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Journal

Thermoelectric Performance of Zn and Ge Co-Doped In_2O_3 Fine-Grained Ceramics by the Spark Plasma Sintering

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Zn and Ge co-doped In_2O_3-based ceramics have been prepared by the spark plasma sintering (SPS) technique. Microstructure studies show that dense and fine-grained ceramic samples can be obtained at low temperature sintered by SPS, and the grain size is about 100–300 nm. These In_2O_3-based ceramics show higher electrical conductivity (~10^3 S/cm) as compared with the pure In_2O_3 (~50 S/cm). In addition, the samples also exhibited large power factor, especially the $In_{1.98}Zn_{0.01}Ge_{0.01}O_3$ sample ~ 7.5 × 10^{-4} W/mK^2. The evaluated maximum ZT value is 0.20 at 973 K, which makes them promising materials to be used in thermoelectric devices.

I. Introduction

Thermoelectric materials, especially oxide thermoelectric materials, have attracted considerable attention for the mutual conversion of heat and electricity in solids. Complex metal oxide polycrystalline ceramics, such as heavily electron-doped $SrTiO_3$,[1] TiO_2,[2] Al-doped ZnO,[3,4] and misfit layered cobaltites[5,6] have excellent high-temperature stability and environmentally favorable aspects. These make them much more enticing for high-temperature applications than conventional low-temperature applied thermoelectric alloys (e.g., Bi_2Te_3).[7] However, many researchers on thermoelectric are working to find better oxide materials. Indium oxide, which is a good candidate, has become a hot topic for electronic materials due to the peculiar thermoelectric character when the cubic bixbyite structure becomes disordered with various cations substituting for indium ions.[8] Bérardan *et al.*[9] have studied the co-substituted $In_{2-2x}M_xSn_xO_3$ (M = Zn, Cu, or Ni) recently. They found that co-substitution can significantly enhance the solubility of the dopant, which can significantly decrease the electrical resistivity and thermal conductivity. In contrast to single element doped oxides, isovalent co-substitution can theoretically make charge compensated well and does not induce any oxygen (or electron) excess or deficiency.[9] Therefore, it is a good way to enhance the thermoelectric properties of oxide materials by co-substituting.

In this work, we have prepared $In_{2-2x}Zn_xGe_xO_3$ using Zn and Ge co-doping approach to tune the electrical conductivity, Seebeck coefficient and the thermal conductivity by the spark plasma sintering (SPS) method. The conventional solid state reaction synthesis method needs much more time to accomplish the synthesis procedure, while the SPS method can greatly improve the properties of sintered ceramics with fine grain and high bulk density in short time and low sintering temperature.

II. Materials and Method

The $In_{2-2x}Zn_xGe_xO_3$ ceramics (x = 0, 0.01, 0.03, 0.05, 0.10, abbreviated as IZGO-0, IZGO-1, IZGO-2, IZGO-3, IZGO-4, respectively) were prepared by the spark plasma sintering technique. In_2O_3 (99.99%, Sinopharm), GeO_2 (99.99%, Sinopharm), ZnO (99.99%, Sinopharm) were used as raw materials. These starting powders with the above-mentioned nominal compositions were mixed by ball-milling for 12 h. The mixed powder was calcined in a muffle furnace at 873 K for 2 h to make the desired precursor. All the ceramic samples were sintered by the spark plasma sintering (Sumimoto SPS1010, Tokyo, Japan) under the pressure of 40 MPa in the range of 1173–1213 K for 5 min, and the pressure was from 0 to 40 MPa with the temperature from 0 to 1173 K by manual. The as-sintered ceramics were then annealed at 873 K for 2 h in air to eliminate the carbon on the surface. Finally, the obtained ceramic samples of appropriate size were polished and coated with Ag paste for electrical measurements. The relative density of bulk ceramic samples was measured by the Archimedes method. X-ray diffraction (XRD, Cu$K\alpha$, D/MAX-2500V; Rigaku, Tokyo, Japan) and Scanning Electron Microscopy (SEM, JSM-6460; JEOL, Tokyo, Japan) were used to reveal the phase composition and microstructure of $In_{2-2x}Zn_xGe_xO_3$ ceramics, respectively. The temperature dependence of electrical conductivity and Seebeck coefficient of samples were measured using a self-made apparatus[5,7] in the temperature range of room temperature to 1000 K.

III. Discussion

Figure 1 shows the XRD patterns of various IZGO samples by the SPS. All the samples belong to the single phase of In_2O_3 as $x \leq 0.03$. While further increasing the doping concentration, GeO_2 secondary phase appears. We did not observe the $In_2Ge_2O_7$ phase as previously reported,[10] which may be ascribed to the low sintering temperature by the SPS technology. As it can be seen in the inset of Fig. 1, the peak of IZGO samples tends to shift to higher angle, and the lattice parameter of the cubic phases from the X-ray diffraction pattern drops from a = 1.0118 nm for IZGO-0 to a = 1.0109 nm for IZGO-2, then it decreases to a = 1.0106 nm for IZGO-4, which may be ascribed to the

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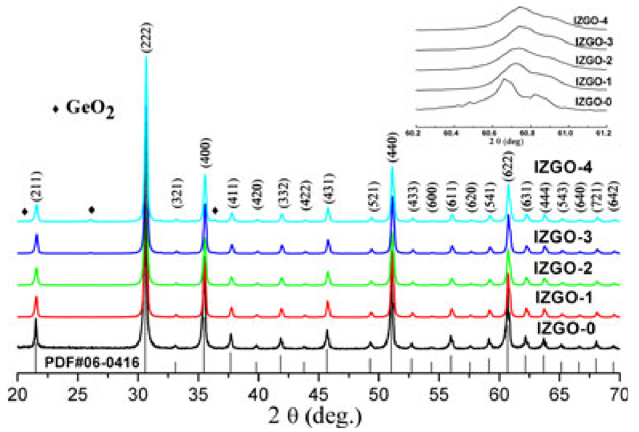

Fig. 1. X-ray diffraction patterns of Indium Oxide-based ceramic samples with the nominal compositions $In_{2-2x}Zn_xGe_xO_3$ (x = 0, 0.01, 0.03, 0.05, 0.10) by the SPS method. Inset: the enlarged XRD patterns for samples around 60°.

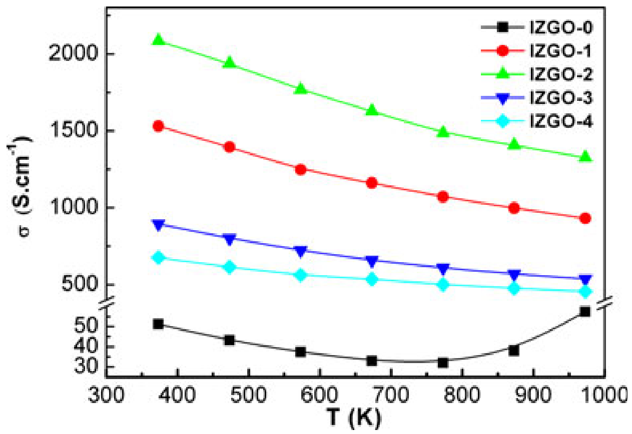

Fig. 3. Temperature dependence of electrical conductivity of the various IZGO samples.

small radius of Ge^{4+} and Zn^{2+} substituting for the In sites, and the lattice parameter decreased with doping. In addition, the XRD results indicate that the Zn and Ge co-doping can significantly enhance the solubility of Ge in the In_2O_3 matrix, which is much more soluble than the solubility limit about 0.5 at.% according to a report by Bérardan *et al.*,[10] and also can be helpful to tune the electrical conductivity in wide doping content.

The SEM images of the fractured cross section and surface of the Zn and Ge co-doped In_2O_3 system are shown in Fig. 2. The results indicate that the relative density of the samples are all about 95% measured by the Archimedes method. The density of the samples is summarized in Table I. The In_2O_3-based ceramics are composed of fine grains of 100–300 nm, which indicates that the SPS method can yield finer grains as compared with conventional solid state reaction method.

Figure 3 shows the temperature dependence of electrical conductivity of specimens. The electrical conductivity of the samples monotonically decreases with decreasing temperature. The electrical conductivity of the $x = 0.03$ sample is about 2.08×10^3 S/cm and 1.35×10^3 S/cm at 373 and 973 K, respectively. This is about two orders higher than that of pure In_2O_3, which may be ascribed to the related defects caused by the volatility of ZnO. Moreover, the conductivity of the samples first increased then decreased over a wide range with the increase of doping content of x and it reaches the highest point in IZGO-2 sample, which indicated that the electric conductivity of the samples can be tuned by the concentration of Zn and Ge.

According to the polaron theory,[11] the temperature dependence of the conductivity is generally described as:

$$\sigma = nea^2(A/T)\exp(-E_a/k_BT)\infty T^{-1}\exp(-E_a/k_BT),$$

where n is the carrier concentration, e is the electron charge of carrier, and a is the intersite distance of hopping. A, E_a, k_B, and T are the pre-exponential terms related to the scattering mechanism, the activation energy, Boltzmann constant, and absolute temperature, respectively. As shown in Fig. 4, there is a linear correlation between ln(σT) and $1000/T$ in IZGO-1, IZGO-2, IZGO-3, and IZGO-4 samples. The results indicate that the activation energy is in the range of 0.0221–0.0290 eV. The activation energy E_a drops from 0.0240 eV for $x = 0.01$ to 0.0221 eV for $x = 0.05$, then it increases to 0.029 eV for $x = 0.10$. The decrease of the activation energy indicates that the transport of the polarons becomes easier with co-substitution. However, it indicates that as $x > 0.05$, the activation energy increases, suggesting that higher doping content is not effective in changing the electrical transport properties. In addition, the related defect characteristic (e.g., defect size and position) and microstructure (e.g., grain and grain boundary) will also influence the activation energy and the electrical conductivity.

Figure 5 shows the thermoelectric power as a function of temperature for various In_2O_3-based samples. A negative

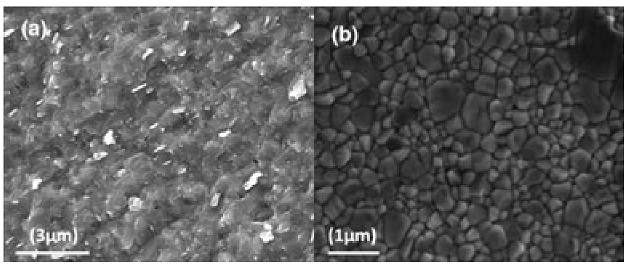

Fig. 2. Scanning electron microscopy images of (a) the fractured cross section and (b) surface for IZGO-2.

Table I. The Density of the Samples

Samples	IZGO-0	IZGO-1	IZGO-2	IZGO-3	IZGO-4
Relative density (%)	96.1	95.3	95.1	97.8	94.5

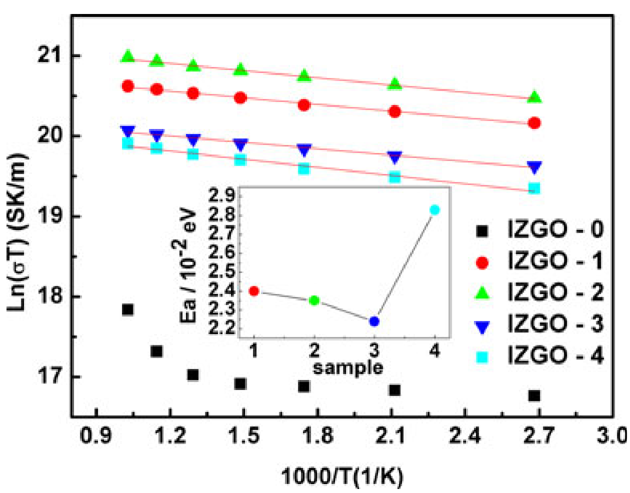

Fig. 4. The plots of ln(σT) vs $1000/T$ plots for various IZGO samples (*solid lines*). Inset: the activation energy for samples.

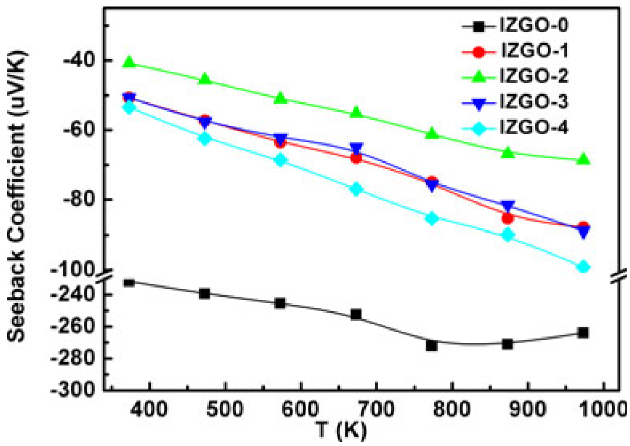

Fig. 5. Temperature dependence of Seebeck coefficients for the various IZGO samples.

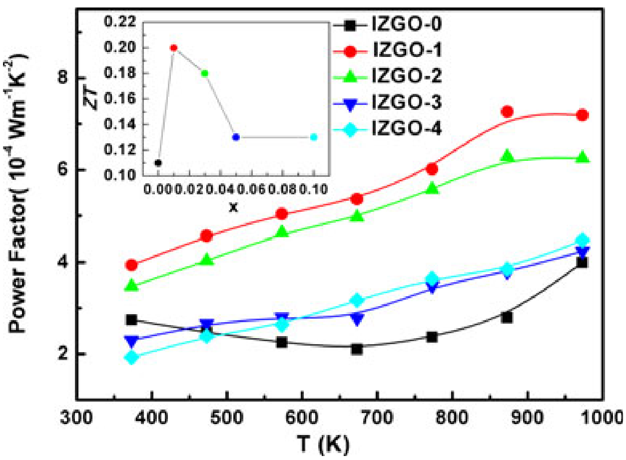

Fig. 6. Temperature dependence of power factor of various IZGO samples. Inset: the *ZT* values of the ceramics at 973 K.

Seebeck coefficient indicates that this system is a typical *n*-type thermoelectric semiconductor. The value of Seebeck coefficient of all doped samples is increasing with an increase of Zn and Ge co-doping respect to In_2O_3, which should be due to the fact that the Seebeck coefficient is inversely proportional to the carrier concentration. Therefore, the high conductivity leads to a low Seebeck coefficient. We also calculated the power factor (PF) of these ceramic materials. As seen from Fig. 6, the power factor of the samples monotonically increases with increasing the temperature and the PF values for $x = 0.01$ samples reached 7.5×10^{-4} W/mK^2 at 973 K. Consequently, the co-substitution can obviously enhance the power factor of the pure In_2O_3 almost over the whole temperature range. According to previously reported $In_{2-2x}M_xSn_xO_3$ (M = Zn, Cu, or Ni) systems,[9] Bérardan *et al.* reported that the best $In_{1.6}Zn_{0.2}Sn_{0.2}O_3$ ceramic sample shows $\sigma \sim 830$ S/cm at 973 K, and power factor is about 5×10^{-4} W/mK^2 at 973 K. Our studies show that the PF of IZGO-1 and IZGO-2 is 7.5×10^{-4} W/mK^2 (σ = 930 S/cm) and 6.2 W/mK^2 (σ = 1325 S/cm), respectively, which indicate that Zn/Ge co-doped IZGO systems can also enhance the electric conductivity and PF values, which may be due to the increase of these ceramic samples' density by this SPS sintering method. As shown in Table II, according to the thermal conductivity expression $\lambda = \lambda_L + \lambda_{el}$, where λ_L originating from the phonon contribution and λ_{el} from the charge carriers contribution, and considering the Weidman–Franz law $\lambda_{el} = L_0 T\sigma$ ($L_0 = 2.45 \times 10^{-8}$ $V^2 \cdot K^{-2}$), we can evaluate the λ_L of IZGO-1 and IZGO-2 is 1.6 and 0.25 W·(m·K)$^{-1}$, respectively, which indicates that the finer grains of IZGO samples can decrease greatly the lattice thermal conductivity, and thus improving the figure of merit (ZT ~ 0.20 at 973 K). These results indicate that a better TE performance can be desirable in these fine-grained In_2O_3-based ceramics by a suitable doping and an optimal processing technology.

Table II. The Thermal Conductivity of the IZGO-1,IZGO-2, and IZGO-3 Samples

	Thermal conductivity W·(m·K)$^{-1}$		
Temperature (K)	IZGO-1	IZGO-2	IZGO-3
373	7.612	5.628	5.729
573	5.258	4.374	4.537
773	4.368	3.799	4.038
873	4.067	3.614	3.896
973	3.840	3.478	3.820

IV. Conclusion

In conclusion, $In_{2\text{-}2x}Zn_xGe_xO_3$, ceramics prepared by the SPS method exhibit very high electrical properties, thermoelectric power, and power factor. Furthermore, Zn and Ge co-doping can tune the electrical behaviors and the thermal conductivity, and the *ZT* of IZGO-1 can be 0.20 at 973 K. Our results indicate that such In_2O_3-based ceramics are promising thermoelectric materials.

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