**Synthesis and structural chemistry of cation ordered double perovskite Ba$_3$Fe$_2$TeO$_9$ and Sr$_3$Fe$_2$TeO$_9$ via novel sol-gel route**

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The term “perovskite” having general formula ABX$_3$, 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 A$_2$B’B”O$_6$ 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 (A3B2B”O9) have been investigated (Sr$_3$Fe$_2$MoO$_9$ and Sr$_3$Fe$_2$UO$_9$) 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 Ba$_3$Fe$_2$TeO$_9$ and Sr$_3$Fe$_2$TeO$_9$ 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.


**Keywords:** Multiferroic, Double perovskite, sol-gel

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

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Certain oxides with the composition R$_x$MO$_y$ (R = rare earth, M = transition metal) crystallizing in the K$_2$NiF$_4$ 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 La$_2$CuO$_4$+$d$ (d = 0 ... 0.07) oxygen intercalation changes the electronic properties from an antiferromagnetic semiconductor to a high-temperature superconductor [2]. In Pr$_2$NiO$_4$+$d$ (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 Å$^3$. In Pr$_2$NiO$_4$+$d$ 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, Pr$_2$NiO$_4$+$d$ 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 Pr$_2$NiO$_4$+$d$ 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 Ni$^{3+}$/Ni$^{2+}$ 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.
**MS16-P7** On the tetragonal phase of sodium bismuth titanate, Na$_{0.5}$Bi$_{0.5}$TiO$_3$ (NBT)

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Sodium bismuth titanate, Na$_{0.5}$Bi$_{0.5}$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 morphotropic pseudo-rhombohedral on average (space group Cc or disordered R3c). Above ~ 573K on heating, the structure is tetragonal, solved by Jones & Thomas [1] in P4$_{bm}$. Above ~ 833K it becomes cubic (Pm-3m).

NBT can be combined with BaTiO$_3$ (BT) amongst other useful perovskites, to make the solid-solution NBT$_x$-BT$_{1-x}$ (NBT-BT). BT is tetragonal (P4$_{mm}$) 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 P4$_{mm}$ 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 P4$_{bm}$. 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 P4$_{bm}$ phase.

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(±5)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.


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

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**Figure 1.** HKO maps of PrNiO$_3$ single crystals with d=0.25 (left) and .12 (right) at $T=100\text{K}$ collected at DMC@SINQ (a=b=3.8Å, c=12.3Å). 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