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Preparation and thermoelectric properties of rare-earth-metal-doped SrO(SrTiO$_3$)$_n$ oxides

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Abstract

Rare-earth-metal-doped (Sr$_{0.95}$R$_{0.05}$)$_3$Ti$_2$O$_7$ (R=Nd, Eu) bulk samples were prepared by a conventional solid state reaction and Spark Plasma Sintering (SPS). The effect of calcining temperature $T_{\text{cal}}$ and atmosphere on the phase composition of samples were investigated. The results show that (Sr$_{0.95}$R$_{0.05}$)$_3$Ti$_2$O$_7$ (R=Eu) samples with pure Ruddlesden–Popper (RP) phases can be obtained at $T_{\text{cal}}=1500$ °C in the atmosphere consisting of mixture H$_2$ and Ar with their volume ratio of 5:95. Thermoelectric property measurements (300K-1000K) indicate that both the electrical resistivity $\rho$ and the absolute value of thermopower $S$ increase with elevating temperature, showing a typical behavior of a degenerate semiconductor. In comparison, the Eu-doped samples have larger dimensionless figure of merit ($ZT$) than the Nd-doped samples at the temperatures below 550K. The largest $ZT$ of (Sr$_{0.95}$Nd$_{0.05}$)$_3$Ti$_2$O$_7$ obtained in the present study is 0.087 (at 919K).

Keywords: (Sr$_{0.95}$R$_{0.05}$)$_3$Ti$_2$O$_7$ (R= Nd, Eu); solid state reaction; Spark Plasma Sintering

1. Introduction

Metal oxides have attract a great deal of interest because they are basically stable and environmental friendly at higher temperatures[1,5]. P-type oxide semiconductors such as Na$_x$CoO$_2$,Ca$_{3}$Co$_4$O$_9$ exhibit rather large $ZT$ ($ZT=S^2\sigma/\kappa$, where $S$, $\sigma$, $\kappa$, $T$ and $Z$ are Seebeck coefficient, the electrical conductivity, the thermal conductivity, absolute temperature and a figure of merit, respectively.), while n-type oxide semiconductors which are inevitably required to develop a thermoelectric power generation module exhibit rather low $ZT$ of 0.37 at 1000K in Nb-doped SrTiO$_3$ [1-4,6-9]. The poor performance of SrTiO$_3$

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can be ascribed to the relatively higher thermal conductivity. In recent years, some researchers have found that the layered perovskite-type Rudlesdden-Popper (RP) \((\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}, n=\text{integer})\) phase structure comprised of \((\text{SrTiO}_3)_n\) block layer and alternative stacks of salt rock \(\text{SrO}\) layer can reduce the thermal conductivity efficiently due to the enhanced phonon scattering at the internal interfaces of \(\text{SrO}/(\text{SrTiO}_3)_n\)[1,10-11]. Up to now, the largest \(\text{ZT}\) of 0.24 at 1000K have been obtained in \((\text{Sr}_{0.95}\text{Gd}_{0.05})_3\text{Ti}_2\text{O}_7\) indicating a promising thermoelectric(TE) materials[1,12-13]. However, the \(\text{ZT}\) is still too low to take into practice. In the present study, \((\text{Sr}_{0.95}\text{R}_{0.05})_3\text{Ti}_2\text{O}_7\) (\(\text{R}=\text{Eu, Nd}\)) oxides were successfully prepared using the conventional solid state reaction and Spark Plasma Sintering (SPS). We studied the effect of the calcining temperature \(T_{\text{cal}}\) and atmosphere on the phase composition of \((\text{Sr}_{0.95}\text{R}_{0.05})_3\text{Ti}_2\text{O}_7\) (\(\text{R}=\text{Eu}\)). Thermoelectric properties of the bulk samples were investigated in the temperature range of 300-1000K.

2. Experimental

All the samples were prepared by combining the conventional solid-state reaction method with Spark Plasma Sintering (SPS). The starting powder of \(\text{SrCO}_3\) (AR), \(\text{TiO}_2\) (AR), \(\text{Eu}_2\text{O}_3\) (99.99%) and \(\text{Nd}_2\text{O}_3\) (99.99%) were ball-milled in a planetary ball mill according to the chemical stoichiometric and calcined at 1200 \(^\circ\text{C}\) for 12h two times with a intermediate grinding for the purpose of the decomposition of carbonate. In order to form RP phase and generate the carrier electrons, the calcined powders were heated three times for 2h in Ar and \(\text{H}_2\) atmosphere. We prepared a series of powder samples at different calcining temperatures \((T_{\text{cal}}=1485 \text{ }^\circ\text{C}, 1500 \text{ }^\circ\text{C}, 1510 \text{ }^\circ\text{C})\) in Ar and \(\text{H}_2\) atmosphere(\(\text{H}_2:\text{Ar}=5:95\)) and at different volume ratios of \(\text{H}_2\) and \(\text{Ar}\) (\(\text{H}_2:\text{Ar}=5:95,10:90\)) holding \(T_{\text{cal}}=1500 \text{ }^\circ\text{C}\). After that, the powder samples with pure R-P phases were Spark Plasma Sintered at 40MPa, 1500 \(^\circ\text{C}\) for 5min in Ar flow. In order to investigate the effect of annealing on the samples, the obtained bulk samples of \((\text{Sr}_{0.95}\text{Eu}_{0.05})_3\text{Ti}_2\text{O}_7\) prepared by SPS, were annealed at 1500 \(^\circ\text{C}\) for 2h in Ar and \(\text{H}_2\) flow. The phase analysis of the powder samples were characterized by X-ray diffraction (XRD). The electrical resistivity \(\rho\) and the Seebeck coefficient \(S\) were measured by ZEM3 in He flow. The thermal conductivity \(\kappa\) were calculated from separate measurements of a laser flash method for thermal diffusivity and differential scanning calorimetry(DSC) for heat capacity \(C_p\) and bulk density measured through the Archimedes method.

3. Results and Discussion

3.1. Phase analysis and structural characterization

Fig.1 shows the powder XRD patterns of \((\text{Sr}_{0.95}\text{Eu}_{0.05})_3\text{Ti}_2\text{O}_7\) at different volume ratios of \(\text{H}_2\) and \(\text{Ar}\) holding \(T_{\text{cal}}=1500 \text{ }^\circ\text{C}\). It can be seen that peaks for other phase were not detected in \((\text{Sr}_{0.95}\text{Eu}_{0.05})_3\text{Ti}_2\text{O}_7\) when the volume ratio of \(\text{H}_2\) and \(\text{Ar}\) is about 5:95,while there are a amount of \(\text{TiO}\) and \(\text{Sr}_2\text{TiO}_4\) peaks when the ratio is about 10:90.Although a small amount of \(\text{H}_2\) might have favorable effects on reducing the electrical resistivity \(\rho\), too much \(\text{H}_2\) may result in undesirable phases which might make the thermoelectric performance deteriorate.

The powder XRD patterns of \((\text{Sr}_{0.95}\text{Eu}_{0.05})_3\text{Ti}_2\text{O}_7\) at different calcining temperatures \(T_{\text{cal}}\) with a fixed volume ratio of \(\text{H}_2:\text{Ar}=5:95\) are shown in Fig.2. We can see that the Rudlesdden-Popper(RP) phases were basically formed in this three calcining temperatures and the best calcining temperature is about 1500 \(^\circ\text{C}\) because there are some other peaks detected in the other two conditions.
3.2. Thermoelectric properties

The temperature dependence of the electrical resistivity $\rho$ and Seebeck coefficient $S$ are shown in Fig.3 and Fig.4, respectively. For all the $(\text{Sr}_{0.95}\text{R}_{0.05})_3\text{Ti}_2\text{O}_7$ (R=Eu, Nd) samples in the temperature range investigated, both the electrical resistivity $\rho$ and the absolute value of $S$ increase with temperature, and the value of $S$ are all negative, indicating that all the samples are n-type degenerate semiconductors. The $\rho$ for all the samples are higher than that of the perovskite-type SrTiO$_3$[14], which can be attributed to the insulating SrO layers randomly distributed in polycrystalline samples. For the sample of $(\text{Sr}_{0.95}\text{Eu}_{0.05})_3\text{Ti}_2\text{O}_7$, the annealed sample has higher electrical resistivity $\rho$ and larger $|S|$. The larger $|S|$ of the annealed sample can reflect the lower carrier concentration $n_e$ which might account for the increased electrical resistivity. The larger difference in $\rho$ between Eu-doped and Nd-doped $(\text{Sr}_{1-x}\text{R}_x)_3\text{Ti}_2\text{O}_7$ oxide might be attributed to the variable valence state in Eu which have two valence states: Eu$^{2+}$ and Eu$^{3+}$.
Fig. 3. The temperature dependence of the electrical resistivity $\rho$ for (Sr$_{1-x}$R$_x$)$_3$Ti$_2$O$_7$ (a) $R$=Eu, $x=0.05$, (b) $R$=Eu, $x=0.05$, annealed, (c) $R$=Nd, $x=0.05$.

Fig. 4. The temperature dependence of Seebeck coefficient $S$ for (Sr$_{1-x}$R$_x$)$_3$Ti$_2$O$_7$ (a) $R$=Eu, $x=0.05$, (b) $R$=Eu, $x=0.05$, annealed, (c) $R$=Nd, $x=0.05$.

Fig. 5. The temperature dependence of the total thermal conductivity $\kappa_{\text{total}}$ and the electronic thermal conductivity $\kappa_{\text{ele}}$ for (Sr$_{1-x}$R$_x$)$_3$Ti$_2$O$_7$ (a) $R$=Eu, $x=0.05$, $\kappa_{\text{total}}$ (b) $R$=Eu, $x=0.05$, $\kappa_{\text{total}}$ of the annealed sample, (c) $R$=Eu, $x=0.05$, $\kappa_{\text{ele}}$, (d) $R$=Eu, $x=0.05$, $\kappa_{\text{ele}}$ of the annealed sample, (f) $R$=Nd, $x=0.05$. The total thermal conductivity $\kappa_{\text{total}}$ for 5% Nd-doped were taken from ref. [12].
Fig. 6. The temperature dependence of power factor for (Sr$_{1-x}$R$_x$)$_3$Ti$_2$O$_7$ (a)R=Eu, x=0.05, (b)R=Eu, x=0.05, annealed, (c) R=Nd, x=0.05

Fig. 7. The temperature dependence of power factor for (Sr$_{1-x}$R$_x$)$_3$Ti$_2$O$_7$ (a)R=Eu, x=0.05, (b)R=Eu, x=0.05, annealed, (c) R=Nd, x=0.05.

Fig. 5 shows the temperature dependence of thermal conductivity $\kappa$ for (Sr$_{1-x}$R$_x$)$_3$Ti$_2$O$_7$ (R=Eu, Nd, x=0.05). The total thermal conductivity $\kappa_{total}$ can be expressed by the sum of the carriers contribution in $\kappa$ ($\kappa_{ele}$) and the lattice component($\kappa_L$), where the $\kappa_{ele}$ can be estimated according to the Wiedemann-Franz' law[11]. We can see that the contribution of $\kappa_{ele}$ to $\kappa_{total}$ is very small, indicating that the phonon contribution to $\kappa_{total}$ is predominant, and annealing treatment have little effect on the total thermal conductivity of (Sr$_{1-x}$R$_x$)$_3$Ti$_2$O$_7$ (R=Eu, x=0.05) oxide. Therefore, the reduction in the thermal conductivity can be attributed to the enhanced phonon scattering at the internal interfaces of SrO/(SrTiO$_3$)$_n$.

Fig. 6 and Fig. 7 show the temperature dependence of power factor (PF) and dimensionless figure of merit (ZT) for (Sr$_{1-x}$R$_x$)$_3$Ti$_2$O$_7$ (R=Eu, Nd, x=0.05) respectively. The PF can be calculated by the electrical resistivity $\rho$ and Seebeck coefficient $S$ with the formula $PF=S^2/\rho$. The PF of (Sr$_{0.95}$Eu$_{0.05}$)$_3$Ti$_2$O$_7$ basically decrease with temperature, while the PF of (Sr$_{0.95}$Nd$_{0.05}$)$_3$Ti$_2$O$_7$ increase. The decrease of PF with temperature for (Sr$_{0.95}$Eu$_{0.05}$)$_3$Ti$_2$O$_7$ might result from the rapid increase in $\rho$ accompanying a slow increase in $|S|$. Below 700K, the annealed sample have higher PF. However, when the temperature is higher than 700K, both the annealed sample and the unannealed sample basically have the same value of PF. The maximum PF is 384$\mu$Wm$^{-1}$K$^{-2}$ at 301.78K obtained in the annealed sample of (Sr$_{0.95}$Eu$_{0.05}$)$_3$Ti$_2$O$_7$. For all the samples in the investigated temperature range, the ZT increase with temperature. The largest ZT at room temperature is 0.024 achieved in the annealed sample of (Sr$_{0.95}$Eu$_{0.05}$)$_3$Ti$_2$O$_7$, while the maximum ZT is 0.087 obtained in (Sr$_{0.95}$Nd$_{0.05}$)$_3$Ti$_2$O$_7$ at 919K.
4. Summary

The (Sr_{1-x}R_x)_{3}Ti_2O_{7} (R=Eu, Nd; x=0.05) oxide were successfully prepared. The pure R-P phases powders were obtained at $T_{cal}=1500 \, ^\circ C$ with the volume ratio of H$_2$ and Ar about 5:95. Thermoelectric properties of the bulk samples were measured in the temperature range of 300K-1000K. All the samples exhibited electrical resistivity $\rho$ and the seebeck coefficient $S$, and both $\rho$ and $|S|$ with a negative value increase with temperature indicating a typical n-type degenerate semiconducting behavior. The total thermal conductivity $\kappa_{total}$ for all samples decrease with elevating temperature and the decrease in $\kappa_{total}$ might be ascribed to the enhanced phonon at the internal interfaces of SrO/SrTiO$_3$. The maximum ZT value reaches 0.087 at 919K for (Sr$_{0.95}$Nd$_{0.05}$)$_3$Ti$_7$.

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References


