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Microstructure characterization and thermoelectric properties of $Sr_{0.9}La_{0.1}TiO_3$ ceramics with nano-sized Ag as additive

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ABSTRACT

$Sr_{0.9}La_{0.1}TiO_3$ thermoelectric ceramics with different contents of nano-sized Ag metal particles as additive were prepared by conventional solid state reaction method, and the influences of Ag adding content on the microstructure and thermoelectric properties were investigated. XRD characterization confirmed that the main phase was perovskite $Sr_{0.9}La_{0.1}TiO_3$, along with a small amount of metal Ag phase. SEM images showed that all of the samples were dense, and the results of TEM indicated that the Ag particles accumulated at the grain boundaries to form a percolating network, contributing to increasing the electrical conductivity. Raman spectra of $Sr_{0.9}La_{0.1}TiO_3/x$Ag samples before and after annealing in Ar+C atmosphere showed a great difference, resulting from the creation of oxygen vacancies and changes in the Ti–O bond vibration and rotation mode. With increasing Ag adding content, the absolute value of Seebeck coefficient increased. Ag addition caused an increase in carrier concentration and acted as electrical connections between the grains, which improved the electrical conductivity and reduced the thermal conductivity to 1.4–3.4 W/m/K. Finally, the maximum ZT value of $ZT_{883K} = 0.30$ was obtained for $x = 20$ *wt*% samples.

1. Introduction

Dramatic progress has been made in recent years in the development of renewable energy technology that can reduce greenhouse gas emissions, fossil fuel usage, and environmental contamination. Direct conversion between thermal and electrical energy using thermoelectric (TE) materials may revolutionize energy efficiency throughout modern society [1,2]. As with many technologies, the TE materials themselves limit the overall performance. Enhancement of thermoelectric properties can be achieved by lowering the thermal conductivity (κ) while avoiding a significant deterioration of the Seebeck coefficient (S) and the electrical conductivity (σ) [3,4].

Oxide thermoelectric materials have relatively low carrier mobility and were generally not recognized as good thermoelectric materials [5]. However, oxides do have many potential advantages as thermoelectric materials, such as non-toxic, low-cost, and good chemical and thermal robustness, etc., and have attracted great interest all over the world [6].

In particular, carrier-doped $SrTiO_3$ with a cubic perovskite structure is a promising candidate n-type oxide due to its high figure-of-merit ZT at high temperatures. Based on the $SrTiO_3$ system, $Sr_{0.9}La_{0.1}TiO_3$ has been shown to have good thermoelectric properties [7–12]. Lanthanum doped $SrTiO_3$ single crystal exhibits a high power factor at room temperature, 28–36 μW/(K^2cm), which is comparable to that of Bi-Te and Zn-Sb alloys [13,14]. However, the obtained results are still insufficient for the practical application of thermoelectric power generation. The drawbacks are their low electrical conductivity, which consequently needs to be improved [15,16]. It is known that an effective way to enhance thermoelectric properties is to introduce a small amount of dopants [17–20]. But most of them are doped in the form of oxides, and there are no studies on the influencing mechanism.

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Considering the high electrical conductivity of metallic materials, it is reasonable to improve the electrical properties of $Sr_{0.9}La_{0.1}TiO_3$ with the introduction of a small amount of metallic powders [21]. And strontium (Sr), lanthanum (La) and titanium (Ti) are candidate metal dopants.

However, metal Sr and La are a kind of chemically active metal. At room temperature, Sr can react with water to generate strontium hydroxide and hydrogen, so it should be stored in kerosene. Metal La can be easily oxidized and is vulnerable to the erosion by inorganic acids in the air. It is usually stored in solid paraffin or immersed in kerosene. Thus metal Sr and La cannot be doped in the form of powders. Ti is a chemically stable transition metal. It can be doped in the form of powders. In our previously work [22], metal Ti powders were used as raw materials to dope into $Sr_{09}La_{01}TiO_3$ ceramics. Unfortunately, it was oxidized to form TiO_2 in the calcination stage, difficult to be preserved in the form of metal after sintering.

Besides Sr, La and Ti metal powders, some other metal materials having high electrical conductivity can be used to improve electrical conductivity, such as gold (Au), palladium (Pa), platinum (Pt), silver (Ag), copper (Cu), nickel (Ni), etc. Among them, silver (Ag) is also a chemically stable transition metal, and has good electrical conductivity ($\rho = 1.58 \times 10^{-8}\,\Omega\,m$). It can be doped in the form of metal powders [23]. A proper amount of Ag added in $Ca_3Co_4O_{9+\delta}$ ceramics resulted in an increase of the power factor, since Ag could improve electrical connections between cobaltite grains, resulting in a significant increase in σ without largely increasing κ [24]. G.H. Zheng et al. [25] prepared $Sr_{0.9}La_{0.1}TiO_3/x$Ag compounds via hydrothermal method and sintered, and use high purity strontium, lanthanum and silver nitrate as raw materials. It revealed that the addition of Ag increased the electrical conductivity to 200–1000 S/cm for $Sr_{0.9}La_{0.1}TiO_3$ compounds. But a tedious chemical reaction was used to provide Ag materials and they did not show the influencing mechanism.

In this paper, ceramic samples of $Sr_{0.9}La_{0.1}TiO_3/x$Ag with $0.05 \le x \le 0.20$ have been prepared by the conventional solid-state reaction method, which is practical to produce in bulk. X-ray photoelectron spectroscopy (XPS) was used to study the valence of each element, and Raman spectroscopy was used to study the bonding relationships among the elements. The effects of Ag adding content on the microstructure and thermoelectric properties of $Sr_{0.9}La_{0.1}TiO_3$ ceramics were investigated, and the mechanisms were discussed.

2. Experimental procedure

$Sr_{0.9}La_{0.1}TiO_3/x$Ag compounds ($x = 5$ *wt%*, 10 *wt%*, 15 *wt%*, 20 *wt%*, numbered as SLA1#, SLA2#, SLA3#, SLA4#, respectively) were prepared by using the conventional solid state reaction method. Reagent-grade strontium carbonate ($SrCO_3$), titanium oxide (TiO_2), lanthanum oxide (La_2O_3), bismuth oxide (Bi_2O_3) and nano-sized silver (Ag) powders (the average particle size is 30–40 nm) were used as raw materials. Bi_2O_3 (10 *wt%*) was added to form a liquid phase to decrease the sintering temperature. Firstly, the mixtures of $SrCO_3$, TiO_2, La_2O_3 and Bi_2O_3 were weighed in stoichiometric proportions, and ball milled in ethanol with zirconia balls as the grinding media for 12 h. After drying, the mixtures were calcined at 1200 °C for 4 h in air. Then nano-sized Ag powders were added to the calcined powders in stoichiometric proportions and ball milled again in ethanol for 12 h. After the wet mixtures dried, the powders were granulated with PVA as a binder and then pressed into pellets (Φ30 mm × 4 mm and Φ12 mm × 3 mm). The compacts were heated to 500 °C for 2 h to burn out the binder and then sintered at 1450 °C for 2 h in argon (Ar) atmosphere. In order to further reduce electrical resistivity, an annealing process was performed at 1350 °C for 8 h in argon+graphite (Ar+C) atmosphere. The annealed samples were cut into rectangular columns with dimensions of 15 × 4 × 3 mm^3 to measure the thermoelectric properties.

The phase structure of as-prepared ceramics was characterized using an X'Pert PRO X-ray diffraction (XRD, Dutch Panalytical Company) over the 2θ range of 20–80°. The microstructure was examined using a Quanta 600 FEG Scanning Electron Microscopy (SEM). The lattice dynamics of $Sr_{0.9}La_{0.1}TiO_3/x$Ag samples were investigated by means of Raman scattering using a micro-Raman spectrometer (Renishaw plc InVia plus, 514.5 nm). The surface chemistry of the $Sr_{0.9}La_{0.1}TiO_3/x$Ag samples was characterized by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD) using Al Ka emission. The binding energies and oxidation states were obtained from high-resolution scans. The energy scale was calibrated by assigning 284.6- eV to the C 1 s peak.

The electrical resistivity and the Seebeck coefficient were measured simultaneously in the temperature range between 343 K and 1073 K using LINSEIS LSR-3/1100 equipment in Helium (He) atmosphere. The thermal diffusivity (λ) and specific capacity (C_p) were measured with a laser flash apparatus (Netzsch LFA427, Netzsch, Selb, Germany). Then the thermal conductivity (κ) was calculated from the thermal diffusivity, the specific heat capacity, and the density (ρ) by applying the following equation:

$$k = \lambda \rho C_p \tag{1}$$

The thermoelectric figure of merit ZT was calculated using the following equation:

$$ZT = S^2 \sigma T / k \tag{2}$$

Where S, T, σ, and κ represent the Seebeck coefficient, absolute temperature, electrical conductivity and thermal conductivity, respectively.

3. Results and discussion

3.1. The microstructure of $Sr_{0.9}La_{0.1}TiO_3/x$Ag ceramics

The results of XRD for calcined powders show that the reaction of $SrCO_3$, TiO_2 and La_2O_3 generated $Sr_{0.9}La_{0.1}TiO_3$. The equation is shown as follows:

$$0.9SrCO_3 + 0.05La_2O_3 + TiO_2 \rightarrow Sr_{0.9}La_{0.1}TiO_3 + 0.9CO_2\uparrow \tag{3}$$

After sintering, the X-ray diffraction patterns of $Sr_{0.9}La_{0.1}TiO_3/x$Ag ceramics are shown in Fig. 1. The major diffraction peaks can be indexed as $Sr_{0.9}La_{0.1}TiO_3$ with the cubic perovskite structure belonging to the $Pm3\,m$ space group. A second phase, metal Ag, can be easily identified according to the PDF card No. 65–2871. The diffraction intensity of the Ag phase increases with increasing Ag -adding content. The lattice parameters (a) and cell volumes (V) are calculated from these XRD data using the Unit Cell software (Table 1), and the lattice constants are almost same within the error bar.

Scanning electronic microscopy (SEM) images of the cross section microstructures for $Sr_{0.9}La_{0.1}TiO_3/x$Ag ceramics are shown in Fig. 2. The results show that the grain size of samples with different Ag content is similar, and that the grains are mostly equiaxed, which means that Ag particles have few influence on the grain growth of the matrix materials. Besides, there are some spheroidal particles in each sample, whose size is smaller than 1 μm (Point 1–4).