10th Summer School on Condensed Matter Research Zug, August 13 – 19, 2011

Abstract

Oxygen Induced Phase Transitions

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Non-stoichiometric oxides are able to uptake or release oxygen atoms, sometimes up to an important amount. Usually these reactions require high temperatures to perform, related to the limited mobility of oxygen when reducing temperature. The reasons for this originates from the fact that oxygen ions are doubly charged and have a rather large radius of about 1.4 Å, the associated energy barriers to overcome during the diffusion process are therefore high.

For a very few oxides, however, oxygen is mobile even down to ambient temperature, which has potential technological applications for sensors or membranes/electrolytes for Solid Oxide Fuel Cells (SOFC). Low temperature oxygen mobility in solid oxides with metallic conductivity, enables to control the oxygen stoichiometry by electrochemical methods or soft chemistry. Performing oxygen intercalation reactions at ambient temperature, i.e. far away from thermodynamic equilibrium, allows obtaining new metastable phases, often associated to oxygen ordering on an impressive scale, and also accompanied by interesting changes in the physical properties.

Low temperature oxygen mobility can thus be used as a concept to synthesize new and unpredictable phases. Appropriate tools like electrochemistry also directly allow controlling quantitatively the oxygen uptake/release and rendering the reaction kinetics accessible for *in situ* investigations of structure and dynamic properties.

We will present here selected examples, mainly of oxides with Perovskite and Rudlessden-Popper type frameworks, where changes in the oxygen stoichiometry go along with phase transitions. These reactions may either allow to access new and metastable phases, or to induce charge ordering and long range order of the intercalated oxygen atoms. These structural phase transitions are discussed together with lattice dynamical aspects in terms of low temperature oxygen mobility mechanisms, allowing to propose a new concept to conceive new materials for energy conversion based on fast oxygen ion conduction at moderate temperature such as 2nd generation SOFC.

References:

1. Lattice Dynamics to Trigger Low Temperature Oxygen Mobility in Solid Oxide Ion Conductors, W.Paulus, H. Schober, S. Eibl, M. Johnson, T. Berthier, O. Hernandez, M. Ceretti, M. Plazanet, K. Conder, C. Lamberti, *J. Am. Chem. Soc.* 130 (47) 16080-85 (2008)
2. On the role of lattice dynamics on low-temperature oxygen mobility in solid oxides: a neutron diffraction and first-principles investigation of $La_2CuO_{4+\partial}$, Antoine Villesuzanne, Werner Paulus, Alain Cousson, Shoichi Hosoya, Loïc Le Dréau, Olivier Hernandez, Carmelo Prestipino, Mohamed Ikbel Houchati, Juerg Schefer, *J Solid State Electrochem* (2011) 15:357–366
3. Time-Resolved in situ studies of oxygen intercalation into $SrCoO_{2.5}$ performed by neutron diffraction and X-ray absorption spectroscopy, Ronan Le Toquin, Werner Paulus, Alain Cousson, Carmelo Prestipino, Carlo Lamberti, *J. Am. Chem. Soc.* 128 (2006) 13161-13174

4. Infinite layer iron oxide with a square-planar coordination by low temperature synthesis, Y. Tsujimoto, C. Tassel, N. Hayashi, T. Watanabe, H. Kageyama, K. Yoshimura, M. Takano, M. Ceretti, C. Ritter, & W. Paulus, *Nature* 450 (2007) 1062-66

5. Anisotropic oxygen diffusion at low temperature in perovskite-structure iron oxides, Satoru Inoue, Masanori Kawai, Noriya Ichikawa, Hiroshi Kageyama, Werner Paulus, Yuichi Shimakawa, Nature Chemistry, 2 (2010) 213-217