

K around the transition temperature. In order to determine precisely the structure at high and low temperatures, Rietveld refinements of a complete 2θ range were performed on the patterns collected below and above the transition temperature either for PLT20 or PLT30. The temperature dependence of the relative dielectric permittivity was also performed. From the final Rietveld refinements it was observed important structural trends and it was possible to determine the range where the ferroelectric-to-paraelectric phase transition takes place. The results observed with the XRD refinements agree with that one observed by electric measurements. Structural details, in terms of short and long-range order, are presented and the correlation between the XRD and XANES/EXAFS data is discussed.

Keywords: Rietveld structural refinement, perovskite structures, phase transitions and structure

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Different models for the polar nanodomain structure of PZN and other relaxor ferroelectrics

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Computer simulations have been carried out to test the recently proposed model [1] for the nano domain structure of relaxor ferroelectrics such as lead zinc niobate (PZN). In this recent model it was supposed that the polar nanodomains are three dimensional, that the observed diffuse rods of scattering originate from the boundaries between domains and that the Pb displacements may be directed along $\langle 100 \rangle$, $\langle 111 \rangle$ or $\langle 110 \rangle$. This is in marked contrast to our previously published model [2] which described the polar domains as thin plates with Pb displacements confined to $\langle 110 \rangle$ directions within the essentially 2D domains. The present results confirm that $\langle 100 \rangle$ and $\langle 111 \rangle$ types of Pb displacement are viable possibilities but the number of domain boundaries required to produce sufficiently strong diffuse rods of scattering means that individual domains cannot be described as three dimensional and must still be relatively thin. The current work has been carried out with no direct involvement of the B-site cation ordering that many workers assume is necessary to understand the formation of the polar nanodomains. While it may be true that the B-site cation distribution could provide an underlying perturbation field that might ultimately limit the extent of any polar domain, it is certainly not necessary to produce the observed scattering effects. In an attempt to establish which of the now available models is correct the behaviour of each in an electric field has been explored.

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[2] Welberry, T.R., Goossens, D.J. & Gutmann, M.J. (2006). *Phys. Rev.* B74, 224108.

Keywords: diffuse scattering, relaxor ferroelectrics, PZN

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Structural aspects of the effect of NaNbO₃ substitution on quantum paraelectric behavior of CaTiO₃

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Several perovskite titanates like SrTiO₃, CaTiO₃ (CT), EuTiO₃, La_{1/2}Na_{1/2}TiO₃ and KTaO₃ are known to exhibit unusual phenomenon of quantum paraelectricity. For these materials, the dielectric constant increases with decreasing temperature but does not show a peak corresponding to a ferroelectric (FE) or antiferroelectric (AFE) transition. Instead, their dielectric constant becomes temperature independent at very low temperatures. This has been attributed to the suppression of FE/AFE transition due to zero point quantum fluctuations of the lattice. We have recently shown that substitution of Pb²⁺ in CT can stabilise AFE phase with negative Curie-Weiss temperature [1]. In this work, we present evidence for a phase transition at low temperatures in the system (1-x)CaTiO₃-xNaNbO₃ (CT-xNN), as a result of Na⁺ and Nb⁵⁺ substitutions at Ca²⁺ and Ti⁴⁺ sites. NaNbO₃ substitution leads to a dielectric anomaly superimposed over a continuously rising paraelectric background of pure CT. This anomaly is characterized by a negative Curie-Weiss temperature indicating an AFE transition. Temperature dependent XRD studies reveal the appearance of weak superlattice reflections below the AFE transition temperature. One of the unit cell parameters of the AFE phase is found to be 6 times that of the paraelectric phase. The paraelectric to AFE transition is shown to be first order as evidenced by a discontinuous change in the unit cell parameters. Our previous study on Pb²⁺ substituted CT [1] and the present study on CT-xNN suggest that CT is an incipient AFE. We also show that the mixed CT-xNN system exhibits morphotropic phase boundary like characteristics [2].

References:

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[2]. S. Tripathi et al, *Phys. Rev. B* **77**, 052104 (2008).

Keywords: quantum paraelectric, morphotropic phase boundary, antiferroelectric

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Synthesis and characterization of Bi(Ni_{0.5}Ti_{0.5})O₃

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Ferroelectric lead zirconate titanate is widely used as integral parts of electrical devices due to the high dielectric and electromechanical properties. However, the toxicity of lead oxide results in serious environmental problems and hence alternative compounds free from lead are urgently under development. Since Bi³⁺ ion has the same electronic structure as the Pb²⁺ ions, Bi-containing perovskites are promising candidates for lead-free ferroelectric ceramics. Bi(Ni_{0.5}Ti_{0.5})O₃, BNT, ceramic was

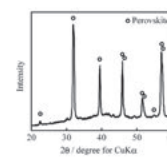


Fig. 1. Powder x-ray diffraction pattern of the BNT ceramic synthesized at 6 GPa, 1000 °C.

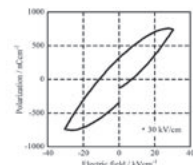


Fig. 2. P-E hysteresis loop of the BNT ceramic.

synthesized using reagent-grade Bi_2O_3 , TiO_2 and $\text{NiCO}_3 \cdot n\text{H}_2\text{O}$ as starting materials. A mixture of the starting materials was calcined in air and then grounded to fine powder to fill up densely a high-pressure reaction cell. The sample was initially compressed and successively heated on keeping constant pressure. Figure 1 shows powder x-ray diffraction pattern of a recovered BNT ceramic synthesized at 6 GPa and 1000 °C. The single-phase perovskite structure was formed. P-E hysteresis loop shows that the BNT ceramic is ferroelectric (Fig. 2). A multi domain structure of the BNT ceramic was also measured by scanning nonlinear dielectric microscopy.

Keywords: high-pressure synthesis, perovskites, solid phase reactions

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X-ray magnetic circular dichroism and electronic state of cobalt atoms in $\text{La}_{1-x}\text{M}_x\text{CoO}_3$ ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$)

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The doping effect of Ca, Sr and Ba has been studied on the magnetic structure of $\text{La}_{1-x}\text{M}_x\text{CoO}_3$ ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$) by X-ray magnetic circular dichroism (XMCD) and theoretical calculation of a DV- $X\alpha$ discrete-variational Hartree-Fock-Slater method. XMCD experiments were carried out at the Co *K* absorption edge in the BL-6C(3A) station of Photon Factory, where Si(111) double-crystal monochromator and diamond(001) phase retarder were used in the Faraday arrangement of rare-earth magnets. A nonmagnetic LaCoO_3 transforms into a paramagnetic semiconductor above $T = 90$ K and a ferromagnetic metal above 500 K. A negative XMCD peak was clearly observed for pure LaCoO_3 at $E = 7.719$ keV of a Co *K* main edge above $T = 90$ K, suggesting a mixed valence state and intermediate spin states. By substituting divalent Ca, Sr or Ba ion for La^{3+} , the negative peak was associated with a positive peak at $E = 7.723$ keV. A pair of peaks forms a dispersion type, which is rationalized with the double-exchange interaction between Co^{3+} and Co^{4+} . First-principles calculations of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ can reproduce the experimental XMCD spectra, where a hybridization of Co 3*d*, 4*p* and O 2*p* stabilizes a magnetic state and the molecular orbital may contribute to produce the intermediate state of Co^{3+} or Co^{4+} . The Ca^{2+} substitution for La^{3+} is expected to have the hole doping with weaker lattice distortion because the ionic radii *IR* resemble each other ($IR = 1.32$ Å for La, 1.35 Å for Ca, 1.44 Å for Sr, 1.61 Å for Ba). The negative XMCD peak for $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ ($x = 0.1$ and 0.15) appeared at $E = 7.721$ keV, while the peak for $x \geq 0.2$ returned to the common position of $E = 7.719$ keV. The presentation will discuss the electronic structures and spin states of cobalt ions in the solid solution.

Keywords: X-ray magnetic circular dichroism, mixed-valence transition-metal compounds, electronic structure and magnetism

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Tuning of magnetic properties by building blocks assembly in halogeno-cobaltites perovskites

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Cobaltites have attracted considerable interest in the last decade because of spectacular properties such as thermoelectric or superconducting effects. In that field, our investigation of the Ba-Co-X ($\text{X}=\text{O}, \text{F}, \text{Cl}, \text{Br}$) system has led to a number of new mixed-valent CoIII/IV materials that turned out to display complex physical properties. From a structural point of view, these compounds can be deduced from each other by the reorganization of structural blocks isolated by anionic layers. We have investigated the dependence of the connectivity between the building blocks on the magnetic orderings and we have evidenced a main conservation of intra-block properties. The role of the inter-block connectivity on the local Co moments has been pointed out. We have shown (from both Squid measurements and neutron diffraction) that magnetic orderings can vary, depending on the connectivity between the blocks, from ferromagnetic to antiferromagnetic and eventually metamagnetic transition. Crystal, magnetic structure and geometrical features at the interblocks

junction for

a) 2H-BaCoO_3 : Ferrimagnetic
 b) 5H-BaCoO_3 -d: Ferromagnetic
 c - d) $10\text{H-Ba}_6\text{Co}_6\text{XO}_{15.5}$: Antiferromagnetic
 e) $18\text{R-Ba}_7\text{Co}_6\text{BrO}_{15.5}$: Metamagnetic

Compound	Co-Co (Å)	Co-O (Å)	O-O (Å)	Co-O-O (°)
(a) 2H-BaCoO ₃	4.7	1.9	3.3	85°
(b) 5H-Ba ₆ Co ₆ O _{15.5}	3.3	1.9	3.3	125°
(c) 10H-Ba ₆ Co ₆ XO _{15.5}	3.2	1.8	3.3	155°
(d) 10H-Ba ₆ Co ₆ XO _{15.5}	3.2	1.8	3.3	155°
(e) 18R-Ba ₇ Co ₆ BrO _{15.5}	6.6	1.8	3.7	130°

Keywords: perovskite layered compounds, magnetic structure determination, structure-physical properties relationships

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Synthesis of KNbO_3 at different conditions

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The main problem of stabilization of perovskite structure of KNbO_3 is keeping the stoichiometry of consistence as a result of calcining at high temperatures at which K_2O evaporates. Moreover, during preparation of KNbO_3 at low temperatures nanoparticle generation occurs. It is known that at the crystalline sizes lesser than critical ferroelectric properties are suppressed: at room temperature the values of spontaneous polarization lessen and changes of symmetry up to generation of cubic paraelectric phases occur. That is why the study of nanoscale effects at KNbO_3 synthesis is of interest. The aim of current work is the study of dependencies of generation of perovskite phases from synthesis temperatures. Part of this work is done with