Intergrowth and thermoelectric properties in the Bi-Ca-Co-O system

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Abstract

Single crystals of the Bi-Ca-Co-O system have been grown using the flux method with cooling from 900°C and 950°C, respectively. The single crystals are characterized by transmission electron microscopy and X-ray diffraction. The misfit cobaltite \([\text{Ca}_2\text{Bi}_{1.4}\text{Co}_{0.6}\text{O}_4]^{\text{RS}}[\text{CoO}_2]_{1.69}\) single crystals with quadruple \((n=4)\) rocksalt (RS) layer are achieved with cooling from 900°C. Such crystal exhibits room-temperature thermoelectric power (TEP) of 180\(\mu\)V/K, much larger than that in Sr-based misfit cobaltites with quadruple RS layer. However, intergrowth of single crystals of quadruple \((n=4)\) and triple \((n=3)\) RS-type layer-based misfit cobaltites is observed with cooling from 950°C. Both of TEP and resistivity were obviously enhanced by the intergrowth compared to \([\text{Ca}_2\text{Bi}_{1.4}\text{Co}_{0.6}\text{O}_4]^{\text{RS}}[\text{CoO}_2]_{1.69}\) single crystal, while the power factor at room temperature remains unchanged.

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I. INTRODUCTION

The first cobaltite Na$_x$CoO$_2$ exhibiting large TEP ($S \sim 100 \mu$V/K at room temperature) as well as low electrical resistivity was discovered by Terasaki et al. in 1997 [1]. Since then, the misfit cobaltites have also been thought to be the potential candidates for thermoelectric applications. The crystal structure of the misfit cobaltites consists of alternatively stacking three ($n=3$, such as [Ca$_2$CoO$_3$]$^{RS}$[CoO$_2$]$_{1.62}$) or four ($n=4$, such as namely [M$_2$Bi$_2$O$_4$]$^{RS}$[CoO$_2$]$_{a}$, M=Ca, Sr, Ba) RS-type layers and one CoO$_2$ hexagonal CdI$_2$-type layer with edge-shared CoO$_6$ octahedra [2,3], which is similar to that found in Na$_x$CoO$_2$. For simplicity, we take them as $n=3$ phase and $n=4$ phase, respectively. The two sublattices of rocksalt block and hexagonal CdI$_2$-type CoO$_2$ layer possess the common $a$- and $c$-axis lattice parameters and $\beta$ angles but different $b$-axis length causing a misfit along $b$-direction. Among all the misfit cobaltites, TEP varies from $S = 90 \mu$V/K for [Sr$_2$Co$_{1-x}$Tl$_x$O$_3$]$^{RS}$[CoO$_2$]$_{1.8}$ up to $S = 165 \mu$V/K for [Ca$_2$Co$_{0.6}$Pb$_{0.4}$O$_3$]$^{RS}$[CoO$_2$]$_{1.61}$ [4, 5, 6]. Bi$^{3+}$ seems to be the most beneficial to be included in these cobaltites in terms of the thermoelectric figure of merit ($ZT = S^2T/\rho\kappa$, $S, \rho$ and $\kappa$ are TEP, electrical resistivity and thermal conductivity, respectively) and is now used in the development for oxide-based thermogenerators [7]. In the [Ca$_2$CoO$_3$]$^{RS}$[CoO$_2$]$_{1.62}$ ($n=3$) cobaltite, its room-temperature TEP value increases from 125 to 140 $\mu$V/K by low bismuth amounts substitution for Ca [8]. The polycrystalline [Bi$_{1.7}$Co$_{0.3}$Ca$_2$O$_4$]$^{RS}$[CoO$_2$]$_{1.67}$ ($n=4$) [10] with large amounts of bismuth shows about 140 $\mu$V/K at room temperature. The RS block in [Bi$_{1.7}$Co$_{0.3}$Ca$_2$O$_4$]$^{RS}$[CoO$_2$]$_{1.67}$ is constructed with two deficient [BiO] layers sandwiched by two [CaO] layers. In contrast, the RS block in [Ca$_2$CoO$_3$]$^{RS}$[CoO$_2$]$_{1.62}$ is built up from two [CaO] layers sandwiching one [CoO] layer [3,10]. Though the number of the RS layers is different, they show almost the same $b_{RS}/b_H$ ratio ($b_{RS}$ and $b_H$ are the lattice parameters along b-axis for RS and hexagonal layer, respectively) [2]. The common ground between Bi-doped [Ca$_2$CoO$_3$]$^{RS}$[CoO$_2$]$_{1.62}$ and [Bi$_{1.7}$Co$_{0.3}$Ca$_2$O$_4$]$^{RS}$[CoO$_2$]$_{1.67}$ evokes the sufficient interest of the role of $n=3/n=4$ RS layer to the thermoelectric properties. In this article, single crystals of Bi-Ca-Co-O were grown by the flux method cooling from different melting temperatures. It is found that single crystals with pure $n=4$ phase were obtained with cooling from 900°C, while intergrowth of single crystals of quadruple ($n=4$) and triple ($n=3$) RS-type layer-based misfit cobaltites were achieved with cooling from 950°C. Structural analysis and thermoelectric properties
were systematically studied on these single crystals.

II. EXPERIMENTAL DETAIL

The Bi-Ca-Co-O single crystals were grown by the solution method using K$_2$CO$_3$-KCl fluxes. In the first step, polycrystalline Bi$_2$Ca$_2$Co$_2$O$_y$ was prepared by a solid-state reaction method. Starting materials Bi$_2$O$_3$, CaCO$_3$ and Co$_3$O$_4$ were mixed in a proportion of Bi:Ca:Co = 2:2:2, with a total weigh to be 2.7 grams. The powders were heated at 800°C for 10 hours. Then the prepared Bi$_2$Ca$_2$Co$_2$O$_y$ and the mixture of KCl and K$_2$CO$_3$ by a molar proportion of 1:4 (20.5 grams) were mixed and loaded in an aluminum crucible having 30 ml volume. The solute concentration was about 1.5 mol%. A lidded crucible was used to prevent the solution from evaporating and to grow crystals under stable conditions. The powder-flux mixture was melted at 900°C or 950°C for 20 hours, respectively, and then slowly cooled down to 600°C at a rate of 5-6°C/hr. The single crystals were separated from the melt by washing with distilled water. The single crystals obtained with cooling from 900°C and 950°C were denoted as crystal 1 and crystal 2 in the following text, respectively. The crystals were large thin platelets and black in color, as shown in Fig.1. As shown in Fig.1, typical dimensions of the crystal 1 and crystal 2 are around $3 \times 3 \times 0.05$ mm$^3$ and $5 \times 5 \times 0.05$ mm$^3$, respectively.

The structural characterization of the single crystals was performed by X-ray diffraction (XRD) and transmission electron diffraction (TEM). The analysis of the actual composition was made by the inductively coupled plasma (ICP) atomic emission spectroscopy (AES) (ICP-AES) technique. Resistivity was measured using a standard four probe method through an alternative current (AC) resistance bridge (LR700, Linear Research Inc.). The TEP was measured using the steady-state technique.

III. RESULTS AND DISCUSSION

A. Structural Characterization

The XRD patterns recorded for crystal 1 and crystal 2 are shown in Fig. 2. The presence of only 00$l$ reflections indicates that the crystals are grown along c-axis. The XRD pattern for crystal 1 grown from 900°C indicates good single $n=4$ phase. The $c$-axis lattice parameter
was estimated to be 14.651 Å based on the d-spacing values of 00l reflections. The ICP-AES
gave that the actual composition for crystal 1 is Bi : Ca : Co = 1.40 : 2.00 : 2.29. The XRD
pattern for crystal 2 shows two sets of 00l reflections. Based on d-spacing values for the
two sets of the reflections, the c-axis lattice parameters for the two sets of 00l reflections are
14.659 Å and 10.800 Å, respectively. It suggests that there exist two phases in the crystal
2. The 00l reflections arises from the structure of the n=4 phase (c = 14.659 Å) as the
crystal 1, while the set of 00l reflections with c = 10.800 Å is the same as that observed in
[Ca₂CoO₃]RS[CoO₂]₁.₆₂ (n=3) phase. Therefore, it indicates that an intergrowth of the n=4
phase and [Ca₂CoO₃]RS[CoO₂]₁.₆₂ (n=3) phase occurs in crystal 2. Similar intergrowth has
been reported in polycrystalline Sr-Bi-Co-O system, where the major phase is n=3 layer-
based cobaltite [⁶]. The XRD pattern of crystal 2 shows that the dominated phase is n=4.
The ICP-AES gave the actual composition for crystal 2 to be Bi : Ca : Co = 1.40 : 2.37 :
2.77.

The electron diffraction (ED) patterns are shown in Fig. 3 for the crystal 1 and crystal 2.
In Fig.3a, one can clearly see RS diffraction spots from the [Bi₂Ca₂O₄] layer and hexagonal
diffraction spots from the [CoO₂] layer for crystal 1. The a- and b-axis length of the hexagonal
[CoO₂] layer (aₕ, bₕ) is estimated to be 2.87(9) and 2.83(2) Å, respectively. The a- and
b-axis length of the RS [Bi₂Ca₂O₄] layer (aₙ, bₙ) is estimated to be 4.98(9) (≈ \(\sqrt{3}aₕ\))
and 4.784 Å, respectively. From the above structural analysis, crystal 1 shows the misfit
structure along b-axis (bₙ/bₕ = 1.69); while along a-axis, length of the rock-layer matches
with that of the hexagonal layer (aₙ ≈ \(\sqrt{3}aₕ\)), being consistent with previous report in
polycrystalline sample [¹³]. Therefore, the structural formula of the crystal 1 can be written
as [Ca₂Bi₁.₄Co₀.₆O₄]⁹⁸[R₆O₂]₁₆₉.

Fig.3b shows similar main ED pattern for crystal 2 to that observed in crystal 1 shown
in Fig.3a. It gives the same in-plane lattice parameters of RS and hexagonal layers. In
Fig.3b, there are satellite reflections along b* direction, in contrast to the ED pattern for
crystal 1, which shows no satellite reflections as shown in Fig.3a. Because the XRD patterns
of the two single crystals have shown that crystal 1 is pure n=4 phase, while crystal 2 is
intergrowth of n=4 and n=3 phases, therefore, the satellite reflections should come from the
modulation structure in n=3 phase. Superposition of the main reflections is consistent with
almost the same in-plane lattice parameters between two compounds. Actually, the misfit
ratio (1.62) in [Ca₂CoO₃]⁹⁸[CoO₂]₁₆₉ is slightly smaller than that in crystal 1. But if Ca is
partly substituted by Bi in \([\text{Ca}_2\text{CoO}_3]^{RS}[\text{CoO}_2]_{1.62}\), the lattice parameter of the RS layer is enhanced and the same misfit ratio could be obtained as that in crystal 1 [8].

The intergrowth of the \(n=3\) and \(n=4\) phases in Bi-Ca-Co-O system arises from the thermodynamical competition for the two phases. Pure single crystal of the \(n=4\) phase can be grown with cooling the melting solution from 900°C, while single crystal intergrowth of \(n=3\) and \(n=4\) phases can be obtained with cooling the same melting solution from 950°C. It definitely indicates that the single crystal of \(n=3\) phase can be grown only above 900°C. The melting solution was slowly cooled from 950°C, the single crystal of \(n=3\) phase starts to grow. When the melting solution was cooled to below 900°C, the \(n=4\) phase is thermodynamically more stable than the \(n=3\) phase. Therefore, the single crystal of \(n=4\) phase begins to grow with the \(n=3\) phase. In addition, the two phases have the same lattice parameters in plane, which provides a condition for the epitaxial intergrowth of the two phases. This is possible intergrowth mechanism for the \(n=3\) and \(n=4\) phases in Bi-Ca-Co-O system.

### B. Physical Properties

Temperature dependence of the in-plane resistivity for crystal 1 and 2 is plotted in Fig. 4. The room-temperature values of \(\rho_{ab}\) are 12.7 mΩ cm for crystal 1 and 13.6 mΩ cm for crystal 2, respectively. They are larger than those in \([\text{Ca}_2\text{CoO}_3]^{RS}[\text{CoO}_2]_{1.62}\) (8.5 mΩ) and \([\text{Bi}_{0.87}\text{SrO}_2]^{RS}[\text{CoO}_2]_{1.82}\) (4.0 mΩ) [11, 12]. \(\rho_{ab}\) shows metallic behavior (\(d\rho/dT > 0\)) at high temperature and exhibits a minimum at 156 K and 206 K for crystal 1 and crystal 2, respectively. These temperatures corresponding to the minimum of \(\rho_{ab}\) (\(T_{min}\)) are much higher than those observed in \([\text{Ca}_2\text{CoO}_3]^{RS}[\text{CoO}_2]_{1.62}\) (70 K) and \([\text{Bi}_{0.87}\text{SrO}_2]^{RS}[\text{CoO}_2]_{1.82}\) (80 K) single crystals [11, 12]. The room-temperature resistivity \(\rho_{ab}\) and the temperature corresponding to the minimum resistivity \(T_{min}\) indicate that Bi-Ca-Co-O system has the weaker metallicity compared to \([\text{Ca}_2\text{CoO}_3]^{RS}[\text{CoO}_2]_{1.62}\) and \([\text{Bi}_{0.87}\text{SrO}_2]^{RS}[\text{CoO}_2]_{1.82}\). Fig. 5 shows that the insulator-like behavior at low temperature for the two types of crystal follows different transport laws. Resistivity for crystal 1 below 150 K can be fitted using two thermal activation behavior (\(\rho \propto exp[\Delta_g/k_BT]\), where \(\Delta_g\) is the energy gap), which gives the thermal activation energy (\(\Delta_g\)) to be 2.4 meV below 20 K and 4.3 meV between 25 K and 90 K. Resistivity for crystal 2 can be fitted using thermal activation law above 40 K, with \(\Delta_g=4.8\) meV. Below 40 K, variable range hopping (VRH, \(\rho \propto exp[(T_0/T)^{1/4}]\))
resistivity was observed.

Temperature dependence of the in-plane TEP is shown in the Fig.6 for crystal 1 and crystal 2, as well as for $[\text{Ca}_2\text{CoO}_3]^{RS}[\text{CoO}_2]_{1.62}$ crystal. The magnitudes of 180 $\mu$V/K for crystal 1 and 190 $\mu$V/K for crystal 2 are much larger than that observed in $[\text{Ca}_2\text{CoO}_3]^{RS}[\text{CoO}_2]_{1.62}$ (125 $\mu$V/K) and Pb-doped $[\text{Bi}_{0.87}\text{SrO}_2]_2^{RS}[\text{CoO}_2]_{1.82}$ (highest of 150 $\mu$V/K as x=0). This is consistent with the weaker metallicity in Bi-Ca-Co-O system inferred by Fig. 4. The in-plane TEP changes slightly at high temperature and decreases obviously below 100 K, similar to that observed in $[\text{Ca}_2\text{CoO}_3]^{RS}[\text{CoO}_2]_{1.62}$ and $[\text{Bi}_{0.87}\text{SrO}_2]^{RS}[\text{CoO}_2]_{1.82}$. A model for the TEP in layered cobaltites has be proposed by Koshibae. The result for cobalt ions in low spin state is that the TEP depends on the fraction of holes, $x=\text{Co}^{4+}/\text{Co}$, according to the expression derived from the generalized Heikes formula

$$S = -\frac{k_B}{|e|} \ln\left(\frac{1}{6} \frac{x}{1-x}\right)$$

(1)

where $k_B$ is the Boltzmann constant and $e$ is the charge of electron. From this formula, the average valence of cobalt ions in $[\text{Ca}_2\text{Bi}_{1.4}\text{Co}_{0.6}\text{O}_4]^{RS}[\text{CoO}_2]_{1.69}$ could be 3.42. The thermoelectric power factor ($Q=S^2/\rho$) calculated from the data in Fig.6 and Fig.4 is shown in Fig.7. The two crystals have almost the same value of $Q=2.7\times10^{-4}$ W/mK$^2$ at room temperature, which is close to that obtained in Na$_x$CoO$_2$. However, Fig.7 shows that the room-temperature values of $Q$ for crystal 1 with $n=4$ and crystal 2 with intergrowth is obviously higher than that in $[\text{Ca}_2\text{CoO}_3]^{RS}[\text{CoO}_2]_{1.62}$ single crystal with $n=3$. Unchange in $Q$ at room temperature for crystal 2 with intergrowth of $n=3$ and $n=4$ in Bi-Ca-Co-O system can be ascribed to the simultaneous enhancement of TEP and resistivity. The enhancement of the TEP together with the resistivity due to intergrowth in Bi-Ca-Co-Co system is different from the case of the Sr-based system, in which the intergrowth of $n=3$ and $n=4$ phase enhances the TEP but reduces the resistivity relative to the pure $n=3$ phase. Nevertheless, relative to pure $n=3$ phase, the power factor is enhanced by the intergrowth of $n=4$ and $n=3$ phase in Ca- and Sr-based system. It seems that the $n=4$ component plays the major role in the transport properties in the single crystal with intergrowth of $n=4$ and $n=3$ phase.
IV. CONCLUSION

Single crystals of Bi-Ca-Co-O have been grown using K$_2$CO$_3$+KCl flux. Single crystals with pure $n=4$ phase were grown from 900°C, while intergrowth of $n=4$ and $n=3$ phase was obtained as crystals were grown from 950°C. At room temperature, Ca-based $n=4$ crystal have the much larger TEP (180 $\mu$V/K) than that in Sr-based one and $n=3$ [Ca$_2$CoO$_3$]$^{RS}[CoO_2]_{1.62}$. The intergrowth of $n = 4$ and $n = 3$ phase enhances the TEP value and resistivity, but does not change the power factor at room temperature. As pointed by Klein et al. [6], the presence of such intergrowth could be an important structural feature of the misfit cobaltites in generating larger values of TEP.

V. ACKNOWLEDGEMENT

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FIG. 1: Photographs of crystal 1 and 2.
FIG. 2: The XRD patterns for crystal 1 (grown from 900 °C) and crystal 2 (grown from 950°C). ♦ and * are referred to the reflections from $n=4$ phase and $n=3$ phase, respectively. Intergrowth can be clearly observed in the pattern for crystal 2.
FIG. 3: The [001] ED patterns for the crystal 1 (a) and crystal 2 (b).
FIG. 4: Temperature dependence of in-plane resistivity for crystal 1 and 2. The inset shows the closeup of the in-plane resistivity at high temperature, in which metallic behavior and minimum of resistivity can be observed.
FIG. 5: Thermal activation ($\rho \propto \exp[\Delta_g/k_BT]$, where $\Delta_g$ is the energy gap) and variable range hopping ($\rho \propto \exp[(T_0/T)^{1/4}]$) fitting of the resistivity for crystal 1 and crystal 2.
FIG. 6: Temperature dependence of Seebeck coefficient for crystal 1, crystal 2. That of 
$[\text{Ca}_2\text{CoO}_3]^\text{RS}[\text{CoO}_2]_{1.62}$ single crystal is also shown in the figure as comparison [11].
FIG. 7: Temperature dependence of power factor ($Q$) for crystal 1, crystal 2, and $\left[\text{Ca}_2\text{CoO}_3\right]^{\text{RS}}\left[\text{CoO}_2\right]_{1.62}$ single crystal [11].