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Pb-for-Bi substitution for enhancing thermoelectric characteristics of [(Bi , Pb) 2 Ba 2 O 4 ± ω] 0.5 Co O 2

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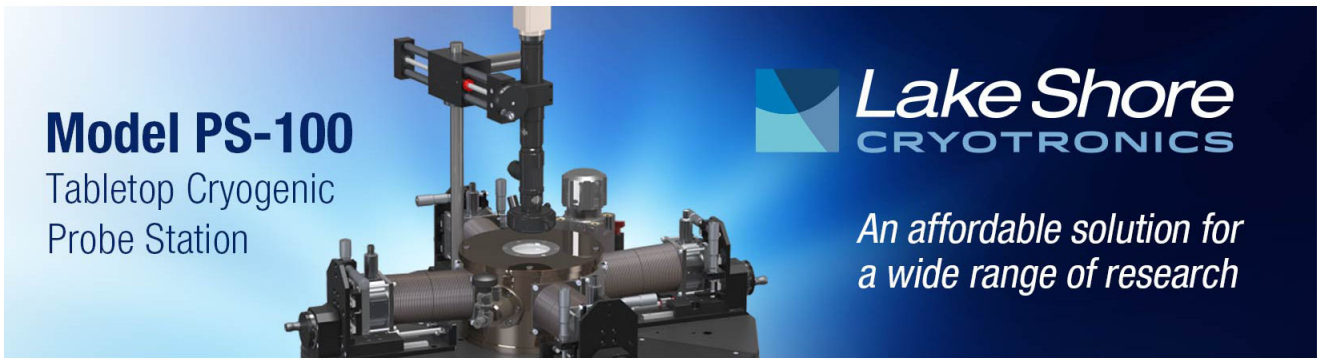

Pb-for-Bi substitution for enhancing thermoelectric characteristics of $[(Bi,Pb)_2Ba_2O_{4\pm\omega}]_{0.5}CoO_2$

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We report strongly enhanced thermoelectric characteristics for a misfit-layered oxide, $[Bi_2Ba_2O_{4\pm\omega}]_{0.5}CoO_2$, in a wide temperature range, as achieved through substituting up to 20% of Bi by Pb. The Pb substitution kept the thermal conductivity (κ) unchanged but decreased the electrical resistivity (ρ) and increased the Seebeck coefficient (S) simultaneously, such that a three-fold enhancement in the thermoelectric figure of merit, Z ($\equiv S^2/\rho\kappa$), was realized. At the same time x-ray absorption near-edge structure data indicated that the valence and spin states of Co are not affected by the Pb-for-Bi substitution. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2206134]

Today the advantages of thermoelectric (TE) devices have become deeply recognized from the viewpoint of clean generation and usage of energy.[1] The major obstacle towards wider applications is in the efficiency of the TE material itself. TE efficiency is evaluated in terms of "figure of merit" Z ($\equiv S^2/\rho\kappa$), and the difficulty lies in the fact that the individual parameters of Z, i.e., electrical conductivity (ρ), Seebeck coefficient (S), and thermal conductivity (κ), are not totally independent such that an enhancement in one parameter is often achieved at the expense of the other(s). Recent material discoveries have highlighted oxides as notable candidates for high-efficiency TE materials.[2–5] Highly promising p-type oxide thermoelectrics all contain hexagonal CoO_2 layers in their crystal structures. In the first-generation TE oxide, Na_xCoO_2, the adjacent CoO_2 layers are separated by a single, nonstoichiometric Na^+ layer, whereas in the so-called misfit-layered (ML) cobalt oxides, $[M_mA_2O_{m+2\pm\omega}]_qCoO_2$ (M=Co, Bi, etc.; A=Ca, Sr, etc.; m=0, 1, or 2), the hexagonal (H) CoO_2 layer is incoherently coupled with square-planar (S) $M_mA_2O_{m+2}$ layers.[6,7] Here, combination of highly conducting CoO_2 layers with strongly correlated electrons and insulating layers of a random/disturbed atomic arrangement is likely to be the crucial feature for the materials to show excellent TE characteristics as a whole.

For a $[M_mA_2O_{m+2\pm\omega}]_qCoO_2$ phase, the "stoichiometry parameter" q is defined by the ratio of the b-axis lengths of the lattices of the two layers, H and S, i.e., $q \equiv b_H/b_S$. Hence it also serves the role of "misfit parameter" as it quantifies the degree of misfitness. Recently Hervieu *et al.*[8] synthesized the first Ba-based ML cobalt oxide, $[Bi_2(Ba_{1.8}Co_{0.2})O_{4\pm\omega}]_qCoO_2$. Unlike the other ML cobalt oxides, this compound with the large Ba as the A-site constituent was found to be commensurate, i.e., q=0.5. Nevertheless, it showed—besides enhanced metallic conduction—a value for the room-temperature Seebeck coefficient not significantly lower than those for the incommensurate ($q>0.5$) ML cobalt oxides. Here we report further enhancement in the TE characteristics as achieved in a wide temperature range for the phase through partial Pb-for-Bi substitution.

Polycrystalline samples of $[(Bi_{1-x}Pb_x)_2(Ba_{1-y}Co_y)_2O_{4\pm\omega}]_{0.5}CoO_2$ corresponding to the nominal cation compositions of y=0.2 and x=0.0, 0.1, or 0.2 were synthesized from appropriate amounts of Bi_2O_3, PbO_2, BaO_2, and Co_3O_4 in 0.1% O_2/Ar gas flow at 775 °C for 12 h (in a pellet form). From inductively coupled plasma (ICP) analysis the actual cation composition was found (presumably due to some Co loss during the synthesis process) to be closer to the y=0 situation than to the nominal y=0.2 one, hence suggesting—along with chemistry arguments—that in practice there is no Co occupation at the A (=Ba) site. For all the three samples XRD and electron diffraction (ED) patterns (not shown here) were found fully compatible with a $[M_mA_2O_{m+2\pm\omega}]_qCoO_2$-type structure with m=2 and q=0.5. In our preliminary work on the $[(Bi_{1-x}Pb_x)_2Ba_2O_{4\pm\omega}]_{0.5}CoO_2$ system it was seen that with increasing Pb-substitution level x, the lattice parameter c decreases, whereas the lattice parameters a and b remain essentially constant.[9] Moreover, from the ED patterns it could be concluded that parallel to the case of its Sr-based $[(Bi_{1-x}Pb_x)_2Sr_2O_{4\pm\omega}]_qCoO_2$ analog,[10] the modulation seen within the $[(Bi_{1-x}Pb_x)_2Ba_2O_{4\pm\omega}]$ block in $[(Bi_{1-x}Pb_x)_2Ba_2O_{4\pm\omega}]_{0.5}CoO_2$ at x=0 (Ref. 8) gradually disappears with increasing x.[9] This is presumably due to a concomitant decrease in oxygen content of the (Bi,Pb)O layer, as commonly seen for many other

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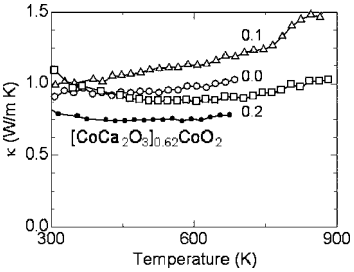

FIG. 1. Temperature dependence of thermal conductivity (κ) for the $[(Bi_{1-x}Pb_x)_2Ba_2O_{4\pm\omega}]_{0.5}CoO_2$ samples with $x=0.0$, 0.1, and 0.2. Also given are data for a polycrystalline reference sample of $[CoCa_2O_{3\pm\omega}]_{0.62}CoO_2$.

Bi-based layered oxides when replacing Bi partially by Pb.[11,12]

The samples were characterized for their TE properties in two temperature ranges. At low temperatures ($T<300$ K) the resistivity measurements were performed with a four-point-probe apparatus (Quantum Design: PPMS) and the thermoelectric power was measured using a steady-state technique. In the high-temperature region ($T>300$ K) the measurements for ρ and S were performed using a high-temperature-Seebeck-probe apparatus (HTSP-2000), and the thermal conductivity data were collected by a laser-flush technique in vacuum (ULVAC: TC-7000).

Figure 1 displays the thermal conductivity data for the samples. For a reference, included are the data collected under similar conditions for a polycrystalline sample of $[CoCa_2O_{3\pm\omega}]_{0.62}CoO_2$. The thermal conductivity values for our reference sample are in reasonable agreement with those previously reported for low-density randomly oriented samples of the same phase.[3] We conclude from Fig. 1 that the thermal conductivity levels for the $[(Bi_{1-x}Pb_x)_2Ba_2O_{4\pm\omega}]_{0.5}CoO_2$ samples are close to that for the $[CoCa_2O_3]_{0.62}CoO_2$ phase. It also seems that within the $[(Bi_{1-x}Pb_x)_2Ba_2O_{4\pm\omega}]_{0.5}CoO_2$ series the Pb-for-Bi substitution affects little the thermal conductivity characteristics.

In Fig. 2, given are the electrical resistivity data for the three samples. At high temperatures all the samples show metallic behavior. However, as for most of other ML cobalt oxides,[4,10,13,14] an upturn of the ρ-T curve is seen for the Pb-free sample around 140 K (in accordance with the data previously reported for the phase by Hervieu *et al.*[8]). With increasing Pb content, the upturn temperature is significantly lowered, i.e., down to 26 K (53 K) for $x=0.2$ ($x=0.1$). Also the absolute values of resistivity decrease with increasing x. Hence Pb substitution markedly enhances the metallicity in the $[(Bi_{1-x}Pb_x)_2Ba_2O_{4\pm\omega}]_{0.5}CoO_2$ system. Moreover, the thermoelectric power is increased with increasing x (Fig. 3). The room-temperature values of S are 80 μV/K for $x=0.0$, 95 μV/K for $x=0.1$, and 120 μV/K for $x=0.2$. Note that

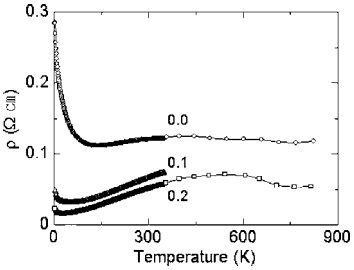

FIG. 2. Temperature dependence of electrical resistivity (ρ) for the $[(Bi_{1-x}Pb_x)_2Ba_2O_{4\pm\omega}]_{0.5}CoO_2$ samples with $x=0.0$, 0.1, and 0.2.

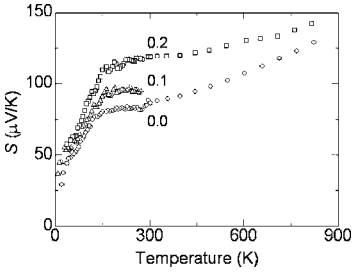

FIG. 3. Temperature dependence of thermoelectric power (S) for the $[(Bi_{1-x}Pb_x)_2Ba_2O_{4\pm\omega}]_{0.5}CoO_2$ samples with $x=0.0$, 0.1, and 0.2.

parallel results have been reported for the Sr-based system, $[(Bi_{1-x}Pb_x)_2Sr_2O_{4\pm\omega}]_qCoO_2$.[15] Thanks to the simultaneously decreased ρ and increased S values, the Pb-substituted $[(Bi,Pb)_2Ba_2O_{4\pm\omega}]_{0.5}CoO_2$ phase appears to be a highly attractive candidate for TE applications. In terms of the Z value, the enhancement is roughly three-fold, i.e., the Z value (in the units of 10^{-5} K^{-1}) is ca. 0.7 (2.5) for $x=0.0$ ($x=0.2$) at 300 K and ca. 1.2 (3.6) for $x=0.0$ ($x=0.2$) at 700 K.[15] Here we should mention that previous studies have demonstrated simultaneously enhanced electrical conductivity and thermoelectric power characteristics for the $[(Bi,Pb)_2Sr_2O_{4\pm\omega}]_qCoO_2$ system upon Pb substitution[16–19] and for the Na_xCoO_2 system upon increasing Na content,[20] whereas oxygen-content control in $[CoCa_2O_{3\pm\omega}]_{0.62}CoO_2$ enhanced one of the two parameters at the expense of the other.[21]

To gain some insight into the possible effects of the Pb substitution on the electronic structure of the $[(Bi,Pb)_2Ba_2O_{4\pm\omega}]_{0.5}CoO_2$ phase, we carried out x-ray absorption near-edge structure (XANES) spectroscopy measurements at both Co L and O K edges. The spectra were collected at room temperature at the BL20A high-energy spherical grating monochromator (HSGM) beam line of the National Synchrotron Radiation Research Center (NSRRC) of Taiwan, in x-ray fluorescence-yield mode at the O K edge and in total-electron-yield mode at the Co L edge with photon energy resolutions of ~0.15 and ~0.30 eV, respectively. The photon energies were calibrated with an accuracy of 0.1 eV against the known absorption peaks of reference compounds. Figure 4 displays the Co L-edge spectra for the samples normalized by adjusting to a common value the height of the Ba M_4-edge peak that appears in the same energy range as the Co L-edge absorption. To the Co L-edge spectra, the major contribution is from the empty $3d$ states: the main dipole-allowed transition of $2p\rightarrow 3d$ is mixed with a small amount of $2p\rightarrow 3s$ only. Due to the Co $2p$ core-hole spin-orbit coupling the Co L-edge spectra are split into two parts, L_3 (~778 eV) and L_2 (~793 eV). The detailed line

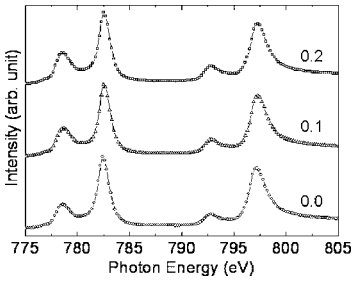

FIG. 4. Co $L_{2,3}$-edge XANES spectra for the $[(Bi_{1-x}Pb_x)_2Ba_2O_{4\pm\omega}]_{0.5}CoO_2$ samples with x=0.0, 0.1, and 0.2, normalized at the Ba M_4 absorption peak around 783 eV.

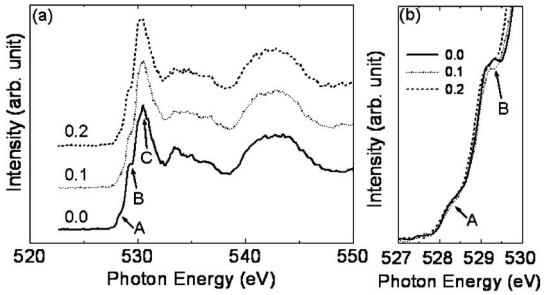

FIG. 5. O *K*-edge XANES spectra for the $[(Bi_{1-x}Pb_x)_2Ba_2O_{4\pm\omega}]_{0.5}CoO_2$ samples with $x=0.0$, 0.1, and 0.2. The spectra are (a) self-absorption corrected and (b) normalized at peak *B*.

shapes in the two regions should sensitively depend on the valence, orbital, and spin states of cobalt. The present spectra for the $[(Bi_{1-x}Pb_x)_2Ba_2O_{4\pm\omega}]_{0.5}CoO_2$ samples closely resemble those previously reported for other ML and related cobalt oxides based on hexagonal CoO_2 layers of Co^{III}/Co^{IV}.[22–24] Moreover, no visible differences are observed within the sample series either, suggesting that the Pb-for-Bi substitution has no significant effect on the valence state of cobalt. Regarding the spin state, the most indicative parameter is the so-called branching ratio, $BR=I_3/(I_3+I_2)$,[25] that is commonly used to compare the relative intensities of the L_3 and L_2 regions. In the case of high-spin state, the exchange coupling between the core-hole and 3*d* electrons tends to increase the BR value beyond $\sim 2/3$.[25,26] For each of the present samples, a BR value of around 0.6 or lower was obtained, hence verifying the (expected) low-spin state.

The O *K*-edge spectra (corrected for the self-absorption effects) are shown in Fig. 5(a). Referring to the previous works on various ML cobalt oxides,[23,24] we assign the first three features with increasing photon energy to the transitions from the O 1*s* core level to the O 2*p* states hybridized with the unoccupied $3d$-t_{2g} ($\sim$528.3 eV; peak *A*) and Co $3d$-e_g ($\sim$529.2 eV; peak *B*) states of Co and those of Bi/Pb 6*p* ($\sim$530.5 eV; peak *C*) orbitals. We fitted the spectra using Gaussian functions for the three peaks, and then normalized the spectra at peak *B* which should be of equal intensity in all the three samples as it is in each case believed to originate from completely empty e_g orbitals of low-spin Co. In the spectra thus normalized, the relative intensity of peak *A* (due to hole states in the t_{2g} orbitals) can then be used to compare the Co valence values in the three samples (the higher the intensity is, the higher should be the Co valence). From Fig. 5(b), it is seen that with increasing *x*, both the intensity and the energy of peak *A* remain constant, hence telling us that the Pb-for-Bi substitution does not significantly affect the Co valence in $[(Bi_{1-x}Pb_x)_2Ba_2O_{4\pm\omega}]_{0.5}CoO_2$. Hence the O *K*-edge data confirm the conclusion already made based on the Co *L*-edge data. Parallel conclusions have also been made for other layered oxides, e.g., $[(Bi,Pb)_2Sr_2O_{4\pm\omega}]_qCoO_2$ and $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$.[11,12,23] Apparently, the presently revealed enhancement in the TE characteristics of $[(Bi,Pb)_2Ba_2O_{4\pm\omega}]_{0.5}CoO_2$ due to Pb-for-Bi substitution should have its origin in something other than an increase in the hole-doping level of the CoO_2 layer.

In conclusion, we have systematically presented the advantageous effect of partial substitution of Bi by Pb on the thermoelectric characteristics of the misfit-layered cobalt oxide, $[(Bi_{1-x}Pb_x)_2Ba_2O_{4\pm\omega}]_{0.5}CoO_2$, in a wide temperature range (5–800 K) using single-phase polycrystalline samples with *x* up to 0.2. Most profoundly, both the electrical conductivity and the Seebeck coefficient were found to be simultaneously enhanced by Pb-for-Bi substitution, whereas thermal conductivity remained constantly low. From XANES spectroscopy data collected for the samples at both the Co *L* and O *K* edges, it was concluded that upon Pb-for-Bi substitution the Co valence remains essentially unchanged and the low-spin state is preserved for all the samples.

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