

synthesized using reagent-grade  $\text{Bi}_2\text{O}_3$ ,  $\text{TiO}_2$  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  $\text{LaCoO}_3$  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  $\text{LaCoO}_3$  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  $\text{La}^{3+}$ , 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  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$ . 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  $\text{Co}^{3+}$  or  $\text{Co}^{4+}$ . The  $\text{Ca}^{2+}$  substitution for  $\text{La}^{3+}$  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  $\text{Ba-Co-X}$  ( $\text{X}=\text{O}, \text{F}, \text{Cl}, \text{Br}$ ) 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)  $2\text{H-BaCoO}_3$ : Ferrimagnetic  
 b)  $5\text{H-BaCoO}_3$ : Ferromagnetic  
 c)  $10\text{H-Ba}_6\text{Co}_6\text{XO}_{15.5}$ : Antiferromagnetic  
 d)  $18\text{R-Ba}_7\text{Co}_6\text{BrO}_{15.5}$ : Metamagnetic

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

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#### Synthesis of $\text{KNbO}_3$ at different conditions

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The main problem of stabilization of perovskite structure of  $\text{KNbO}_3$  is keeping the stoichiometry of consistence as a result of calcining at high temperatures at which  $\text{K}_2\text{O}$  evaporates. Moreover, during preparation of  $\text{KNbO}_3$  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  $\text{KNbO}_3$  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

the use of *in situ* method on X-ray diffractometer. The phase changes observed may be explained in the following way: at low synthesis temperatures and relatively short-time calcinating (2 hours) the generation of KNbO<sub>3</sub> as least(possibly nano) particles. This supposal is proved by the fact that known ferroelectrics (BaTiO<sub>3</sub>, PbTiO<sub>3</sub> etc.) in nanocrystal condition are characterized by the increased cell sizes and lessened values of spontaneous deformation. The increased cell volumes could be the consequence of large concentrations of defects. On increase of calcinating temperatures, the reduce of the cell volume might be the consequence of either increase of crystalline sizes or of the reduce of defects number. Until now the phenomenological study of ferroelectric phase conditions was observed from the point of view of outer effects(temperatures, pressures, electric fields) that's why including the parameters of real conditions of objects into complete theoretical observation.

Keywords: ferroelectrics, phase transitions, synthesis

### P11.11.54

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#### Modulated crystal structure of RE<sub>1.67</sub>AE<sub>0.33</sub>NiO<sub>4</sub> in charge ordering state

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Stripe-type charge ordering (CO) [1], as found in some layered perovskite-type transition-metal oxides, is a typical example of self-organized electrons and also responsible for novel electric properties, such as the colossal magnetoresistance and electroresistance that are expected to be applied to the next generation memories [2]. Therefore, investigation of the CO structure is important for material design in layered transition metal oxide systems [3]. In this work, we report on the modulated crystal structure associated with the CO in the single-layered nickelates RE<sub>1.67</sub>AE<sub>0.33</sub>NiO<sub>4</sub> (RE and AE are rare-earth and alkaline-earth ions, respectively). The relation between A-site cations and CO structure has been investigated systematically by means of transmission electron microscopy (TEM). Long-range ordered charge stripes with a commensurate modulation wave number along the b-axis (the longer axis in the ab plane) are observed in the orthorhombic single crystal Pr<sub>1.67</sub>Ca<sub>0.33</sub>NiO<sub>4</sub> with minimal disorder effect. Change of A-site combination to Sm and Sr, the CO correlation along the b-axis becomes short-range. An abrupt decrease of the CO correlation length along the c-axis with the increase of disorder revealed that the charge stripe ordering collapses via the stacking faults of the charge stripes, indicating that the quenched disorder affects the CO structure in the layered nickelates.

Keywords: modulated crystals, transition-metal oxides, TEM

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#### Investigation of differently synthesized Co-Ni-Al spinels and precision of the crystallographic data

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Spinelns comprise a large group of compounds with high importance in industry. Our investigations focus on the influence of different synthesis methods on both, the crystallization path and on the crystal chemistry of the spinel product. Additionally to the materials aspects, the precision and reproducibility of the crystallographic analyses are of major interest. (Co,Ni)Al<sub>2</sub>O<sub>4</sub> spinels with four different Ni:Co ratios were synthesized by 4 different methods: from impregnated carbons, by sol-gel methods, and by calcination of oxides and of salts. Samples were calcined at temperatures between 550°C and 1300°C. All samples were measured in Bragg-Brentano geometry with Cu-K  $\alpha$  radiation. Additionally, selected samples were analyzed in Debye-Scherrer geometry with Mo-K $\alpha_1$  radiation and by neutron diffraction at the E6 instrument at the Hahn-Meitner facility (Berlin). Rietveld refinements of diffraction patterns revealed that the synthesis path indeed has an influence on the spinels formed. Due to the different precursor materials spinels with different chemical compositions and varying amounts of by-phases are obtained. Neutron diffraction experiments performed on selected samples calcined between 1050°C and 1300°C show only minor changes of the Co and Ni distribution on the octahedral and the tetrahedral position with temperature. This indicates that already at lower temperatures the spinels formed are in equilibrium. Structure refinement strategies as well as the selection of instrument geometry and radiation source shows a strong influence on the refined structure data.

Keywords: spinel, crystallization of materials, data precision

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#### Phase transition studies in multiferroic Pb(Fe<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub> and its solid solution with PbTiO<sub>3</sub>

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Recent years have witnessed enormous interest in the multiferroic materials because of the presence of more than one ferroic/ anti-ferroic orders: such as ferroelectric, ferroelastic and ferromagnetic/ antiferromagnetic. Pb(Fe<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub> (PFN), is a multiferroic exhibiting a diffuse ferroelectric phase transition at 385K and two antiferromagnetic transitions at 143K and 9K, respectively. It is an attractive material for use in multilayer ceramic capacitors and other electronic devices due to its high dielectric constant, diffuse phase transition behaviour and low sintering temperature. The phase diagram of its solid solution with PbTiO<sub>3</sub> ( i.e. (1-x)Pb(Fe<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub>-xPbTiO<sub>3</sub> or PFN-xPT) shows a morphotropic phase boundary (MPB) similar to that in the well known Pb(Zr<sub>x</sub>Ti<sub>1-x</sub>)O<sub>3</sub> (PZT), (1-x)Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-xPbTiO<sub>3</sub> (PMN-xPT) and (1-x)Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub> (PZN-xPT) ceramics. We present here the results of synchrotron powder x-ray diffraction, dielectric and magnetization studies on 'phase-pure' PFN and PFN-xPT. It was found for the