

层状钴氧化物 $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ 的高温热电性能及 XPS 研究

李中华 陈 刚* 裴 健 刘璞生

(哈尔滨工业大学应用化学系, 哈尔滨 150001)

摘要: 采用固相反应法制备了组成为 $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ ($x=0.0, 0.4, 0.8$, 略写为 BAC-222) 的层状钴氧化物陶瓷。利用 X-射线光电子能谱考察该类化合物的电子结构, 结果表明钴离子以 Co^{3+} 和 Co^{4+} 混合价态形式存在, $n_{\text{Co}^{4+}}/n_{\text{Co}^{3+}}$ 的比例随着 Ag 掺杂的量增加而增加。O1s 光电子谱显示在所有样品中均存在点阵氧和吸附氧。热电性能测试结果显示, 随着 Ag 掺杂量的增加, 电导率显著增加而 Seebeck 系数几乎保持不变, Ag 的引入极大的影响了 BAC-222 的电子输运性质, 其功率因子在 1 123 K 时达到了 $1.23 \times 10^{-4} \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-2}$, 是一种具有很好应用前景的热电材料。

关键词: 层状钴氧化物陶瓷; 热电; XPS; BC-222

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High-temperature Thermoelectric Properties and X-ray Photoemission Spectra of Layered Co-based Oxides $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$

LI Zhong-Hua CHEN Gang* PEI Jian LIU Pu-Sheng

(Department of Applied Chemistry, Harbin Institute of Technology, Harbin 150001)

Abstract: Layered Co-based ceramics with a nominal composition of $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ ($x=0.0, 0.4, 0.8$, denoted by BAC-222) were prepared using conventional solid state reaction method. X-ray photoemission spectroscopy(XPS) was used to investigate their electronic structures. The cobalt ions are existed in mixed states of Co^{3+} and Co^{4+} . It is found that the $n_{\text{Co}^{4+}}/n_{\text{Co}^{3+}}$ ratio increases with the Ag doping content. The O1s photoemission spectra show that there are lattice oxygen and chemical absorbed oxygen in all the samples. Meanwhile, the conductivity and Seebeck coefficient of $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ were studied. The substitution of Bi^{3+} by Ag^+ results in dramatically increase of the electrical conductivity while the Seebeck coefficient is kept almost unchanged. This abnormal phenomenon means that Ag^+ ions play an important role in the electrical transport property of BAC-222. The power factor of $\text{Bi}_{1.6}\text{Ag}_{0.4}\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ reaches $1.23 \times 10^{-4} \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-2}$ at 1 123 K, which suggests that $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ are good potential oxides for thermoelectric application.

Key words: layered Co-based ceramic; thermalelectric; XPS; BC-222

Thermoelectric generation systems can convert heat energy into electric energy directly without using moving parts and without producing carbon dioxide gas, radioactive substances, or other emissions. Studies on this subject have been accelerated by the global need to

utilize exhausted waste heat. Metal oxides are very suitable for this purpose compared with conventional thermoelectric materials^[1,2], due to their high thermal and chemical stability at high temperatures in air for thermoelectric conversion. Among various metal oxides,

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*通讯联系人。E-mail: gchen@hit.edu.cn

第一作者: 李中华, 男, 32 岁, 博士, 副教授; 研究方向: 材料化学和计算化学。

layered cobalt oxides such as NaCo_2O_4 (Co-124)^[3], $\text{Ca}_2\text{Co}_2\text{O}_5$ or $\text{Ca}_3\text{Co}_4\text{O}_9$ (Co-349)^[4-6], and $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ (BC-222)^[7-10] have attracted a great deal of interest. The conversion efficiency of a thermoelectric material is expressed by the figure of merit, Z , defined as $S^2/(\rho\kappa)$, or ZT , where S , ρ , κ , and T are the thermoelectric power, electrical resistivity, thermal conductivity, and temperature, respectively. Large S coexisting with low ρ values is necessary to the realization of excellent thermoelectric performance, therefore, much effort has been made to increase the power factor (S^2/ρ) of thermoelectric materials.

The single crystal of BC-222 exhibits good thermoelectric performance ($ZT > 1.1$ at 1000 K)^[8], which is competitive with that of conventional degenerate semiconductors such as Bi_2Te_3 , PbTe , and $\text{Si}_{1-x}\text{Ge}_x$ ^[2]. However, it is difficult to grow single crystals large enough for the construction of a thermoelectric device. Therefore, many research group focus on the increase of ZT values of polycrystalline bulk material for practical applications. For polycrystalline BC-222^[9], κ value ($1.6 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$) is almost the same as single crystal (about $2.0 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$), S value ($180 \mu\text{V} \cdot \text{K}^{-1}$) is more than half of single crystal (about $300 \mu\text{V} \cdot \text{K}^{-1}$), ρ value ($17 \text{ m}\Omega$) is more than five times of single crystal ($3 \text{ m}\Omega$) at 1000 K. As mentioned above, reducing ρ value looks like the most effective way to improve the thermoelectric property of polycrystalline BC-222.

Recently, it has been reported that the addition of Ag metal to polycrystalline $\text{Na}_x\text{Co}_2\text{O}_4$ ^[11] and AgO to Co-349^[12] can successfully reduce and consequently improve the thermoelectric power factor (S^2/ρ or $S^2\sigma$). In the present study, we examined the effect of Ag substitution on the thermoelectric properties of BC-222 bulk materials.

1 Experimental

Polycrystalline samples of $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ were prepared from reagent grade Bi_2O_3 , SrCO_3 , Co_3O_4 and AgNO_3 powders in stoichiometric ratios. The mixtures were pressed in the form of dish-shaped pellets and heated in alumina crucible in air at 1123 K for 12 h.

X-ray diffraction (XRD) patterns of the powders

were obtained on Rigaku D/max-2000 diffractometer operated at 40 kV and 100 mA with Cu $K\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) using curved graphite monochromator to examine the sample purities. Electrical conductivity (σ) was measured by a dc four-probe technique. Thermopower (σ) was calculated from the thermoelectric voltage and the temperature difference between the two ends of sample. XPS experiment was carried out on VG ESCALAB MK II spectrometer using Al $K\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$). The binding energy scale was calibrated by assigning 284.6 eV to the C1s signal.

2 Results and discussion

In the synthesis of $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$, the effects of sintering temperature and time were examined. Fig.1 (a) shows XRD patterns of the $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ products synthesized by conventional solid state reaction method at

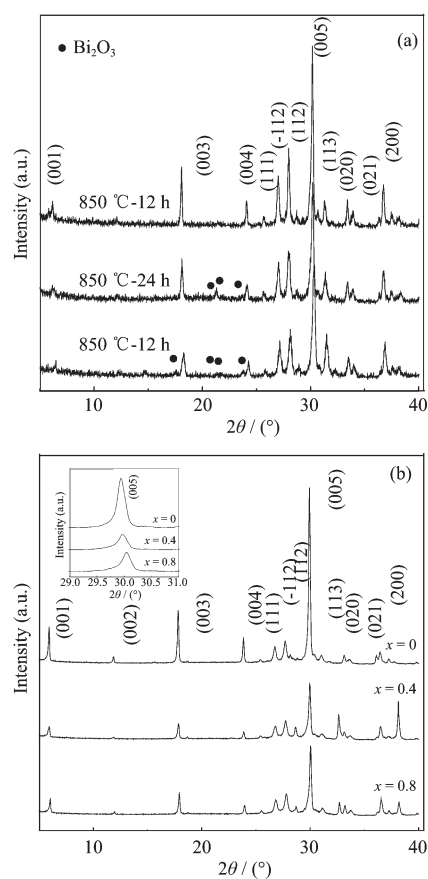


Fig.1 XRD patterns of $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ synthesized at different temperatures without Ag doping (a) and Ag doped at 1123 K, $x=0$, $x=0.4$ and $x=0.8$ (b). The inset shows x axis enlarged figure and the peaks shift can be seen clearly

different sintering temperatures for different periods of time. When the sample is sintered at 1 073 K for 12 h, we can obtain $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ and unreacted Bi_2O_3 in the products. When the sintering time increases from 12 h to 24 h, the unreacted Bi_2O_3 still exists.

Whereas, there is nearly no Bi_2O_3 impurity in the products obtained at 1 123 K for 12 h. It means that sintering temperature, instead of sintering time, is a critical factor for the preparation of single phase $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$. Therefore, Ag substituted $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ ($x=0.0, 0.4, 0.8$) were all prepared at 1 123 K. XRD analysis confirms that the $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ samples are crystallized in a monoclinic structure as shown in Fig.1 (b). XRD patterns of $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ powders are slightly shifted to higher 2θ value with the increase in the amounts of doped silver as shown in the inset of Fig.1 (b). The shift indicates that a part of silver at least is homogeneously doped into the $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ lattice.

Fig.2 shows the temperature dependence of conductivity for $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ samples. Ag substitution is effective in increasing the conductivity with all three samples showing metallic-like behavior (i.e., $d\sigma/dT < 0$) within the measured temperature range. For the $x=0.4$ sample the conductivity is as high as $62.1 \text{ S} \cdot \text{cm}^{-1}$ at 333 K, which is about 1.47 times of that of undoped polycrystalline samples ($42.2 \text{ S} \cdot \text{cm}^{-1}$). The high conductivity may originate from the substitution of monovalent Ag^+ for trivalent Bi^{3+} . It could increase hole concentration of the system, which can be further approved by XPS analysis

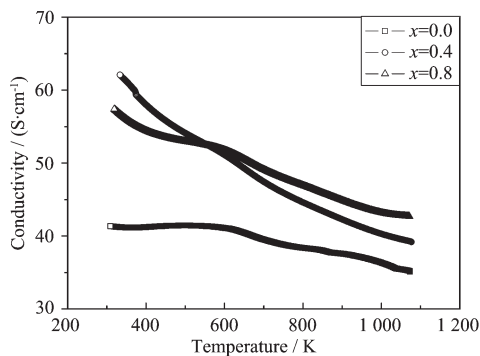


Fig.2 Electrical conductivity σ for $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ as a function of temperature

As shown in Fig.3, all samples show positive values of the thermoelectric power, suggesting p-type

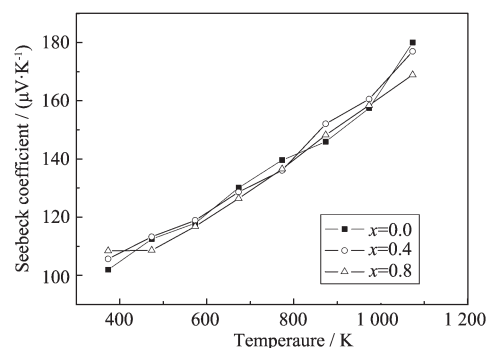


Fig.3 Seebeck coefficient (S) for $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ as a function of temperature

conductors. This temperature dependence is similar to single-crystal BC-222. Contrary to the Ag concentration dependence of conductivity, the addition of Ag has little effect on S . For the three samples the values of thermoelectric power all increase with increasing temperature in the whole temperature range measured. The above σ and S data indicate that Ag substitution is fairly effective for improving the BC-222 systems thermoelectric properties.

The thermoelectric power factor ($\text{PF} = S^2 \cdot \sigma$) was calculated from measured σ and S values (Fig.4). The PF of each sample increases with increasing temperature. Because the addition of Ag to BC-222 increases σ , and S almost keeps unchanged, the PF of Ag doped samples are all increased. The values of calculated power factor at 1 123 K are about 1.06, 1.23, and $1.22 \times 10^{-4} \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-2}$ for the $x=0, 0.4$, and 0.8 samples, respectively. The decrease in the conductivity value suggests an increase in the carrier concentration, which is in agreement with the substitution of Ag^+ for Bi^{3+} . However, the change in thermoelectric power value

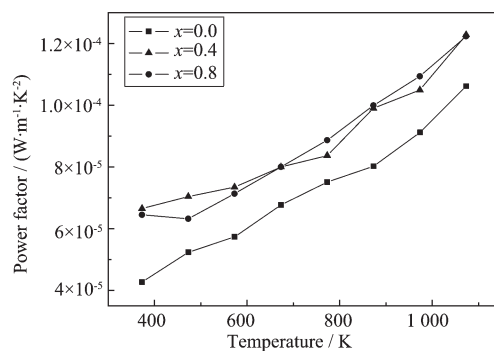


Fig.4 Temperature dependence of PF for $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$

indicates the opposite. It should be noted that the increase of conductivity and unchanged Seebeck coefficient with Ag substitution are difficult to understand by conventional theory.

The valence states of cobalt ions in $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ were examined with XPS. Fig.5 shows the spectra for the $\text{Co}2p$ level of the samples at $x=0.2, 0.4, 0.5$. The three spectra are very similar and exhibit the $2p_{3/2}$ and $2p_{1/2}$ doublets due to the spin-orbit coupling. The peaks positions of the $\text{Co}2p_{3/2}$ level of the $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ at $x=0.0, 0.4$ and 0.8 are observed as 781.4, 781.2 and 781.1 eV, respectively. From these results, it seems to be difficult to discern the valence states of cobalt ions in $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$. The spectral features of these $\text{Co}2p_{3/2}$ peaks in Fig.5 are broad and the asymmetric bands show the structure information about cobalt ions. If the Co^{3+} coexists with the Co^{4+} , it should lead to asymmetry of $\text{Co}2p_{3/2}$ peak feature^[13]. Here we use an asymmetric index β , where β is defined as the ratio of half-width at the half-maximum on a high-binding-energy side, W_H , to half-width at the half-maximum on a low-binding-energy side, W_L . The value of β increases as 1.0($x=0.0$), 1.1($x=0.4$) and 1.3($x=0.8$) with x in $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$. This indicates that Co^{3+} coexists with the Co^{4+} . From these spectra of $\text{Co}2p$ level, we conclude that the cobalt ions have a mixed state of Co^{3+} and Co^{4+} . The fraction of Co^{4+} is increased with the increase of x .

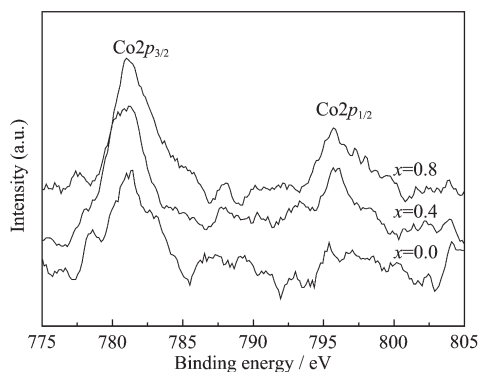


Fig.5 $\text{Co}2p$ photoelectron spectra of $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$

Moreover, the oxygen states of $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ were studied by XPS. Fig.6 shows the spectra for the $\text{O}1s$ level of $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ ($x=0.0, 0.4$ and 0.8). Every $\text{O}1s$ spectrum of $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ shows two peaks. The peak at low-binding-energy side is assigned

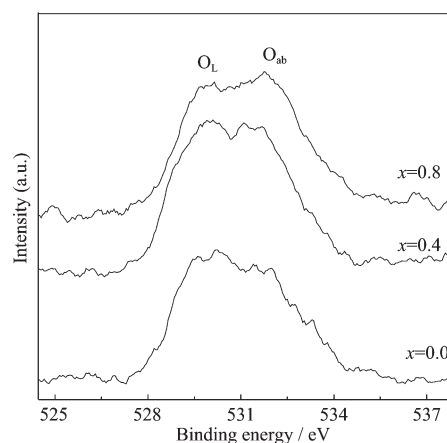


Fig.6 $\text{O}1s$ photoelectron spectra of $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$

as lattice oxygen O^{2-} , and the other peak at high-binding-energy side is assigned as adsorbed oxygen species^[14]. The binding energy of lattice (O_L), adsorbed oxygen (O_{ad}) and their relative intensity are shown in Table 1. The binding energy of lattice oxygen (O_L) decreases with increasing x , which indicates that O-Co bond is strengthened by doping of Ag and the increase of Co^{4+} . It is well known that CoO_2 layers are responsible for the electric conduction of layered Co-based oxides, therefore, the strengthening of O-Co bond suggests an increase of electric conductivity of Ag substitution $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$. On the other hand, the increase of relative intensity ratio of O_{ad}/O_L is a natural result of Ag^+ substitution for Bi^{3+} , which means an increase of hole concentration in the system and the increase of conductivity.

Table 1 Positions of lattice(O_L) and adsorbed oxygen(O_{ad}) for the $\text{O}1s$ XPS spectra of $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ ($x=0.2, 0.4, 0.5$), as well as their relative intensity ratios(R)

x	$\text{O}1s$		
	O_L / eV (Intensity/counts)	O_{ad} / eV (Intensity/counts)	$R(\text{O}_{ad}/\text{O}_L)$
0.0	530.1(5 802)	531.6(5 526)	0.95
0.4	530.0(7 540)	531.4(7 455)	0.99
0.8	529.8(8 015)	531.7(8 186)	1.02

3 Conclusions

$\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ ($x=0.25, 0.3, 0.4$) ceramics were prepared by solid-state reaction. The crystalline phases, electronic structure and high temperature thermoelectr-

ic property of $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$ have been investigated. XPS results show that cobalt is in mixed states of Co^{3+} and Co^{4+} and the $n_{\text{Co}^{4+}}/n_{\text{Co}^{3+}}$ ratio increases with the Ag doping content increasing. The O-Co bond is strengthened by doping of Ag and the increase of Co^{4+} . The increase of relative intensity ratio of O_{ad}/O_L results in hole concentration increase in the system, which is responsible for the positive effective in increasing conductivity of Ag substitution $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{Co}_2\text{O}_{8-\delta}$. Because it provides a significant increase of conductivity without changing S value, Ag substitution has been proved to be an effective way to obtain high thermoelectric performance materials.

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