

DAY 1

Keynote Forum



3rd Edition of International Conference on

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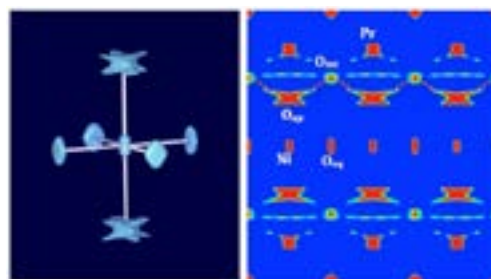
PHONON ASSISTED OXYGEN DIFFUSION VS. OXYGEN AND ELECTRONIC ORDERING MECHANISMS IN NON-STOICHIOMETRIC CORRELATED OXIDES

Werner Paulus

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Transition Metal Oxides with strongly correlated electrons have been studied intensively due their interesting physical properties. This includes colossal magnetoresistance (CMR) where huge variations in resistance are achieved just by small changes in the applied magnetic field, or high temperature superconductivity (HTC) to name two of them [3-6]. These materials are characterized by the existence of several competing states such as charge, spin and orbital ordering, interacting in a synergetic way and leading to fairly complex phase diagrams. Thereby the physical properties can be tuned in a wide range via hole doping, e.g. by cation substitution as is the case for RE₂-xSr_xMO₄. An alternative way of hole doping presents oxygen intercalation, generally proceeding at ambient temperature via a topotactic oxygen uptake along shallow potential diffusion pathways. Contrary to the cation substitution, requiring high reaction temperatures, oxygen intercalation reactions allow the controlled synthesis of strongly correlated oxides far away from thermodynamic equilibrium, essentially resulting in kinetically stabilized and thus metastable phases. Low temperature reactivity of solids may thus be used as a concept, to investigate the limits of available structural and electronic complexity in transition metal oxides. The reaction pathway to insert oxygen at low temperatures in solid oxides becomes a decisive parameter to tune correlations, leading to extremely complex phase relations as physical and structural properties are not only depending on the overall stoichiometry, but decisively on the sample history. Taking these oxides as oxygen 'sponges' operating at low reaction temperatures down to ambient, structural and electronic correlation lengths could then be influenced by the reaction conditions and kinetics. We here discuss here the challenges, low temperature solid state reactivity implies for the synthesis of new complex oxides but equally the current understanding of the relying oxygen diffusion

mechanisms, having a huge fundamental and technological interest.



Pr₂NiO_{4.25}: Representations of the NiO₆ isosurfaces (left) for indicate the anharmonic double potential of the apical oxygen atoms present at 673 K, obtained from single crystal neutron diffraction and Maximum Entropy Analysis. The large anisotropic displacements of the apical oxygen atoms along [110] directly point towards the interstitial oxygen sites, forming a shallow oxygen diffusion pathway which is dynamically activated

Recent Publications

1. From T to T'-La₂CuO₄ via Oxygen Vacancy Ordered La₂CuO_{3.5}, M. Ikbel Houchati, M. Ceretti, C. Ritter and W. Paulus, Chem. Mater. 2012, 24, 3811-3815
2. One-dimensional oxygen diffusion mechanism in Sr₂ScGaO₅ electrolyte explored by neutron and synchrotron diffraction, 17O-NMR and DFT calculations, S. Corallini M. Ceretti, G. Silly, A. Piovano, S. Singh, J. Stern, C. Ritter, J. Ren, H. Eckert, K. Conder, Wei-tin Chen, Fang-Cheng Chou, N. Ichikawa, Y. Shimakawa, W. Paulus, J. Phys. Chem. C, 2015, 119 (21), 11447-11458

3. Low temperature oxygen diffusion mechanisms in Nd₂NiO_{4+δ} and Pr₂NiO_{4+δ} via large anharmonic displacements, explored by single crystal neutron diffraction, M. Ceretti, O. Wahyudi, A. Cousson, A. Villesuzanne, M. Meven, B. Pedersen, J.-M. Bassat, W. Paulus, JOURNAL OF MATERIALS CHEMISTRY A, 3, 42 (2015) p21140-48
4. Solid-state reactivity explored in situ by synchrotron radiation on single crystals: from SrFeO_{2.5} to SrFeO₃ via electrochemical oxygen intercalation, A. Maity, B. Penkala, R. Dutta, M. Ceretti, A. Lebranchu, D. Chernyshov, A. Perrichon, A. Piovano, A. Bossak, M. Meven, W. Paulus, J Physics D: Applied Physics, Special issue: 100 years of crystallography: new dimensions offered by large scale facilities, J. Phys. D: Appl. Phys. 48 (2015)
5. Positional Recurrence Maps: a powerful tool to de-correlate static and dynamical disorder in distribution maps from molecular dynamics simulations, Piovano, Andrea, Perrichon, Adrien, Boehm, Martin, Johnson, Mark, Paulus, Werner, Physical Chemistry Chemical Physics, 2016,
6. Anisotropic Oxygen Diffusion Properties in Pr₂NiO_{4+δ} and Nd₂NiO_{4+δ} Single Crystals, J-M Bassat, M. Burriel, O. Wahyudi, M. Ceretti, P. Veber, I. Weill, A. Villesuzanne, J-C Grenier, W. Paulus, and John A. Kilner, J PhysChemC, 2013, 117, 26466-26472,
7. A. Perrichon, A. Piovano, M. Boehm, M. Zbiri, M. Johnson, H. Schober, M. Ceretti and W. Paulus, Lattice Dynamics Modified by Excess Oxygen in Nd₂NiO_{4+δ}; Triggering Low-Temperature Oxygen Diffusion, J. Phys. Chem. C 2015, 119, 1557-1564.

Biography

Werner Paulus is exploring low temperature oxygen diffusion mechanisms in transition metal oxides. Oxygen doping, via topotactic reaction mechanisms while proceeding at ambient temperature is a powerful tool to access structural and electronic complexity in a controlled way. It also allows to better explore the underlying diffusion mechanisms on an atomic scale, having huge importance in solid state ionics, e.g. for the optimisation of battery materials, fuel cell membranes/electrolytes or sensors. Research activities cover synthesis methods from powder to large single crystals and to explore oxygen intercalation reactions in especially dedicated electrochemical cells on single crystals and polycrystalline electrodes by neutron and X-ray diffraction (synchrotron & laboratory), spectroscopy (XAFS, Raman, INS, IXS, NMR) combined with ¹⁸O/¹⁶O oxygen isotope exchange reactions and sophisticated data analysis (Maximum Entropy, twinning).

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CRYSTALLOGRAPHY OF PHASE TRANSFORMATIONS IN SOLIDS AND ITS APPLICATIONS

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Properties of materials are governed by their microstructures, which in turn are controlled by the phase transformations at a given composition. To obtain the desired microstructure, it is essential to understand the phase transformations that occur in the material. Crystallography of phase transformations defines the morphology of microstructures, explains the actual phase transformation process at an atomic level and describes the relationship between the new phase and the parent phase. Hence, the crystallography controls the final properties of materials. In the past decades, although a number of theories/models have been developed to understand the crystallography of phase transformations, none of them can be used to design new materials and processes until the edge-to-edge matching (E2EM) model became available [1]. Development of the E2EM model was based on the principles that the nature of a coherent or semi-coherent interface and the associated crystallographic relationships are governed by minimisation of interfacial energy between two crystals; and that the necessary and sufficient condition for minimisation of the interfacial energy is to maximize the atom matching. The best and most effective approach to achieve the maximum atom matching is the matching of atom rows that are close packed or nearly close packed and are contained in the matching planes that are arranged to meet in the "edge to edge" manner as shown in following figure. Major advantage of the E2EM model over all other previous models is its predictive capacity from the first principle. Thus, it can be used to design new alloys and processes. In this presentation, after briefly reviewing the success of this model in predictions of the crystallographic features of diffusion controlled phase transformations in solids [1], its applications in development of new and more effective grain refiners for cast metals, including magnesium alloys [2], zinc alloys [3] and steels [4], are introduced. Predictions of the textures and growth features of epitaxial growth and crystalline nanowires [5] are also presented.

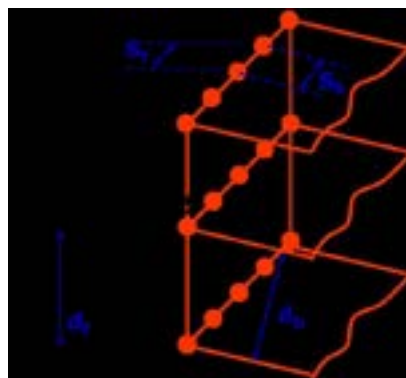


Figure: Schematic illustration of the edge-to-edge matching model

Recent Publications

1. Zhang M-X, Kelly P (2014) Crystallographic features of phase transformations in solids *Progress in Materials Science*, 54:1101-1170.
2. Ali Y, Qiu D, Jiang B, Pan F-S, Zhang M-X (2016) The influence of CaO addition on grain refinement of cast magnesium alloys *Scripta Materialia*, 114:103-107.
3. Liu Z-L, Qiu D, Wang F, Taylor J, Zhang M-X (2015) Crystallography of grain refinement in cast zinc-copper alloys. *Journal of Applied Crystallography* 48:890-900.
4. Li M, Li J, Qiu D, Zheng Q, Wang G, Zhang M-X (2016) Crystallographic study of grain refinement in low and medium carbon steels. *Philosophical Magazine* 96:1556-1578.
5. Liu Z, Zhang Z, Jiang R, Li X, Zhang M-X, Qiu D (2016) Crystallography of phase transformation in the self-inclined InAs nanowires grown on GaAs{111} *Scripta Materialia*, 121:79-83.

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Biography

Professor Mingxing Zhang has his expertise in crystallography of phase transformations in solids and crystallography of grain refinement of cast metals. His research focuses on development of new metallic materials and their processing in order to improve the properties of the alloys. He is also an expert on surface engineering of engineering metallic materials. He is one of the two inventors of the well-known edge-to-edge matching model and proposes the research theme on crystallography of grain refinement for cast metals. He is currently a professor in materials science and engineering in the School of Mechanical and Mining Engineering, the University of Queensland. (orcid.org/0000-0001-8363-6968).

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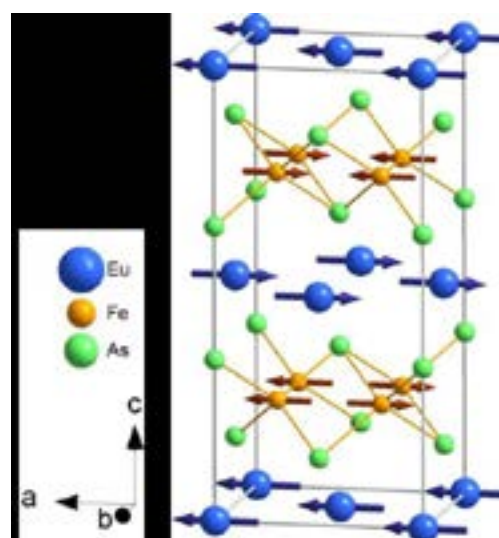
ADVANCES AND APPLICATIONS OF NEUTRON SCATTERING AND DIFFRACTION

Martin Meven

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The unique features of Neutrons make them a valuable tool for many crystallographic studies on hot topics in physics, chemistry, biology and material sciences. Their interaction with nuclei yields not only high penetration depths but also interaction strengths that differ significantly from the those well known for X-rays, e.g. some light elements (H, O) show relative large scattering cross sections compared to many heavy elements while neighbored elements can differ strongly. Therefore, Neutron imaging can be used to perform in situ radiography of engines to study the different moving parts and liquids involved in its operation. In the area of energy applications are the non-destructive spacial reconstruction of the distribution of elements inside new battery types during charge-discharge-cycles. This can be combined with neutron diffraction studies on the underlying chemical processes to develop new materials, e.g. for Li-ion or sodium metal halide batteries [1, 2]. The sensitivity of neutrons for light elements plays also an important role, e.g. for the understanding of energy relevant compounds like ionic conductors based on layered perovskites [3]. This holds true also for detailed studies on complex H bonds in minerals (phosphates, silicates, etc.) or organic matter/biological systems in life sciences, e.g. antibiotics [4]. The magnetic moment of neutrons allows detailed insights into magnetic order and related phase transitions. This feature is widely used in recent studies on multiferroics but also on modern high temperature superconductors based on cuprates [5] or iron arsenides [6] and played also an important role in the discovery of skyrmions [7].

The successful contribution of neutrons to various scientific applications has been made possible by advances in methods and instrumentation at existing neutron sources (e.g. in Europe ILL, MLZ, ISIS, etc.) in recent years. This and the installation of the new European Spallation Source ESS will support this trend also for the future.



Magnetic structure of EuFe_2As_2 at $T=2.5\text{K}$ derived from neutron single crystal diffraction [6]

Recent Publications

1. A. Senyshyn et al. (FRM II & KIT), Journal of power sources, 282, 235-240 (2015).
2. Veronika Zinth et al., Journal of the Electrochemical Society 162 (3), A384 – A391 (2015).
3. O. Wahyudi, M. Ceretti, I. Weill, A. Cousson, F. Weill, M. Meven, M. Guerre, A. Villesuzanne, J.M. Bassat, W. Paulus, CrystEngComm, 17 (2015) 6278-6285.
4. A. Ostermann, T. Schrader, Tomanicek et al., J. Biol. Chem., 288, 4715 (2013)..

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5. M. Braden, M. Meven, W. Reichardt, L. Pintschovius, M.T. Fernandez-Diaz, G. Heger, F. Nakamura, and T. Fujita; *Phys. Rev. B* **63**, 140510 (2001).
6. Y. Xiao, Y. Su, M. Meven, R. Mittal, C. M. N. Kumar, T. Chatterji, S. Price, J. Persson, N. Kumar, S. K. Dhar, A. Thamizhavel, and Th. Brueckel, *Phys. Rev. B* **80**, 174424 (2009).
7. Mühlbauer S, Binz B, Jonietz F, Pfeleiderer C, Rosch A, Neubauer A, Georgii R, Böni P; *Science*. 2009; **323**: 915.

Biography

Dr. Martin Meven received his PhD in natural sciences at the Institute of Crystallography at RWTH Aachen University in 2001. Aside from his scientific

work on HT superconductors during this time he gained experience in scattering methods with X-ray diffractometry including instrument development. He extended his expertise as postdoc at Munich, where he developed a new single crystal diffractometer for hot neutrons at the neutron source FRM II of the Heinz Maier-Leibnitz Zentrum (MLZ) in Garching, Germany. Since then he has been working as instrument scientist on various topics in the fields of crystallography, solid state chemistry and solid matter physics and material sciences. He has served as a board member of various scientific conferences and scientific referee at review panels at various neutron sources in Europe. He is the speaker of the Special Interest Group on Neutron Scattering (SG # 7) of the German Society of Crystallography (DGK) and organizes workshops on neutron scattering techniques for crystallographers to young scientists on a regular basis. (orcid.org/0000-0002-8079-5848).

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DAY 2

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IDENTIFICATION OF THE DEFECT CLUSTERS IN CONGRUENT LITHIUM TANTALATE

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The combination of the extraordinary physical properties of lithium tantalate LiTaO_3 (LT) offers a great potential for applications in modern optics and photovoltaics. A large fraction of such applications is based on the defect chemistry. The congruently grown composition of LT using the Czochralsky method yields the cation concentration ratios of $[\text{Li}]/[\text{Ta}]=48.75/51.25$. Li deficiency suggests several possible configurations of a defect cluster in congruent crystals, which guarantee charge neutrality. Several intrinsic defect models have been considered in literature over several decades. Here, using a combinational approach based on DFT and solid-state NMR, we demonstrate that distribution of electric field gradients (EFGs) on a ${}^7\text{Li}$ site may be regarded as a fingerprint of a specific defect configuration. The defect structure in one of two congruent LT crystals after annealing was identified experimentally and proved by the defect formation energy consideration. We found that the defect cluster in this crystal corresponded to the empty site model. The identification of the defect structure in the second LT sample was more challenging, implying the presence of extrinsic defects and an inhomogeneous defect distribution. After thermal treatment, hydrogen out-diffusion and homogeneous distribution of other defects in both LT samples were observed in the NMR and FTIR spectra. The approach of searching for the EFG fingerprints from DFT calculations in NMR spectra can be applied for identification of the defect clusters in other complex oxides.

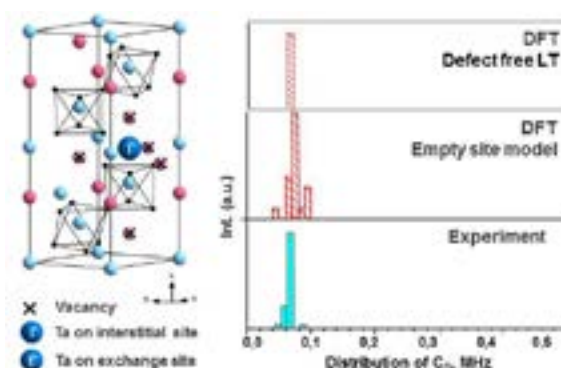


Figure. Left panel: Crystal structure of empty site defect model for non-stoichiometric lithium tantalate. Crosses and large dark blue spheres denote modified atom as compared to defect-free structure. Right panel: Classification of calculated quadrupolar coupling constants C_Q for defect-free and empty site defect models, and for experimental quadrupolar coupling constants in lithium tantalate crystal.

Recent Publications

1. V. A. Vizgalov, T. Nestler, L. A. Trusov, I. A. Bobrikov, O.I. Ivankov, M.V. Avdeev, M. Motylenko, E. Brendler, A. Vyalykh, D.C. Meyer, D. M. Itkis (2018) Enhancing Lithium-Ion Conductivity in NASICON Glass-Ceramics by Adding Yttria. *Cryst. Eng. Comm.*, accepted DOI: 10.1039/C7CE01910F
2. A. Vyalykh, M. Zschornak, Th. Köhler, M. Nentwich, T. Weigel, J. Hanzig, R. Zaripov, E. Vavilova, S. Gemming, E. Brendler, D.C. Meyer (2018) Analysis of the defect clusters in congruent lithium tantalate. *Phys. Rev.*

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- Materials 2:013804.
3. V.O. Koroteev, W. Münchgesang, Yu.V. Shubin, Yu.N. Palyanov, P.E. Plyusnin, D.A. Smirnov, K.A. Kovalenko, M. Bobnar, R. Gumeniuk, E. Brendler, D.C. Meyer, L.G. Bulusheva, A.V. Okotrub, A. Vyalikh (2017) Multiscale characterization of ¹³C-enriched fine-grained graphitic materials for chemical and electrochemical applications. *Carbon*, 124:161–169.
 4. S. A. Rounaghi, H. Eshghi, S. Scudino, A. Vyalikh, D. E. P. Vanpoucke, W. Gruner, S. Oswald, A.-R. Kiani-Rashid, M. Samadi-Khoshkhou, U. Scheler, J. Eckert (2016) Mechanochemical route to the synthesis of nanostructured Aluminium nitride. *Sci. Rep.* 6:33375
 5. M. T. Atanasova, A. Vyalikh, U. Scheler and W. W. Focke (2016) Characterization of rectorite from the Beatrix Gold Mine in South Africa. *Appl. Clay Sci.* 126:7-16

6. D. M. Itkis, J. J. Velasco-Velez, A. Knop-Gericke, A. Vyalikh, M. V. Avdeev and L. V. Yashina (2015) Probing Operating Electrochemical Interfaces by Photons and Neutrons. *ChemElectroChem*, 2(10):1427-1445 .

Biography

Anastasia Vyalykh is a research group leader at the Technical University Bergakademie Freiberg since 2014. She received her Master degree in physics at the State University Saint-Petersburg (1999). As PhD in physical chemistry (Free University of Berlin, 2005) she focuses on the application of solid-state NMR and quantum-chemical calculations for structure determination in functional oxides, solid ionic conductors, low-dimensional carbon materials. Current research interests include studies of interfacial phenomena in organic - inorganic nanocomposites, conducting glass-ceramics, carbon-based nanohybrids as well as implementation of the in-situ methods for studies of electrochemical processes. (orcid.org/0000-0003-2326-8889).

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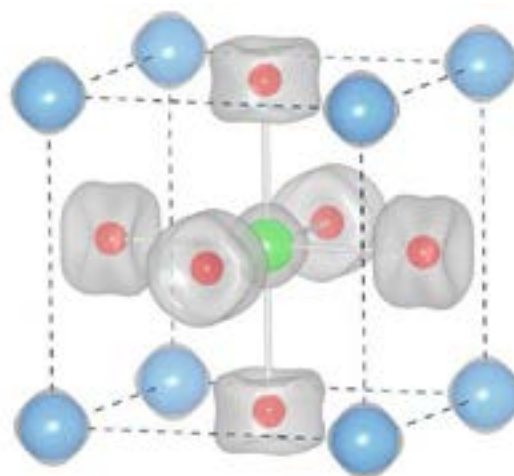
STRUCTURAL FEATURES OF A NEW OXYGEN DEFICIENT PEROVSKITE $\text{Sr}_2\text{ScGaO}_5$, A PROMISING OXYGEN ION CONDUCTOR AT MODERATE TEMPERATURE

Monica Ceretti

Institut Charles Gerhardt Montpellier, France

Oxygen ion conductors are materials of major interest for a series of application in the area of solid state ionic (fuel cells, batteries, electrodes, sensors, catalysts, etc...). In this respect oxides with brownmillerite type structure ($\text{A}_2\text{BB}'\text{O}_5$), have attracted much attention, especially as they show oxygen ion mobility down to ambient temperature. This mobility is a result of a phonon assisted diffusion mechanism, based on a dynamic oxygen disorder scenario of the infinite BO_4 chains [1, 2]. Brownmillerite type frameworks containing B-cations with saturated or empty electron shells (d_0 or d_{10} configurations) present a special case, as they impose a fixed oxygen stoichiometry, making them good candidates to study oxygen diffusion mechanisms on a microscopic level. In this context, we have synthesized a new phase $\text{Sr}_2\text{ScGaO}_5$, having pure oxygen ion conductivity. Depending on the synthesis route, it shows two polymorphs: orthorhombic Brownmillerite type structure or an oxygen deficient cubic perovskite structure. When synthesizing $\text{Sr}_2\text{ScGaO}_5$ by classical solid state reaction at 1200°C , the thermodynamically stable phase obtained shows the brownmillerite framework [3]. Heating at higher temperature, it shows a phase transition to the cubic perovskite structure completed at 1500°C , associated with improved oxygen ion conduction [4]. Since the cubic symmetry can be maintained down to ambient temperature, we were able to grow high quality single crystal of the cubic phase [5]. We report here on a combination of characterization on the brownmillerite as well on the cubic $\text{Sr}_2\text{ScGaO}_5$. High-resolution structure analysis has been performed using X-rays (synchrotron and laboratory) and neutron diffraction methods, combined with NMR analysis for local environment [3]. In particular, single crystal neutron diffraction with subsequent analysis of the nuclear scattering density by the Maximum Entropy Method has been performed

in order to describe in more detail oxygen displacement factors and associated diffusion pathways [5]. To better understand the oxygen mobility mechanisms, these studies were complemented by Raman and impedance spectroscopy.



Nuclear scattering density (in grey) of the $\text{Sr}_2\text{ScGaO}_5$ obtained at room temperature from neutron single crystal diffraction and subsequent Maximum Entropy reconstruction. The perovskite unit cell and the $(\text{Sc}/\text{Ga})\text{O}_6$ octahedra are outlined. While isotropic displacements are found for Sr and (Sc/Ga) , oxygen atoms (in red) show an anisotropic disk shape distribution

Recent Publications

1. Paulus W. et al. (2008) Lattice Dynamics To Trigger Low Temperature Oxygen Mobility in Solid Oxide Ion

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- Conductors. *Journal of the American Chemical Society*, 130(47): p. 16080-16085.
2. Ceretti M. et al. (2015) Low temperature oxygen diffusion mechanisms in Nd₂NiO₄⁺ and Pr₂NiO₄⁺ via large anharmonic displacements, explored by single crystal neutron diffraction. *Journal of Materials Chemistry A*, 3(42): p. 21140-21148.
 3. Corallini S. et al. (2015) One-Dimensional Oxygen Diffusion Mechanism in Sr₂ScGaO₅ Electrolyte Explored by Neutron and Synchrotron Diffraction, 170 NMR, and Density Functional Theory Calculations. *The Journal of Physical Chemistry C*, 119(21): p. 11447-11458.
 4. Ceretti M. et al. (2016) Influence of Phase Transformations on Crystal Growth of Stoichiometric Brownmillerite Oxides: Sr₂ScGaO₅ and Ca₂Fe₂O₅. *Crystals*, 6(11): p. 146.
 5. Corallini S. et al. (2017) Cubic Sr₂ScGaO₅ Perovskite: Structural Stability, Oxygen Defect Structure, and Ion Conductivity Explored on Single Crystals. *Inorganic Chemistry*, 56(5): p. 2977-2984.

Biography

Monica Ceretti has an expertise in neutron diffraction for crystal structural studies. After 14 years at the Laboratoire Léon Brillouin (Saclay, France) as scientific responsible of a neutron diffractometer, she first moved to the University of Rennes and then in Montpellier (chemistry department), where she is in charge for structural studies of correlated oxides by neutron and X-ray diffraction. Member of several panels for proposals review at large scale facilities (at the ILL in the past and now at FRM2) in the crystallography committees, she is involved in training activities in neutron scattering for structural studies in the frame of master courses as well as in specialized schools.

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