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High pressure synthesis and properties of $\text{Bi}_{0.5}\text{Pb}_{0.5}\text{CrO}_3$: A novel $\text{Cr}^{4+}/\text{Cr}^{3+}$ perovskite



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ABSTRACT

We have synthesized a new $\text{Bi}_{0.5}\text{Pb}_{0.5}\text{CrO}_3$ perovskite phase by means of a high pressure reaction at 70 kbar and 1000 °C. The distorted orthorhombic perovskite structure can be indexed in the space group $Pnma$ with lattice parameters $a=5.4768$ (1) Å, $b=7.7450$ (2) Å, and $c=5.4574$ (1) Å at room temperature, but undergoes a structural phase transition and enters into a $P2_1/m$ monoclinic distorted perovskite phase below 150 K with $a=5.4173$ (2), $b=7.7286$ (4) and $c=5.4930$ (3). The structural transition is coincident with the onset of magnetic interactions. At lower temperatures a weak ferromagnetic structure is evident related to antiferromagnetic Cr-spin canting and a spin-glass transition is observed at ≈ 40 K. The semiconducting-type electrical resistivity is relatively low, associated with $\text{Cr}^{3+}/\text{Cr}^{4+}$ electron hopping, and shows considerable magneto-resistance (up to 15%). Due to the low resistivity the dielectric permittivity ϵ_r could be determined only below $T < 80$ K to be ≈ 300 and did not show any strong temperature-dependence. Ferroelectricity was not detected in the T -range investigated and no magnetocapacitance effects were observed.

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1. Introduction

Among mixed oxide phases, perovskites represent one of the most important and well-studied structures. Perovskites or perovskite related structures can accommodate a vast range of different cations, which can lead to distinct properties such as superconductivity (e.g. in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$), colossal magneto-resistance ($\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$), itinerant electron ferromagnetism (SrRuO_3), ferroelectricity (BaTiO_3), piezoelectricity ($\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$), ionic conductivity ($\text{La}_{0.67-x}\text{Li}_{3x}\text{TiO}_3$, BaCeO_{3-x}) [1,2], as well as multiferroic behavior (TbMnO_3) which has attracted particularly strong interest in recent years [3,4]. One among the different strategies for the chemical search for new candidate multiferroic materials is the accommodation of different cations on the A - and B -site of the perovskite structure. The B -site cation would possess partially filled d or f electron levels as a source

for magnetism, whereas the A -site cation would exhibit lone-pair electrons to induce non-centrosymmetry into the crystal structure and possibly ferroelectric polarization. The parent compounds for the title material, BiCrO_3 and PbCrO_3 , are both high pressure/high temperature (HP/HT) phases and require 40 kbar and 55 kbar respectively, and temperatures of $800 < T < 1000$ to be synthesized [5–10].

The HP synthesis of BiCrO_3 at 35–55 kbar has been largely studied in the past. The compound undergoes a structural phase transition at ≈ 410 – 420 K from a high temperature monoclinic to a low temperature non-centrosymmetric triclinic perovskite phase, and the Cr^{3+} cations order antiferromagnetically below ≈ 120 K [7]. Across the structural transition the dielectric permittivity exhibits an anomaly, which signals ferroelectricity and a concomitant ferroelectric polarization. Therefore, BiCrO_3 may be regarded a multiferroic system due to the coexistence of ferroelectric and magnetic ordering below ≈ 120 K.

PbCrO_3 has been synthesized and characterized for the first time by Roth and De Vries [6]. They reported a cubic perovskite

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symmetry ($a=4.00$ Å), and an antiferromagnetic structure with $T_N \approx 240$ K. More recently, a deeper investigation revealed the coexistence of an occupational and displacive modulation of Pb^{2+} cations [9]. Further magnetic measurements validated the AFM behavior and revealed a novel temperature-driven and gradual spin reorientation between 185 and 62 K [9,10], which was believed to be correlated to the occupational and displacive Pb^{2+} modulations. Within the context of the solid solution $\text{Bi}_{1-x}\text{Pb}_x\text{CrO}_3$ that we have recently investigated [11], we here describe the synthesis and characterization of the double perovskite $\text{Bi}_{0.5}\text{Pb}_{0.5}\text{CrO}_3$. Our work is motivated by the above-mentioned strategy of combining two different cations on the perovskite A-site with both having lone-pair electrons and a magnetic cation in the B-site leading to an $A_{0.5}A'_{0.5}BO_3$ perovskite.

2. Experimental section

$\text{Bi}_{0.5}\text{Pb}_{0.5}\text{CrO}_3$ was prepared under HP/HT conditions using a Belt-type press located in the “Laboratorio Complutense de Altas Presiones”. Stoichiometric amounts of α - PbO , Bi_2O_3 , Cr_2O_3 and CrO_2 were intimately mixed and ground in an agate mortar and placed in a Pt capsule for HP/HT, the synthesis conditions being explored at temperatures in the 900–1100 °C range, at pressures between 40–80 kbar and reaction times between 3 and 30 min. The resulting powders were examined by powder X-ray diffraction (XRD) using a Panalytical model X’Pert PRO MPD Alfa1 diffractometer with monochromatic CuK_α ($\lambda=1.5405$ (6) Å) radiation obtained with a germanium primary monochromator. Data were collected in the range of $2\theta=5$ –120°, with a step size of 0.017° (2θ) over a total exposure time period of 12 h. The powder diffraction patterns were indexed by TREOR and DICVOL software [12,13], and fitted to a structural model using the Rietveld method by means of the FullProf-Suite program [14,15].

Low temperature thermodiffraction measurements have been performed in an X’Pert PRO-TT diffractometer using Cu radiation ($K_{\alpha 1}=1.5405$ (6) Å and $K_{\alpha 2}=1.5443$ (9) Å). The temperature was varied between 14 and 298 K in a Phenix Oxford Cryosystems low temperature chamber.

Samples for high resolution transmission electron microscopy (HRTEM) and convergent beam electron diffraction (CBED) were prepared by grinding the powder, dispersing it in *n*-butyl alcohol and collecting few drops of the suspension on a holey carbon-coated copper grid. Selected area electron diffraction (SAED) was performed using a JEOL JEM FX2000 microscope, equipped with a double tilt $\pm 45^\circ$ holder, working at 200 kV. HRTEM was carried out on a JEOL JEM 3000FEG microscope, with $C_s=0.6$ nm, operating at 300 kV. Both microscopes were equipped with an analyzer for Energy Dispersive Analysis of X-rays (EDAX) to verify the stoichiometry of $\text{Bi}_{0.5}\text{Pb}_{0.5}\text{CrO}_3$.

HRTEM images have also been simulated using Mac Tempas software, whereby the focus was varied in the model and optimized between -600 Å and -100 Å in 6 steps of 100 Å, and the sample thickness between 11 and 93.1 Å in 4 steps [16,17].

A SQUID Quantum Design XLMPM was used to perform measurements of magnetic susceptibility (χ) vs temperature (T) under ZFC and FC conditions (1 and 5 kOe) between 2 and 300 K, magnetization M vs applied field (H) at 5 K between $H=0$ –5 T, and magnetic AC susceptibility (χ) vs T at 33, 330, 660 and 1000 Hz between 20 and 60 K.

A QuadTech impedance analyzer was used for dielectric spectroscopy with an applied ac amplitude of 20 mV operating between 20 Hz and 1 MHz. Data were collected in the format of real and imaginary part of the impedance (Z'' – Z'). To facilitate frequency (f), T and H dependent dielectric measurements a special sample holder was used (Janis Research Ltd., USA), which can fit into a Quantum

Design PPMS measurement system providing variable H (up to 140 kOe) and variable T (10–320 K). The custom built probe was necessary to minimize the internal probe capacitance (≈ 0.2 pF) and maximize the internal probe resistance (≈ 10 GΩ), which is both detrimental for reliable alternating current (ac) dielectric measurements. The sample tray at the bottom of the probe was equipped with spring loaded drop-down pins to ensure optimal contact between the pins and sample electrodes. As an electrode material Au was sputter-deposited onto two opposing faces of the $\text{Bi}_{0.5}\text{Pb}_{0.5}\text{CrO}_3$ bulk samples and both such electrodes were covered with Ag paint.

Equivalent circuit fitting of the dielectric data collected at variable f , T and H was performed by employing commercial Z-View[®] fitting software, where each equivalent circuit model was fitted to both the real and imaginary parts of the f -dependent impedance data by minimizing the statistically weighted linear least-squares.

3. Results and discussion

3.1. Optimization of the synthesis conditions

For the synthesis of $\text{Bi}_{0.5}\text{Pb}_{0.5}\text{CrO}_3$ the reaction temperature, pressure and time needed to be optimized by trial and error. For any of these 3 parameters, too low a value leads to an incomplete reaction of the precursors, whereas too high values lead to decomposition. The optimum conditions were found to be 70 kbar and 1000 °C with a reaction time of 15 min.

3.2. Structural characterization

3.2.1. Room temperature phase

The room temperature Rietveld refinement provided good agreement between model and data (Fig. 1). No indications for a $\text{Bi}^{3+}/\text{Pb}^{2+}$ A-site cation order were found by XRD. This is not surprising though, because Pb^{2+} and Bi^{3+} are isoelectronic ions and X-ray diffraction cannot distinguish between them. The $\text{Bi}_{0.5}\text{Pb}_{0.5}\text{CrO}_3$ phase was indexed as an orthorhombic perovskite structure, because we observe an unusual broadening of the 220 peak in the XRD pattern at around 40° . We interpret this as a weak orthorhombic distortion in $\text{Bi}_{0.5}\text{Pb}_{0.5}\text{CrO}_3$ perovskite, which cannot fully split the 220 reflection. Rietveld refinements using tetragonal settings give significantly higher fitting errors.

Refinements were carried out with space group (S. G.) $Pnma$, with lattice parameters $a=5.4768$ (1) Å, $b=7.7450$ (2) Å and $c=5.4574$ (1) Å. This can be regarded as the diagonal cell $\sqrt{2}a_c \times 2a_c \times \sqrt{2}a_c$ in a pseudo-cubic perovskite setting with $a_c \approx 3.8$ Å [18,19]. The ED micrographs of the room temperature phase shown below suggest $Pnma$ orthorhombic symmetry due

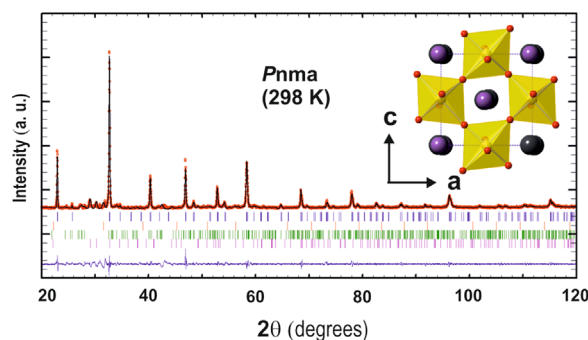


Fig. 1. Experimental and calculated XRD patterns and their difference for perovskite $\text{Bi}_{0.5}\text{Pb}_{0.5}\text{CrO}_3$ at 298 K. Tic marks show positions of expected peaks. The bottom curve shows the difference between observed and calculated patterns. Secondary phases are PbCrO_3 and $\delta\text{-Bi}_2\text{O}_3$.

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