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Effect of Ca doping on the thermoelectric properties of $SrCu_2O_2$

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The thermoelectric properties of p-type oxide $SrCu_2O_2$ doped with Ca with amounts of 0, 3, 10, and 15% have been studied. The Seebeck coefficients were found to be positive for all the samples in the temperature range between 423 and 923 K. Although no effective enhancement of the electrical conductivity was observed, doping with Ca clearly improved the Seebeck coefficients and the thermal conductivity of $SrCu_2O_2$. $SrCu_2O_2$ doped with 10% Ca showed the lowest thermal conductivity that varied from 0.32 W/mK at 423 K to 0.66 W/mK at 923 K. Overall, the value of ZT of Ca-doped $SrCu_2O_2$ was slightly larger than that of the un-doped $SrCu_2O_2$. $SrCu_2O_2$ doped with 15% of Ca showed the highest ZT of 2.67×10^{-3} at 423 K and 4.38×10^{-3} at 923 K.

Key words: $SrCu_2O_2$, Thermoelectric property, Calcium, Doping.

Introduction

These days, as the demand for energy becomes higher, the development of thermoelectric materials has received much more attention. Thermoelectric materials exhibit the Seebeck effect induced by a temperature difference in the materials, so they are widely used for energy conversion between electricity and heat. The performance of a thermoelectric material is evaluated in terms of a figure of merit, $Z = \alpha^2\sigma/\kappa$, which requires a low thermal conductivity (κ), a high electrical conductivity (σ), and a large thermoelectromotive force (Seebeck coefficient, α) [1]. The discovery of layered cobalt oxides, such as $NaCo_2O_4$ [2], $Ca_2Co_2O_5$ [3], and delafossite-type oxides $CuMO_2$ [4-6], as promising p-type thermoelectric materials have stimulated thermoelectric studies of oxide materials. Although it has been known that the figure of merit values of metal oxides are smaller compared to those of semiconductors and alloys, the oxides gain research attention as high-temperature thermoelectric materials for power generation due to their high thermal stability, oxidation resistance, and reduced toxicity [7].

A transparent conducting oxide (TCO) is a unique type of material that combines electrical conductivity and optical transparency in a single material, possessing carrier concentrations of at least 10^{20} cm^{-3} and optical band gaps greater than 3 eV [8]. Due to their appealing properties, TCOs are widely used in solar cells and other optoelectronic devices. Development of functional p-n junctions solely using TCO materials is currently a major challenge, as this would open up the possibility of "transparent electronics" [9], which necessitates the production of good quality n- and p-type TCO materials.

$SrCu_2O_2$ (SCO) is a p-type transparent conductive oxide with a wide band gap (3.3 eV) which makes this material a promising candidate not only for full oxide electronic devices but also for thermoelectric applications [10]. Many efforts has focused on exploiting this material as a p-type wide band gap semiconducting oxide in transparent thin film electronics [11-12]. These activities have included epitaxial thin film materials, yielding the possibility of developing epitaxial oxide electronics [13-14]. Recently we observed that the figure of merit of SCO increases as the measurement temperature increased, and the dimensionless ZT value reaches up to 2×10^{-3} at 923 K [15]. Unfortunately, the conductivity of SCO has been far smaller than of the other p-type TCOs. It has been reported that for SCO thin film the addition of a small amount of K and Ca increased the conductivity slightly [10, 16]. The effect of dopants, however, has not yet been fully understood.

In this paper, we report on the thermoelectric properties of Ca-doped SCO ceramics fabricated by a solid state reaction. The resulting ceramics showed an improvement in the Seebeck coefficient and the thermal conductivity, which resulted in a slightly larger figure of merit. On the other hand, the electrical conductivity did not show an obvious change as compared to the un-doped SCO ceramics.

Experimental

The Ca-doped SCO ceramics were synthesized by a solid-state reaction from high purity CuO and $SrCO_3$

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powders with the addition of $CaCO_3$. After being well mixed and ground, the powders were rapidly heated once and slowly heated 3 times to 1073 K. Mixing and grinding were done after every heating. A hydrostatic pressure of approximately 113 MPa was applied to make a compact pellets that were then sintered in a N_2 ambient at 1143 K for 10 h. The detailed synthesis process of the SCO ceramic has been reported previously [15]. Different Ca levels (0, 3, 10, and 15%) were used to investigate the effect of doping.

The structural properties were studied from X-ray diffraction patterns (Rigaku Miniflex Diffractometer) and scanning electron microscope images (CX-100S). The electrical conductivity and the Seebeck coefficient were measured using an Ulvac-Riko ZEM2 system, and the thermal conductivity was measured using an Ulvac-Riko TC7000 system. The thermoelectric measurements were carried out from 423 to 923 K.

Results and Discussion

The XRD patterns in Fig. 1 shows that all the SCO ceramics are of a tetragonal crystalline structure. No significant additional phase was observed when the doping level is lower than 10%. In the SCO doped with 15% Ca, several non-identified peaks appeared in the spectrum. The lattice parameters of un-doped SCO calculated from the XRD pattern are $a = 5.466$ Å and $c = 9.826$ Å, similar to those reported [17]. The peaks of Ca–doped SCO shift toward higher diffraction angles with increasing Ca levels, indicating that the lattice parameters of the Ca-doped SCO were decreased due to Ca doping. This result is consistent with the expectation that the Ca^{2+} ions (radius ~ 1.14 Å) substitute on the sites of the Sr^{2+} ions (radius ~ 1.32 Å) in SCO. The lattice parameters of SCO samples as a function of Ca doping level are shown in Fig. 2.

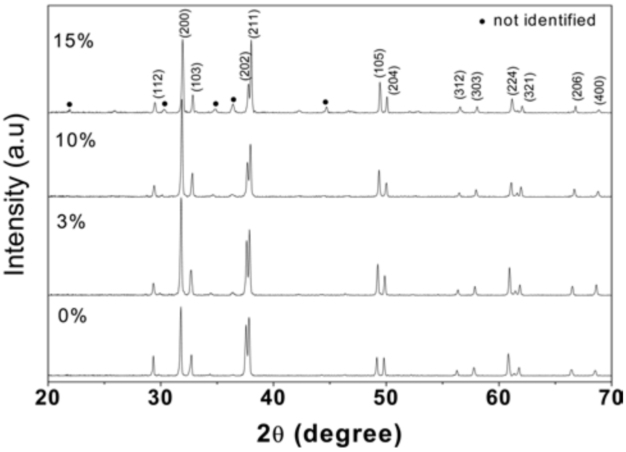

Fig.1. XRD patterns of $SrCu_2O_2$ doped with 0, 3, 10, and 15% Ca. The peaks labeled with dots were not identified.

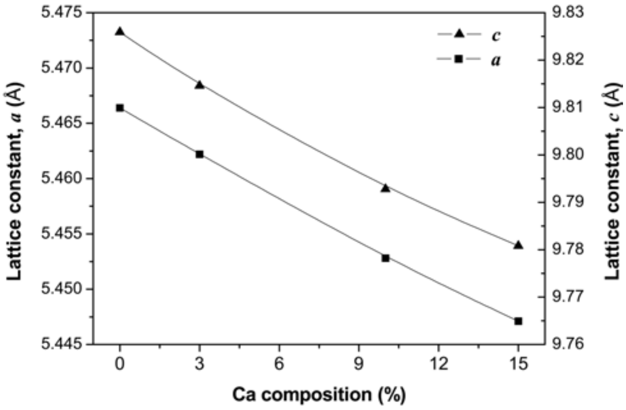

Fig. 2. Lattice parameters of $SrCu_2O_2$ as a function of Ca composition.

Figure 3 shows the SEM images of the as-sintered SCO with different Ca levels. A larger grain size was

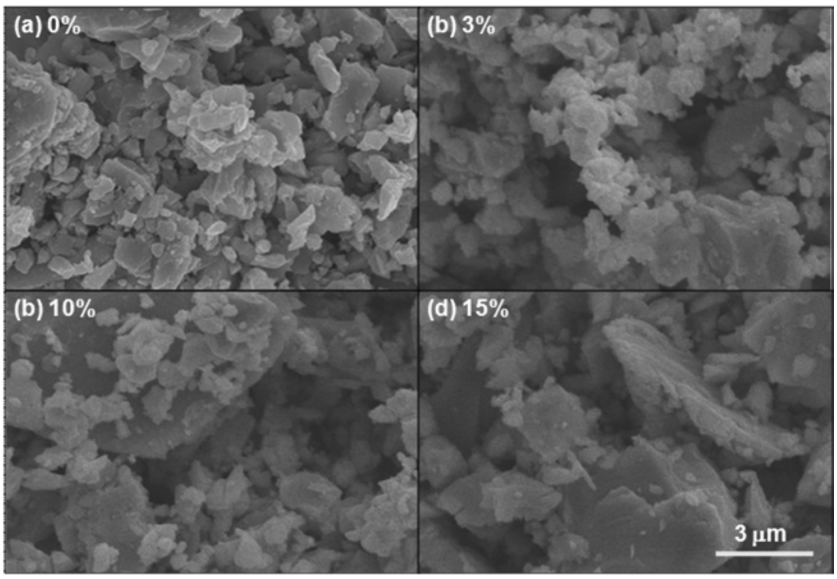

Fig. 3. SEM images of the surface of $SrCu_2O_2$ doped with Ca (a) 0%, (b) 3%, (c)10%, and (d) 15%.

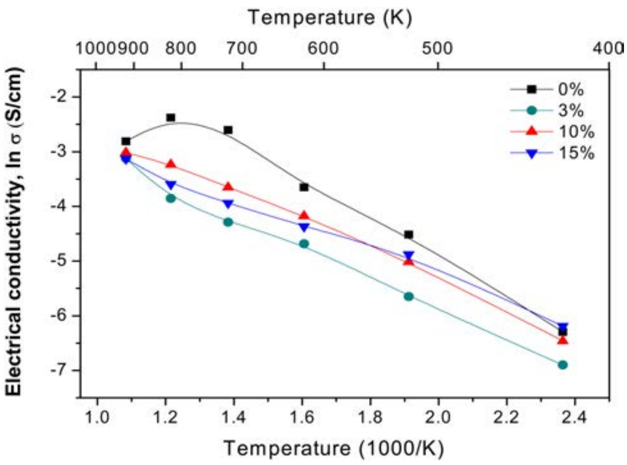

Fig. 4. Temperature dependence of the electrical conductivity of $SrCu_2O_2$ doped with different Ca levels.

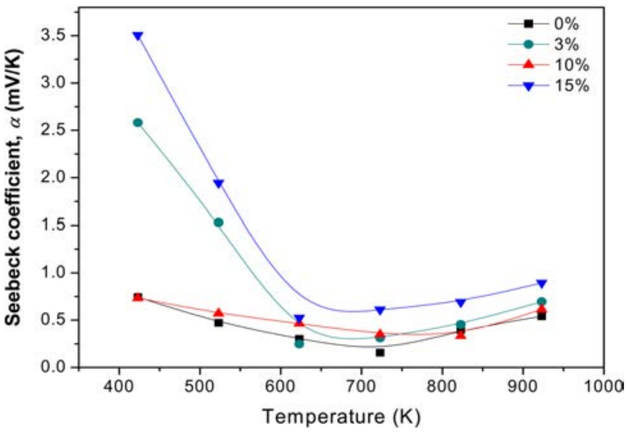

Fig. 5. Seebeck coefficients as a function of temperature of $SrCu_2O_2$ doped with different Ca levels.

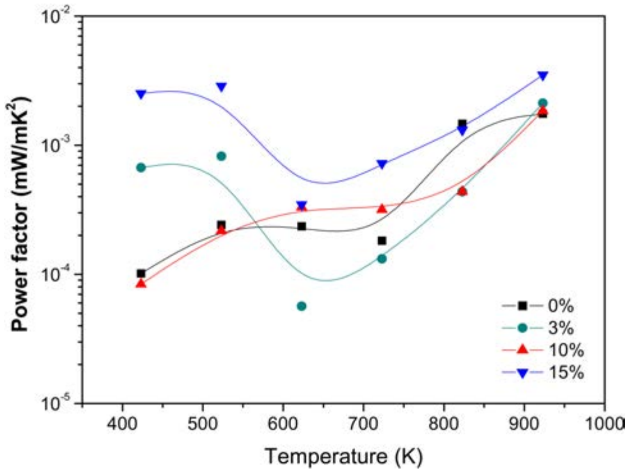

Fig. 6. Power factor of $SrCu_2O_2$ doped with different Ca levels as a function of temperature.

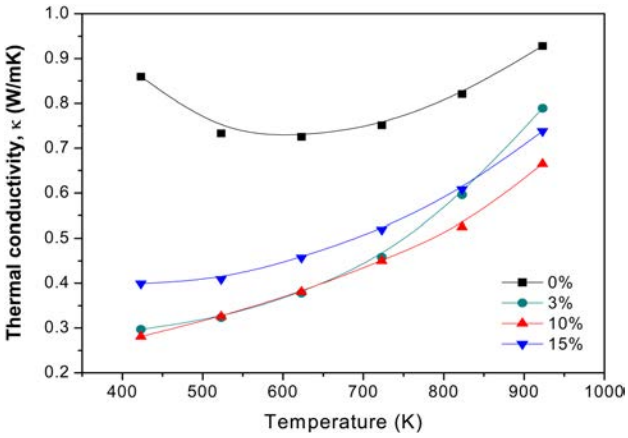

Fig. 7. Temperature dependence of the thermal conductivity of $SrCu_2O_2$ doped with different Ca levels.

observed for the 15% Ca-doped SCO. The porosity increased with an increase of the Ca level, resulting in a decrease in the density. The bulk densities are 4.510, 4.432, 4.101, and 3.938 g/cm^3 for SCO ceramics with Ca level of 0, 3, 10, and 15%, respectively.

The temperature dependence of the electrical conductivity (σ) is shown in Fig. 4. The electrical conductivity increased with the temperature from 423 to 923 K for Ca-doped samples, confirming a semiconducting behavior. Although the electrical conductivity did not show a clear dependence on the Ca level, the overall electrical conductivities of Ca-doped SCO samples was lower than that of the un-doped SCO. The above observation might be due to the increased porosity from Ca doping, since a high porosity is responsible for a decrease in the electrical conductivity and also the thermal conductivity [18].

Seebeck coefficient (α) measurements have been carried out to identify the major conduction type of SCO and the results are shown in Fig. 5. The Seebeck coefficients are positive for all samples, indicating a p-type semiconducting behavior. Near room temperature, the Seebeck coefficients from samples doped with 3 and 15% Ca increased significantly, but fell down around 623 K then increased slightly till 923 K. The decrease of the Seebeck coefficient might be due to an increase of the carrier concentration, which is consistent with the increase of the electrical conductivity observed in Fig. 4. A high Seebeck coefficient indicates a large thermoelectric force, which is needed to obtain a high voltage. Therefore, our results indicate that the addition of Ca to SCO can increase the thermoelectric force at temperatures lower than 600 K. The highest value of the Seebeck coefficient (3.51 mV/K at 423 K) was attained in the SCO doped with 15% Ca.

The power factor ($\alpha^2\sigma$) is calculated by using the Seebeck coefficient and electrical conductivity, which represents the electrical contribution to the thermoelectric performance. The calculated data are plotted in Fig. 6. Since the power factor was more strongly affected by the Seebeck coefficient than the electrical conductivity, consequently the power factor values from the SCO with higher amounts of Ca were significantly higher than for the un-doped SCO sample near room temperature. At

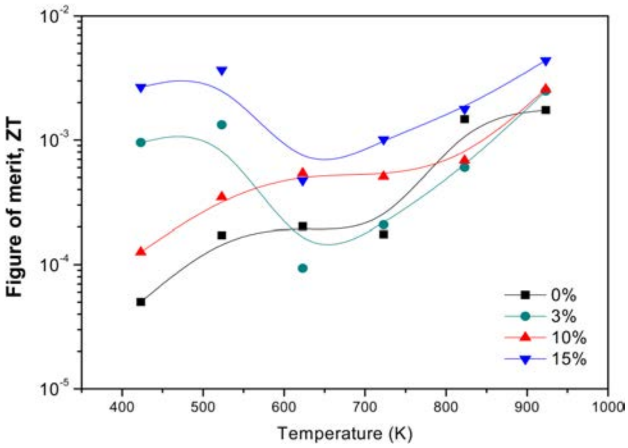

Fig. 8. Dimensionless figure of merit as a function of temperature of $SrCu_2O_2$ doped with different Ca levels.

423 K, the power factor of the SCO sample doped with 15% of Ca is about 2.52 $\times 10^{-6}$ W/mK^2.

Figure 7 shows the temperature dependence of the thermal conductivity (κ). For the Ca-doped SCO samples the thermal conductivity increased as the measurement temperature became higher. Moreover, the effect of doping clearly reduced the thermal conductivity as compared to the un-doped SCO sample. The SCO sample doped with 10% Ca showed a κ between 0.32 and 0.66 W/mK, whereas that un-doped SCO sample had a κ varying from 0.73 to 0.93 W/mK. These values are lower than other oxides reported previously [3, 6]. A high mean atomic mass and strong phonon scattering were suggested as the main contributions to the low thermal conductivity [19]. The substitution of Ca ions in the Sr sites might cause more inelastic phonon scattering, thereby decreasing the phonon mean free path and the thermal conductivity.

From the measured values of σ, α, and κ, the dimensionless figure of merit ZT was calculated and is plotted in Fig. 8. The addition of Ca to SCO slightly improved ZT. The highest ZT was attained from the SCO sample doped with 15% Ca in the measured temperature range. The values of ZT from the SCO sample doped with 15% Ca are 2.67×10^{-3} at 423 K and 4.38×10^{-3} at 923 K. These values were comparable with other delafossite-type oxides in the same temperature range, such as $CuFe_{1-x}Ni_xO_2$ or $CuCrO_2$ [6, 20].

Summary

We have investigated the thermoelectric properties of $SrCu_2O_2$ doped with Ca (0, 3, 10, and 15%). The electrical performance was not improved effectively as expected, but the Seebeck coefficient and the thermal conductivity showed improvements as the level of Ca was increased. Although the overall ZT showed a slightly higher value than that of the un-doped SCO sample, our results indicate that in order to effectively improve the thermoelectric properties of SCO by doping, further investigation is necessary.

Acknowledgement

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