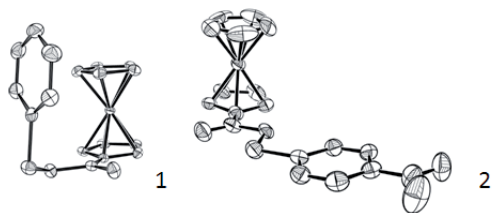


contributing to the stability of the molecule and promoting the packing of molecules in dimers formed by C(Cp)-H...O(nitro) hydrogen bonds.



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Keywords: structure, supramolecular, substituent

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A transmission electron microscopy study of the atomic structure of $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ (NBT)

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Piezoelectric and ferroelectric, perovskite ceramics (chemical formula, ABO_3) are widely used in electromechanical devices such as transducers, sensors and so forth for a variety of applications ranging from smart car shock absorbers to pressure sensors. $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$, (abbreviated as PZT) is currently the most important and commonly used perovskite in this field. However, from the perspective of environmental protection, the presence of lead makes the use of PZT undesirable. Therefore, in an attempt to replace PZT and other lead-containing perovskites, much effort has been devoted to developing a lead-free perovskite with attractive electromechanical properties. The compound $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$, (abbreviated as NBT) is one of the most promising such candidates.

NBT is one of the rare lead-free perovskites with A-site substitution. Neutron powder diffraction has shown that NBT undergoes (at least) two structural phase transitions on cooling. This study has confirmed that the room temperature phase of NBT belongs to the polar $R3c$ space group. However, many experiments (in-situ neutron scattering of NBT single crystal and transmission electron microscopy (TEM) studies) have revealed deviations from the ideal $R3c$ structure. Since these local structural deviations are critical in understanding NBT's ferroelectric properties, studying the local microstructure of NBT is essential. Detecting and characterising subtle changes in structure at the nano-scale requires the use of transmission electron microscopy.

Results will be presented of a detailed TEM study of NBT and NBT-doped with barium titanate using a combination of high resolution imaging and electron diffraction in order to investigate and understand the local structure of the rhombohedral phase at room temperature. A sequence of electron diffraction patterns obtained at different crystal orientations shows weak streaks of structured diffuse scattering, suggesting local structural modulation. This reciprocal space feature appears to be associated with "striped contrast" in TEM bright field images. The geometry of the structured diffuse scattering and the associated structural modulation will be described and its relationship with features observed in the images will be discussed.

Key words: sodium bismuth titanate, transmission electron microscopy, modulated structure

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Structural phase transitions in the $\text{Pb}_2\text{MnW}_{1-x}\text{Re}_x\text{O}_6$ perovskites.

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We here report on the structural properties of a new series of double perovskites, $\text{Pb}_2\text{MnW}_{1-x}\text{Re}_x\text{O}_6$. The edges of the series have been studied previously. Pb_2MnWO_6 is orthorhombic at room temperature, space group $Pnma$ [1]. It is isostructural with Pb_2CoWO_6 . The Pb atoms adopt distorted environments which arise from displacements out from the center of the oxygen polyhedron along the [100] cubic direction. On warming, this compound undergoes a crystal phase transition from orthorhombic to cubic. This structural modification is coupled to a change in the dielectric permittivity suggesting an antiferroelectric ground state. X-ray absorption spectroscopy revealed that this is an order-disorder transition as the local structure around Pb atoms show similar distortion degree in both cubic and orthorhombic phases. In this way, dynamic distortions in the cubic phase are frozen in the orthorhombic one [2]. $\text{Pb}_2\text{MnReO}_6$ is monoclinic at room temperature (space group $C2/m$) and it also transforms into a cubic phase at 410 K. The transition can be understood as the condensation of two primary modes, Γ_4^+ associated to the anti-phase tilting of ReO_6 and MnO_6 octahedra and Σ_2 associated to the collinear movement in opposite directions of, mainly, 2/3 of the Pb^{2+} cations [3]. The entropy content for this transition is smaller than the one expected for an order-disorder transition suggesting the presence of significant disorder in the low temperature phase.

The x-ray diffraction patterns of $\text{Pb}_2\text{MnW}_{1-x}\text{Re}_x\text{O}_6$ samples ($0 \leq x \leq 1$) were measured in the temperature range between 123 and 523 K. These measurements have allowed us to obtain the structural phase diagram for the whole series. All samples are cubic at high temperature and undergo a structural phase transition on cooling from cubic phase to either orthorhombic or monoclinic phases. The transition temperature (T_c) slightly decreases as the Re content increases. Below T_c , the Rietveld analysis confirms that the orthorhombic cell is maintained for $x \leq 0.2$ whereas the samples adopt the monoclinic structure for the composition range $x \geq 0.5$. Solid solution between W and Re atoms exists in the abovementioned ranges of the phase diagram. Samples included in the $0.25 \leq x \leq 0.45$ range show the coexistence of both orthorhombic and monoclinic phases. The weight fractions of each phase vary almost linearly in opposite ways in this concentration range. These features agree with the presence of a miscibility gap in the phase diagram for $0.25 \leq x \leq 0.45$.

The structural study was completed measuring EXAFS spectra at the Pb L_3 , Re L_3 , W L_3 and Mn K edges. In the low temperature phase, all samples show similar local structure for each atom independently of the chemical composition. This result indicates a similar degree of local distortion for these atoms in the whole series in spite of the differences in the crystal structure. The local structure has been also monitored in function of the temperature for $x = 0$, $x = 0.5$ and $x = 1$ samples. No changes with temperature are appreciated at all in any of these samples. This result reveals that dynamic distortions are still present in the cubic phase for the whole composition range.

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Keywords: X-ray_diffraction, EXAFS, miscibility

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Reversible phase transition of metal-organic framework by de/rehydration

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The phase transition of a new coordination polymer, [Zn(HBTC)(BPE)_{0.5}(H₂O)]_n·nH₂O, HBTC²⁻=dianion of trimesic acid, DPE = 1,2-bis-(4-pyridyl)ethane, during dehydration and rehydration processes has been monitored by in-situ synchrotron powder X-ray diffractometry. The complex with an extended 1D ladderlike metal-organic framework (MOF) has been synthesized and structural characterized by single-crystal X-ray diffraction method. Structural determination reveals that the Zn(II) ion is four-coordinated in a distorted tetrahedral geometry, bonded to one nitrogen atom from one BPE ligand, and three oxygen atoms from two monodentate carboxylate groups of two HBTC²⁻ ligands and one coordinated water molecule. The 1D ladderlike MOF **1** dehydrates up heating of the solid to 180°C to form a new 2D MOF, [Zn(HBTC)(DPE)0.5]n (**2**). The reversible solid-state structural transformation between crystalline **1** with 1D ladderlike framework and its dehydrated powder **2** with 2D framework via the displacement of coordinated water molecule to HBTC²⁻ ligand, by thermal de/rehydrated processes has been monitoring by in situ PXRD measurements. In the crystal lattice, during heating process, one oxygen atom of the uncoordinated carboxylate group of HBTC²⁻ ligand moves toward the neighboring Zn(II) ion, with concomitant removal of the water molecule, and form a new Zn-O bond without expanding the coordination geometry of metal center. The dehydrated structure for **2** at 180°C was determined from the powder diffraction data with program DASH. Powder pattern was indexed with Dicvol and Treor programs. The structure factors of the powder patterns were extracted with Pawley's method, and simulated annealing method was employed to determine the crystal structure. The final refinement with the Rietveld method was performed using GSAS-EXPGUI program.

Keywords: powder crystallography, metal-organic framework, dehydration

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Origin of giant tetragonal lattice strain in (1-x)BiFeO₃-xPbTiO₃ System

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Electron charge density studies are carried out to reveal the origin of the large tetragonal lattice distortion in multiferroic perovskites (1-x)BiFeO₃-xPbTiO₃ (BF-xPT) by analyzing synchrotron radiation powder diffraction data measured at SPring-8 BL02B2 using the MEM/Rietveld method. The characteristic chemical bondings that are Fe/Ti in 5-fold O coordination and covalent Bi/Pb-O bonding are clearly visualized in the MEM charge density maps in the entire tetragonal composition range $x > 0.31$, which implies BF-xPT is a layered material in the tetragonal phase. The largest tetragonal lattice strain of $c/a = 1.187$ is observed at $x = 0.31$ in the vicinity of the morphotropic phase boundary (MPB) to the rhombohedral structure [1]. Note that all perovskite-type solid solutions with tetragonal structures never show the largest tetragonal distortion near the MPB, for example the smallest tetragonal distortion in PZT near the MPB [2, 3]. The crystal structure of BF-0.31PT, together with PT, is shown in Fig. 1. With decreasing x from 1 (PT) to 0.31, the lattice parameter a decreases, while c increases. Significant changes in the lattice parameters a and c are attributed to changes in the Bi/Pb-O (covalent) and Fe/Ti-O (ionic) bond lengths, respectively. The extrapolated lattice parameters and bond lengths at $x = 0$ (BF) on the basis of the experimentally observed ones well coincide with those optimized by *ab initio* calculations assuming the tetragonal structure with $P4mm$ symmetry. We consider that the tetragonal structure of BF-0.31PT with large tetragonal distortion is originated from the hidden tetragonal structure of BF. By substituting BF for PT in the BF-xPT system, the rotational mode of the Fe/Ti-O₆ octahedron is suppressed, and the tetragonal structure is established by the dominated soft phonon at the Γ point in the Brillouin zone. The Bi/Pb-O covalent bonding plays an important role for the large tetragonal distortion. It is quite natural to consider that the layered structure involving the Fe/Ti-O₅ pyramids are materialized by the contraction on the Bi/Pb-O bonding.

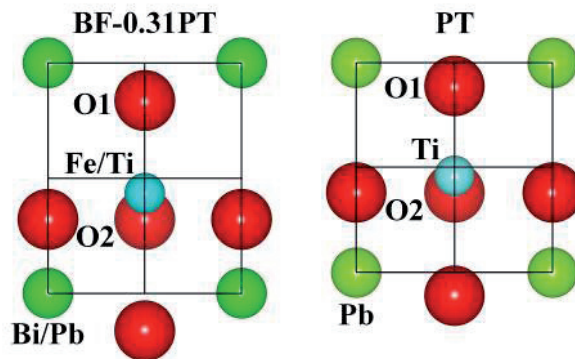


Fig. 1 Crystal structure of BF-0.31PT and PT.

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Keywords: X-ray_diffraction, ferroelectric, perovskite

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Crystal structure of BaTiO₃-based ceramics in MLCCs under applied high voltage

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