

MS16-P5 Synthesis and structural chemistry of cation ordered double perovskite Ba₃Fe₂TeO₉ and Sr₃Fe₂TeO₉ via novel sol-gel route

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The term “perovskite” having general formula ABX₃, can accommodate a wide variety of elements with the advantage of manipulation in stoichiometry for advanced technologies including magnetism, dielectric behavior, conductivity or even multiferroic behavior. The stoichiometric changes can lead to obtain double perovskite with general formula A₂B'B''O₆ which are widely studied so far [1-3], where six coordinate sites are occupied by B' and B'', while 12-coordinate sites are occupied by A cation. Additionally another interesting class of multiferroic compounds with more complex geometry (A₃B'2B''O₉) have been investigated (Sr₃Fe₂MoO₉ and Sr₃Fe₂UO₉) and reported with strong ferromagnetic properties with TC well above room temperature [4-5]. The major drawback while synthesizing above mentioned metal oxides is the tedious solid state synthesis which require high temperature calcination and more time for phase purity. Here we report a successful synthesis of double perovskite Ba₃Fe₂TeO₉ and Sr₃Fe₂TeO₉ by novel environmental friendly 'sol-gel' process using citric acid as complexing medium followed by calcination step. Both compounds have been studied by powder X-ray diffraction (Rietveld), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and magnetic measurements. At room temperature, the crystal structure of Ba₃Fe₂TeO₉ is hexagonal, space group P6₃/mmc (194), with *a* = 5.7665, *c* = 14.2024 Å; while Sr₃Fe₂TeO₉ the crystal structure is cubic, with space group Pm-3m (221), and *a* = 3.9353 Å. Ideally, Ba₃Fe₂TeO₉ and Sr₃Fe₂TeO₉ double perovskite contains Fe³⁺ and Te⁶⁺ cations, ordered in a way that superexchange interactions between neighboring Fe³⁺ spins are the nominal mechanism accounts for the magnetism of these materials. We acknowledge financial support from the Unity through Knowledge Fund (www.ukf.hr) of the Croatian Ministry of Science, Education and Sports (Grant Agreement No. 7/13). 1. Y. D. Li, C. C. Wang, R. L. Cheng, Q. L. Lu, S. G. Huang and C. S. Liu, *Journal of Alloys and Compounds*, 2014, 598, 1-5. 2. A. Sasaki, Y. Doi and Y. Hinatsu, *Journal of Alloys and Compounds*, 2009, 477, 900-904. 3. M. P. Singh, K. D. Truong, S. Jandl and P. Fournier, *Journal of Applied Physics*, 2010, V107. 4. M. C. Viola, J. A. Alonso, J. C. Pedregosa and R. E. Carbonio, *Eur. J. Inorg. Chem.*, 2005, 1559. 5. R. M. Pinacca, M. C. Viola, J. C. Pedregosa, R. E. Carbonio and J. A. Alonso, *J. Mater. Chem.*, 2005, 15, 4648.

Keywords: Multiferroic, Double perovskite, sol-gel

MS16-P6 Structural complexity in non-stoichiometric oxides: From fundamental aspects to application

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Certain oxides with the composition R₂MO₄ (R = rare earth, M = transition metal) crystallizing in the K₂NiF₄ structure have been found to intercalate oxygen at ambient temperatures through a topotactic reaction. The intercalated oxygen strongly influences the oxygen mobility [1] and the electronic properties presumably both through structural order and change of valence for the transition metal ions. In La₂CuO_{4+d} (d = 0 ... 0.07) oxygen intercalation changes the electronic properties from an antiferromagnetic semiconductor to a high-temperature superconductor [2]. In Pr₂NiO_{4+d} (d = 0 ... 0.25) small amounts of intercalated oxygen suppresses the antiferromagnetic order of the Ni-sublattice [3,4]. Further oxygenation leads to defined, long-range ordered superstructures over the full crystal volume with unit cells up to cell volumes of 3,000,000 Å³. In Pr₂NiO_{4+d} these oxygen-rich phases can be electrochemically prepared at room temperature leading to kinetically stabilized phases which are inaccessible through high temperature synthesis. Moreover, the electrochemical process allows varying the oxygen content with precision thus allowing tuning electronic state and resulting superstructure. Therefore, Pr₂NiO_{4+d} is especially suited to study the correlation between structural, charge and orbital order and the resulting electronic properties. In our contribution we will present a detailed single crystal study on electrochemically prepared Pr₂NiO_{4+d} using single crystal neutron and x-ray diffraction data. Exemplarily shown in Fig. 1 these data show the complex oxygen superstructures as a function of the oxygen content d. With the complementary use of neutrons and x-ray we are able to distinguish charge, spin and orbital order. Apparently the presence of intercalated oxygen implies valence order of Ni²⁺/Ni³⁺ stemming from orbital ordering. Further, the long-range oxygen order points to the presence of an organizing interaction. Based on neutron spectroscopic measurements we will show that in the oxygen rich phases additional phonon modes are present. These modes are the fundamental interaction leading to the structural order and also to the room temperature mobility of the intercalated oxygen ions. This phonon-assisted transport would be new phenomenon of oxygen transport and its understanding could lead to solid oxide fuel cells application at room temperature.

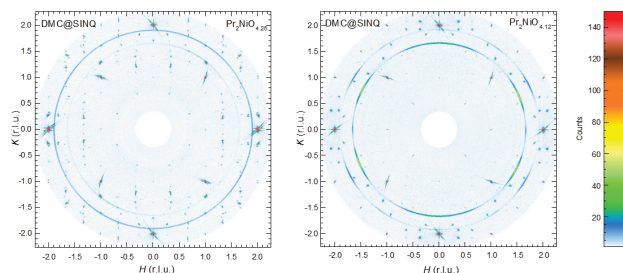


Figure 1. HK0 maps of $\text{Pr}_x\text{Ni}_{1-x}$ single crystals with $d=0.25$ (left) and $.12$ (right) at $T=100\text{K}$ collected at DMC@SINQ ($a=b\sim 3.8\text{\AA}$, $c\sim 12.3\text{\AA}$). Additional peaks originate from the oxygen superstructure which in the case of $d=0.12$ partly vanish at room temperature.

Keywords: oxygen diffusion, perovskites, functional structures, sustainable materials

MS16-P7 On the tetragonal phase of sodium bismuth titanate, $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT)

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Sodium bismuth titanate, $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT), has attracted attention as a potential component of lead-free piezoelectrics with the ultimate aim of replacing the industrial standard material lead zirconate titanate (PZT). At room temperature the crystal structure is monoclinic pseudo-rhombohedral on average (space group Cc or disordered $R3c$). Above $\sim 573\text{K}$ on heating, the structure is tetragonal, solved by Jones & Thomas [1] in $P4bm$. Above $\sim 833\text{K}$ it becomes cubic ($Pm-3m$).

NBT can be combined with BaTiO_3 (BT) amongst other useful perovskites, to make the solid-solution $\text{NBT}_{1-x}\text{BT}_x$ (NBT-BT). BT is tetragonal ($P4mm$) at room temperature and its solid-solution with NBT can be described by $R3c$ up to $x \sim 0.06$. At $x = 0.06$, it was thought that the structure changed abruptly from rhombohedral to tetragonal in an analogous fashion to the so-called morphotropic phase boundary in PZT. However, subsequent works showed that the transition is rather more gradual and that a fully tetragonal polar structure described by $P4mm$ is not established until $x > 0.1-0.15$ [2]. Ma & Tan reported that the transition between the ferroelectric rhombohedral and tetragonal phases in NBT-BT takes place via a pseudo-cubic weakly polar region of composition space assigned as $P4bm$. This phase can be prompted into a more strongly polar phase by application of an electric field [3], referred to as an E-field induced phase transition if the new state persists after the E-field is removed. The understanding of this E-field induced behaviour and the favourable physical properties that accompany it are predicated on understanding the structure and nature of the $P4bm$ phase itself.

New detailed parametric structural data for NBT are presented in the temperature range from 573-943K. The tetragonal phase region is bounded by metrically cubic phases at both high and low temperatures, with the high temperature phase being the cubic aristotype. The tetragonal strain is maximum at $670(\pm 5)\text{K}$. New structural refinements in key regions of the temperature phase diagram are presented and correlated with physical property data, particularly optical birefringence measurements from single crystals [4] and results of pair distribution function (PDF) analysis.

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Keywords: Ferroelectrics, X-ray Diffraction, Non-ambient Diffraction, NBT