

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 $\text{La}_{1-x}\text{M}_x\text{CoO}_3$ ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$)

Satoshi Sasaki¹, Hiroyuki Katsuragawa¹, Maki Okube¹, Takayasu Hanashima²

¹Tokyo Institute of Technology, Materials and Structures Laboratory, Nagatsuta 4259, Midori-ku, Yokohama, Kanagawa, 226-8503, Japan, ²Ritsumeikan University, Nojihigashi 1-1-1, Kusatsu, Shiga 525-8577, Japan, E-mail: sasaki@n.cc.titech.ac.jp

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

Pascal Roussel, Ghislaine Ehora, Sylvie Daviero-Minaud, Olivier Mentre

CNRS UMR 8181 - UCCS, Solid State Chemistry, ENSCL - Bat C7a, Villeneuve d'Ascq, Nord, 59652, France, E-mail: pascal.roussel@ensc-lille.fr

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

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

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Synthesis of KNbO_3 at different conditions

Pavel Teslenko, Yulia Kuprina, Natalia Kofanova, Yuri Kabirov, Michael Kupriyanov

Southern Federal University, Physics faculty, 5, Zorge str., Rostov-on-Don, Rostov region, 344090, Russia, E-mail: kupri@phys.rsu.ru

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