1. Introduction

Thermoelectric (TE) energy conversion has received more attention in the past decade on account of its promising application to directly convert waste heat into electricity.1-4 This means that a huge amount of waste heat, including from human activities, can be converted into useful energy, helping to increase the production efficiency and improve living conditions. The TE figure-of-merit ($ZT$) is given by

$$ZT = \frac{\sigma^2 T}{k}$$

where $\sigma$, $\alpha$, $T$ and $k$ are the electrical conductivity, the Seebeck coefficient, absolute temperature and the thermal conductivity, respectively.5-8 According to the eqn (1), TE material which has good performance needs a large electrical conductivity, a Seebeck coefficient and a low thermal conductivity.

Semiconductor oxides are great prospective alternatives to conventional high temperature thermoelectric materials because of their high temperature stability and relatively wide bandgap. Currently, Si-Ge alloy and Yb4MnSb11 (ref. 8) have high $ZT$ value in high temperature, all of which possess problems such as high cost and toxic raw materials, especially Ge, Yb and Sb. BiCuSeO9,10 maximum application temperature is 600 °C because of oxygen will disappear with the temperature increases. Therefore, the cheaper, high temperature stability and more environmental friendly TE materials are receiving increased attention.

ZnO has a wurtzite structure with space group $P6_3/m$. It is pyroelectric and piezoelectric, what represents the basis for applications in electromechanical or thermoelectric coupling devices. Moreover, ZnO which with a direct bandgap of 3.37 eV at room temperature is a semiconductor. In2O3 is also a wide bandgap transparent semiconductor ($E_g \approx 3.6$ eV) and has a high electrical conductivity.12-15 Indium is sixfold coordinated in the In2O3 bixbyte structure, while zinc adopts fourfold coordination in the ZnO wurtzite structure.16 The homologous compounds, In2O3(ZnO)k ($k = \text{integer}$), have very unique crystal structures with space groups of $R3m$ (for $k$ = odd) or $P6_3/mmc$ (for $k$ = even) and are composed of layers of InO3, In2O3 and ZnO, what are stacked sequentially along the $c$-axis of the hexagonal system.17,18 We can learn a lot from quite many previous studies on the inherent n-type behavior in In2O3 and ZnO.19-22 The zinces disappear during the high temperature solid state reaction. So, the cation antisite defect, indium on zinc (InZn), also should be considered. V8/Zn0 defect in ZnO and V8/In0 in In2O3 for binaries are up to be the origin of n-type conductivity in un-doped ZnO and In2O3. In2O3(ZnO)5 intrinsic superlattice ceramics have three advantages for application in thermoelectric materials. First of all, it possesses excellent structure and chemical stability even at high temperature (under 800 °C). Secondly its wide band gap prevents thermal excitation of “minor” carriers and thus allow the $ZT$ increases at high temperature forward. For the layered structure, the carrier mobility along the layer direction is higher than that cross the layer direction. Thirdly, In2O3(ZnO)5 has a very unique crystal structure composed of layers of InO3− and InZn5O15, periodically stacking in the $c$-axis direction. This layered structure gives rise to low thermal conductivity which is attributed to the reduced mean free path of the phonon between layers.

Enhanced thermoelectric properties of In2O3(ZnO)5 intrinsic superlattice ceramics by optimizing the sintering process

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Thermoelectric (TE) materials have a promising application as they can interconvert thermal energy to electrical energy directly. Oxide TE materials have attracted more attention for this application due to their high temperature stability. In this work, In$_2$O$_3$(ZnO)$_5$ intrinsic superlattice ceramics with a layered structure were synthesized by reaction sintering a mixed powder of In$_2$O$_3$ and ZnO at 1200 °C for different holding times ($t = 6, 8, 10, 12$ and 15 h) in air. Their thermoelectric properties including the electrical conductivity, Seebeck coefficient and thermal conductivity, were measured from 323 to 973 K. The thermoelectric properties depended on the holding time. The highest $ZT$ value of 0.19 at 973 K was obtained for the sample with a 12 h holding time.
In this work, the n-type In$_2$O$_3$(ZnO)$_5$ intrinsic superlattice ceramics were fabricated by a standard solid reaction 1200 °C for 6 h, 8 h, 10 h, 12 h and 15 h. There are In$_2$Zn$_{10}$O$_{19}$ impurity phase of 6 h, 8 h and 10 h. When the holding time is 15 h, the impurity phase appears in the sample and correspond well to In$_2$Zn$_4$O$_7$. Only the 12 h sample contain supreme phase of 6 h, 8 h, 10 h, 12 h and 15 h. When the holding time is 15 h, the superlattice In$_2$O$_3$(ZnO)$_5$ samples were fabricated by a standard solid reaction route. Starting powders, In$_2$O$_3$ (Aladdin, 99.99%) and ZnO (Aladdin, 99.99%), were weighed in stoichiometric amounts and ground together by ball milling using agate balls and vial. The resulting powers were pressed uniaxially under 30 MPa, forming parallel disc with dimensions of 15 mm × 8 mm pellets. The pellets were transfer into an alumina crucible and calcined at 1200 °C for 6–15 h.

The samples were characterized by X-ray diffraction (XRD: Cu-Kz Bruker D8, Germany) and the density (ρ) of the sample was determined by Archimedes method. The fractographs were measured by a scanning electron microscope (SEM, ZEISS, EVO 18-21-57).

The Seebeck coefficient and electrical resistance were measured using a Seebeck coefficient/electrical resistance measuring system (ZEM-3, Ulvac-Riko, Japan) in a He atmosphere (0.015 MPa pressure) which use the 2 × 2 × 8 mm cuboid sample. The Seebeck coefficient was calculated from thermoelectric voltage generated between both ends of a sample ΔV and temperature difference between the two ends ΔT. The thermal diffusivity (D) was measured by laser flash method (NETZSCH, LFA457, Germany) in flow argon atmosphere (80 ml min$^{-1}$) which requires that the samples are discs with a diameter of 6 mm. The electrical and thermal properties of the samples were tested perpendicular to pressure direction. The Hall coefficients (R_H) of the samples were measured at 293 K using a physical properties measurement system (HMS-7000), and a magnetic field of 2 T and electrical current of 30 mA were applied. The carrier concentration ($n_i$) was calculated by $n_i = 1/\epsilon R_H$, where $\epsilon$ is the electronic charge. The carrier mobility ($\mu_i$) was calculated by $\mu_i = R_H/\rho$. The thermal conductivity ($\kappa$) was calculated from the density ($\rho$), specific heat and thermal diffusivity using the relationship $\kappa = DC_\rho\rho$. These thermoelectric properties were measured in the temperature range of 323–973 K.

### 2. Experiments

All samples, belonging to the In$_2$O$_3$(ZnO)$_5$ series, were prepared using a standard solid reaction route. Starting powders, In$_2$O$_3$ (Aladdin, 99.99%) and ZnO (Aladdin, 99.99%), were weighed in stoichiometric amounts and ground together by ball milling using agate balls and vial. The resulting powers were pressed uniaxially under 30 MPa, forming parallel disc with dimensions of 15 mm × 8 mm pellets. The pellets were transfer into an alumina crucible and calcined at 1200 °C for 6–15 h.

### 3. Result and discussion

#### 3.1 Phase and microstructure

Fig. 1 shows the schematic representation of crystal structure from [010] direction for In$_2$O$_3$(ZnO)$_5$. Parent oxides ZnO and In$_2$O$_3$ are also shown for comparison. Unit cells are marked by the blue lines. In the primitive cell of In$_2$O$_3$(ZnO)$_5$ has 150 atoms. Both Zn and In atoms occupy the crystallographic positions. In other words, incorporation of In into ZnO slab is random, as is shown in the schematic representation of refined crystal structures (Fig. 1). In atomic ordered into the ZnO slab in our case can be obtained by high temperature calcinations which using a dilatory cooling.

### Table 1 The elemental mapping were performed for In$_2$O$_3$(ZnO)$_5$ with different holding time ($t = 6, 8, 10, 12$ and 15 h)

| Bulk samples | Indium mass norm [%] | Zinc mass norm [%] | Oxygen mass norm [%] | Indium atom [%] | Zinc atom [%] | Oxygen atom [%] | Abs. error [%] | Rel. error [%] |
|--------------|----------------------|--------------------|----------------------|----------------|--------------|----------------|----------------|----------------|
| 6 h          | 81.32                | 79.21              | 9.47                 | 49.15          | 9.77         | 41.08          | 2.64           | 22.33          |
| 8 h          | 40.19                | 49.35              | 10.46                | 16.65          | 40.09        | 42.46          | 3.55           | 16.09          |
| 10 h         | 37.97                | 50.65              | 11.38                | 15.72          | 37.17        | 47.11          | 3.12           | 17.12          |
| 12 h         | 33.04                | 49.79              | 17.17                | 13.02          | 34.58        | 47.94          | 2.16           | 9.18           |
| 15 h         | 24.48                | 54.95              | 20.57                | 9.11           | 35.92        | 54.97          | 3.98           | 15.89          |
It is worthy to mention that the refined crystal structures of homologous compounds clearly indicate a close relationship to their parent oxides ZnO and In₂O₃. According to their distinct coordination numbers (k), we can identify easily the layers of wurtzite type and bixbyite type structure. Wurtzite type structure similar with ZnO is largely maintained in these homologous compounds although deviation from the trigonal-bipyramidal coordination (k = 5) occurs.

As the data in Table 1 indicate, the content of In decreased with the increase of holding time. And the In atomic ratio is 49.15% in the In₂O₃(ZnO)₅ dispersed with 6 h, however, In₂O₃(ZnO)₅ dispersed with 15 h bulk sample In atomic ratio decreased to 9.11%. Because heating for longer time results into potential loss of indium. The In₂O₃(ZnO)₅ intrinsic superlattice ceramics were synthesized at 1200 °C for different holding time (6–15 h) as shown in Fig. 2. There are rhombohedral symmetry In₂O₃(ZnO)₅ of all specimens, which corresponds well to the PDF#89-8974 card. These results are consistent with the previous reports that In₂O₃(ZnO)₅ crystallize in group R3̅m for odd k values and P6₃/mmc for even k values. Heating for longer time brings about potential loss of indium and zinc. There are In₂Zn₇O₁₀ impurity phase in 6 h, 8 h and 10 h samples. In addition, there are ZnO impurity in the 6 h and 8 h sample. When the holding time is 15 h, the impurity phase appears in the sample and correspond well to In₂Zn₄O₇. Only the 12 h holding time sample is In₂O₃(ZnO)₅ pure phase. The crystallinity of all samples is showed in Table 2. As shown in Fig. 2, the peak intensity in 2θ ranges 30–47° for all the samples have obvious changes, indicating that there is texture in all the
samples. As the holding time is 15 h, the \( B \) of peaks increased, indicating the grain refinement according the Debye–Schererrer formula, \( d = \frac{K \gamma}{B \cos \theta} \) \(^{34}\) (\( K \) is the Scherrer constant, \( d \) is the average thickness of the crystal grains perpendicular to the crystal plane direction, \( B \) is the diffraction width of the measured sample, \( \theta \) is the diffraction angle, \( \gamma \) is the X-ray wavelength, 0.154056 nm).

Fig. 3 shows the scanning electron microscopy (SEM) images of \( \text{In}_2\text{O}_3(\text{ZnO})_5 \) at 1200 °C for 6 h (a), 8 h (b), 10 h (c), 12 h (d), 15 h (e). From the Fig. 3 the grain distribution is relatively uniform. The powders were sintered to bulk at high temperature. The bulk samples have the large grain size of several micrometers. In other words, all the grains were observed with the sharp edge, and their layered structure was described in terraced fields (indicated by the purple arrow on the SEM images). The density of the samples shows the tendency of decreased with the increase of holding time, as is shown Fig. 3(f). It is because that as the extension of holding time from 6 h to 15 h, the \( \text{In}_2\text{O}_3(\text{ZnO})_5 \) ceramic samples possess more and more pores because of potential loss of indium and zinc.

3.2 Thermoelectric properties

Fig. 4 shows that the temperature dependence of electrical transport properties for the \( \text{In}_2\text{O}_3(\text{ZnO})_5 \) ceramics at 1200 °C for 6–15 h. The electrical conductivity (\( \sigma \)) of 6 h and 8 h samples increased with the increasing temperature, being indicative of the semiconductor behavior in Fig. 4(a). When the holding time is 10 h, 12 h or 15 h, which \( \sigma \) decreased with the increasing temperature, showed a metallic behavior. As H. Ohta et al.\(^{33}\) research work shows that \( \text{In}_2\text{Zn}_7\text{O}_{10} \) and \( (\text{ZnO})_5\text{In}_2\text{O}_3 \) showed a metallic behavior and the pure \( \text{ZnO} \) showed a semiconductor behavior. Hence the 6 h and 8 h samples showed a metallic behavior, while the 10 h, 12 h and 15 h samples showed a semiconductor behavior. The concentration of conduction electrons is rather high and fixed in the present temperature range possibly. It is possibly induced by certain small deviations from stoichiometric compositions because the carrier concentration is determined by the valence control mechanism expressed as the following eqn (2),

\[
\text{InO}_1.5 = \text{In}^{2+} + e^- + \text{O}^2_\text{aq} + \frac{1}{4} \text{O}_2(g)
\]  

The \( \sigma \) depends on both carrier concentration \( n \) and mobility \( \mu \) as the following eqn (3),

\[
\sigma = ne\mu
\]

where \( e \) is the electronic charge. The sample for 12 h show higher electrical conductivity than other holding time samples. As reported in previous work,\(^{44}\) the electrical conductivity of \( \text{In}_2\text{Zn}_7\text{O}_{10} \) is lower than the \( \text{In}_2\text{O}_3(\text{ZnO})_5 \). Hence the electrical conductivity of 6 h, 8 h and 10 h samples lower than the 12 h sample. The space group of \( \text{In}_2\text{Zn}_4\text{O}_2 \) is \( P6_3/mmc \), which structure is different with \( \text{In}_2\text{Zn}_2\text{O}_2 \) and \( \text{In}_2\text{Zn}_2\text{O}_{10} \). We infer the existence of \( \text{In}_2\text{Zn}_4\text{O}_2 \) led the lower electrical conductivity. The sample of 12 h has the highest electrical conductivity due to its pure \( \text{In}_2\text{O}_3(\text{ZnO})_5 \) which has the noticeably higher density of the \( \text{InO}_2^- \) planar defects, representing highly conductive paths in the homologous phase. The holding time dependence of the carrier concentration (\( n \)) and the carrier mobility (\( \mu \)) at room temperature has shown in Fig. 5. The extension of the holding time result into the potential loss of indium and zinc. Meanwhile indium substituted zinc and it produce electrons. Hence the carrier concentration increases with the extension of the holding time. The raised carrier concentration given rise to the reducing of carrier mobility in line with their calculation method. As shown in Fig. 4(b), the Seebeck coefficients (\( \alpha \)) of all specimens were observed to be positive what account for \( \text{ZnO–In}_2\text{O}_3 \) ceramics are n-type semiconductor, meaning that the main carrier is electron. The absolute value of \( \alpha \) increased with the increasing of temperature within the scope of the measuring temperature, which corresponding to the electrical conductivity. \( \alpha \) is from the eqn (4) obtained,\(^{34}\)

Fig. 4 The (a) temperature dependence of the electrical conductivity (\( \sigma \)), (b) the Seebeck coefficient (\( \alpha \)), and (c) power factor (\( \sigma^2\alpha \)) for each bulk sample.
The temperature dependence of thermal diﬀusivity (D) (Fig. 6(a)), the carrier thermal conductivity (κc) and the lattice thermal conductivity (κl) (b), the totally thermal conductivity (κ) (c) and ZT value (d) for all bulk samples.

Reduced Fermi energy was used to calculate Lorenz number (eqn (5)) varies as Seebeck value changes (eqn (6)) with temperature or composition. The L calculation was estimated in a traditional single parabolic band model (resulting in an L with a deviation of less than 10% as compared with a more rigorous single non-parabolic band and multiple band models calculation) as described in ref. 35 and 36, where the reduced Fermi energy implicitly determined by the Seebeck values (eqn (2)).

The difference in thermal conductivity is the contribution of the low relative density and anisotropic structure of In2O3(ZnO). We assumed that interface scattering was generated by

\[
\alpha \approx \frac{2k_B^2}{e^2} m^* T \left(3\pi^2 n\right)^{\frac{3}{2}}
\]

where \( \frac{k_B}{e} \) is the Seebeck coefficient for a classical electron gas. The diﬀerent holding times make diﬀerent carrier concentrations of the samples. The temperature dependence of power factor (σα^2) for In2O3(ZnO)5 (1200 °C for 6–15 h) bulks is shown in Fig. 4(c). The material has high power factor (σα^2 > 2), despite having diﬀerent slopes. With the increasing testing temperature, the power factor of the samples increased signiﬁcantly because the Seebeck coeﬃcient increased rapidly with temperature, and the power factor and the square of Seebeck coeﬃcient were proportional. The diﬀerence were proportional. The diﬀerence were proportional.
porosity and difference in local density which arises from the anisotropic structure. One major perspective of nanostructure engineering to enhance thermoelectric properties is to design and create the (defect) structure with appropriate length scale, which is smaller than the mean free path of phonons but larger than that of electrons or holes.\(^1\) The effect of superlattice structures on reducing thermal conductivity has been attributed to various mechanisms, including the modification of phonon spectrum,\(^2\) phonon localizations, phonon scatterings at interfaces due to acoustic mismatch or defects formed arising from lattice mismatch\(^3\)\(^4\) etc. It should be noted that phonon mean free path depends on both temperature and microstructural features, since temperature determines density of states of phonons and thereby affects phonon–phonon interactions/lattice imperfections introduce defect scatterings of phonons (eqn (7)).

\[
\frac{1}{\ell_{\text{tot}}} = \frac{1}{\ell_{\text{ph-ph}}} + \sum \frac{1}{\ell_{\text{ph-def}}}
\]  

Assuming the scattering mechanisms are additive, the total phonon mean free path can be written as ref. 40. Superlattice belong to a surface defect. According to Zhao et al.,\(^5\) its special layered structure introduces additional phonon scattering, reducing the mean free path of the phonon. Thereby the thermal conductivity of the samples is reduced. The values are agreement with the previous ones.\(^6\)\(^7\)\(^8\) In addition to the \(\kappa\) value of all samples are very low and have a little reduction along with the increase of temperature. The total thermal conductivity trend consistent with the lattice thermal conductivity makes clear that \(\kappa_{\text{f}}\) occupies a leading position. The temperature dependence of the thermoelectric dimensionless figure of merit, \(ZT\), is shown in Fig. 6(d). As shown in the eqn (8),\(^9\)

\[
ZT = \frac{\sigma^2 T}{\kappa}
\]  

The supreme \(ZT\) value of 0.19 was measured for the 12 h holding time sample at 973 K. 

Fig. 7 shows the figure of merit of this work compared with other In\(_2\)O\(_3\)–ZnO system using different synthesis process. This work has an obvious improvement makes it an excellent candidate for further research and optimization for high-temperature thermoelectric applications.

4. Conclusions

Intrinsic superlattice ceramics \(\text{In}_2\text{O}_3(\text{ZnO})_5\) with layered structures were synthesized by reaction sintering mixed powders of \(\text{In}_2\text{O}_3\) and \(\text{ZnO}\) at 1200 °C for different holding time, \(t = 6, 8, 10, 12\) and 15 h, in air. There are \(\text{In}_2\text{O}_3(\text{ZnO})_5\) impurity phase of 6 h, 8 h and 10 h samples. When the holding time is 15 h, the impurity phase appears in the sample and correspond well to \(\text{In}_2\text{O}_3(\text{ZnO})_5\). Only the 12 h holding time sample is \(\text{In}_2\text{O}_3(\text{ZnO})_5\) pure phase. They were dense and a number of stripes possibly corresponding to stacking faults were observed in every grain. This layered structure gives rise to low thermal conductivity due to it is attributed to the reduced mean free path of the phonon between layers. The thermoelectric \(ZT\) increasing with increasing temperature and holding time (6–12 h) with the exception of 15 h. The maximum figure of merit of 0.19 was detected for the 12 h holding time sample at 973 K. \(\text{In}_2\text{O}_3(\text{ZnO})_5\) intrinsic superlattice ceramics were found be the huge potential candidates materials for high temperature thermoelectric energy conversion.

Conflicts of interest

There are no conflicts to declare.

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