

state conversion. Ordering of the spin states is manifested in the corresponding superstructure reflections; these can be traced in a diffraction experiment as a function of external stimuli. By mapping reciprocal space with an area detector and synchrotron light, we have studied the temperature dependence of the superstructure reflections for $\text{NdBaCo}_2\text{O}_{5.5}$ and $\text{TbBaCo}_2\text{O}_{5.48}$. We have found that above the metal-insulator transition there are two different Co ions in the asymmetric unit, one sitting in a pyramidal and one in an octahedral environment. Below the transition temperature there are four structurally different Co ions. This observation agrees with the "spin blockade" mechanism suggested for the metal-insulator transition in cobaltites. We also present results of structural analyzes illustrating how the corresponding powder diffraction measurements could easily overlook the correct structure. A symmetry analysis bracketing the observed phase transitions within the context of Landau theory is also given.

Keywords: cobaltites, spin transition, spin ordering

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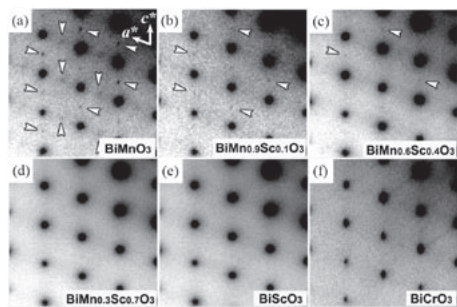
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Investigation of the crystal symmetry of BiMnO_3 : Electron diffraction study

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BiMnO_3 has been considered as a multiferroic material due to the ferroelectric and ferromagnetic properties. The crystal symmetry is, however, controversial today. We investigated the crystal symmetry of BiMnO_3 by Convergent-Beam and Selected-Area Electron Diffraction (CBED and SAED, respectively). CBED, which was used in order to discriminate the crystal axes of BiMnO_3 , showed that BiMnO_3 belongs to space group $C2/c$. In the [010] SAED pattern, however, the very weak but sharp $h0l$ ($l=2n+1$) reflections were observed indicating the noncentrosymmetric long-range ordered structure ($C2$) [1]. This implies that the weak reflections had quite little influence on the CBED patterns [2]. The $h0l$ ($l=2n+1$) reflections could not be detected in structurally related BiScO_3 and BiCrO_3 indicating centrosymmetric $C2/c$, respectively [1]. This strongly suggests that the noncentrosymmetric long-range ordered structure ($C2$) of BiMnO_3 is attributed not only to Bi^{3+} ions with lone electron pair but also to Mn^{3+} ions, that is, to correlation between Bi^{3+} and Mn^{3+} ions. [1]T. Yokosawa, et al. *Phys. Rev. B* **77**, 024111 (2008) [2]M. Tanaka, M. Terauchi, and T. Kaneyama, *CBED II* (JEOL, Tokyo, 1988), pp. 120-139.



Keywords: ferroantiferro-magnetic ferroelectrics, perovskite oxides, electron diffraction

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Structural and magnetic phase transitions in the complex perovskite systems $\text{BiMn}_7\text{O}_{12}$ and $\text{LaMn}_7\text{O}_{12}$

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By means of neutron powder diffraction as a function of temperature, we have investigated the nuclear and magnetic structures of the new systems $(\text{BiMn}_3^{3+})(\text{Mn}_4^{4+})\text{O}_{12}$ and $(\text{LaMn}_3^{3+})(\text{Mn}_4^{4+})\text{O}_{12}$. Single-phase powder samples of both phases were recently synthesized under high pressures at the IMEM-CNR in Parma. In both systems, the A' cation is trivalent, thus all of the Mn B-cations are expected to be trivalent. Both systems crystallize in the $A_3B_4\text{O}_{12}$ complex perovskite structure consisting of a pseudo-cubic network of corner-shared BO_6 octahedra. This system may display a rich manifold of charge, spin and orbital orderings characteristic of mixed-valence systems. In both systems, we have determined precisely the nuclear and magnetic structures as a function of temperature, between room temperature and 2K. We have observed two magnetic transitions at low temperature in the La compound, involving crystallographically different Mn ions. Between 65K and 20K, the propagation vector k is $(0,0,0)$, and only the Mn ions in the B-site are ordered. Below 20K, additional magnetic reflections appear, the lattice is no longer body centered, and magnetic moments of manganese atoms belonging to the A site are ordered. The magnetic structure has been solved by simulated annealing techniques, with help of symmetry analysis. It will be discussed in comparison with the Na analog which had been studied before. For the Bi compound, the effect of the lone pair of Bi on the structure will be discussed, as well as the magnetic structures observed at low temperature.

Keywords: magnetic structures, perovskite structures, neutron powder diffraction

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Coupling of Tb- and Mn-magnetic orders in multiferroic TbMnO_3

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While ferroelectricity and magnetism are chemically incompatible, it has recently been shown that inversion and time-reversal symmetry can be broken simultaneously if magnetic spins order in a cycloidal arrangement as in RMnO_3 . It has been also shown that although the magnetic ordering of Mn-spins drives multiferroicity, R-ions strongly modulate it and thus significantly influence multiferroic properties. Irrespective of the mechanism that drives multiferroic behavior, the magnetic coupling between R- and Mn-spins needs to be understood in order to arrive at a detailed and quantitative model of multiferroics. Here we report on diffraction measurements which demonstrate that the Tb- and Mn- magnetic ordering in multiferroic TbMnO_3 remain

coupled below the ferroelectric temperature $T_{FE} = 28$ K. While below T_{FE} it is known that Tb-spins are induced to order with $\tau^{Tb} = \tau^{Mn}$, below 7 K we find that τ^{Tb} and τ^{Mn} lock-in to rational values of $3/7 b^*$ and $2/7 b^*$, respectively, and obey the relationship $3\tau^{Tb} - \tau^{Mn} = 1$. We explain the novel matching of Tb and Mn wave vectors within the frustrated ANNNI model coupled to a periodic external field produced by the Mn-spin ordering. The $\tau^{Tb} = \tau^{Mn}$ behavior is recovered when Tb magnetization is small, while the $\tau^{Tb} = 3/7$ regime is stabilized at low temperatures by a peculiar arrangement of domain walls in the ordered state of Ising-like Tb spins. Our phase diagram not only reproduces the experimentally observed value of τ^{Tb} but also explains magnetic ordering for R-spins that is realized for R = Dy and Ho.

Keywords: magnetic perovskite materials, magnetic phase transitions, ferroelectricity

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Structure of Sr and Ti codoped LaAlO₃ perovskite

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Rare-earth aluminates, LnAlO₃ (Ln is abbreviated for lanthanide metals such as Ln = La, Ce, Pr, Nd, Pm, Sm, Eu and Gd) are known to possess excellent dielectric properties. In particular, the sintered samples of (La_{1-x}Sr_x)(Al_{1-x}Ti_x)O₃ perovskite-type solid solution have higher quality factors than that of LaAlO₃, peaking Qf=165000 MHz at $x = 0.2$ ¹⁾. This paper aims at clarifying the structure-property relation in the solid solution. Single crystals of $x=0.005$ and 0.20 were grown by the floating-zone method²⁾ and examined by the single-crystal x-ray diffraction method. The crystals possessed weak but significant intensities at the reciprocal lattice points forbidden for the space group $R-3c$ which is commonly assumed for the rhombohedral distortion of the perovskite as in LaAlO₃. The present study revealed that the crystals ($x=0.005$ and 0.2) belong to $R-3$ which accommodates two crystallographically independent octahedral sites for Al(Ti). Ti atoms are preferentially concentrated on the larger Al(Ti)O₆ octahedra. The selective distribution of Ti provides in the $R-3$ structure a less distorted Al(Ti)-O-Al(Ti) bond angle than that in $R-3c$. This is consistent with the physical property that the Sr and Ti codoped compounds have higher Qf than the pure LaAlO₃. Discussion will be given on the reasons why the symmetry of Sr and Ti codoped crystals differs from the pure LaAlO₃³⁻⁴⁾, the end member of the 'solid solution'.

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Keywords: perovskite, new rhombohedral, distortion

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Mobile oxygen form and structural stability of La_{1-x}Sr_xFeO_{3-y} perovskites

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Using thermogravimetry with mass spectrum analysis, low and high-temperature X-ray powder diffraction La_{1-x}Sr_xFeO_{3-y} solid solutions with perovskite-related structure were investigated. From -190 °C and up to room temperature under heating of samples in vacuum perovskite structure preserved. Oxygen loss under heating of samples ($0 \leq x \leq 1$) in air and in vacuum ($x < 0.75$) under temperature of synthesis (1200 °C) leaved the structure unaltered, however, resulted in increase of unit cell volume. Heating in vacuum of compositions $x \Rightarrow 0.75$ resulted in vacancies-ordered phase formation. These structural changes (increase of unit cell parameter, oxygen vacancies ordering) are reversible and reoxidation leads to restoring of initial oxide parameters in process of cooling down in air or in a second heating in air of "vacuum-processed" samples. Loss of oxygen for initial samples under heating and reoxidation process for "vacuum-processed" samples occurred at the same temperature about 400 °C. Amount of emitted oxygen under heating in vacuum and in helium atmosphere increased as compared with those of realised under heating in air.

Keywords: perovskites, high-temperature X-ray diffraction, mobile oxygen form

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X-ray study of the impact of a weak electric field on the domain structure in PbTiO₃ thin films

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Thin films of PbTiO₃ (PTO) deposited on SrTiO₃ (STO) single crystal (001) faces have been studied by SR X-ray scattering to investigate domain size and orientation as a function of film thickness and the impact of a weak electric field. The nearly perfect lattice match between cubic STO and the *ab*-plane of tetragonal PTO ensures that the polar PTO *c*-axis will be well aligned in the growth direction of the film, favouring the formation of *c*-oriented domains. Thin films of PTO in the thickness range 207-24.5 Å deposited by RF magnetron sputtering on insulating STO substrates were studied, using a sample holder allowing the application of an electric field, about 4000 V/cm, onto the sample along the polar axis. In order to study the field effects on the domain structure, scans of reflections $0\ 0\ l$, $h\ 0\ l$ and $0\ k\ l$ were made without field, with field, and again without field after a period with the field turned off. Reconstructions of the diffuse scattering display a surprising complexity which is different for various film thicknesses. The field effects are most prominent for the thickest film (50 uc). Before exposure to the field the major part of the diffuse intensity describes an annular ring relating the average period of the