CPSSC 16

Challenges and Prospects for Solid State Chemistry



Book of Abstracts









Book of Abstracts

CHALLENGES AND PROSPECTS FOR SOLID STATE CHEMISTRY

University of Sevilla, 9 and 10 September 2016

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CHALLENGES AND PROSPECTS FOR SOLID STATE CHEMISTRY

This Discussion Meeting of the EuCheMS Division of Solid State and Materials Chemistry is focused on the latest developments in synthesis, properties, and structural investigations of solids. The meeting has been held just before the 6th EuCheMS Congress, 11-15 September (euchemsseville2016.eu/).

Topics included:

- Frontiers of solid materials synthesis FSM
- Structural advances through new methodology SAM
- Solid state chemistry and applications SSC
- Rationales for functional materials synthesis RFM

The conference includes plenary invited talks and poster presentations.

ORGANIZING COMMITTEE

Paul Attfield, University of Edinburgh Alfonso Caballero, University of Seville and ICMS-CSIC Martin Jansen, MPI Stuttgart Antoine Maignan, University of Caen Emilio Moran, Complutense University Madrid Jose Antonio Odriozola, University of Seville and ICMS-CSIC

CHALLENGES AND PROSPECTS FOR SOLID STATE CHEMISTRY

University of Sevilla, 9 and 10 September 2016

Program

Friday, 9 September 2016

| 09:00 - 09:30 | Registration |
|---------------|--|
| 09:30 - 10:00 | Opening Remarks |
| | Prof. José Antonio Odriozola, Organizing Committee Prof. Pilar Malet Maenner, Dean of the Chemistry Department Prof. Martin Jansen, Chair of Division |
| | Frontiers of solid materials synthesis |
| | Chair: Maria Gracia Francesconi |
| 10:00 - 10:50 | Ullrich Haussermann, Stockholm University "Hydrogen incorporation in Zintl phases and transition metal oxides– new environments for the lightest element in the solid state" |
| 10:50 - 11:30 | COFFEE BREAK |
| | Chair: Alfonso Caballero Martínez |
| 11:30 - 12:20 | Andrei Shevelkov, Moscow State University "Back to the Iron Age: Structure and properties of iron compounds with strong electron correlations" |
| 12:20 - 13:10 | Amparo Fuertes, ICMAB Barcelona "New developments in the chemistry of oxynitride materials" |
| 13:10 - 15:00 | LUNCH |
| | Structural advances through new methodology |
| | Chair: Paul Attfield |
| 15:00 - 15:50 | Florence Babonneau, UMPC Paris "Solid-state NMR characterization of organic-inorganic materials: some recent advances" |
| 15:50 - 16:50 | COFFEE BREAK AND POSTER SESSION |
| | Chair: Wolfgang Bensch |
| 16:50 - 17:40 | Thierry Epicier, INSA Lyon "Life materials chemistry at the nano scale in environmental transmission electron microscopy" |

17:40 - 18:30Andrew Goodwin, Oxford University
"Local symmetry and hidden order"

Saturday, 10 September 2016

| | Solid state chemistry and applications |
|---------------|--|
| | Chair: Colin Greaves |
| 10:00 - 10:50 | Barbara Albert, TU Darmstadt "Complexity in borides: exotic solids or useful materials?" |
| 10:50 - 11:40 | Clare Grey, Cambridge University "Challenges for rechargeable batteries - new characterisation approaches and new chemistries" |
| 11:40 - 12:20 | COFFEE BREAK |
| | Chair: Antoine Maignan |
| 12:20 - 13:10 | Teofilo Rojo, CIC energiGUNE "Towards all solid state batteries" |
| 13:10 - 15:00 | LUNCH |
| | Rationales for functional materials synthesis |
| | Chair: Edmund Cussen |
| 15:00 - 15:50 | Claudia Felser, MPI-CPS Dresden "Topology – from the materials perspective" |
| 15:50 - 16:40 | Maarit Karpinnen, Aalto University "Layer-engineering of novel functional oxide materials" |
| 16:40 - 17:10 | COFFEE BREAK |
| | Chair: <i>Emilio Moran</i> |
| 17:10 - 18:00 | Joao Rocha, Aveiro University "Microporous lanthanide silicates and coordination polymers for optical sensing and nanothermometry" |
| 18:00 - 18:30 | Quo vadimus? |
| | Panel and audience: Concluding discussion |

INDEX

| New Double Cation Ordering in High Pressure Double Perovskites A.M. Arévalo-López, E. Solana-Madruga, A.J. Dos Santos-García, R. Sáez- Puche, J.P. Attfield | FSM1 |
|--|------|
| Uncommon morphological shapes of graphene: 3D graphenes A. Benítez de la Torre, C. Hernández Rentero | FSM2 |
| Structural and orbital orders in Ga-V oxide spinels A.J. Browne, J.P. Attfield | FSM3 |
| Hydrides of CrB-structure type Zintl phases – An in situ investigation H. Auer, H. Kohlmann | FSM4 |
| Microcrystalline calcium phosphate synthesis in non-aqueous medium M. Kuzina, D. Larionov, V. Putlyaev | FSM5 |
| Towards All Solid State Batteries T. Rojo | FSM6 |
| Conversion reactions of binary of ternary chalcogenides S. Rommel, S. Haumann, F. Pielnhofer, A. S. Tragl, F. Bachhuber, J. Rothballer, W. Yan, P. Peter, A. Krach, A. Furtner, R. Weihrich | FSM7 |
| The parent Li(OH)FeSe phase of lithium iron hydroxide selenide superconductors D.N. Woodruff, F. Schild, C.V. Topping, S.J. Cassidy, J.N. Blandy, S.J. Blundell, A.L. Thompson, S.J. Clarke | FSM8 |
| Microstructural Flexibility and Magnetic Structure of SbxV _{1-x} O ₂ (0 <x<0.5) solid="" solution<br="">A.R. Landa-Cánovas, P. Vilanova-Martínez, F. Agulló-Rueda, J. Hernández- Velasco</x<0.5)> | SAM1 |
| Functionalized Gold Nanoparticles as Platforms for Ligand-Receptor- Interactions F. Machka, E. Pouokam, M. Diener, M.S. Wickleder | SAM2 |
| Synthesis and Characterization of Rare Earth doped ZrO ₂ Nanoparticles A.S. Schulze, M.S. Wickleder | SAM3 |
| Orbital Dinner model for Spin-Glass State in Y₂Mo₂O₇ P.M.M. Thygesent, J.A.M. Paddison, R. Zhang, K.A. Beyer, K.W. Chapman, H.Y. Playford, M.G. Tucker, D.A. Keen, M.A. Hayward, A.L. Goodwin | SAM4 |

| Exploration of the Na-Mn-O system as electrode material for Na-ion battery E. Adamczyk, O.I. Lebedev, V. Pralong | SSC1 |
|--|-------|
| In-situ X-ray diffraction investigations of the catalyst during the partial oxidation of acrolein to acrylic acid Jörg Steffan, Kathrin Hofmann, Stefan Knoche, Alfons Drochner, Herbert Vogel, B. Albert | SSC2 |
| Solid state phase transformations, proton conductivity and Iuminescence properties of Ianthanide triphosphonates M. Bazaga-García, I. R. Salcedo, R.P. Colodrero, P. Olivera-Pastor, E.R. Losilla, G.K. Angeli, K.E. Papathanasiou, G.B. Hix, K.D. Demadis, A. Cabeza | SSC3 |
| Graphene-based materials as electrodes for Li-S batteries A. Benítez, A. Caballero, J. Morales | SSC4 |
| Anion-Deficient Solids for CO ₂ Capture – Towards New Materials M.J. Bennett, D.M. Benoit, I. Dobson, M.G. Francesconi | SSC5 |
| Dicyanamide-bridge ligands as building blocks for multifunctional and multistimuli responsive organic-inorganic hybrid perovskites J.M. Bermúdez-García, S. Yáñez-Vilar, M. Sánchez-Andújar, J. López-Beceiro, S. Castro García, R. Artiaga, M.A. Señarís-Rodríguez | SSC6 |
| Soft Chemical Control of the Structure and Magnetism of Layered Oxychalcogenides J.N. Blandy, C.F. Smura, S.J.C. Herkelrath, S.J. Clarke | SSC7 |
| Orbital Order in Prussian Blue Analogues H. Boström, A. Goodwin | SSC8 |
| New IT-SOCF members of Co-based A_{n+1}B_nO_{3n+1} serie K. Boulahya, D. Muñoz, S. García Martin, U. Amador | SSC9 |
| In situ XAS study of the a strontium substituted cobalt perovskites J.L. Hueso, J.P. Holgado, R. Pereñíguez, A. Caballero | SSC10 |
| Nanoparticles Pt-Cu: In situ analysis by DRX and NAP-XPS R. Castillo Barrero, F. Romero Sarria, J.A. Odriozola Gordon | SSC11 |
| Ammonia Effects on Proton Conductivity Properties of Coordination Polymers R.M.P. Colodrero, I.R. Salcedo, M. Bazaga-García, P. Olivera-Pastor, L. Moreno- Real, E.R. Losilla, A. Cabeza | SSC12 |
| Variable temperature study of the Verwey structure of magnetite M.S. Senn, J.P. Wright, J.Cumby, J.P. Attfield | SSC13 |
| Magnetic Study of Spin Transition in a Dinuclear Iron(II) D. Fedaoui, P. Rosa, Y. Bouhadja | SSC14 |

| Structural features and properties of Pr _{2-x} M _x Ru ₂ O ₇ J. Fernández-Sanjulián, E. Morán, M.A. Alario-Franco | SSC15 |
|---|-------|
| Synthesis and impedance spectroscopy of doped Zirconia based ionic conductors N. García-Moncada, R. Poyato, F. Romero-Sarria, J.A. Odriozola | SSC16 |
| Rh/MgAl₂O₄ structured catalyst for syngas production via dry reforming of biogas V. Garcilaso, M.A. Centeno, J.A. Odriozola | SSC17 |
| Electrochemical oxidation influence in molybdocuprates with «1212» structure I. Herrero-Ansorregui, J. Fernandez-Sanjulian, A.R. González-Elipe, E. Morán, M.A. Alario-Franco | SSC18 |
| Structures and Magnetic Properties of 12-Layered Perovskites Ba ₄ LnM ₃ O ₁₂ (Ln = rare Earths; M = Ru, Ir) Y. Hinatsu, Y. Doi, M. Wakeshima | SSC19 |
| High UV-photocatalytic activity of ZnO synthesized by three different procedures: A comparative assessment C. Jaramillo-Páez, J.A. Navío, M.C. Hidalgo, M. Macías | SSC20 |
| Remarkable enhancement in photocatalytic activity of {001} faceted TiO2 loaded with Pt M.A. Lara, J.A. Navío, M.C.Hidalgo | SSC21 |
| Modifying the superconducting properties in the Fe _x Cu _{1-x} YSr ₂ Cu ₂ O _y system S.A.López-Paz, R. Saez-Puche, E. Morán-Miguélez, M.Á. Alario-Franco | SSC22 |
| Rare earth RE(= Pr, Nd, Gd and Tm) influence in the superconducting properties of the Mo _{0.3} Cu _{0.7} Sr ₂ RECu ₂ O _y system X. Martínez de Irujo-Labalde, J. Fernández-Sanjulián, E. Morán-Miguélez, S. García-Martín, M.A. Alario-Franco | SSC23 |
| Rutheno-Cuprates 1212: Cu/Ru substitution at room pressure A. González-Pérez, X. Martínez de Irujo-Labalde, E. Morán-Miguélez, M.A. Alario-Franco | SSC24 |
| Ultrasonic metal welding – The influence of polymer additives S. Matos, S. Matos, F. Veloso | SSC25 |
| Crystal structure of new polyoxometalate/ionic liquid hybrids and their application in catalysis C. Megías-Sayago, E. Alvarez, S. Ivanova, J.A. Odriozola | SSC26 |
| Ruthenium nanoparticles in CO ₂ methanation: influence of the synthesis method in catalytic behaviour S. Navarro-Jaén, A.E. Szego, O.H. Laguna Espitia, F. Romero-Sarria, J.A. Odriozola | SSC27 |

| Efficient UV-photocatalytic activity of ZnO and Ag/ZnO synthesized by a facile method C. Jaramillo-Páez, J.A. Navío*, M.C. Hidalgo, M. Macías | SSC28 |
|---|-------|
| Solid solutions of layered tetrel antimony chalcogenides R. Schlegel, S. Schwarzmüller, J. Barnes, H. Hölzig, O. Oeckler | SSC29 |
| Disorder-phonon coupling in crystal-like aperiodic solids A. Overy, A. Cairns, M. Cliffe, A. Simonov, P. Chater, M. Tucker, A. Goodwin | SSC30 |
| Perturbation of the Verwey structure of Fe₃O₄ E. Pachoud, G. Perversi, J. Cumby, J.P. Wright, J.P. Attfield | SSC31 |
| Mixed ionic-electronic conductors based on lanthanum molybdates J.M. Porras-Vázquez, L. dos Santos-Gómez, C. Frontera, J. Canales-Vázquez, D. Marrero-López, E. Ramírez-Losilla | SSC32 |
| Magnesium secondary battery: New electrolytes and cathode materials E. Anger, I. Dez, A.C. Gaumont, V. Pralong | SSC33 |
| Synthesis, Physico-chemical and Electrochemical Characterizations of Na4VO(PO4)2 as Cathode Material for Na-ion Batteries W. Deriouche, M. Freire, N. Amdouni, A. Maignan, V. Pralong | SSC34 |
| An active Li-Mn-O compound for high energy density Li-ion batteries M. Freire, N.V. Kosova, C. Jordy, D. Chateigner, O.I. Lebedev, A. Maignan, V. Pralong | SSC35 |
| Fe[HO ₃ PCH(OH)CO ₂]-2,5H ₂ O and doped metal derivates: photocatalytic properties I.R. Salcedo, M. Bazaga-García, R.M.P. Colodrero, A.S. Albean, P.Olivera- Pastor, A. Cabeza | SSC36 |
| Obtainment of polyethyleneimine modified ZnO nanoparticles for bioanalytical applications M. Shiriaev, J. Young Jeong, B. Hyun Chung, A. Baranov | SSC37 |
| Insertion of diols into a layered niobate C.I. Thomas, M. Stenholm, M.J. Karppinen | SSC38 |
| Effect of preparation pH on Bismuth Titanate materials with high visible light photocatalytic activity P. Zambrano, J.A. Navío, M.C.Hidalgo | SSC39 |
| Synthesis and scale-up of non-active and active Belite-Alite- Ye'elimite Clinker (BAY) J.D. Zea-García, M.A.G. Aranda, A.G. De la Torre, I. Santacruz | SSC40 |

| Fast microwave-assisted synthesis and lithium-ion diffusion studies of lithium stuffed garnets M. Amores, T. E. Ashton, P. J. Baker, E.J. Cussen, S.A. Corr | SSC41 |
|--|-------|
| New representatives and physical properties of 3d-5d double perovskites P. Adler, A. Kumar Paul, M. Reehuis, A. Sarapulova, B. Yan, S. Kanungo, W. Schnelle, K.K. Wolff, L. Hao Tjeng, C. Felser, M. Jansen | RFM1 |
| Synthesis of zinc deposits by pulsed current A. Boukhouiete, Z. Habes, M. Baccouche | RFM2 |
| A new family of topological insulators based on β-Bi4l4 A. Isaeva, A. Weiz, M. Groh, T. Doert, G. Autes, O.V. Yazyev | RFM3 |

Abstracts

NEW DOUBLE CATION ORDERING IN HIGH PRESSURE DOUBLE PEROVSKITES

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Cation order in ABO₃ perovskites adds to their chemical variety and can lead to properties such as ferrimagnetism and magnetoresistance in Sr_2FeMoO_6 .^[1] Through high pressure and temperature synthesis we have discovered a new type of 'double double perovskite' structure in the family MnRMnSbO₆ (R = La, Pr, Nd and Sm). This tetragonal structure has 1:1 order of cations on both A and B sites; A-site Mn²⁺ and R³⁺ cations are ordered in columns while Mn²⁺ and Sb⁵⁺ have rock salt order on the B sites.^[2] The A-site Mn²⁺ positions are further divided into tetrahedral and square planar environments as shown in Figure 1.

The MnRMnSbO₆ double double perovskites are ferrimagnetic at low temperatures with additional spin-reorientation transitions. The ordering direction of ferrimagnetic Mn spins in MnNdMnSbO₆ changes from parallel to [001] below $T_C = 76$ K to perpendicular below the reorientation transition at 42 K at which Nd moments also order.

Smaller rare earths lead to conventional monoclinic double perovskites (MnR)MnSbO₆ for Eu and Gd, where Mn^{2+} and R^{3+} are disordered over the A sites while Mn^{2+} and Sb^{5+} have rock salt order at the B sites.



Figure 1. Double double perovskite structure of MnRMnSbO₆ oxides (R = La, Pr, Nd and Sm). B site MnO₆ and SbO₆ octahedra have a rocksalt type order while A site Mn and R are ordered in columns parallel to the unique z-axis. Mn A-sites are further split into Mn_A and Mn_A[,] environments with tetrahedral and square planar coordinations as shown on the right.

[1] D. Serrate, J.M. De Teresa, M.R. Ibarra, J. Phys. :Condens. Matter, 19 (200) 023201.

[2] E. Solana-Madruga, A.M. Arévalo-López, A.J. Dos Santos-García, E. Urones-Garrote, D. Ávila-Brande, R. Sáez-Puche, J.P. Attfield, Angew. Chem. Int. Ed, 2016, DOI: 10.1002/anie.201603526.

Uncommon morphological shapes of graphene: 3D graphenes

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Research field: Frontiers of solid materials synthesis

Abstract:

The "graphene" term is the name initially given to a monolayer of graphite, successfully isolated in 2004 [1]. The term has evolved by adding a prefix, few-layer or multilayer or suffixes as "sheet" to describe graphene materials. Implicitly, a 2D structure is associated to these terms. The flexibility is one of the more outstanding properties of the carbon monolayer. The layers can not only be stacked but also rolled or wrapped, emerging new forms of graphenes such as graphene fibers (1D) or three dimensional graphenes (3D). The sheets assembly into 3D macrostructures provides superior physiochemical properties. The 3D network prevents aggregation and guarantees mass transport.



Fig. 1. SEM image of a 3D graphene synthesized by hydrothermal treatment of GO (unpublished results)

In this communication we will describe synthesis methods of 3D graphenes grouped in two bottom-up (CVD methodologies: of molecular precursors on metal foams, followed by the removal of the substrate) and top-down (e.g. hydrothermal reduction of graphitic oxide, GO, and the formation of a hydrogel, Fig. 1) [2]. The resulting materials possess 3D structures, large surface area due to an interconnected pore system, flexibility and elasticity. These properties increase the applications compared with conventional graphenes. Here, we will also outline some applications of 3D graphenes, mainly related with their use as electrodes for electrochemical energy storage and conversion devices.

- [1] Novoselov K S, Geim A K, et al. 2004 Science 306 666.
- [2] Wang H, Yuan X, Zeng G, Wu Y, Liu Y 2015 Adv. Colloid Interface Sci. 221 41.

Structural and orbital orders in Ga-V oxide spinels

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Research field: Frontiers of solid materials synthesis

Abstract:

Transition metal oxides adopting the AB_2O_4 spinel structure type can have complex ground states that arise from coupling between the crystal lattice and spin, charge, and orbital degrees of freedom. In certain spinels, orbital ordering results in an unusual ground state in which atoms are directly bonded to each other and form small clusters called 'orbital molecules'. [1] Examples include helically arranged dimers in MgTi₂O₄ [2] and trimers formed below the Verwey transition in Fe₃O₄. [3] The largest known orbital molecules are formed in AlV₂O₄, which distorts below 700 K from a cubic spinel to a trigonal structure with seven-atom orbital molecule heptamers. [4]

We have recently synthesised GaV_2O_4 , a new orbital molecule material. High-resolution neutron and synchrotron powder diffraction has been used to determine its structure over a range of temperatures and identify the existence of heptamers, akin to those found in AIV_2O_4 , which form in the ground state. Further characterisation of the orbital molecule state in GaV_2O_4 has been achieved by measuring magnetic and physical properties. The effects of chemical substitutions on orbital molecule formation are also being studied.

- [1] J. P. Attfield, APL Mater. **3**, 041510 (2015).
- [2] M. Schmidt, W. Ratcliff, P. G. Radaelli, K. Refson, N. M. Harrison, and S. W. Cheong, Phys. Rev. Lett. 92, 056402 (2004).
- [3] M. S. Senn, J. P. Wright, and J. P. Attfield, Nature **481**, 173 (2012).
- [4] Y. Horibe, M. Shingu, K. Kurushima, H. Ishibashi, N. Ikeda, K. Kato, Y. Motome, N. Furukawa, S. Mori, and T. Katsufuji, Phys. Rev. Lett. **96**, 086406 (2006).

Hydrides of CrB-structure type Zintl phases – An *in situ* investigation

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Research field: Frontiers of solid materials synthesis

Abstract:

Hydrogen can act as an oxidation agent on Zintl phases. It is either incorporated into the cation packing as an interstitial hydride anion or binds to the polyanion covalently as negatively polarized partner (for a recent overview see Häussermann [1]).

We investigated the hydrogenation of the Zintl phases AeTt (Ae = Ca-Ba, Tt = Ge and Sn) of the CrB-structure type. Using ex situ diffraction methods we could show the existence of hydrogen (deuterium) rich compounds (γ -phases) SrGeD_{4/3-x} (x = 0.139(3), Z = 12, *Pnma*, a = 15.2692(11), b = 4.0600(2), c = 11.9113(9) Å) and BaSnD_{4/3-x} (x = 0.055(2), Z = 12, *Pnma*, a = 16.3097(10), b = 4.5554(2), c = 12.9169(7) Å), which crystallize in the CaSiH_{1.3}-structure type [2] as well as BaGeD_{5/3-x} (x = 0.10(3), Z=24, *Pnma*, a = 15.647(3), b = 4.1149(6), c = 26.866(4) Å), which has its own structure type that resembles similar structural features.

In situ neutron diffraction and *in situ* differential scanning calorimetry under 50 bar hydrogen or deuterium pressure revealed that the γ -phases form at temperatures from 100°C to 200°C. At higher temperatures the covalent Ge-H(D) or Sn-H(D) bonds are not stable any longer and the phases release hydrogen (deuterium). The existence of two additional phase types can be established. They are both related to the structure of the parent Zintl phase, but show different hydrogen (deuterium) occupation of tetrahedral alkaline earth metal voids. There are α -phases AeTtD_y, y \approx 0.25 (Z = 4, *Cmcm*: α -SrGeD_y: 50 bar D₂, 320°C, *a* = 4.7659(5), b = 11.8280(14), c = 4.1542(5) Å; α -BaGeD_y: vacuum, 230°C, *a* = 5.0336(9), *b* = 12.215(2), *c* = 4.2734(8) Å; α -BaSnD_y: 50 bar D₂, 200°C, *a* = 5.2280(9), *b* = 12.944(2), *c* = 4.6684(9), *b* = 12.500(3), *c* = 4.1164(8) Å; β -BaGeD_y. 2-50 bar D₂, 230°C, *a* = 4.947(2), *b* = 13.078(8), *c* = 4.205(3) Å). Upon cooling under hydrogen (deuterium) pressure the γ -phases are always reformed.

- [1] U. Häussermann, V. F. Kranak, K. Puhakainen, Struct. Bond. 2011, 139, 143-162.
- [2] Ohba, N.; Aoki, M.; Noritake, T.; Miwa, K.; Towata, S.-i. Phys. Rev. B 2005, 72, 075104.

Microcrystalline calcium phosphate synthesis in non-aqueous medium

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Research field: Frontiers of solid materials synthesis

Abstract:

The manufacture of biomaterials based on calcium phosphates for bone tissue replacement is a topical issue of modern material science. The latest developments are related to the regenerative approach, which requires the investigation of highly resorbable materials based on calcium phosphates with Ca/P ratio < 1.5. The usage of non-aqueous medium for the calcium phosphate synthesis is a promising tool to avoid the impurities, eliminate water influence and gain more control of the material.

The key object of the research was calcium orthophosphate $(Ca(H_2PO_4)_2)$. It was obtained using two methods. According to the first method, calcium oxide or calcium carbonate was mixed with calcium hydrophosphate $(CaHPO_4 \cdot 2H_2O)$ or octacalcium phosphate $(Ca_8H_2(PO_4)_6 \cdot 5H_2O)$ suspension in a solvent (ethanol, diethylene glycol and ethylene glycol) under 110, 130 or 150 °C for 4-5 hours.

The second method was based on the following requirement. The only coproduct of the reaction should be the solvent itself. Calcium orthophosphate was obtained by adding of hot 0.1M calcium glycolate ($C_2H_4O_2Ca$) solution to 0.1M orthophosphoric acid (H_3PO_4) solution in ethylene glycol. The synthesis was carried out under 110, 130 or 150 °C. Calcium glycolate was obtained by pure calcium dissolution in preliminary dehydrated ethylene glycol. In order to eliminate water influence, a new method of crystal orthophosphoric acid synthesis was developed. The acid was obtained in the process of the reaction of phosphorus oxide with the calculated amount of water under low (<39 °C) temperatures.

The main aspects of samples sintering, as well as the microstructure and qualities, were analyzed with the help of X-ray diffraction (XRD) and the scanning electron microscopy (SEM).

TOWARDS ALL SOLID STATE BATTERIES

Professor Teófilo ROJO

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Energy storage possesses an important role in order to rationalize the use of both fossil and renewable energy sources. Electrochemical Energy Storage (EES) is a valuable approach for improving the reliability and overall use of the entire power system (generation, transmission and distribution). Between the EES system, the batteries could bring significant improvements in pollution reduction and efficient use of renewable energy sources. Rechargeable batteries have actually played a key role of the technological progress in recent years. A clear example of this is the indispensable role of the rechargeable Li-ion batteries in facilitating the revolution of portable electronics.

Li-ion batteries ,however, have almost reached their limits in terms of energy density (75-200 Wh/kg), cycle life (1000 cycles at > 80% of capacity), and charge/discharge rate capabilities (1C). To satisfy the industrial needs such as electrical vehicle(EV) and/or stationary grid storage developing of new batteries is required. Metal-oxygen/air batteries are considered the most attractive alternative to Li-ion batteries when high energy density is a critical requirement.

Performance requirements of electrochemical energy storage (EES) for stationary use depend on the application markets that are broad and varied in power and energy ratings, the ratio of power to energy, the discharging time, etc. A number of battery technologies such as lead-acid, Ni-metal, were developed over the last century. An important effort to improve the safety in the Na-S and Zebra technologies has been carried out by reducing the operating temperature. It is worth mentioning the evolution of the research developed in the last four years in the non-aqueous sodium ion systems.

The reliability, durability, and cost play an important role in the energy storage systems. However, safety is especially crucial for large-format batteries, which are developed for application in automotive industry and stationary applications. In most of commercial batteries a liquid solution of different salts in organic carbonates is used as dominating electrolytes. However, at elevated temperature, detrimental impacts on the performance and safety of the battery arise due to the instability of the salts and flammability of organic solvents. This is especially crucial for large-format batteries, which are developed for application in automotive industry and stationary applications. Solid electrolytes (ceramic and polymeric) are an alternative to liquid electrolytes.

In this talk we will present a general overview of the current challenges on battery technologies and the future trends on solid state batteries for electrical vehicles and stationary applications.

Conversion reactions of binary to ternary chalcogenides

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Research field: Frontiers of solid materials synthesis.

Abstract:

Along the ternary phase diagram of main group metals A, transition metals M and chalcogenides X compounds of compositions $M_{3/2}AX$ attracted recent interest. Within the solid solutions $Co_{3,x}Ni_xSn_{2,y}In_yS_2$ thermoelectric and magnetic properties can be tuned [1, 2]. The compounds can be prepared by reaction of binary chalcogenides like SnS with transition metals M = Co, Ni by high temperature reactions (T > 800°C). The formation was studied by in situ X-ray diffraction. Due to recent studies nano size SnS can be converted with Ni²⁺ to Ni₃Sn₂S₂ under surprisingly mild reductive conditions (T < 197°C) in ethylene glycole (EG) [3]. By careful changes of reaction conditions the formation of products like Ni₃S₂, Ni@SnS, Ni₃Sn₂S₂, Ni₃Sn or NiS is observed. Further, the reaction mechanism of Bi₂X₃ (X = S, Se) with Ni²⁺ in EG was studied to detail [4]. Consequently, intermediate Bi and NiBi nanoparticles are formed. Depending on reaction conditions superconducting Ni₃Bi₂X₂ or NiBiSe is formed. As both compositions are found along the line M+AX in the phase diagram the given methods shown ways towards directed product formation. With the help of DFT methods calculations on the relative stabilities of different M_xAX compositions were performed and compared to experimental results. [5]

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The parent Li(OH)FeSe phase of lithium iron hydroxide selenide superconductors

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Research field: Frontiers of solid materials synthesis *and* Solid state chemistry and applications.

Abstract:

The recently discovered ^[1] hydroxide selenides $Li_{1-x}Fe_x(OH)Fe_{1-y}Se$, synthesised hydrothermally with $x \sim 0.2$ and $0.02 \le y \le 0.15$ show high temperature superconductivity when y < 0.05 and the iron within the FeSe layer is reduced below the +2 oxidation state.^[2] We have quantified the relationship between composition, structure and superconducting T_c in these hydroxide selenides and have shown that reductive lithiation using Li in liquid ammonia (Li/NH₃), following the hydrothermal synthesis, reduces *y* to zero: incoming lithium displaces iron ions from the hydroxide layers into the vacant sites in the selenide layers yielding bulk superconducting compositions $Li_{1-x+y}Fe_{x-y}(OH)FeSe$. This report of the control of these compounds was in principle not able to disentangle the importance of reduction of Fe below the +2 oxidation state and full occupancy of the Fe sites in the selenide layer. Here we extend the soft chemistry of these compounds to approach the composition Li(OH)FeSe which is not a superconductor, showing that reduction of iron below the +2 oxidation state is essential for superconductivity, in line with a recent computational report.^[3]

Furthermore, some superconducting compositions synthesised hydrothermally show an apparent magnetic ordering transition around 12 K which has been ascribed to ferromagnetic ordering of the Fe²⁺ moments in the Li_{0.8}Fe_{0.2}(OH) layers.^[4] Although other experiments initially suggested that these iron ions participate in antiferromagnetism.^[5] In this communication we clarify this magnetism in the Li_{0.8}Fe_{0.2}(OH) layers of hydrothermally synthesised samples that lie outside the superconducting regime.



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Microstructural Flexibility and Magnetic Structure of $Sb_xV_{1-x}O_2$ (0<x<0.5) Solid Solution

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Research field: Structural advances through new methodology.

Abstract:

Rutile phase ~SbVO4 plays a key role in the catalyst for the ammoxidation of propane to acrylonitrile. It exhibits an intense structural flexibility involving cation vacancies, changes in oxidation states and different degrees of order-disorder, from Short Range Order (SRO) to superstructures and structural modulations [1, 2]. We have studied the solid solution Sb_xV_{1-x}O₂, that ranges from SbVO₄ (x=0.5) to Sb_{0.1}V_{0.9}O₂ (x=0.1). All the Sb cations are Sb⁵⁺ while the V cations are V⁴⁺ and V³⁺. In the Sb-richest phase, ~SbVO4, vanadium is V³⁺, as confirmed by EELS, magnetic susceptibility and neutron diffraction, showing the latter antiferromagnetic ordering at TN < 50K. Electron diffraction shows the presence of intense SRO as wavy twodimensional sheets of diffuse intensity in the reciprocal space, running perpendicularly to c*. Very weak SRO can be observed at Sb_{0.33}V_{0.67}O₂ and magnetic ordering happens at lower temperatures (TN~6K). For Sb_{0.25}V_{0.75}O₂ compositions, a different type of SRO appears and it can be observed by ED as very intense two-dimensional sheets of diffuse intensity forming a three-dimensional net of edge-sharing octahedra in reciprocal space. At $Sb_{0.1}V_{0.9}O_2$ the same SRO can also be observed by ED but this phase presents a structural transition similar to that of VO_2 but at lower temperature (51°C), observed by ED. The magnetic susceptibility curve is very similar to VO_2 curve, with magnetic phase transitions above room temperature, indicating the presence of spin-Peierls distortion due to V^{4+} (S=¹/₂) pairing. For VO₂ (x=0) the Raman spectrum is strong and the peaks correspond to the monoclinic phase. For x=0.1, 0.25, and 0.33, the spectrum becomes very weak and broad, due to the transition to the semiconducting phase and the electrostatic screening by free charges, as in the rutile phase of VO₂. For x=0.25 the Raman spectrum becomes strong again due to the transition to an insulating monoclinic phase.

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SAM - 2

Functionalized Gold Nanoparticles as Platforms for Ligand-Receptor-Interactions

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Research field: Structural advances through new methodology

Abstract:

Gold nanoparticles proved to be versatile materials for applications as medicinal and pharmaceutical agents.[1] As their dimension ranges in the same size of some biomolecules like proteins and receptors gold nanoparticles are promising carriers for active compounds. The spatial arrangement allows multivalent interactions between nanoparticle and receptors, meaning simultaneous binding of multiple ligands on one entity with receptors on another.

Unmodified gold nanoparticles can be prepared with a narrow size distribution via different synthetic approaches. Modification of the ligand shell with mercaptocarboxylic acids by ligand exchange reaction gives water solubility and stability. Bioactive ligands were attached covalently via peptide bonds to the gold nanoparticles surface. In an interdisciplinary approach new insights and understanding of interactions between nanoparticles and biological compounds were obtained. Different neurotransmitters were attached to gold nanoparticles and their biological activity was demonstrated.

The developed conjugates were applied as new agonists in classical ligand-receptor interactions. Multivalent presentation seems to enhance the interactions. The large surface covered with multiple active ligands lead to a strong improvement of biological activity of receptors at very low activation concentrations.[2]

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Synthesis and Characterization of Rare Earth doped ZrO₂ Nanoparticles

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Research field: Structural advances through new methodology.

Abstract:

The interest in rare earth materials increased steadily in the past years. Especially optical technologies like LEDs are in the focus but due to their broad optical properties also other applications are possible. Since semiconductor nanoparticles like quantum dots often contain toxic metals like cadmium, rare earth doped nanoparticles could be an alternative as luminescent nanomaterials. Because the luminescence of these nanoparticles is caused by 4f transitions the emission bands are very narrow and therefore easy to distinguish. It is also possible to cover an optical spectrum between the visible and the near infra-red range of the electromagnetic spectrum.[1] Cubic zirconium dioxide nanoparticles (ZrO₂ NPs) with an edge length of 8 nm were synthesized by using a hydrothermal method. The nanocrystals were doped with different rare earth metals to cover a wide range of the electromagnetic spectrum with their luminescence. Different concentrations of the rare earth elements were incorporated to investigate the influence on the emission properties. The particles were characterized with TEM. EDX, powder diffraction and emission measurements. For an application for example in biological system the nanoparticles have to be dispersible in water. Furthermore it is necessary to provide a possibility for specific functionalization. For this propose the ZrO₂ NPs were coated with a shell of silicon dioxide made form tetraethoxysilane and (3-aminopropyl)triethoxysilane. The free amine moieties on the surface can be used to introduce different moieties through coupling and the particles can be functionalized for a specific target.

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Orbital Dimer model for Spin-Glass State in Y₂Mo₂O₇ <u>P. M. M. Thygesent^a</u>, J. A. M. Paddison^{a,b,c}, R. Zhang^b, K. A. Beyer^d, K. W. Chapman^d H. Y. Playford^b M. G. Tucker^b, D. A. Keen^b, M. A. Hayward^a, A. L. Goodwin^a ^aDepartment of Chemistry, University of Oxford, UK ^bISIS Facility, Didcot, UK ^cSchool of Physics, Georgia Institute of Technology, USA ^dAdvanced Photon Source, Argonne, USA E-mail: peter.thygesen@chem.ox.ac.uk

In recent years there has been increasing interest in materials where degrees of freedom are determined by coupling between spin orientation and orbital order. $Y_2Mo_2O_7$ is a spin glass with Jahn-Teller active Mo^{4+} ions, which occupy the vertices of corner-sharing tetrahedra in a frustrated pyrochlore lattice. In most pyrochlore oxides both frustration and positional disorder must be present simultaneously to show spin glass behaviour [1]. Previous work on $Y_2Mo_2O_7$ has shown a small distortion in the Mo position to be present, which has been ascribed to anisotropic vibration, but it is insufficiently large to explain the spin glass behaviour.

In this study, neutron and X-ray total scattering data have been collected to much higher resolution than previous work [2] on a powder sample above and below spin glass transition at 22.5 K [3]. The data have been refined using PDFGui with various constraints. Our key result is a model that reconciles the apparent contradictions of previous experimental studies and presents how combination of local symmetry-breaking and geometric frustration can lead positional disorder to drive the spin glass state in $Y_2Mo_2O_7$.

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Keywords: Total scattering, Orbital order, Spin-Glass, Frustration

Exploration of the Na-Mn-O system as electrode material for Na-ion battery

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Research field: Solid state chemistry and applications

Abstract:

Over the past two decades, lithium-ion has gained great popularity because of their high voltage, good energy density and long life. However, the cost of materials is increasing due to the commercialization of lithium batteries and in addition the lithium global resources are unevenly distributed. One of the most appealing alternatives is to use sodium instead of lithium. Indeed, sodium is a thousand times more abundant and geographically spread [1].

In this context, due to the low cost and non toxic character of manganese oxides, the Na-Mn-O system is an interesting topic of research as potential new material for Na-ion positive electrode.

In this presentation, we will discuss on the reversible sodium insertion in the layered type structures that present many advantages such as facilitated insertion/extraction of the Na ions. Thus, several phases with the composition Na_{1-x}MnO₂ system ($0 \le x \le 1$) have been reported in this system. Among these studies, nanoplates of Na_{0.7}MnO₂ were hydrothermally synthesized by Su and coworkers [2] and present a capacity of 164 mAh/g at a current density of 40 mA/g. The two layered phases of NaMnO₂, α and β , have also been electrochemically tested and show good capacities of 210 [3] and 190 mAh/g [4], respectively at the average voltage of 2.8V vs Na^{+/}Na. The structure, morphology and electrochemical properties relationship will be presented.

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SSC - 2

In-situ X-ray diffraction investigations of the catalyst during the partial oxidation of acrolein to acrylic acid

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Research field : Solid state chemistry and applications

Abstract:

The partial oxidation of acrolein (ACR) to acrylic acid on Mo/V/W-mixed oxides is of major industrial interest. Little knowledge exist on the selectiv oxidation of acrolein to acrylic acid on heteropoly acids. To gain new insights into the reaction mechanisms at elevated temperatures and under catalytic conditions an *in-situ* X-ray diffraction system was used. Structural changes of molybdatovanadophosphate heteropoly acids are discussed.

The heteropoly acid $Cs_2H_2[PVMO_{11}O_{40}]_* \times H_2O$ (HPA) and further Keggin-ion containing compounds were studied by DTA/TGA under argon and by *in-situ* X-ray diffraction under inert (N₂), reducing (ACR), humid (H₂O) and oxidizing (ACR + O₂ + vapour) atmospheres. HPA crystallizes with a cubic structure (P $n\overline{3}m$, $a_{298 K}$ = 1180,94(2) pm).

During heat treatment in nitrogen a loss of crystal water is observed between 473 and 573 K, followed by a loss of structural water in the temperature range of 573 and 723 K. Above 773 K the compound totally decomposes, yielding a mixture of the binary oxides MoO_3 , V_2O_5 , Cs_2O , P_2O_5 .

Under reducing conditions (5 vol-% ACR) further changes in the diffraction pattern are observed, which will be discussed.

Investigating heterogeneous catalytic reactions in a reaction chamber by *in-situ* X-ray diffraction proves to be a valuable method for the analysis of changes in the catalyst in the presence of organic compounds and under different atmospheres.

Solid state phase transformations, proton conductivity and luminescence properties of lanthanide triphosphonates

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Research field: Solid state chemistry and applications.

Abstract:

Metal phosphonates are multifunctional coordination polymers with high chemical and thermal stability and tunable properties, such as internal H-bond networks [1]. These features together with the combination of the lanthanide cations in their frameworks make them interesting solids due to their potential luminescent and proton conductivity properties [2].

In the present work, we describe the crystal structure and solid state transformations of a new family of isostructural compounds with general formula $Ln(H_4NMP)(H_2O)_2]Cl\cdot 2H_2O$ [Ln = La^{3+} , Pr^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , H_6NMP = nitrilotris(methylphosphonic acid)]. These solids, formed by positively charged layers compensated by chloride ions in the interlamellar space, show reversible dehydration/hydration processes at low humidity (up to 170 °C), while become to be unstable upon heating at 80 °C and 95% RH. Under these conditions, the solids experiment different solid state transformations which are accompanied by a metal/ligand reorganization leading to phases with higher proton conductivities [3]. In addition, the luminescent properties of these solids will be discussed.

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SSC - 4

Graphene-based materials as electrodes for Li-S batteries

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Research field : Solid state chemistry and applications

Abstract:

To mitigate and reduce the dependence of our society on fossil fuels (mainly oil and natural gas) and to achieve satisfy our energy demand, it has thought about the use of renewable energy sources (solar, wind, etc.) as the best alternative. Because of the intermittency in the generation of these renewable energy storage systems require energy efficient. At this point, the rechargeable batteries can be strong competition in the market.

The rechargeable lithium-sulfur battery, due to its high theoretical capacity of 1675 mAh g⁻¹ and its high energy density of 2600 Wh kg⁻¹ is an ideal technology for this purpose [1].

The direct use of sulfur as a cathode Li/S battery is not practical due to its low conductivity and the solubility of the reaction intermediates generated in the cycling. To overcome these drawbacks is necessary a second component acting as conductive matrix and host sulfur. The optimal host material for impregnation of sulfur should be light, with a high conductivity and high surface area. Graphene is presented as a key material to meet this challenge [2].

20

In this communication the use of graphenes of different features is proposed to prepare graphene-sulfur composites. These composites will be used as electrodes for Li/S batteries. The synthesis of these graphene is carried out from graphite, transforming it into graphitic oxide (GO). Then, a graphitic oxide reduction is performed, obtaining graphene nanosheets (GNS). Synthetized graphenes exhibit morphological properties (porosity and surface) required to be used as sulfur electrodes matrix. GNS-Sulfur composites show good electrochemical performance, achieving remarkable values of both capacity and energy released and stability testing for long cycling.

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Intensity / a.u.

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Anion-Deficient Solids for CO₂ Capture – Towards New Materials

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Research field: Solid state chemistry and applications

Abstract:

In the field of CO_2 capture and storage, two well-researched approaches are the reaction of alkali earth metal oxides, AO (A = Ca, Sr, Ba) with CO_2 to form carbonates ACO₃ and, the physisorption of CO_2 molecules in the channels of zeolites.¹ This work investigates a new approach derived from merging these strategies. Oxides of the general formula A_2MO_3 (A = Ca, Sr, Ba and M = Cu, Pd) contain alkali metals, which tend to react readily with CO_2 to form stable carbonates and, also show a K_2NiF_4 -type structure with anion deficiencies, which can be host sites for $(CO_3)^{2^-}$ anions. In fact, in the crystal structure of these materials, the transition metal is coordinated by the oxide anion in square planar fashion and forms chains of corner-linked M-O polyhedral, along which the anion vacancies are ordered.

We intend to exploit these vacant sites for CO_2 storage, aided by the presence of an alkaline earth metal, which will form stable bond with the $(CO_3)^{2^-}$ anions. The advantage of this approach is the use of CO_2 as chemical reagent, to modify the anionic lattice in inorganic solids, hence either modify their properties or prepare new materials.

There have been reports of the formation of novel compounds via "filling" of the anion vacancies in A₂MO₃ compounds. In A₂CuO₃ (A = Sr, Ca) the anion stoichiometry was increased via the substitution of 1 oxide with 2 fluoride anions, leading to the formation of A₂CuO₂F_{2+δ}, $(0 \le \delta \le 0.35)$.² A₂PdO₃ has also been reported to form the oxide-fluoride A₂PdO₂F₂, via the same process.³ Furthermore, Sr₂CuO₃ can form the oxide carbonate Sr₂CuO₂(CO₃) as a result of O²⁻ anions being partially replaced by $(CO_3)^{2-}$ anions. Sr₂CuO₃ can therefore be considered a very good candidate for CO₂ capture, as it contains widely available low cost elements and is easy to prepare.

We have monitored the incorporation of CO₂ into Sr_2CuO_3 and Ba_2PdO_3 using a combination of Thermo Gravimetric Analysis and Powder X-Ray Diffraction. The results showed that we were able to prepare $Sr_2CuO_2(CO_3)$ and $Ba_{11}Pd_{11}O_{20}(CO_3)_2$ with $BaCO_3$ respectively by direct reaction of Sr_2CuO_3 and Ba_2PdO_3 with CO_2 .^{4,5} The removal of CO_2 from $Sr_2CuO_2(CO_3)$ has also been explored and preliminary results show reversibility to Sr_2CuO_3 for more than one cycle.

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Dicyanamide-bridge ligands as building blocks for multifunctional and multistimuli responsive organic-inorganic hybrid perovskites

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Research field: Solid state chemistry and applications.

Abstract:

Organic-inorganic hybrid perovskites have suffered an accelerated widespread all over the materials science community during the last years due to their remarkable functional properties, such as photovoltaic properties in the MAPbI₃ or magnetoelectric-multiferroic properties in the $[CH_3NH_3][Co(HCOO)_3].[1]$ Parallely, during the last decade, cyanide, $[CN]^-$, and dicyanometallates, $[NC-M-CN]^-$ (M = Cu⁺, Ag⁺, Au⁺, etc.), anions have attracted great attention as building blocks for organic-inorganic frameworks and coordination polymers with a wide structural diversity and remarkably functional properties.[2] Nevertheless, studies on cyanide-based and related perovskites remains relatively scarce up-to date.[3]

In this work, we present a novel family of organic-inorganic hybrid ABX₃ perovskites containing dicianamides (dca = $[NC-N-CN]^{-}$) as bridging ligands in the X sites, with molecular formula $[TPrA][M(dca)_3]$ (TPrA = $[CH_3CH_2CH_2]_4N^+$; M = Mn^{2+} , Fe²⁺, Co²⁺ and Ni²⁺). As we will show, these compounds which from the structural point of view exhibit very interesting order-disorder phenomena, display a peculiar coexistence of multifunctional and multistimuli responsive properties, namely: colossal thermal expansion, multiferroicity, electric order and multiple phase and dielectric transitions that can be easily modulated by temperature, external hydrostatic/uniaxial pressure as well as internal chemical pressure.[4]

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Soft Chemical Control of the Structure and Magnetism of Layered Oxychalcogenides

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Research field: Solid state chemistry and applications

Abstract:

 $Sr_2CoO_2Cu_2Se_2$ and $Sr_2CoO_2Ag_2Se_2$ are isostructural, layered oxychalcogenides. [1] In this work we describe the effect on the structure and magnetic properties of these compounds as they are oxidized using I_2 /MeCN solution under an inert atmosphere. This technique has previously been successfully used to oxidize Mn in $Sr_2MnO_2Cu_{1.5}S_2$, thereby deintercalating Cu to maintain charge balance. This fundamentally changed the Cu vacancy ordering and caused a change in the low-temperature magnetic structure. [2]

For $Sr_2CoO_2Cu_2Se_2$ and $Sr_2CoO_2Ag_2Se_2$, it is found that, despite the compounds' similar structure, their behavior when Cu/Ag is removed is very different. $Sr_2CoO_2Cu_2Se_2$ shows a decrease in cell volume as a function of Cu-content, in which the relationship between lattice parameters *a* and *c* is linear. A general loss of magnetism is also observed, consistent with a loss of unpaired electrons as Co is oxidized, but no rearrangement of magnetic structure is observed.

As Ag is removed in $Sr_2CoO_2Ag_2Se_2$, two distinct regimes are observed: a regime in which the removal of Ag causes a reduction in the *a* lattice parameter, but not in *c*. In this regime, the material is antiferromagnetic but with increasing glassiness as Co is oxidized. In the second regime, there is a dramatic change in *c* as a function of Ag occupancy. Here the material appears to be ferromagnetic from magnetometry measurements, but no intensity arising from magnetism is observed in neutron diffraction measurements.



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Orbital Order in Prussian Blue Analogues

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Abstract:

Functional metal oxides are known for their exotic physical properties, such as colossal magnetoresistance or ferroelectricity.¹ The understanding of these systems is complicated, due to the strong correlation between orbital, magnetic and transport degrees of freedom. Thus, the study of materials with weaker correlation between the different degrees of freedom is of interest. Metal-organic frameworks may form similar topologies to metal oxide systems, but the longer molecular linker alters the correlation strength.

Prussian Blue Analogues (PBAs) are a class of metal-organic frameworks with the general formula $A_xM_y[M'(CN)_6]_z$, where A is an alkali metal ion and M and M' are transition metals. These compounds display a wide range of interesting magnetic functionality, however, the orbital properties are less understood. A number of Jahn-Teller distorted PBAs are known, where cooperative alignment of the long axes leads to tetragonal distortion, as opposed to the ideal cubic symmetry.²⁻³ Yet, there are few studies about the possibility of orbitally disordered states. As the typical intermetallic separation is larger (5 Å) in PBAs than in oxides perovskites (4 Å), the energy scale for metal-metal correlation should be reduced. Thus, the transition to the disordered orbital state may occur at lower temperature for PBAs, relative to oxide perovskites. By creating doped series of PBAs, we intend to investigate the functional similarities and differences compared to the properties of doped oxide systems

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New IT-SOCF members of Co-based A_{n+1}B_nO_{3n+1} serie

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Research field : Solid state chemistry and applications

Abstract:

Precise knowledge of the relationships between structure and properties is crucial for the design of efficient materials. In the search for these relationships, the great flexibility of perovskite-type oxides ABO₃ to accommodate the insertion of AO rock salt layers is extremely useful. By varying the composition of perovskites further, a large number of phases can be formed based on the intergrowth of various structure types with blocks of perovskite. The simplest of these phases are those based on the intergrowth of rock salt (AO) and perovskite (ABO₃) blocks, represented by the Ruddlesden-Popper phases [1].

The excellent chemical and thermal stability of cobaltites perovskite related oxides that belong to the Ruddlesden–Popper (R–P) series with the general formula $A_{n+1}Co_nO_{3n+1}$ ((ACoO₃)_nAO) (A=Rare and/or alkaline earth elements), in which the multiple perovskite layers that are n octahedra thick alternate with single AO rock salt layers makes them very attractive materials as IT-SOFC [2,3], which are the object of study for this work.

We present in this communication the structural characterization and electrochemical properties of new members of Ruddlesden–Popper (R–P) series (Nd,Sr)_{n+1}Co_nO_{3n+1} as promising cathode materials for intermediate temperature SOFC. The effect of Mn/Fe doping on the electrical conductivity, chemical compatibility, and electrochemical performance is presented.

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In situ XAS study of the a strontium substituted cobalt perovskites

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Research field: Solid stated chemistry and applications.

Abstract:

Oxides with perovskite structure (ABO₃) are of interest because of their electric, magnetic or catalytic properties. Many papers have been published related to the partial substitution of atoms A and/or B. Sr doped cobaltites have been investigated, and some authors have found that the spin configuration of the LaCoO₃ changes by introducing Sr(II) atoms. But there is no agreement about the origin of these characteristics: formation of Co(IV) ions or oxygen vacancies.

Two cobaltites, LaCoO₃ and La_{0.5}Sr_{0.5}CoO_{3- δ}, have been studied by Co K-edge XAS. The substitution of La(III) by Sr(II) species induces changes in the reactivity and electronic state of the perovskite, while little or no changes can be detected in the formal oxidation state of cobalt atoms. The presence of Sr induces a modification in the electronic behavior of the perovskite, but maintaining the oxidation state of cobalt atoms (Co³⁺). So, oxygen vacancies are formed throughout the network, increasing the reactivity of the perovskite, now much more reducible than the original perovskite. By reduction and oxidation, the structure of the perovskite can be recovered, although in a disordered state. As detected by *in situ* XAS, the reduction treatment produces metallic cobalt in the Sr-perovskite, while after the oxidation treatment a Co(III) phase with spinel structure is obtained. Surprisingly, no Co(II) species are detected in this new spinel phase.

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Nanoparticles Pt-Cu: In situ analysis by DRX and NAP-XPS

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Research field: Solid stated chemistry and applications.

Abstract:

Preferential oxidation of CO in an excess amount of hydrogen (PROX) is an important process for obtaining CO-free hydrogen for proton exchange membrane fuel cells (PEMFCs). Pt-Cu based catalysts are one of the most studied catalysts because it suppresses side reactions like rWGS, they are chemically and mechanically resistant to temperature cycling due to start-up/shut-down procedures during fuel processors real operation. Recently, there are numerous studies of Pt-Cu nanoparticle based catalysts for PROX reactions [1].

In this work, Pt-Cu nanoparticles of controlled size and morphology were synthetized. Structural composition was studied by XRD in a temperature chamber. We apply the Soleil Synchrotron illuminated near ambient pressure X-ray photoelectron spectroscopy to study the surface structure modification of a Pt-Cu model system [2]. We used an energy source of 200eV to study Pt 4f and Cu 3p core levels. The escape depth was 0,5 nm. We found that, after temperature treatment, there are surface and structural composition variation in the nanoparticles (figure 1).



Figure 1. Surface and structural composition variation studies by XRD and NAP-XPS.

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Ammonia Effects on Proton Conductivity Properties of Coordination Polymers.

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Research field: Solid state chemistry and applications.

Abstract:

Crystalline metal phosphonates are referred to as a type of structurally versatile coordination polymers [1]. Many of them contain guest molecules (H₂O, heterocyclics, etc.), acidic sites and, furthermore, their structure can be also amenable for post-synthesis modifications in order to enhance desired properties [2].

In the present work, we examine the relationships between crystal structure and proton conductivity for several metal phosphonates derive from multifunctional ligands, such as 5-(dihydroxyphosphoryl)isophthalic acid (PiPhtA) [3] and 2-hydroxyphosphonoacetic acid (H₃HPAA). Crystalline divalent metal derivatives show a great structural diversity, from 1D to 3D open-frameworks, possessing hydrogen-bonded water molecules and acid groups. These solids present a proton conductivity range between $7.2 \cdot 10^{-6}$ and $1.3 \cdot 10^{-3}$ S·cm⁻¹. Upon exposure to ammonia vapor, from an aqueous solution, solid state transformations are observed accompanied of enhance proton conductivities. The stability of these solids under different environment conditions (temperature and relative humidities) as well as the influence of the ammonia adsorption on the proton conduction properties of the resulting solids will be discussed.

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Variable temperature study of the Verwey structure of magnetite

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Research field: Solid state chemistry and applications

Abstract:

The electronic state of magnetite (Fe₃O₄) has been studied extensively for over 75 years since Verwey proposed a charge ordering of Fe²⁺ and Fe³⁺ ions below the 125 K transition temperature.[1] At this temperature a discontinuity is observed in most physical measurements, including an increase in resistivity of two orders of magnitude.[1] The charge order of these octahedral B sites in spinel-type AB₂O₄ could not be verified during earlier studies due to the complexity of the low temperature superstructure, and significant crystallographic challenges.

Recently, an unconstrained refinement of all atomic coordinates within the full *Cc* supercell was achieved through the use of microcrystal X-ray diffraction of a 40 μ m grain at 90 K.[2] This revealed charge and orbital ordering of the degenerate Fe²⁺ t_{2g}⁴e_g² states, confirming Verwey's original hypothesis to a first approximation. However, additional structural distortions in which the B site Fe-Fe distances are anomalously shortened show that the Fe²⁺ states are not fully localised, instead forming linear three-site polarons known as trimerons. This orbital molecule description is also supported by DFT bandstructure calculations.[3]

Here we report the detailed crystal structure study of magnetite between 20 K and the Verwey transition and the associated changes in the complex Verwey structure with temperature.

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Magnetic Study of Spin Transition in a Dinuclear Iron(II)

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Research field : Solid state chemistry and applications

Abstract

From its discovery in the 1930's till now, spin crossover has been the subject of extensive applications. One of the problems remaining is the ability to organize at will spin crossover systems with the desired properties, since spin crossover remains an elusive property very much depending on the surroundings of the metallic center.

In this context, a very interesting family is the bis(pyrazolyl)pyridine one. With these analogues of the widely-used terpyridine system, many of their homoleptic complexes show spin crossover behaviour [1]. It has also been shown in our laboratory that many complexes can be photoconverted at low temperatures, with long lifetimes of photoexcited high-spin state [2a,b]. They constitute thus interesting building blocks for the obtention of organized systems.

During the course of our present investigations of functionalized subunits of the kind, we have also looked at the possibility of controlling the coordination behaviour of bis(pyrazolyl)pyridine ligands through the use of blocking ancillary ligands. This poster will show the results we have found with pseudohalogens in particular thiocyanate and selenocyanate.

The complexes { $[Fe(3-bpp)(NCS)_2]_24,4'$ -bpy} was synthesized in good yield. The infrared spectrum of the powder showed only one absorption in the cyanide region at 2079 cm⁻¹. The complex crystallizes in the centrosymmetric $P2_1/n$ space group with an inversion center lying in the middle of the 4.4_-bipyridine moiety. On the high-energy end, a strong absorption takes place below 600 nm, which corresponds to both the MLCT (metal-to-ligand charge transfer) and the d–d bands of the LS (low-spin) state of the complex. The other absorption band centered around 820 nm is very likely to be the d–d transition band of the HS (high-spin) state. A further decrease in the temperature to 80 K led to some changes in the valley around 700 nm and an apparent shift in the high-energy.

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STRUCTURAL FEATURES AND PROPERTIES OF Pr_{2-x}M_xRu₂O₇ PYROCHLORES

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Research field: pyrochlores, magnetic and electric properties.

Abstract:

Most of the $A_2B_2O_7$ ternary oxides present the pyrochlore structure. This structure is cubic and belongs to the *Fd-3m* space group, the A cation being placed in a distorted cube with 8 coordination and the B cation being hexacoordinated and located in a trigonal antiprism . The $A_2B_2O_7$ pyrochlores have been the subject of a great number of studies because, when B cation is a magnetic transition metal, they show magnetic frustration together with very interesting electrical properties [1-3]. Moreover, some pyrochlores can be used as catalysts or electrocatalysts [4] or as conducting components in thick-film resistors [5].

 $Pr_2Ru_2O_7$ was first prepared by Montmory *et al.* in 1959 [6]. Its magnetic properties were studied by Hinatsu *et al.* showing a spin glass behavior below the 150 K transition temperature [2]. But, on the other hand, more recent studies by Seshadri *et al.* define an antiferromagnetic behavior [7].

In an attempt to obtain new materials with eventually interesting electronic, i. e. magnetic and electrical properties, praseodymium partial substitution for strontium and calcium has been performed yielding the solid solution Pr_{2-x}M_xRu₂O₇ (M=Sr, Ca). Results obtained by X-ray diffraction, transmission electron microscopy and magnetic and electric measurements will be presented and discussed in the present communication.

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Synthesis and Impedance Spectroscopy of doped Zirconia based Ionic Conductors

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Research field: Solid state chemistry and applications.

Abstract:

lonic conductors are very interesting for many industrial applications, for example, pure ionic conductors can be used as oxygen sensors or as electrolytes for SOFCs (solid oxide fuel cells) [1], and mixed ionic-electronic conductors are extensively used as membranes in separation processes of O_2 , H_2 , etc. [2]. Generally, a mixed oxide is able to accommodate defects or oxygen vacancies in its lattice by doping or substitution of some cations for an aliovalent metal ion, creating ionic or mixed conductivity in stable structures, like perovskite structures [2, 3, 4].

In this context, and in order to improve catalytic reactions where the water diffusion is a ratelimiting step, it has been synthesized ZrO_2 doped with 5, 7 and 12 mol. % of Eu_2O_3 . The synthesis was carried out by a co-precipitation method at pH 8 using their nitrates as precursors. The characterization by XRD showed the formation of the solid solution in all cases. N₂ physisorption, XRF spectrometry, X-Ray Photoelectron Spectroscopy (XPS) and Transmission Electron Microscopy (TEM) were also measured to characterize the mixed oxides.

The conductivity of these materials was analyzed by impedance spectroscopy over a frequency range 100 Hz to 4 MHz with an ac voltage of 0.1 V. The experiments were evaluated from room temperature to 700 °C in Ar, O_2 /Ar and H_2O /Ar atmospheres, thereby studying O_2 and H_2O pressure influences. The results show pure ionic conductors ($E_a \approx 1 \text{ eV}$) and the effects in the conductivity behaviour when water is used, indicating the conduction of H⁺ and/or OH⁻ ions happens. It is also observed the influence of europium amount in the mixed oxide, having a maximum in the conductivity for 5 mol. % of Eu₂O₃ compound.

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Rh/MgAl₂O₄ structured catalyst for syngas production via dry reforming of biogas

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Research field: Solid state chemistry and applications

Abstract: Synthesis gas (syngas), mainly composed by H₂ and CO, is a key intermediate in the chemical industry for several highly selective syntheses of a wide range of chemicals and synthetic fuels [1]. The syngas production is possible from almost any carbon source ranging from natural gas and oil products to coal and biomass. During decades, conversion of natural gas into liquid fuels has been discussed as an interesting route to the exploitation of biogas coming from e.g wastewater treatment plants [2]. Catalytic autoreforming of biogas, which composition vary between 50-70% of CH₄ and 50-30% CO₂, is feasible via dry reforming of methane (DRM). Most widely used catalyst in DRM are based on nickel, but rapidly deactivation due to carbon deposits make them not useful since biogas high methane contain. Then, the catalyst properties are dictated by the severe operating conditions, including temperatures of 450-950 °C and coke Thus, there is a need to develop a thermally stable catalyst that will resist formation. deactivation due to carbon deposition and sintering [3]. For that propose, rhodium over MgAl₂O₄ catalyst is chosen since dissociation of CH₄ is thermodynamically most favorable over Rh compared to other transition metals [4] and formation of MgAl spinel, in which the Al and Mg form the spinel framework and some basic Mg remains on the surface, acts as a promoter in activation of CO₂ and promotes oxidation of surface carbon [5]. Additionally, the use of metallic monoliths structure as catalyst substrate is well known alternative compare with powder catalyst, as enhance heat and mass transport and decrease pressure drop in conventional fixed beds reactors [6]. In the present work, 1%Rh structured catalyst is synthesized, characterized and evaluated in dry reforming condition. Rhodium average particle size, measured by TEM, remains 1.7 nm after the activation step (50 ml/min of H₂ diluted by N₂ at 800 °C) before the catalytic test. Carbon dioxide conversion present higher values than methane, in the range 150-1300 L/g/h space velocity, indicate the presence of RWGS contribution, which increase notably if residence time decrease. As a consequence H_2/CO also decrease since methane loosed activity. Otherwise. using biogas inlet composition compared with CH₄/CO₂=1, temperature screening shown up to 600°C, %CO₂ is maintain constant, while methane overflow is not converted. Nevertheless, selectivity were preserved in the range $CH_4/CO_2=1-1.5$.

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SSC - 18

Electrochemical oxidation influence in molybdocuprates with «1212» structure

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Research field: Solid state chemistry and applications

Abstract:

Cuprates with «1212» structure present the same structure as YBCO where the cupper situated in chains positions is partially replace by a transition metal (molybdenum in this case) [1]. In the present work $Mo_{0.3}Cu_{0.7}Sr_2TmCu_2O_{8-\delta}$ is studied.

In order to achieve the superconducting state, this cuprates family needs an oxidation process. It can be carried out by several methods as oxygen conventional annealing or high pressure oxidation with KCIO₃ [2,3]. In our case we are centered in a much less used method: electrochemical oxidation. It consists in the application of an electrical current/potential (galvanostatic/potentiostatic procedure) to the electrochemical cell, whose working electrode is a sintered pellet of the material concerned. Oxygen species are generated *in situ* by the decomposition of the electrolyte (water electrolysis in basic media).

In the electrochemical study of $Mo_{0.3}Cu_{0.7}Sr_2TmCu_2O_{8-\delta}$ we have found a superconducting material by potentiostatic (T_c=18K) and galvanostatic (T_c=44K) procedure measured by electrical resistivity.

On the other hand interesting redox equilibrium takes place in the oxidized state studied by XPS:

 $Mo_{0.12}^{V}Mo_{0.18}^{VI} + Cu_{2.28}^{II}Cu_{0.41}^{III}$ $Mo_{0.19}^{V}Mo_{0.20}^{VI} + Cu_{2.39}^{III}Cu_{0.31}^{III}$

After electrochemical oxidation cupper decreases its oxidation state and molybdenum increases it (contrary to the usual behavior in other superconductors like YBCO).

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Structures and Magnetic Properties of 12-Layered Perovskites $Ba_4LnM_3O_{12}$ (*Ln* = rare Earths; *M* = Ru, Ir)

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Research field: Solid state chemistry and applications

Abstract:

Preparation, crystal structures and magnetic properties of guaternary rare earth oxides $Ba_4LnM_3O_{12}$ (*Ln*=Rare earths; *M*=Ru, Ir) were investigated. From the powder x-ray and neutron diffraction measurements, it was found that *M* ions are octahedrally coordinated by six oxide ions, and three MO_6 octahedra share faces forming a M_3O_{12} trimer, and that the M_3O_{12} trimers and LnO_6 octahedra are alternately linked by corner-sharing and form the perovskite-type structure with 12 layers (Fig. 1). The change of lattice parameters a, b, c, and β for $Ba_4LnM_3O_{12}$ against the ionic radius of Ln^{3+} show that except for the compounds having Ln = Ce. Pr. and Tb. they increase monotonously with the Ln^{3+} ionic radius. However, the values for Ln = Ce, Pr, and Tb compounds are considerably smaller than this trend. For both M = Ruand Ir cases, the Ln-O bond lengths are close to the $Ln^{4+}-O^{2-}$ lengths calculated from Shannon's ionic radii. These results show that the Ce, Pr,



Figure 1: Crystal structure of $Ba_4LnM_3O_{12}$

and Tb ions are in the tetravalent state. Therefore, the oxidation states of Ru and Ir are also tetravalent ($Ba_4Ln^{4+}Ru^{4+}_{3}O_{12}$, $Ba_4Ln^{4+}Ir^{4+}_{3}O_{12}$). For other Ln ions, the mean oxidation state of Ru and Ir ions is +4.33 (Ba₄ Ln^{3+} Ru^{4.33+}₃O₁₂, Ba₄ Ln^{3+} Ir^{4.33+}₃O₁₂).

Measurements of the magnetic susceptibility for $Ba_4LnM_3O_{12}$ give the contrastive results between the ruthenium-containing compounds Ba₄LnRu₃O₁₂ and the iridium-containing compounds Ba₄LnIr₃O₁₂ (Table 1). Any of the $Ba_4Ln^{3+}Ru^{4.33+}{}_{3}O_{12}$ compounds shows similar magnetic transitions at very low temperatures, whereas $Ba_4Ln^{3+}Ir^{4.33+}{}_{3}O_{12}$ ($Ln \neq La$, Lu) compounds are paramagnetic down to 1.8 K. Magnetic properties of $Ba_4Ln^{3+}Ir^{4\cdot33+}_{3\cdot}O_{12}$ clearly show that we have to treat the Ir ions as the Ir₃O₁₂ trimer to understand their magnetic behavior. Both compounds $Ba_4Ln^{3+}Ir^{4,33+}{}_{3}O_{12}$ (*Ln* = La, Lu) are diamagnetic, indicating that the $Ir^{4,33+}{}_{3}O_{12}$ trimers are diamagnetic. Other compounds $Ba_4Ln^{3+}Ir^{4\cdot33+}_{3}O_{12}$ (i.e., $Ln \neq$ La, Lu) are paramagnetic down to 1.8 K, and their effective magnetic moments (μ_{eff}) are close to the magnetic moments of Ln^{3+} ions (μ_{ln}). That is, the contribution of the $Ir^{4.33+}_{3}O_{12}$ trimer to the magnetic properties of $Ba_4LnIr_3O_{12}$ is negligible.

 $Ba_4Ce^{4+}Ir^{4+}_{3}O_{12}$ orders antiferromagnetically at 10.5 K, while the corresponding ruthenium-containing compound Ba₄Ce⁴⁺Ru⁴⁺₃O₁₂ is paramagnetic. These magnetic results are



effective magnetic moments and the entropy change for the magnetic ordering show that the trimers $Ru^{4.33+}{}_{3}O_{12}$ and $Ir^{4+}{}_{3}O_{12}$ have the S = 1/2 ground state, and in other cases there is no magnetic contribution from the trimers $Ru^{4+}{}_{3}O_{12}$ or $Ir^{4.33+}{}_{3}O_{12}$.

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Table 1: Magnetic properties of Ba₄*LnM*₃O₁₂

| | Valence | Magnetic properties | |
|----|----------|------------------------------|--------------------|
| Ln | state of | (Transition temperature / K) | |
| | Ln ion | $Ba_4LnRu_3O_{12}$ | $Ba_4LnIr_3O_{12}$ |
| La | 3+ | AF(6.0) | Dia |
| Ce | 4+ | CW | AF (10.5) |
| Pr | 4+ | AF (2.4) | AF (35) |
| Nd | 3+ | F (11) | CW |
| Sm | 3+ | AF (3.2) | van Vleck |
| Eu | 3+ | AF (4.0) | van Vleck |
| Gd | 3+ | AF (2.5) | CW |
| Tb | 4+ | AF (24) | AF (16) |
| Dy | 3+ | AF (30) | CW |
| Но | 3+ | AF (8.5) | CW |
| Er | 3+ | AF (8.0) | CW |
| Tm | 3+ | AF (8.0) | CW |
| Yb | 3+ | AF (4.8) | CW |
| Lu | 3+ | AF (8.0) | Dia |

AF:antiferromagnetic, F:ferromagnetic, CW:Curie-Weiss, Dia:diamagnetic

High UV-photocatalytic activity of ZnO synthesized by three different procedures: A comparative assessment

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Research field. Solid state chemistry and applications.

Abstract:

Heterogeneous photo-catalysis is an Advanced Oxidation Process (AOP), which has been the subject of numerous studies and applications, particularly using TiO₂ (P25) commercial oxide. ZnO has often been considered a valid alternative to TiO_2 because of its good optoelectronic, catalytic and photochemical properties along with its low cost. With the aim to improve the photocatalytic performance of ZnO for practical applications, various kinds of synthetic approaches, including conventional method using aqueous different precursors, hydrothermal/solvothermal growth, sol-gel method, ultrasonic assisted method and chemical vapor deposition, have been developed to prepare ZnO particles with different sizes and morphologies. However, all of these methods require severe reaction conditions such as high temperature, sophisticated techniques, high purity of gas, adjustable gas flow rate, expensive raw materials and so on. Hence, it is important to find a simple and cost-effective method for the synthesis of ZnO nanocrystals. In the present study, we have synthesized ZnO by three different procedures: conventional precipitation method, hydrothermal method and microwaveassisted methods. The following flowchart illustrates the synthesis procedure thereof.



In all three procedures, the same material is obtained, the hydrocincite, which evolves into crystalline ZnO after calcination heat treatments. We have investigated the effect of annealing temperature in the final surface and structural properties. Photocatalytic studies were performed using two selected substrates, Methyl Orange and Phenol, as model substrates. Calcination treatment leads to a significant improvement in the photocatalytic properties up to 500°C for 2 h. Chosen a calcination temperature (400°C) no significant variation was observed in the photocatalytic activities of ZnO obtained by the three methods, so using the preparation by a coprecipitation method, instead of a hydrothermal or microwave assisted method, would be more simple.

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Remarkable enhancement in photocatalytic activity of {001} faceted TiO₂ loaded with Pt

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Research field : Solid state chemistry and applications

Abstract:

One of the most important goals in photocatalysis research continues to be increasing the photocatalytic activity of TiO_2 . For this, among other strategies, metal noble deposition has been widely studied [1] as well as changing anatase crystal morphology to obtain a higher exposition of the more reactive anatase {001} facets [2]. In the present work, both effects have been combined and the influence of Pt deposition on highly reactive 001 facets of TiO_2 for phenol (a well known aromatic contaminant) and methyl orange (widely used dye) photodegradation has been studied

Photodeposition of platinum using hexachloroplatinic acid as metal precursor was carried out over the TiO₂ powder obtained with a large percentage of highly reactive (001) facets exposed prepared by hydrothermal method using different TiO₂ precursors (titanium tetraisopropoxide and titanium butoxide) in the presence of HF as facet controlling agent. The materials were widely characterized and evaluated in the degradation reactions of both substrates under UV illuminationWith the Pt deposition, the enhancement on photodegradation rate of phenol was about 25% regarding the original faceted TiO₂ and about 40% compared to commercial P25. With methyl orange the photodegradation rate exceeded about 50% of the rate obtained over TiO₂ P25 (figure 1).



Figure 1. Initial reaction rates for (a) phenol and (b) methyl orange photo oxidation

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Modifying the superconducting properties in the Fe_xCu_{1-x}YSr₂Cu₂O_y system

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Research field: Solid state chemistry and applications.

Abstract:

Among the factors which are recognized to drive the critical temperature in copper oxide high temperature superconducting cuprates (i.e. number of planes) the local structure around the apical position seems to play a major role. This region of the structure connects the charge reservoir layers to the superconducting planes, controlling the charge transfer process. This process can be modified through partial substitution of copper in the YBCO (123) type structure by other transition metals, leading to the so called M-1212 phases.

Previous results in the study of the $M_xCu_{1-x}RESr_2Cu_2O_y$ (M=Mo; RE= Y, Er, Tm) system [1], show an unexpected relation between the apical distance (Cu(2)-Oap), the O(2)-Cu(2)-O(2) buckling angle and the resulting Tc [2]: the critical temperature increases with decreasing the apical distance and with increasing the buckling angle. Moreover, these structural changes are accompanied by cationic redox equilibrium: molybdenum is oxidized while copper is reduced [3].

In order to evaluate if this tendency is spread over other M-1212 cuprates, we are extending the study to the $Fe_xCu_{1-x}YSr_2Cu_2O_y$ system [4]. Iron could adopt several oxidation states and coordination geometries within the mentioned redox process. Aiming this, several samples of compositions $Fe_xCu_{1-x}YSr_2Cu_2O_y$ (x = 0.25-0.5) have been subjected to different treatments: low temperature oxidizing/reducing annealing, ozonization, electrochemical oxidation and combinations of these treatments. The resulting magnetic and electrical behaviour is shown in this communication.

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SSC - 23

Rare earth RE(= Pr, Nd, Gd and Tm) influence in the superconducting properties of the Mo_{0.3}Cu_{0.7}Sr₂RECu₂O_y system

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Research field: Solid State Chemistry and applications

Abstract:

Since the discovery of high temperature superconductivity in the La-Ba-Cu-O family, with a critical temperature T_c of 30 K, by Bednorz and Muller in 1986 [1], cuprates have attracted the focus on this field. The subsequent appearance of YBCO in 1987 [2] put T_c above the nitrogen boiling point (77 K). In order to search for new superconducting materials based on YBCO the substitution of Barium by Strontium was proposed. Nevertheless, due to the crystal and ionic size restrictions, this compound can only be prepared at high pressure conditions [3]. However, the partial or total substitution of Copper, placed in the basal plane Cu-O chains by certain elements allows the synthesis to be performed at ambient pressure and high temperatures [4].

Molybdenum introduction, partially replacing copper has been widely studied in the last few years in our research group. Our aim is focused in the search of correlations between composition –including oxidation states- structure –in particular apical distances (Cu-O_{apical}) and buckling angles β <> Cu-O-Cu- and Tc. In this sense, we have found an opposite trend to the commonly-accepted one. Moreover, this interesting dependence is accompanied by complex red-ox equilibrium between Copper and Molybdenum [5].

In the present work, we study the role of the rare earth on the $Mo_{0.3}Cu_{0.7}Sr_2RECu_2O_y$ (RE= Pr, Nd, Gd y Tm) system. These compounds have been prepared by the ceramic method and treated under different oxidation conditions. Structural characterization, magnetic properties and transport measurements will be presented and discussed.

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Rutheno-Cuprates 1212: Cu/Ru substitution at room pressure

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Research field: Solid State Chemistry and applications

Abstract:

The coexistence between the antagonistic properties of ferromagnetism (FM) and superconductivity (SC) has been widely studied in the last decades in the family of ruthenocuprates (RuSr₂RECu₂O₈) and still remains under focus [1, 2]. In RuSr₂RECu₂O₈ phases, also known as 1212 HTSC materials, it has been observed (only in certain conditions of very low magnetic fields or in resistivity measurements) a critical temperature T_c of the order of 30 K and a Néel temperature T_N around 164 K. It is also known that these materials can only be prepared at room pressure, when RE = Gd, Sm or Eu [3,4].

We show here that the, partial substitution of Ruthenium by Copper, allows the synthesis to be done at room pressure and, also, produces a substantial modification in the physical properties: an increase in Tc (~40%) and a decrease in T_N of about 10% to ~130 K. This compound has been prepared by the ceramic method and treated under an oxygen atmosphere. Powder X-Ray Diffraction and Selected Area Electron Diffraction have been performed to characterize the structure. Also, the magnetic and superconducting properties have been measured in a Physical Properties Measurement System (PPMS) and a Superconducting Quantum Interference Device (SQUID)

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ULTRASONIC METAL WELDING – THE INFLUENCE OF POLYMER ADDITIVES

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Research field: Solid state chemistry and applications

Abstract:

PVC is considered one of the most versatile polymers due to their ability to react with various additives before being processed into final products. By the choice within a wide range of chemicals, it is possible to obtain PVC compounds with the necessary features for each application. [1] There are a large number of variables that affect the properties of PVC such as the degree of crystallinity, the glass transition temperature, molecular weight or morphology. The mechanical, thermal or chemical properties of the manufactured product may have specific characteristics, primarily due to two main factors: 1) Inclusion of appropriate additives in PVC formulations (plasticizers, pigments, lubricants, colorants, flame retardants, etc.) and 2) a variety of manufacturing processes such as extrusion, injection, etc. [2]

In the insulation of cables, PVC is used in the flexible form, but due to PVC thermal instability, processing it is virtually impossible without the addition of additives. The additives are generally high molecular weight thermoplastic and are added in small quantities with three main functions, accelerate the fusion process; improve the rheological and mechanical properties. [2] The biggest disadvantage of PVC is the easiness to degrade by the action of temperature or ultraviolet radiation. [3,4]

The principle of ultrasonic assembly involves the use of high-frequency mechanical vibrations transmitted through the parts to generate a frictional heat build-up at an interface. It is known that moisture inhibits ultrasonic welding but when welding metal materials like copper alloys it was not expected to have influence coming from cable insulations. [5]The machine should be able to weld over copper alloys oxidized or with certain contamination coming from the plastic insulation. [6,7]

During the time it was seen that whenever the insulation is made of PVC the instability of ultrasonic welding increases versus other type of insulations. In order to identify what are the main items influencing the ultrasonic welding process ability, a study was conducted using electrical cables with PVC insulation.

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Crystal structure of new polyoxometalate/ionic liquid hybrids and their application in catalysis

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Research field: Solid state chemistry and applications

Abstract:

New hybrid systems based on phosphomolybdic acid and three different ionic liquids were synthetized as previously reported [1]. For the $\text{Emim}_3[\text{PMo}_{12}O_{40}]$ (from this point forward Emim-Mo) synthesis, appropriate quantities of prepared $\text{H}_3\text{PMo}_{12}O_{40}$ (0.9 g) and 1-ethyl-3-methylimidazolium methanesulfonate (Alfa Aesar) were dissolved in distilled water (20 mL) separately. When mixed, a precipitate was formed, then filtered and dried at room temperature. Another two hybrids were analogously prepared by using 1-butyl-3-methylimidazolium methanesulfonate (Sigma Aldrich) to produce the $\text{Bmim}_3[\text{PMo}_{12}O_{40}]$ (Bmim-Mo) and 1-hexyl-3-methylimidazolium chloride (Alfa Aesar) for $\text{Hexmim}_3[\text{PMo}_{12}O_{40}]$ (Hexmim-Mo). After completely drying the precipitate under low pressure, the product was recrystallized from an equal volume mixture of acetonitrile and acetone. Upon standing at room temperature for 7 days, yellow crystals were formed, which were used for single crystal X-ray diffraction analysis.

The catalytic activity of all systems was evaluated in the isomerization of glucose to fructose at different temperatures. The results are presented in Fig.1.



Fig. 1. Glucose conversion at different temperatures (100% selectivity to fructose in all cases)

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Ruthenium nanoparticles in CO₂ methanation: influence of the synthesis method in catalytic behaviour

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Research field: Solid state chemistry and applications

Abstract:

A series of Ru/Al₂O₃ catalysts using ruthenium nanoparticles were obtained by means of two different synthesis methods: polyol method [1] and w/o microemulsions [2], modifying the Ruto-surfactant molar ratio and the water-to-surfactant ratio respectively, in order to control the size of the metallic particles. The characterization results demonstrate that, in both cases, the higher the concentration of surfactant the smaller the size of the Ru nanoparticles. Additionally, the obtained catalysts were tested in CO_2 methanation reaction. Catalysts prepared using the polyol method are highly active and 100% selective for this reaction while those prepared by microemulsions give the RWGS reaction and show lower activity, as seen in Figure 1. Selectivity towards CO_2 methanation seems to be related to the presence of carbonaceous species on the catalysts surface. Consequently the presented results remark the close influence of the synthesis method in the catalytic activity of Ruthenium nanoparticles.





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Efficient UV-photocatalytic activity of ZnO and Ag/ZnO synthesized by a facile method

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Research field: Solid state chemistry and applications.

Abstract:

ZnO has been tested in the decomposition of several dyes in aqueous solutions, as well as many other environmental pollutants [1]. In many cases, ZnO has been reported to be more efficient than TiO₂ [2] but the occurrence of photocorrosion [3] and the susceptibility of ZnO to facile dissolution at extreme pH values, have significantly limited its application in photocatalysis. In this work, ZnO nanoparticles have been successfully synthesized by a facile precipitation procedure by mixing aqueous solutions of Zn(II) acetate and dissolved Na₂CO₃ at pH ca. 7.0 without template addition. We have investigated the effect of annealing temperature in the final surface and structural properties. Photocatalytic studies were performed using two selected substrates, Methyl Orange (MO) and Phenol (Ph), both as single model substrates and in mixtures of them. The results are shown in the accompanying figures in terms of values of initial reaction rate of degradation for single substrates. It has been stated that calcination treatments lead to a significant improvement in the photocatalytic properties of the studied samples, even better than TiO₂(P25). As expected, the addition of Aq^+ during the photocatalytic degradation of MO increases the reaction rate of the degradation of MO, giving a resultant Ag/ZnO photocatalyst which, after recovery, can be reused at least 18 times for the MO degradation tests, being even more photoactive than ZnO.



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Solid solutions of layered tetrel antimony chalcogenides

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Research field: Materials Chemistry

Abstract:

Sulfosalt-like chain structures in the system Sn/Sb/Se include those of SnSb₂Se₄ [1] or SnSb₄Se₇.[2] SnSb₂Se₄ exhibits high Seebeck coefficients; however, the thermoelectric performance is limited by rather low electrical conductivity. Formally adding Na₂Se leads to Na₂SnSb₂Se₅, a NaCl-type compound (a = 5.978 Å). It is stable in air; increased ionicity leads to reduced electrical conductivity whereas thermal conductivity κ remains almost the same.

In the system Ge/Bi/Se, annealing stoichiometric mixtures leads to a homogenous GeBi₂Se₄, a new layered compound with GeSb₂Te₄ structure type.[3] Structure refinements as well as EDX data indicate a certain range of homogeneity, which may involve vacancies. Compared to Ge²⁺, Bi³⁺ concentrates the near the van der Waals gaps due to its higher formal charge. Thermal conductivities are low with $\kappa = ~0.5 \text{ Wm}^{-1}\text{K}^{-1}$ from room temperature up to 500 °C. Quenched samples contain a disordered and locally distorted NaCl-type phase (~Ge_{1.3}Bi_{1.4}Se₄, *a* = 5.74 Å). Heterogeneous samples were investigated by TEM and microfocused synchrotron radiation. HRTEM images show many defects and diffraction patterns exhibit various diffuse maxima, some of which indicate a partial (i.e. beginning) transition to the GeSb₂Te₄ structure type.

PbSb₂Te₄ and PbBi₂Te₄ form a complete solid solution series with GeSb₂Te₄-type structure.[4] Its properties as topological insulator have been discussed.[5] Concerning thermoelectric properties, our measurements show that the thermal conductivity of mixed crystals is decreased compared to ternary phases for all homologous phases PbTe[(Bi,Sb)₂Te₃]_m with m \leq 4. PbBi₄Te₇ and PbSb₄Te₇, for instance, are not completely miscible, but substitution with 12.5 % Sb in PbBi_{3.5}Sb_{0.5}Te₇ leads to $\kappa = 1.8 \text{ Wm}^{-1}\text{K}^{-1}$ compared to 2.6 Wm⁻¹K⁻¹ for pristine PbBi₄Te₇, resulting in an increase of the ZT value from 0.23 to 0.28 at 300 °C.

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Disorder-phonon coupling in crystal-like aperiodic solids

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Research field: Solid state chemistry and applications

Abstract:

Functional materials design usually focuses on structurally-ordered systems because the disorder is considered detrimental to many functional properties. This paradigm is challenged by or work, where particular types of strongly correlated disorder are shown to give rise to useful characteristics that are inaccessible in ordered states [1]. A combination of low-symmetry building unit and high-symmetry topological template leads to aperiodic "procrystalline" solids that harbour this type of disorder. We have identified key classes of procrystalline states together with their characteristic diffraction behaviour, and establish mappings onto known and target materials. The strongly-correlated disorder found in these systems is associated with specific sets of modulation periodicities distributed throughout the Brillouin zone. Lattice dynamical calculations reveal selective disorder driven phonon broadening [2] that resembles the poorly-understood "waterfall" effect observed in relaxor ferroelectrics [3]. This property of procrystalline solids suggests a mechanism by which strongly-correlated topological disorder might allow independently-optimised thermal and electronic transport behaviour, such as required for high performance thermoelectrics [4].

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Perturbation of the Verwey structure of Fe₃O₄

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Research field: Solid state chemistry and applications

Abstract:

Magnetite Fe₃O₄ is the oldest known magnetic material and has the cubic spinel structure *Fd-3m* at room temperature. Upon cooling it undergoes significant changes in its magnetism and conductivity at the Verwey transition T_V ~125K, accompanied by a structural transition first thought to be a charge ordering of Fe²⁺ and Fe³⁺ on the octahedral B-sites. The structure at low temperature was only recently solved; it is an acentric $\sqrt{2} \times \sqrt{2} \times 2$ monoclinic *Cc* superstructure with a complex charge ordering, involving distortions of linear Fe-Fe-Fe units into three-site polarons (called trimerons), coupled through orbital ordering and shared electron density [1].

The Verwey ground state of magnetite has been shown to be very sensitive to chemical perturbation, changing both the order of the transition and its temperature [2]. We investigated the modifications in the low temperature Verwey phase of non-stoichiometric $Fe_{3(1-\delta)}O_4$ and substituted $Fe_{3-x}Zn_xO_4$ magnetite samples as well as a natural sample. This poster presents the synthesis, characterisation and synchrotron X-ray diffraction on microcrystals of these modified magnetites.

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Mixed ionic-electronic conductors based on lanthanum molybdates

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Research field: Solid state chemistry and applications.

Abstract:

In this work, La₆MoO₁₂-based compounds were investigated as part of a new family of materials very competitive as PC-SOFC's electrolyte and hydrogen separation membranes [1,2].

La_{5.4}MoO_{11.1} was synthesized by the freeze-drying precursor method and the calcination conditions were optimized in order to obtain single phases. Several cooling rates were applied and different polymorphs were obtained: Fm-3m (quenching), R-3 (50 °C·min⁻¹) and R-3m (0.5 °C·min⁻¹). For the quenched sample, the structural description is satisfactory, however, for the other two compositions, some small reflections were not given any intensity by the model used. Transmission electron microscopy confirmed the presence of superstructures for those samples. All ceramic materials were obtained with relative densities close to 100% after sintering at 1500 °C. Stability studies demonstrated that all three polymorphs were stable in oxidizing and reducing conditions at 800 °C for 48 hours.

All samples present a significant proton contribution to the conductivity at temperatures lower than 800 °C. These results were confirmed by thermogravimetric analysis. The highest conductivity values were observed for the samples prepared by quenching. The three polymorphs present a small p-type electronic contribution to the overall conductivity in oxidizing conditions and n-type electronic one in very reducing conditions, much more significant for the samples cooled by quenching and at 50 °C·min⁻¹.

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Magnesium Secondary Battery:

New electrolytes and cathode materials

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Research field: Solid state chemistry and applications.

Abstract:

Magnesium is one of the alternatives to lithium for battery because of its abundancy, low cost and high energy density. Research on magnesium battery began in the 80s and has led to the first magnesium secondary battery reported by Aurbach in 2000.[1] However, two challenges are still remained for magnesium to compete with lithium ion battery: development of highenergy-density cathode material. Oxides, sulfurs and polyanions derivatives are the most studied materials for the positive electrode.[2] The second challenge concerns the electrolyte which should have a large electrochemical window and should allow plating and striping of magnesium on the negative electrode. Carbonated solvent, (poly)ethers and lonic liquids are mostly used with bis(trifluoromethylsulfonyl)imide, triflate or perchlorate magnesium salt as electrolytes.

Our researches are focused on the study of vanadium oxide derivatives for positive electrode of magnesium battery. Furthermore, ionic liquid-based electrolytes will be investigated.



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Synthesis, Physico-chemical and Electrochemical Characterizations of Na₄VO(PO₄)₂ as Cathode Material for Na-ion Batteries

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Research field: Solid state chemistry and applications.

Abstract:

Regarding the field of energy storage, the design of new materials that are showing high ionic mobility together with being economic and environmental benign is crucial [1].. Our research is focused on the synthesis and the exploration of new frameworks with large tunnels or layered structures that could be used as high potential electrode material for Na ion batteries [2, 3]. In this presentation, we will discuss on the sodium vanadium phosphate phase Na₄VO(PO₄)₂, prepared by a conventional solid state route. This phase is showing a one-dimensional structure built up of corner shared VO₆ and PO₄. The electrochemical properties of Na₄VO(PO₄)₂ was studied as a positive electrode in a sodium ion battery. The first results show the possibility of extracting one sodium through a two-phase process in redox potential of 3.4V versus Na⁺/Na. The structural transformations occurring during the insertion and extraction process will be discuss [4].

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SSC - 35

An active Li-Mn-O compound for high energy density Li-ion batteries

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Research field: Solid state chemistry and applications.

Abstract:

Due to their low weight, high energy densities and long cycle life, the battery scientific community is still trying to develop new high capacity cathodes materials in order to increase the energy density of storage devices [1].

After a composition screening, a new material family has been discovered in the Li-Mn-O system and has been investigated as potential new material for Li-ion batteries to replace conventional NMC materials ($\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$) [2]. In this study, we report for the first time the synthesis, structural and electrochemical characterizations of a new non-lamellar oxide with the highest capacity observed ever before in the Li-Mn-O system. This new patented [3] material with the composition of Li₄Mn₂O₅ shows a discharge capacity of 300 mAh/g. It is a rock-salt type nanostructured material (a = 4.16Å), prepared by a direct mechanochemical synthesis.

The electrochemical performances were performed at a C/20 rate, and show a reversible discharge capacity about 300 mAh/g. During cycling, the derivative curves indicate at least two active redox couples [4]: Mn^{3+}/Mn^{4+} (around 3.3V), Mn^{4+}/Mn^{5+} and/or O^{2-}/O^{-} (around 4.1V). In order to have a better insight of lithium deinsertion process, we used magnetic measurements at various charge states. We will show that magnetic measurements are perfect tools to access to the oxidation level of the material, and in agreement with the values obtained after iodometric redox titrations. We will namely show that this material is oxidized up to Mn^{5+} oxidation state with a competition of the oxygen oxidation [4-5].

In short, in this work are reported the first results of a new electrochemically active compound as positive electrode for Li-ion batteries, with the active participation of both redox centers: Manganese and Oxygen [6].

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Fe[HO₃PCH(OH)CO₂]·2,5H₂O and doped metal derivates: photocatalytic properties

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Research field: Solid state chemistry and applications.

Abstract:

Metal-organic frameworks, and more generally coordination polymers, exhibit multifunctional properties derived from their structural versatility and the specific chemistry of both, the type of metal ion and organic linker [1]. The latter moiety may induce, indeed, a number of properties, such as structural rigidity or flexibility and pore functionality. However, the role of the metal ion in these structures is less studied.

In this communication we report the photocatalytic properties a Fe(II) phosphonate, Fe[HO₃PCH(OH)CO₂]·2,5H₂O, and the corresponding transition metal-doped derivatives for Advanced Oxidation Processes (AOPs) [2]. The possible synergistic effect of TiO₂ has been also studied in order to enhance pollutant removal from water. These systems show heterogeneous photo-Fenton catalytic properties for the degradation of phenol and/or methylene blue in the presence of UVA-Vis light. XRD, XPS and TEM were the techniques used to characterize thoroughly the photocatalysts.

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Obtainment of polyethyleneimine modified ZnO nanoparticles for bioanalytical applications

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Research field: Solid state chemistry and applications

Abstract:

The development of high sensitive, low-cost, reliable biosensors having an excellent selectivity is a key task for medicine, environmental protection and monitoring of chemical spills. Nanomaterial for bioapplications (for instance, zinc oxide (ZnO) nanoparticles) must possess specific physical properties (e.g., optical), be tolerant to surface modification and attachment to biomolecules such as antibodies, enzymes, etc, and also non-toxic and safe. However, stability of nanoparticle dispersions in buffer solutions, which is crucially important for practical use of nanoparticles, is still an issue. Polyethyleneimine (PEI) is a promising candidate both for ZnO nanoparticle stabilization and biofunctionalization.

This study aims to create PEI-modified biofunctionalized ZnO nanoparticles, stable in phosphate buffered saline (PBS). ZnO nanoparticles were synthesized in diethylene glycol media at 150 °C. Different strategies were utilized for ZnO nanoparticle modification in order to disclose the role of PEI in stability of colloidal system. Synthesized and modified ZnO nanoparticles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and infrared spectroscopy measurements, and stability of colloidal system was investigated using dynamic light scattering (DLS) data. Finally, ability of ZnO nanoparticles to attach proteins for potential analytical applications was proved using Bradford protein assay.

Among different strategies of modification, ZnO nanoparticles modified by trisodium citrate, PEI and glutaraldehyde (GA) have showed the best stability in PBS while preserving low aggregation level and high positive surface charge.

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Insertion of diols into a layered niobate.

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Research field: Solid State Chemistry

Abstract:

Ceramics such as those with the Ruddlesden-Popper or Dion-Jacobson structures have been shown to host various organic molecules.¹⁻² The key to this ability are layers of titanium and/or niobium oxide octahedra sandwiched between single layers of rock salt or metal ions. If the metal ions can be replaced with protons intercalation of bases such as amines become possible.

By intercalating an organic layer into the host structure additional functionality can be introduced to the ceramic. Hybrid materials such as these have been proposed for use as heterogeneous catalysts particularly photocatalysts ³ and for electronic devices.

HTiNbO₅, a compound with layered sheets of titanoniobate octahedra was chosen for our investigations. Previously, R-NH₂ have been successfully intercalated into HTiNbO₅⁴ and here we demonstrate the introduction of primary alcohols and diols into the structure. The diols are inserted into the ceramic layers by exchange of butylamine from (ButNH₃)_xH_{1-x}TiNbO₅ using a solvothermal vessel at 70 °C. The product is then filtered and dried in air before characterization by XRD, TGA and FTIR. Compared to diamines the diols appear to bind to the ceramic in a different way. Phenol and carboxylic acid based materials have also been investigated and their binding or lack thereof is discussed with reference to possible mechanisms of inclusion.

The expansion of the organic intercalates of $(TiNbO_5)^{-}$ to include diols further opens up opportunities for the expansion of functional organic-ceramic hybrids. The difference between the interactions of amines, alcohols and diols illustrates the importance of investigating different functional groups for intercalation along with the proven amines.

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Effect of preparation pH on Bismuth Titanate materials with high visible light photocatalytic activity

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Research field : Solid state chemistry and applications

Abstract:

Bismuth titanates have attracted increasing interest in the last years due to their reported photocatalytic activity under visible irradiation [1]. Among the family of titanates, Bi₄Ti₃O₁₂ has been the most widely studied material, however the metastable Bi₂₀TiO₃₂ has also shown interesting photocatalytic properties [2]. In this work, Bi-Ti-O powders were hydrothermally synthesized at different pHs and a full characterization to the obtained materials was performed. The pH value during the synthesis was proven to have a crucial influence on the phase composition and properties of the materials. The photocatalytic activities of the catalysts obtained were evaluated in the degradation of phenol (a well known aromatic contaminant) on aqueous solution under visible light irradiation.



Figure 1. Initial reaction rates for phenol photo oxidation over the different materials

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SSC - 40

Synthesis and scale-up of non-active and active Belite-Alite-Ye'elimite clinker (BAY)

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Research field: Solid state chemistry and applications.

Abstract:

Ordinary Portland cement (OPC) is an environmentally contentious material, as for every ton of OPC produced, ~0.97 tons of CO₂ are released. This opens the need of designing new formulations of cements formed by low calcite-demanding phases, such as ye'elimite, that release less CO₂ during their fabrication. Belite-Alite-Ye'elimite (BAY) cements are promising eco-friendly building materials as OPC substitutes at a large scale [1]. The reaction of alite and ye'elimite with water should develop cements with high mechanical strengths at early ages, while belite will contribute to later curing times. However, they develop lower mechanical strengths at early-medium ages than OPC [2]. It is known that the presence of different polymorphs of belite and ye'elimite affects the hydration due to the different reactivity of those phases [3].

The aim of this work is to process, characterize and scale-up a non-active BAY clinker (with coexisting alite, β -belite and ye'elimite) and an active-BAY clinker (with coexisting alite, α'_{H} -belite and ye'elimite) to develop, in a future step, comparable mechanical strengths to OPC. The parameters evolved in the preparation of the clinker have been optimized, such as the selection of raw materials (including mineralizers and activators), clinkering conditions and scale-up methodology. Finally, the clinker was characterized through laboratory X-ray powder diffraction in combination with the Rietveld methodology.

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Fast microwave-assisted synthesis and lithium-ion diffusion studies of lithium stuffed garnets

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Research field: Solid state chemistry and applications

Abstract:

Lithium-stuffed garnets attract huge attention due to their outstanding potential as solid-state electrolytes for lithium batteries.[1] However, there exists a persistent challenge in the reliable synthesis of these complex functional oxides together with a lack of complete understanding of the lithium-ion diffusion mechanisms in these important materials. Addressing these issues is critical to realizing the application of garnet materials as electrolytes in all solid-state lithium-ion batteries. We have synthesised a cubic phase garnet of nominal composition $Li_{6.5}AI_{0.25}La_{2.92}Zr_2O_{12}$ through a microwave-assisted solid-state route for the first time, reducing considerably the reaction times and heating temperatures. Lithium-ion diffusion behaviour has been investigated by electrochemical impedance spectroscopy (EIS) and state-of-art muon spin relaxation (μ -SR) spectroscopy, displaying activation energies of 0.55 ± 0.03 eV and 0.19 ± 0.01 eV respectively.[2]

This difference arises from the high inter-grain resistance, which contributes to the total resistance in EIS measurements. In contrast, μ -SR acts as a local probe providing insights on the order of the lattice, giving an estimated value of 4.62×10^{-11} cm² s⁻¹ for the lithium diffusion coefficient. These results demonstrate the potential of this lithium-stuffed garnet as a solid-state electrolyte for all solid state lithium-ion batteries, an area of growing interest in the energy storage community.

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RFM - 1

New representatives and physical properties of 3d-5d double perovskites

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Research field: Rationales for functional materials synthesis

Abstract:

Double perovskites $A_2BB'O_6$ feature various possibilities for the design of new magnetic and magnetoelectric materials. Unique properties arise if an electronically more localized 3d ion at the *B* site is combined with an electronically more delocalized 4d or 5d ion on the *B*' site. Important compounds in this field are the half-metallic ferromagnets Sr₂FeMoO₆ [1] and Sr₂FeReO₆ [2]. They exhibit Curie temperatures above room temperature and large magneto-resistance effects, making them promising candidates for applications in spintronics. Another key member in this family is Sr₂CrOsO₆ [3], which is a ferrimagnetic insulator with an unusually high Curie temperature of 720 K. We investigated the magnetic and electronic properties of DP oxides Sr₂BOsO₆ with two magnetic sublattices (*B* = Fe, Co) and a single magnetic sublattice (*B* = Y, In, Sc).

 Sr_2FeOsO_6 [4–6] and Sr_2CoOsO_6 [7,8] turned out to be antiferromagnetic insulators. Magnetic susceptibility and heat capacity studies revealed two magnetic phase transitions for both compounds, namely, at $T_{N1} = 140$ K, $T_{N2} = 67$ K for Sr_2FeOsO_6 and $T_{N1} = 108$ K and $T_{N2} = 67$ K for Sr_2CoOsO_6 . Sr_2FeOsO_6 crystallizes in a tetragonal DP structure (space group *I*–4*m*), with buckling of the Fe-O-Os layers in the *ab* plane, but an ideal Fe-O-Os angle of 180° along *c*. In Sr_2FeOsO_6 Fe^{3+} ($t_{2g}{}^3e_g{}^2$) and Os^{5+} ($t_{2g}{}^3$) ions are present. From neutron diffraction it can be seen that the two antiferromagnetic spin structures formed below T_{N1} (AF1) and T_{N2} (AF2) feature a ferrimagnetic arrangement of the Fe and Os spins in the *ab* plane but differ in the spin sequence along the *c*-direction. Whereas all Fe and Os spins show parallel alignment along *c* in AF1, an up-up, down-down, etc., sequence is observed in AF2. A complex magnetic ordering behavior with two distinct phases, AF1 and AF2, and a tetragonal (*I*–4*m*)-to-monoclinic ($P2_1/n$) phase transition at T_{N1} are found for Sr_2COOsO_6 [7,8], where Co^{2+} ($t_{2g}{}^5e_g{}^2$) and Os^{6+} ($t_{2g}{}^2$) ions occur. Below T_{N1} , a spin structure with partially ordered Co^{2+} and Os^{6+} moments is formed, whereas, below T_{N2} , a canted non-collinear magnetic state occurs, where the Co moments are totally frozen. The detailed spin structure of Sr_2COOsO_6 is still a matter of discussion [9].

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Synthesis of zinc deposits by pulsed current

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Research field: Rationales for functional materials synthesis

Abstract:

In this study, zinc deposits were obtained using continous and pulsed current processes from chloride bath. The optimum conditions of deposition were established. Test of corrosion were undertaken in a stirred and aerated solution of NaCl (30g/l). The morphology of the coatings was characterised by observations in scanning electronic microscopy (SEM). Finally, X-ray diffraction in symetric mode allowed to evaluate the structure and principal crystallographic orientations of the deposits. The results obtained, showed that the development in pulsed induced a marked improvement in the morphology and grain refinement[1, 2].

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A new family of topological insulators based on β -Bi₄I₄

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Research field: Rationales for functional materials synthesis

Abstract:

A recent joint theoretical and experimental study has shown that the long-known β -Bi₄I₄ is a strong topological insulator [1]. Its crystal structure is built by a stack of quasi-one-dimensional bismuth stripes terminated by iodine atoms [2]. Similar halogen-terminated bismuth stripes in different packing arrangements are found in α -Bi₄I₄ [2], Bi₄Br₄ and mixed iodide-bromides [3]. Here we present optimized single-crystal growth for hard-to-access α -Bi₄I₄ and mixed Bi₄Br_xI_{4-x}, and a new Bi₄Br₂I₂ modification.

Single crystals of α - and β -Bi₄I₄ (needles up to 1 mm long) were obtained from Bi and BiI₃ in the Lewis-acidic ionic liquid (IL) [BMIm]I-1.1AII₃ ([BMIm]: 1-butyI-3-methylimidazolium) at 180°C. The Bi:BiI₃ ratio is decisive for the crystal structure of the product. Moreover, the iodide anion of [BMIm]I is mandatory for Bi₄I₄ synthesis; hence the IL is serving both as solvent and as reactant. A DSC study revealed two peritectic melting temperatures for these structural modifications, 312°C and 338°C; thus rationalizing them as two polytypes of bismuth monoiodide. Large crystals of Bi₄Br_xI_{4-x} (needles up to 5 mm long) were obtained via chemical transport reactions with HgBr₂ and HgI₂ [2]. In addition to the structures described in [3], a new modification of Bi₄Br₂I₂ with preferential occupancy of iodine and bromine sites was synthesized (sp. gr. *C2/m*, a = 13.239(1) Å, b = 4.3978(3) Å, c = 10.519(1) Å, $\beta = 110.945(1)^\circ$, $R_{all} = 4\%$). DFT-based band-structure calculations predict the new Bi₄Br₂I₂ to be a weak topological insulator with Z₂ = 0;(001).

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