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Enhancement in thermoelectric characteristics of the misfit-layered cobalt oxide, $[(Bi,Pb)_2Ba_{1.8}Co_{0.2}O_{4\pm\omega}]_{0.5}CoO_2$, through Pb-for-Bi substitution

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Abstract

Thermoelectric characteristics of a newly discovered commensurate (q=0.5) misfit-layered oxide, $[Bi_2Ba_{1.8}Co_{0.2}O_{4\pm\omega}]_qCoO_2$, have been significantly enhanced through partial Pb-for-Bi substitution: such substitution is found not only to reduce electrical resistivity and extend the temperature range for metallic conductivity, but also to raise the Seebeck coefficient. To obtain heavily Pb-substituted samples (up to 20–30% substitution level) requires careful control of both temperature and oxygen partial pressure during synthesis. Upon increasing Pb content, the lattice gets shrunken along the layer-piling (c-axis) direction, while the q value remains constant at 0.5.

Keywords: Misfit-layered compound; Cobalt oxide; Thermoelectric characteristics

1. Introduction

Misfit-layered (ML) cobalt oxides, $[M_mA_2O_{2+m}]_qCoO_2$ (M=Co, Bi, etc.; A=Ca, Sr, etc.; m=1 or 2) [1], based on incoherently coupled hexagonal CoO_2 layers and square-planar $M_mA_2O_{2+m}$ layers of rock-salt (RS) type, are in a focus of current attention owing to their unexpectedly good thermoelectric (TE) characteristics [2–4], i.e. low electrical resistivity (ρ), high Seebeck coefficient (S) and low thermal conductivity (κ), in the scale of "figure-of-merit", Z ($\equiv S^2/\rho\kappa$). For practical applications, the non-dimensional figure, ZT, should be higher than unity at the utilization temperature, T. From material design and optimization points of view, the difficulties arise from the fact that the individual factors for Z, i.e. ρ, S and κ, are not totally independent, as, e.g. all of them are (different) functions of the carrier concentration [5]. For an optimized Z, materials with carrier concentrations of the level of 10^{19} cm^{-3} have been looked for, supposing that the materials obey the conventional band theory: the first-generation thermoelectrics, e.g. Bi_2Te_3 and PbTe, are all degenerate semiconductors.

Compound Na_xCoO_2 was the first oxide material highlighted due to its high TE figure ($S \approx 100$ μV/K and $\rho \approx 200$ μΩ cm at room temperature [6]), being comparable to that of Bi_2Te_3. From the crystal structure of this oxide, a clue was derived that a (multi)layered structure comprising both highly conducting layers with strongly correlated electrons and insulating layers of a random/disturbed atomic arrangement are likely to be crucial features of the next-generation oxide thermoelectrics. Notably, ML oxides also fulfill these criteria.

Comparing the properties of ML oxides of various systems, e.g. Pb-(Sr,Ca)-Co-O [7], Tl-(Sr,Ca)-Co-O [8], Hg-(Sr,Ca)-Co-O [9] and Bi-(Sr,Ca)-Co-O [10], a trend can be derived that substitution of Sr by the smaller Ca at the A site depresses the metallic conductivity. This, on the other hand, suggests that Ba-based ML oxides, if exist, might show enhanced metallicity. Along this, a recently discovered compound, $[Bi_2Ba_{1.8}Co_{0.2}O_{4\pm\omega}]_qCoO_2$, was found highly metallic [11]. [Unlike the other ML cobalt oxides, this compound is commensurate in terms of the misfit-parameter, q ($\equiv b_{CoO_2}/b_{RS}$=0.5).] Here we report further enhancement in its TE characteristics by means of partial Pb-for-Bi substitution, yielding not only lower electrical resistivity and an extended temperature range for metallic conductivity but also a drastic increase in the Seebeck coefficient.

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2. Experimental

Polycrystalline samples of $(Bi_{1-x}Pb_x)_2Ba_{1.8}Co_{2.2}O_{8+\delta}$ with x ranging from 0 to 0.4 were prepared from stoichiometric mixtures of Bi_2O_3, PbO_2, BaO_2 and Co_3O_4 through solid-state reaction. Precursor pellets of thoroughly mixed powders were sintered for 12 h at optimized temperatures in oxygen-partial-pressure controlled atmospheres about 800 °C. Diffraction patterns of the samples were collected by an X-ray diffractometer (Rigaku: RINT-2000; Cu K_α radiation) and refined for the lattice parameters in space group $C2/m(0b0)s0$ using JANA2000 [12]. Electron diffraction (ED) patterns were taken using a transmission-electron microscope (TEM; Hitachi: 9000NAR) with an acceleration voltage of 300 kV. Resistivity measurements were performed with a four-point-probe apparatus (Quantum Design: PPMS). Magnetoresistance data were also collected with the same apparatus. Thermoelectric power was measured using a steady-state technique, below 300 K. Magnetization was measured by a SQUID magnetometer (Quantum Design, MPMS-XL).

3. Results and discussion

The Pb-free ML compound, $Bi_2Ba_{1.8}Co_{2.2}O_{8+\delta}$, readily forms as a single phase at 800 °C in air, as reported earlier [11]. Attempts were made to employ the same synthesis conditions for the Pb-containing samples too, but considerable amounts of Co_3O_4 and $Ba(Pb_{0.75}Bi_{0.25})O_3$ (superconductive with $T_c \approx 7$ K) always appeared as impurity phases. Careful optimization of synthesis conditions was made to obtain XRD-pure samples of the $(Bi_{1-x}Pb_x)_2Ba_{1.8}Co_{2.2}O_{8+\delta}$ phase with x up to 0.3. However, the impurity phase $Ba(Pb_{0.75}Bi_{0.25})O_3$ appeared again at x=0.4 (see Fig. 1 for the XRD patterns). In the inset of Fig. 1, the relationship between the lattice parameter, c and the Pb content, x is shown. With increasing Pb content, the c parameter decreases up to x=0.2 and then saturates for $x \geq 0.3$. (The lattice parameters, a and b, remain essentially constant.) From these results, the solubility limit of Pb in $(Bi_{1-x}Pb_x)_2Ba_{1.8}Co_{2.2}O_{8+\delta}$ is estimated at x=0.2~0.3. Here it should be noted that for the Sr-based system, $(Bi_{1-x}Pb_x)_2Sr_2Co_2O_y$, the solubility limit of Pb at the Bi site was found at $x \approx 0.3$ [13,14].

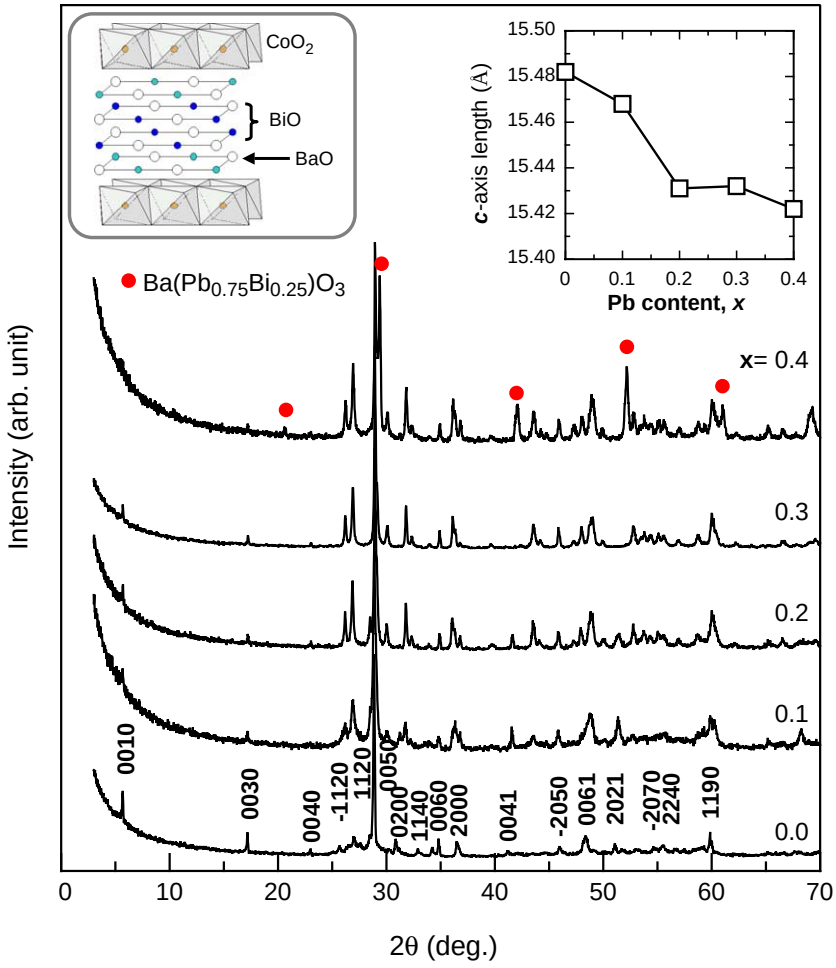

Fig. 1. X-ray diffraction patterns for the $(Bi_{1-x}Pb_x)_2Ba_{1.8}Co_{2.2}O_{8+\delta}$ samples with x=0, 0.1, 0.2, 0.3 and 0.4. In the inset the c lattice parameter refined from the patterns is plotted against the Pb content, x. Note that the four-integer indices given for the x=0 sample are in the form of $hk^{RS}lk^{CoO2}$.