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Characterization and electrical properties of sol-gel synthesized (Sr, Pb)TiO_3 powders

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Y-doped (Sr, Pb)TiO_3 powders were prepared by a sol-gel route as well as the calcination of gel precursors. The results of DTA/TG showed that the thermal decomposition of dry precursors mainly occurred below 600°C. Meanwhile, infrared ray (IR) spectrum meter, X-ray diffraction (XRD) meter and transmission electron microscope (TEM) were used to characterize the synthesized powders, respectively. Using the synthesized powders as starting materials, $Sr_{0.5}Pb_{0.5}TiO_3$ semiconducting ceramics were fabricated at 1050°C. Sample's room temperature resistivity is $1.51 \times 10^2\ \Omega \cdot cm$, its resistivity jumps more than 5 orders of magnitude above the Curie temperature (T_c). With increasing the soaking time, the room temperature resistivity and the negative temperature coefficient of resistance (NTCR) effect below T_c increased, showing the electrical properties of (Sr, Pb)TiO_3 thermistors are obviously affected by PbO loss.

1. Introduction

Positive temperature coefficient of resistance (PTCR) effect in Barium titanate semiconducting ceramics was first found in 1955 [1]. The ceramic resistance abruptly jumped at the phase transformation from tetragonal to cubic. Thereafter, the studies have been actively carried out for improving above peculiar electrical properties and developing practical applications, such as heaters, switching elements, sensors, and automatic demagnetizer of color TV [2–4].

In decade, (Sr, Pb)TiO_3 composite system has also been paid attention since the V-shaped PTCR effect was first observed in 1988 [5]. The ceramics exhibited negative temperature coefficient of resistance (NTCR) effect below the Curie temperature (T_c) and PTCR effect above T_c. The research for lowering the resistivity, improving the thermal sensitivity and revealing the conduction mechanism are still intriguing [6–9]. Wang *et al.* [10] synthesized (Sr, Pb)TiO_3 powders by using oxalate co-precipitation and employed the synthesized powders to successfully fabricate (Sr, Pb)TiO_3 ceramics of low room temperature (RT) resistivity and strong PTCR effect. However the co-precipitation needs many complicate processes, such as repetitious filtration and washing, and the soluble dopant ions was easy to be lost during washing, which caused low reliability and repeatability. Furthermore, it was found in our previous study that suppressing Pb volatilization is important to lower the resistivity of (Sr, Pb)TiO_3 ceramics and their electrical properties are evidently affected by the distribution of Pb^{2+} elements [11]. Therefore it is still interesting to synthesize ultrafine (Sr, Pb)TiO_3 powders and use them to fabricate high-performance thermistors at a relatively low sintering temperature.

At present, sol-gel technique has been widely employed to synthesize inorganic materials [12–15]. Many ultrafine titanate powders could be obtained from a simple chemical reaction as well as the calcination of dry gels [16–18]. The aim of this paper is to prepare strontium-lead titanate powders by a sol-gel process and use the synthesized powders to fabricate thermistors.

2. Experimental

2.1. Preparation of (Sr, Pb)TiO_3 powders

Analytical grade $Sr(CH_3COO)_2$, $Pb(CH_3COO)_2$, $Y(NO_3)_3$ and $Ti(OC_4H_9)_4$ were used as the starting materials to synthesize the precursors of Y-doped (Sr, Pb)TiO_3 powders. The weighted $Sr(CH_3COO)_2$, $Pb(CH_3COO)_2$ and $Y(NO_3)_3$ were dissolved into deionize water to form a clear acetate solution, the ratio of Pb/Sr was 1:0, 4:1, 3:2, 1:1 and 2:3, respectively. The content of Y^{3+} is 0.5 mol%, corresponding to the content of $Ti(OC_4H_9)_4$. Amount of acetic acid was added to adjust the acidity of solution in order to form the gels slowly. At the same time, stoichiometric $Ti(OC_4H_9)_4$ liquids were dissolved into CH_3CH_2OH

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to form 0.5 M solution. Under stirring, both above solutions were mixed slowly at room temperature and the white gels were gradually formed. Subsequently, the gels were heated for 4 h at 60°C in a water bath and then dried at 100°C for 24 h to obtain the dry precursors. Finally, the precursors were calcined at 700°C for 2 h in air to obtain the Y-doped (Sr, Pb)TiO_3 powders.

2.2. Characterization

Thermal decomposition of the Y-doped $Sr_{0.5}Pb_{0.5}TiO_3$ dry precursors was investigated by thermogravimetric and differential thermal analyses from room temperature to 1100°C at a heating rate of 10°C/min by using SETARAM92 TG/DTA apparatus (ref. Al_2O_3). Infrared ray absorption of the dry precursors and 700°C-2 h calcined powders were measured from 400 cm^{-1} to 4000 cm^{-1} by PE883 spectrophotometer, respectively. The crystalline structures of obtained powders with different Pb/Sr ratios were examined by using Regaku D/max IIIB X-ray diffraction meter (Cu $K_{\alpha 1}$). The morphology of Y-doped $Sr_{0.5}Pb_{0.5}TiO_3$ powders was observed by a Hitachi-800 transmission electron microscope (TEM).

2.3. Preparation and electrical properties of thermistors

Small amount of Li^+(0.1 mol/L LiOH water solution) was added into calcined Y-doped $Sr_{0.5}Pb_{0.5}TiO_3$ powders. Then the mixtures were well mixed and pressed into 10 mm diameter discs with about 1 mm thickness. Finally, the green pellets were sintered in air at 1050°C for 1–2 h to obtain Y-doped $Sr_{0.5}Pb_{0.5}TiO_3$ semiconducting ceramics. The sample's microstructure was observed by JSM-6301F scanning electron microscope (SEM), and its resistance-temperature characteristic was measured from room temperature up to 400°C by a dc resistance-temperature measuring meter.

3. Results and discussion

Infrared spectrum is a powerful tool to identify the compound through measuring the characteristic absorption of infrared ray, especially to study the functional groups of organic compounds. Fig. 1 gives the IR spectra of the Y-doped $Sr_{0.5}Pb_{0.5}TiO_3$ dry precursors and 700°C-2 h calcined powders, respectively. It can be seen that the powders only have three simple absorption peaks at wave number 1466, 858 and 611 cm^{-1}, which are originated from the vibrations of $Sr_{0.5}Pb_{0.5}TiO_3$ molecule [17]. However the IR spectrum of dry precursors in Fig. 1 is more complicated. A strong absorption peak appears at wave number 3374 cm^{-1}, corresponding to the O–H vibration of residual acetic acid in the precursors. The characteristic absorption peaks of acetate appear at the wave number 1563, 1427 and 1346 cm^{-1}, which are originated from the asymmetrical stretching vibration and the symmetrical stretching vibration of $-COO^-$.

Thermal decomposition of Y-doped $Sr_{0.5}Pb_{0.5}TiO_3$ dry precursor was investigated by TG/DTA apparatus. Fig. 2 gives the variances of the heat flow and the specimen's gravity from room temperature to 1100°C. Below 280°C, DTA curve appears two endothermatic peaks at 165°C, 218°C, accompanying about 5.6% weight loss in TG curve, which perhaps resulted from the decomposition of acetate to form oxycarbonates. The main decomposition to synthesize (Sr, Pb)TiO_3 occurs in the temperature range of 280–500°C, accompanying a strong exothermic peak at 371°C in DTA curve and about 18% weight loss in TG curve. A small exothermic peak is also observed at 533°C in DTA curve, which corresponds to the crystallization of (Sr, Pb)TiO_3. Furthermore, a weak endothermic peak in DTA curve and more than 1% of weight loss in the TG curve are found around 900°C, which perhaps resulted from the densification of (Sr, Pb)TiO_3 powders and a small amount of PbO loss.

The XRD patterns of prepared Y-doped (Sr, Pb)TiO_3 powders with different Pb/Sr ratio are shown in Fig. 3.

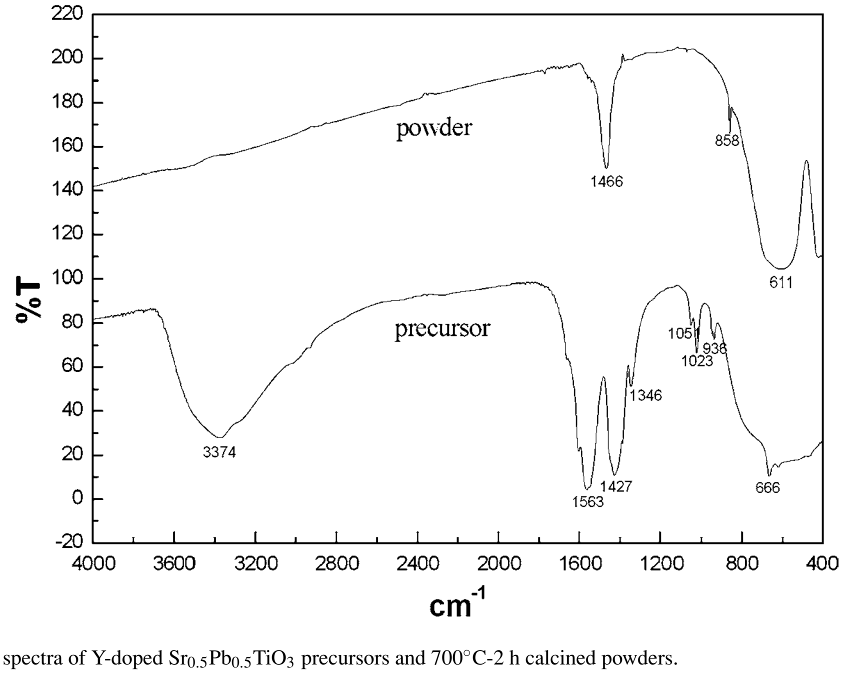

Figure 1 IR absorption spectra of Y-doped $Sr_{0.5}Pb_{0.5}TiO_3$ precursors and 700°C-2 h calcined powders.

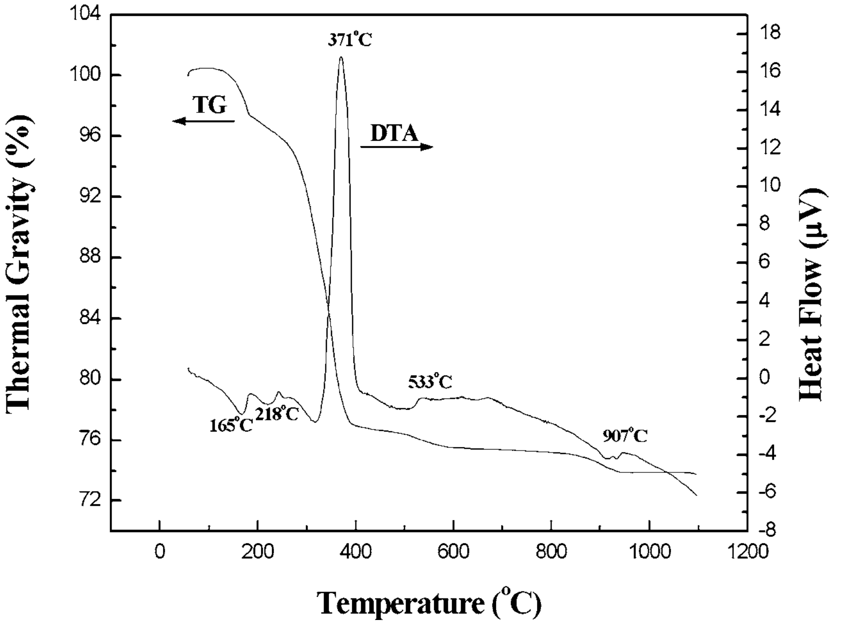

Figure 2 DTA/TG curves of Y-doped $Sr_{0.5}Pb_{0.5}TiO_3$ precursors.

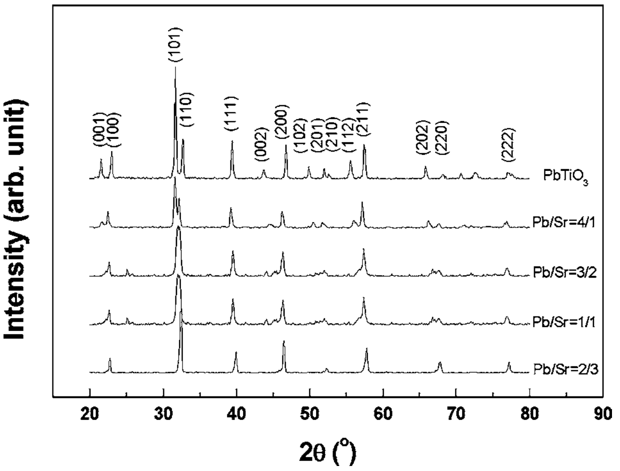

Figure 3 XRD patterns of sol-gel synthesized Y-doped (Sr, Pb)TiO_3 powders calcined at 700°C for 2 h.

It can be seen that the powders have typical ABO_3-type structures with tetragonality at room temperature [10]. With increasing Pb/Sr ratio, the diffraction peak (002) moves to the lower angle, showing that the unit cell of (Sr, Pb)TiO_3 polycrystalline elongates along *c* axis with increasing Pb/Sr ratio.

The morphology of 700°C-2 h calcined Y-doped $Sr_{0.5}Pb_{0.5}TiO_3$ powder is shown in Fig. 4. It can be seen that the most particles are round and their average sizes are less than 100 nm.

Using above synthesized powders as starting materials, Y-doped $Sr_{0.5}Pb_{0.5}TiO_3$ semiconducting ceramics were obtained by sintering at 1050°C for 1–2 h. According to results of XRD, 700°C-2 h calcined (Sr, Pb)TiO_3 powders have ABO_3-type structure with tetrogonality in our experiments. Therefore, Fig. 5 shows that the grains are in shape of rectangle with sizes of 1–3 μm.

The resistivity-temperature characteristics of 1050°C-sintered samples are shown in Fig. 6. The resistivity of sample 1 is 1.51×10^2 $\Omega \cdot$cm at room temperature, which jumps 5.16 orders of magnitude

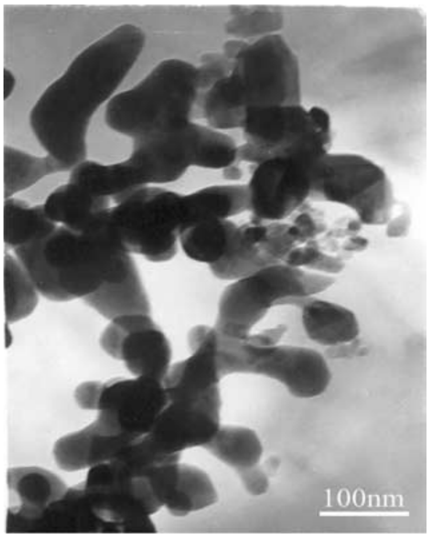

Figure 4 TEM micrography of sol-gel synthesized Y-doped $Sr_{0.5}Pb_{0.5}TiO_3$ powders calcined at 700°C for 2 h.

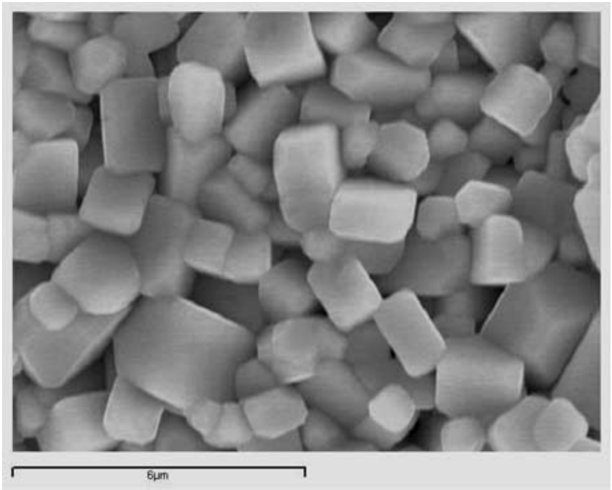

Figure 5 SEM micrography of 1050°C-1 h sintered Y-doped $Sr_{0.5}Pb_{0.5}TiO_3$ ceramic.

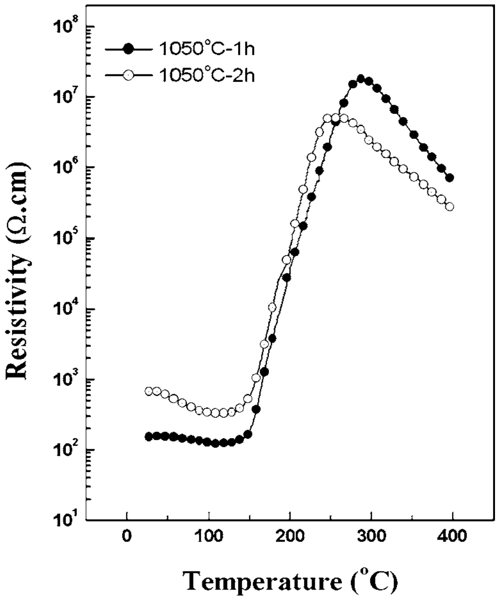

Figure 6 Resistivity-temperature curves of Y-doped $Sr_{0.5}Pb_{0.5}TiO_3$ ceramics.

in the PTCR effect region. The positive temperature coefficient α_{+30} is 14.0%/°C, where α_{+30} is the resistivity differential variability at the temperature 30°C higher than the switching temperature in the PTCR effect region. With increasing the soaking time, the RT resistivity of sample 2 increases to 6.7×10^2 $\Omega \cdot \mathrm{cm}$, its resistivity jumps 4.19 orders of magnitude in the PTCR effect region and the α_{+30} is 14.1%/°C. Meanwhile sample 2 exhibits an obvious drop of resistivity (NTCR effect) below the Curie point.

In our previous study [11], we found that the suppression of Pb volatilization was significant for decreasing the RT resistivity of (Sr, Pb)TiO_3 semiconducting ceramics. It was assumed that much PbO loss produced a large of Pb^{2+} vacancies, which would degrade the electrical conduction of (Sr, Pb)TiO_3 ceramics by forming complex defect $(V''_{\mathrm{Pb}} \cdot 2Y^{\bullet}_{\mathrm{Pb}})$, and the NTCR effect of (Sr, Pb)TiO_3 ceramics should be closely related to the Pb^{2+} vacancies in the grain boundary layers. The excess PbO addition or sintering at lower temperature are effective methods to control PbO loss and keep stable Pb/Ti ratio in (Sr, Pb)TiO_3 lattices. In this paper, using sol-gel synthesized powders as starting materials, (Sr, Pb)TiO_3 semiconducting ceramics with strong PTCR effect were obtained at a relatively low sintering temperature [6, 8]. It will be easy to control the electrical properties of (Sr, Pb)TiO_3 thermistors at a lower sintering temperature because Pb volatilization is relatively slow.

4. Conclusions

Y-doped (Sr, Pb)TiO_3 powders were synthesized by sol-gel process as well as calcinations at 700°C. DTA/TG, IR spectra, XRD and TEM were employed to characterize the prepared powders. The investigation of DTA/TG showed that the dry acetate gels decomposed to form oxygencarbonate blow 280°C and the synthesis of polycrystalline (Sr, Pb)TiO_3, accompanying exothermic reaction and large weight loss, mainly occurred between 280–600°C.

Using synthesized powders as starting materials, Y-doped $Sr_{0.5}Pb_{0.5}TiO_3$ semiconducting ceramics with low room temperature resistivity and strong PTCR effects were fabricated at 1050°C. The changes of sample's room temperature resistivity and its NTCR effect ($T < T_c$) with the soaking time showed that the thermal sensitivity of (Sr, Pb)TiO_3 semiconducting ceramics is obviously affected by PbO loss.

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