

Thermoelectric properties of Bi³⁺ substituted Co-based misfit-layered oxides

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Abstract Highly densified (Ca_{1-x}Bi_x)₃Co₄O₉ thermoelectric ceramics with a layered structure were prepared by a sol-gel method followed by spark plasma sintering (SPS). Thermoelectric (TE) properties of the complex oxide ceramics were measured from room temperature to 700 °C. The results show that Bi³⁺ substitution leads to an increase in both electrical conductivity and Seebeck coefficient simultaneously. Bi³⁺ doped samples also show a lower thermal conductivity than undoped samples. The dimensional figure of merit ZT value of (Ca_{0.95}Bi_{0.05})₃Co₄O₉ samples is 0.25 at 700 °C.

Keywords Thermoelectric properties · SPS · Oxides

1 Introduction

The performance of the thermoelectric materials is characterized by the figure of merit $ZT = T\sigma S^2/\kappa$, where S , σ , κ and T are the Seebeck coefficient, electrical conductivity, thermal conductivity of materials, and the absolute temperature, respectively. Hence good TE materials require high S , high σ and low κ . Over the past several decades, a lot of thermoelectric materials including alloy semiconductors

(e.g., Bi₂Te₃, PbTe and SiGe) have been found and applied in generation power and refrigeration. Recently, new alloys systems with high ZT have been reported, such as skutterudites (e.g., CeFe₄Sb₁₂) [1], CsBi₄Te₆ [2], and AgPb₁₈SbTe₂₀ [3].

But shortages of these conventional materials, such as surface oxidation and vaporization at high temperature, have limited further applications of these materials. Oxides, owing to its natural merits of low thermal conductivity and high-resistance of oxidation at high temperature, have recently been exploited as alternative thermoelectric materials. Terasaki et al. [4] have found that NaCo₂O₄ (NCO) single crystals have good TE performance with a high Seebeck coefficient (100 μV/K at 300 K) and a low resistivity (200 μΩ cm at 300 K). Additionally, Bi₂Sr₂Co₂O_x [5] with high ZT values have also been reported as promising candidates of TE materials. All the Co-based oxides listed above are misfit-layered compounds containing CdI₂-type [CoO₂] layers. Because of the volatility of Bi and Na at high temperature and the toxicity of these elements, their practical applications are quite limited. Among Co-based oxides, crystal structure and physical properties of Ca₃Co₄O₉ (CCO) have been reported recently [6]. This compound is thought to be a misfit-layered oxide consisting of two monoclinic subsystems, namely Ca₂CoO₃ and CoO₂ layers, and the single crystals with a Ca₃Co₄O₉ structure have a figure of merit $ZT \approx 0.87$ at 700 °C in air [7], which is close to that of (Bi_{1-x}Sb_x)₂Te₃ alloys ($ZT \approx 1$).

Although the single crystals of the Co-based TE oxides have a high ZT, single crystal samples are too small to be used in the fabrication of the TE devices. More feasible method is to use polycrystalline materials and enhance their TE properties by improving their composition and preparing process. The SPS method, which can yield highly densified bulk materials and induce grain orientation in the layered Co-based TE oxides, has been verified as an

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effective method of improving TE properties [8]. Besides the improvement on the microstructure and preparation, ions substitution is also an effective method to enhance the ZT value [9]. In this letter, highly densified Bi^{3+} substituted $\text{Ca}_3\text{Co}_4\text{O}_9$ ceramics were prepared by wet chemical method and SPS process to investigate their TE properties from room temperature to 700 °C.

2 Experiment

The pure precursor powders of $(\text{Ca}_{1-x}\text{Bi}_x)_3\text{Co}_4\text{O}_9$ ($x=0.025\text{--}0.10$) were prepared by a citrate sol–gel method [8]. Then the bulk samples were sintered with SPS methods. During the SPS procedure, the precursor powders were placed in a graphite die with a diameter of 20 mm, and a pulsed electric current was passed through it under a pressure of 50 MPa. The samples were sintered at 900 °C for 5 min. Finally the samples were obtained after removing the carbon on the surface by calcining at 800 °C for 8 h in air and then were cut into rectangles of $15\times 3\times 3$ mm for measurement.

The phase compositions of the samples were analyzed by X-ray diffraction (XRD). The microscopic images of ceramics were examined by Tescan scanning electron microscopic (SEM) model 5136. The relative densities of all the samples were measured by Archimedes method. The measurements of electrical conductivity and Seebeck coefficient were carried out in a computer-controlled homemade apparatus from room temperature up to 700 °C. The thermal conductivity κ was obtained from the product of the bulk density, specific heat capacity and thermal diffusivity, which were measured by the laser flash (Shikuriko: TC-7000) method.

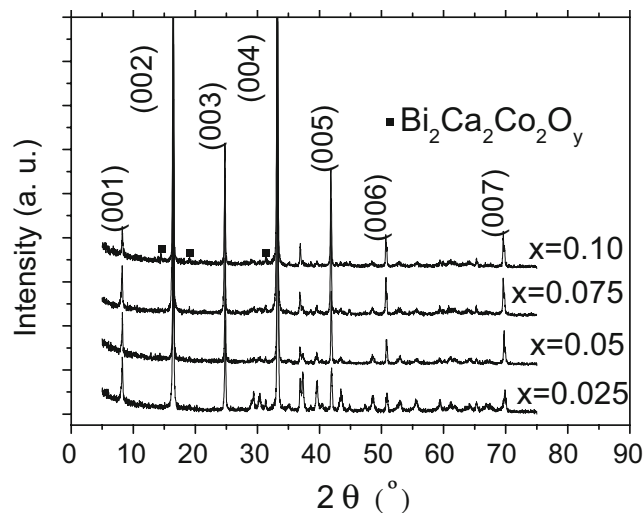


Fig. 1 XRD patterns for the polished surface (perpendicular to the SPS pressing direction) of $(\text{Ca}_{1-x}\text{Bi}_x)_3\text{Co}_4\text{O}_9$

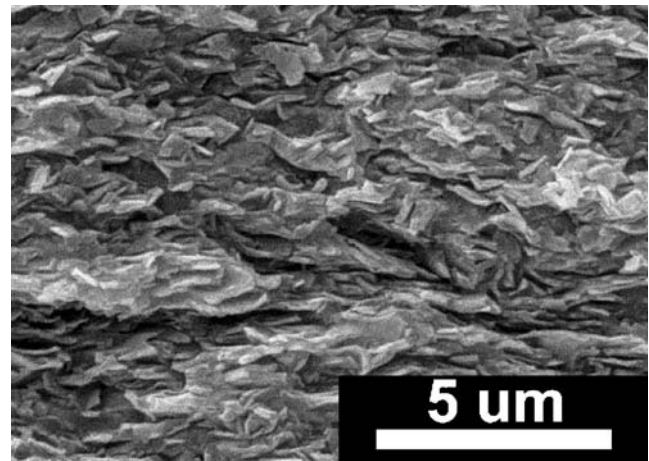


Fig. 2 SEM photograph of the fractured surfaces of the samples $(\text{Ca}_{0.95}\text{Bi}_{0.05})_3\text{Co}_4\text{O}_9$

3 Results and discussion

The XRD patterns for the polished surface (perpendicular to the SPS pressing direction) of $(\text{Ca}_{1-x}\text{Bi}_x)_3\text{Co}_4\text{O}_9$ ($x=0.025, 0.05, 0.075, 0.10$) samples are shown in Fig. 1. It can be seen from Fig. 1 that the samples with a small amount of Bi ($x<0.075$) substitution are almost crystallized in a single CCO phase, since their XRD peaks are exactly the same as that reported by Masset et al. [6]. However, with increasing Bi substitution amount ($x>0.075$), the XRD peaks for an impurity phase $\text{Bi}_2\text{Ca}_2\text{Co}_2\text{O}_x$ appears. The XRD results show that the CCO compound is sensitive to the amount of substitution ions. The XRD patterns that also indicate the samples containing more Bi^{3+} content [e.g. $(\text{Ca}_{0.90}\text{Bi}_{0.10})_3\text{Co}_4\text{O}_9$] have stronger (001) XRD peaks intensity than ones with less Bi^{3+} content and other XRD peaks except (001) crystal planes are obviously depressed. Figure 2 illustrates the SEM images of fractured surface

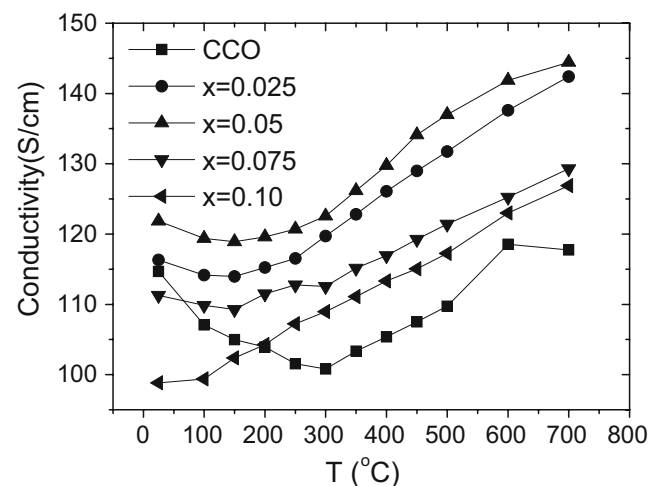


Fig. 3 Temperature dependence of electrical conductivity for Bi^{3+} substituted and undoped samples

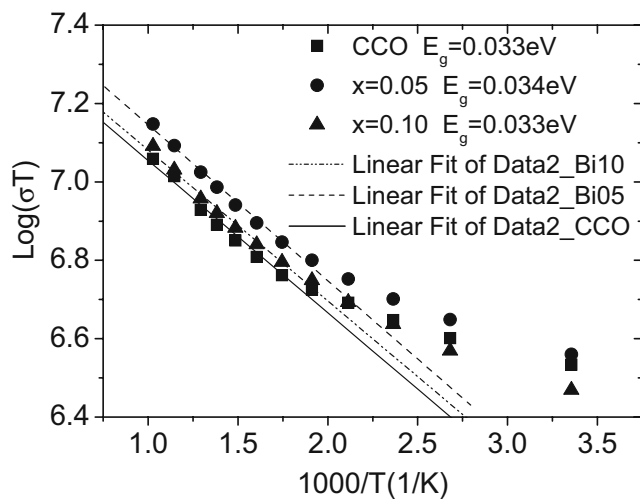


Fig. 4 The activity energy of the samples of $(\text{Ca}_{1-x}\text{Bi}_x)_3\text{Co}_4\text{O}_9$ ($x=0, 0.05$ and 0.10)

(perpendicular to the SPS pressing direction) for the sample of $(\text{Ca}_{0.95}\text{Bi}_{0.05})_3\text{Co}_4\text{O}_9$. The sheet-like grains can be observed due to the layered crystal structure of $\text{Ca}_3\text{Co}_4\text{O}_9$ [8]. The SEM micrograph also shows the textured microstructure of the ceramics as evidenced in the XRD.

Figure 3 shows the temperature dependence of the electrical conductivity for $(\text{Ca}_{1-x}\text{Bi}_x)_3\text{Co}_4\text{O}_9$ samples. The data of pure $\text{Ca}_3\text{Co}_4\text{O}_9$ are shown for comparison [8]. In the high temperature region, the electrical conductivity of all samples increases with increasing temperature, which is a common behavior of $\text{Ca}_3\text{Co}_4\text{O}_9$ oxides in this measured temperature region. The electrical conductivity of $(\text{Ca}_{1-x}\text{Bi}_x)_3\text{Co}_4\text{O}_9$ increases with increasing Bi content as $x < 0.05$, but decreases as $x > 0.05$. The $(\text{Ca}_{0.95}\text{Bi}_{0.05})_3\text{Co}_4\text{O}_9$ sample has the highest conductivity values, which is 144 S/cm at 700 °C. The σ value of CCO without any ion substitution is 118 S/cm at 700 °C. It is expected according to the traditional theory that the Bi^{3+} substitution will decrease the σ value since it

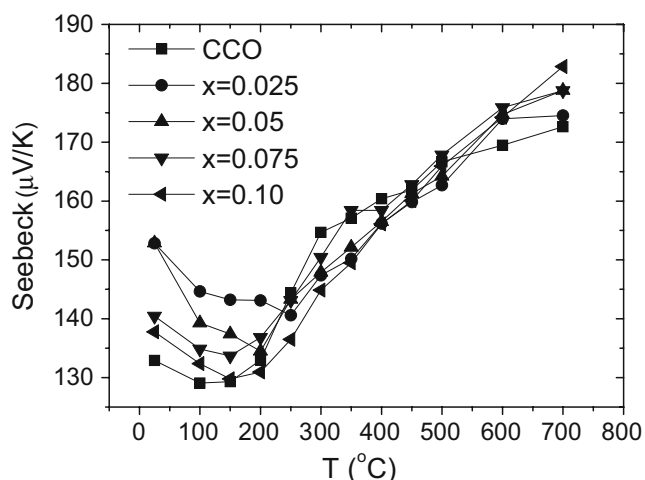


Fig. 5 Temperature dependence of the Seebeck coefficient for Bi^{3+} substituted and undoped samples

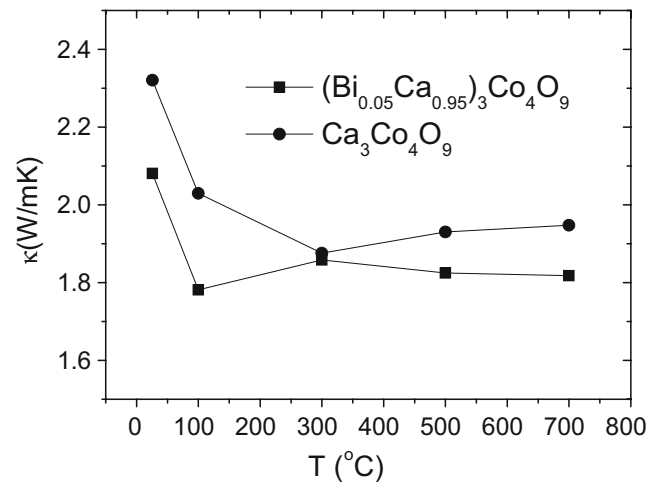


Fig. 6 Dependence of thermal conductivity on temperature for $(\text{Ca}_{0.95}\text{Bi}_{0.05})_3\text{Co}_4\text{O}_9$ and undoped sample

decreases the p-type carrier concentration. Otherwise, our experiment results imply that there exists another factor which influences the electrical conductivity. One possible interpretation is that the Bi^{3+} substitution improves the carrier mobility [10]. The straight linear relationship between $\log(\sigma T)$ and $1/T$ shown in Fig. 4 in the high temperature region ($>573\text{K}$) indicates the character of polaron hopping conduction mechanism [11]. The electrical conductivity of the small polaron hopping can be expressed as

$$\sigma = ne\mu = nea^2(A/T^{-1}) \exp(-E_g/k_B T) \quad (1)$$

where n is the carrier concentration, μ the carrier mobility, a the intersite distance of hopping, E_g the activation energy, k_B the Boltzman constant, and A the pre-exponential term related to the scattering mechanism. Here n , a and E_g could be influenced by ion substitution. Seen from Fig. 4, the activation energy for the pure CCO, the samples with $x=0.05$ and $x=0.10$ is 0.034, 0.034 and 0.033 eV, respectively,

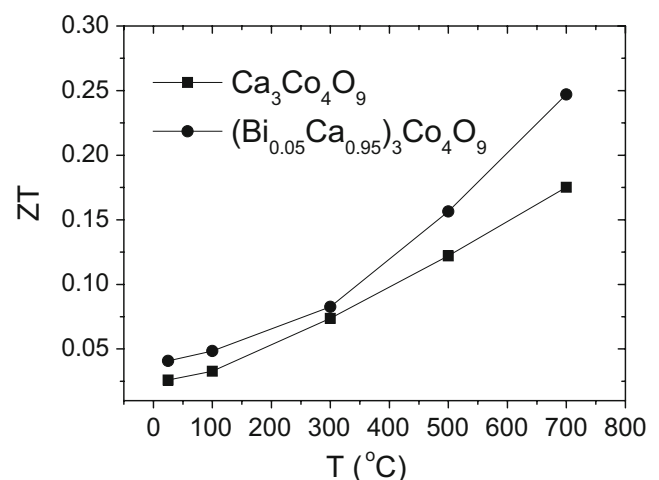


Fig. 7 Temperature dependence of the ZT values for $(\text{Ca}_{0.95}\text{Bi}_{0.05})_3\text{Co}_4\text{O}_9$ and undoped sample

which is almost stable with different Bi content. Therefore, the increase in σ with Bi substitution should be attributed to the change in a , the intersite distance of hopping, which compensates for the reduction of the carrier concentration and may arise from that Bi^{3+} substitution with large ion diameter enlarges the lattice constant of CCO and increases the intersite distance of hopping.

The dependence of Seebeck coefficient S on temperature for $(\text{Ca}_{1-x}\text{Bi}_x)_3\text{Co}_4\text{O}_9$ is presented in Fig. 5. The positive S values indicate that the all samples are p-type semiconductors. For all samples, at high temperature (>573 K), Seebeck coefficient of $(\text{Ca}_{1-x}\text{Bi}_x)_3\text{Co}_4\text{O}_9$ increases with increasing Bi content and temperature. The sample with $x=0.05$ has a Seebeck value of $179 \mu\text{V/K}$, which is larger than that of the pure CCO oxides ($173 \mu\text{V/K}$). This result that S and σ of $(\text{Ca}_{1-x}\text{Bi}_x)_3\text{Co}_4\text{O}_9$ both increase with Bi content seems hard to be understood with a simple band model. Although Bi^{3+} substitution has a depressed effect on the carrier concentration, it changes the energy dependence of mobility and leads to increase in S and σ . This abnormal behavior is quite different from conventional semiconductor materials, implying that it is possible to enhance the thermoelectric properties of Co-based misfit-layered oxides by ions substitution.

Figure 6 shows the temperature dependence of thermal conductivity κ for $(\text{Ca}_{0.925}\text{Bi}_{0.075})_3\text{Co}_4\text{O}_9$ and CCO sample, which has the highest power factor σS^2 in all Bi^{3+} doped samples. It is seen from Fig. 6 that Bi doped sample $(\text{Ca}_{0.95}\text{Bi}_{0.05})_3\text{Co}_4\text{O}_9$ has a lower thermal conductivity (1.81 W/m K at $700 \text{ }^\circ\text{C}$) than pure CCO (2.01 W/m K at $700 \text{ }^\circ\text{C}$). The addition of Bi^{3+} heavy ions decreases κ due to enhanced phonon scattering. Figure 7 gives the temperature dependence of the dimensional figure of merit ZT. The ZT values for $(\text{Ca}_{0.95}\text{Bi}_{0.05})_3\text{Co}_4\text{O}_9$ and undoped sample both increase with increasing temperature. At $700 \text{ }^\circ\text{C}$, the ZT value of the Bi^{3+} substituted sample is 0.25, much larger than that of undoped CCO (0.175), since Bi^{3+} substitution optimizes all three TE parameters (S , σ and κ). This result shows that ion substitution is an effective and feasible method to improve the TE properties of CCO. Further optimization on the ceramic microstructure is needed to

further improve the TE performance of Co-based misfit-layered oxides.

4 Conclusions

The Bi^{3+} substituted CCO samples have been prepared by a sol-gel method followed by SPS treatment. The ZT value of $(\text{Ca}_{0.95}\text{Bi}_{0.05})_3\text{Co}_4\text{O}_9$ is 0.25 at $700 \text{ }^\circ\text{C}$. Bi^{3+} substitution can lead to an increase in the electrical conductivity σ and Seebeck coefficient S simultaneously, which is quite different from traditional semiconductors. The optimization on σ and S by Bi substitution arises from its improvement on carrier mobility of CCO. Bi^{3+} substitution also lowers the thermal conductivity, especially at high temperature. The improvement of TE properties for CCO by Bi^{3+} substitution indicates that there exists a potential to further optimize the TE performance of Co-based misfit-layered oxides.

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