Raman scattering studies on PZT thin films for trigonal–tetragonal phase transition*

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Abstract: PZT thin films were successfully prepared through sol–gel. The annealing temperature was confirmed through DTA analyzing. The trigonal and tetragonal phase transition was analyzed through Raman scattering. The intensity of the $A_1(2TO)$ mode and the $A_1(3TO)_T$ mode were enhanced with the increase of the annealing temperature. So, the conclusions were obtained that the trigonal phase turned into a tetragonal phase as temperature increased.

Key words: PZT; Raman scattering; phase transition
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1. Introduction

Lead zirconate titanate (PZT) thin films have attracted much attention because of their excellent properties such as piezoelectric, ferroelectric, optical and pyroelectric. In recent years, many institutions have been committed to the research of PZT thin film materials which could be used in sensitive units on infrared detectors. The properties of PZT thin films depend on the changes of the microstructure. So it is essential to study the relationship between the film properties and the microstructure.

There are many ways to prepare PZT thin films. The sol–gel method is widely used because of its uniformity, simplicity in fabrication processes and low cost characteristics[1]. To correlate the structure–property relationship in PZT pyroelectric materials, the Raman scattering technique has been widely used to study the lattice modes and phase transition[2]. Frantti and Lantto studied the structure features of PZT material near the MPB (morphotropic phase boundary) between 11 and 680 K through Raman spectroscopy[3]. Fihlo and others have studied the temperature phase transition of PZT which have the composition of MPB through the Raman scattering spectrum, and identified the phase boundary of rhombohedral-monoclinic-tetragonal[4]. But Raman scattering has been rarely used to study the rhombohedral–tetragonal phase transition. This paper uses the sol–gel method to prepare PZT (48/52) pyroelectric thin films, and confirms the range of annealing temperature through DTA (different thermal analysis). Furthermore, the micro-theory of rhombohedral–tetragonal phase transition in the vicinity of morphotropic phase boundary was studied through Raman scattering.

2. Experiment

The substrates used in this experiment are $Pt/Ti/Si_3N_4/SiO_2/Si$. The Si_3N_4 layer will keep better thermal insulation performance[5]. The fabrication processes of PZT films are shown in Fig. 1. $P_{1.1}Z_{0.48}T_{0.52}$ is studied in this work. The ratio of Zr/Ti is standard ratio in the vicinity of the MPB. Under the Curie temperature, this Zr/Ti ratio is propitious to form the perovskite phase, in which the rhombohedral and tetragonal could co-exist. Lead acetate trihydrate $Pb(CH_3COO)_2{\cdot}3H_2O$, tetrabulyl tittanate $Ti(OC_4H_9)_4$, and zirconium n-butoxide $Zr(OC_4H_9)_4$ are selected for raw materials, and acetylacetone is the chelating agent; glycol methyl ether is the solvent. The concentration of PZT dissolved in glycol methyl is 20%; this is conducive for the prepared thin films. The sol was symmetrically spread on the substrate by the spin on method with a speed of 4500 r/m for 30 s, and then sintered at 420 °C. According to the DTA results, the annealing temperatures are 600, 650 and 700 °C. Finally, thin films of

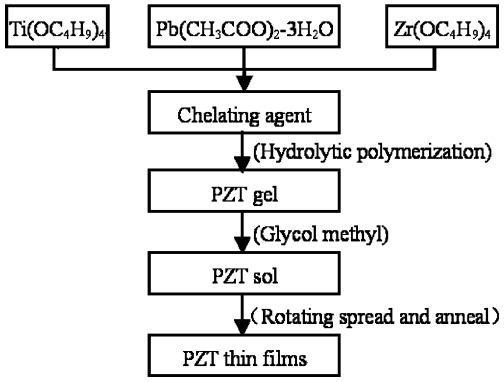

Fig. 1. Processes of preparing PZT thin films by sol–gel.

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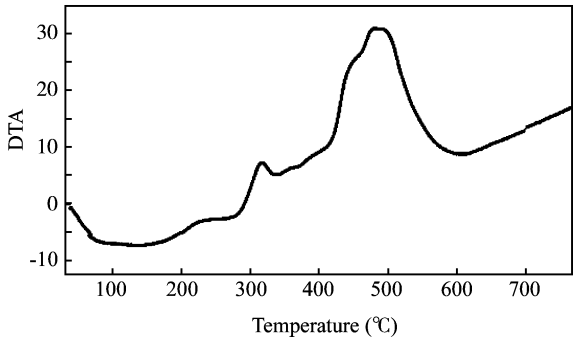

Fig. 2. DTA curve of PZT.

about 200 nm were obtained.

3. Results and discussion

3.1. DTA

Figure 2 is the DTA curve of PZT gel. There is a large temperature range and moderate endothermic peak between 40 and 220 °C. The water evaporation in residual organic solvent is responsible for this phenomenon. The exothermic peak is obviously observed between 280 and 330 °C, which corresponds to the formation processes of –Ti–O–, –Pb–O–, –Zr–O– molecule bonds through hydrolytic polymerization, and the release processes of CO_2 and H_2O formed through organic matter burning. The formation reaction occurs when the temperature exceeds 420 °C. The transformation from the amorphous phase to the crystalline phase occurs in this temperature range. So the sintering temperature was ensured for 420 °C and the annealing temperatures are 600, 650 and 700 °C.

3.2. Raman scattering analysis

There are two constituents of the lattices at the MPB: the Ti and Zr crystal cell in which Ti or Zr locates at the center of the lattices respectively. At the Ti high-margin, Ti is the dominant status, and it forces the Zr cell to come into the tetragonal structure; and at Zr in high-margin, the Zr cell is in a dominant position which could force the Ti cell to come into the trigonal structure. So the rhombohedral and tetragonal could co-exist. This is the transition region, in which the distortion phenomenon of the ferroelectric lattice is mutation occurred[6]. So the ferroelectric structure is laxation. The spontaneous polarization and coercive field reached the best match. The prototype PZT represents 12 optical modes at the center of the Brillouin zone. These modes are simplified as $3T_{1u} + T_{2u}$ above the Curie temperature. T_{2u} mode is non-activity for Raman and IR, and is called the "silent mode". Under the Curie temperature, T_{2u} mode translates into B_1+E in the tetragonal system, and A_2+E in the trigonal system. They are non-activity for IR but activity for Raman. Three T_{1u} modes are activity for IR (infrared ray) but non-activity for Raman in cubic phase above Curie temperature. Under the Curie temperature they translate into A+E and are activity for both IR and Raman[7].

Figure 3 shows the Raman shifts of PZT films prepared

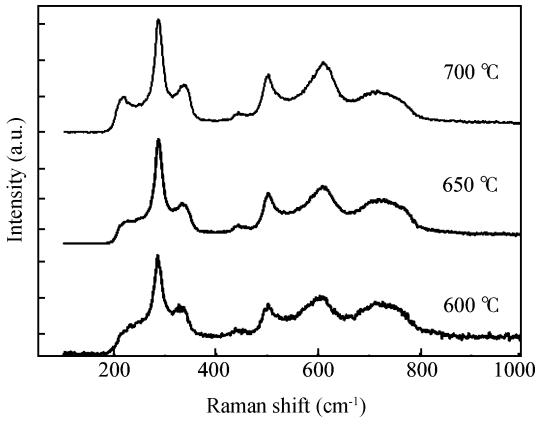

Fig. 3. Raman spectra of PZT at different annealing temperatures.

Table 1. Location of Raman modes in IF (cm^{-1}).

Temperature (°C)	E(2TO)	E+B_1(silent)	A_1(2TO)
600	232.757	285.601	327.137
650	223.095	286.361	334.634
700	218.835	288.260	336.132

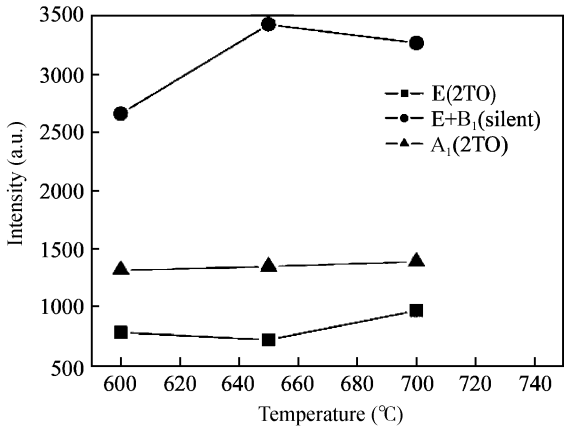

Fig. 4. Intensity of Raman modes in IF.

at different annealing temperatures. It can be seen that the E(1TO) mode at 87.5 cm^{-1} and the A_1(1TO) mode at 150 cm^{-1} do not appear. The reasons for this are due to the responsibility problem of Raman equipment in low-frequency region.

3.2.1. IF (intermediate-frequency) range (200–400 cm^{-1})

In the range of 200–400 cm^{-1}, Raman peaks at different annealing temperatures are fitted by Dat–Lab. The peaks are shown in Table 1.

The E(2TO) mode and A_1(2TO) mode are split from the T_{1u}. E(2TO) mode which moves to low-frequency when the annealing temperature is raised. The E+B_1(silent) mode represents the trigonal–tetragonal coexistence phase. When the temperature gradually increases, the E+B_1 mode moves to high-frequency. Fihlo and others pointed out that the A_1(2TO) mode can be used as a sign of the tetragonal phase[8]. In Fig. 4, as the annealing temperature increases, the intensity of A_1(2TO) mode increases gradually. This indicates that the trigonal phase is turning into the tetragonal phase.

Table 2. Location of Raman modes at high-frequency (cm^{-1}).

Temperature (°C)	E(2LO)	$E(3TO)_T$	$A_1(3TO)_T$	E(3LO)	R_h
600	437.469	502.472	608.704	712.018	752.551
650	442.907	501.405	606.986	709.695	764.635
700	443.269	501.050	609.048	706.372	768.868

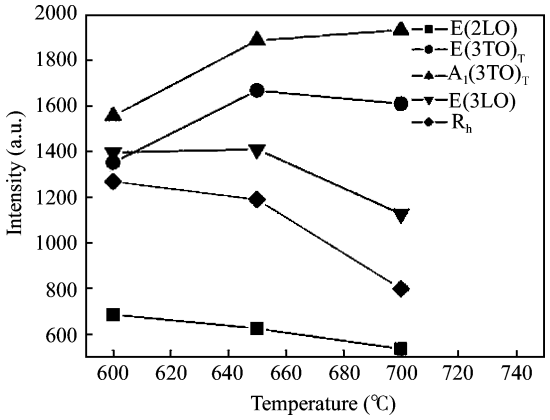

Fig. 5. Intensity of Raman vibration modes at high-frequency.

3.2.2. High-frequency range (400–900 cm^{-1})

Raman spectra at high-frequency are fitted, and the mode locations are shown in Table 2.

The E(2LO) and E (3LO) modes belong to the ferroelectric trigonal–tetragonal co-existence phase. The $E(3TO)_T$ and $A_1(3TO)_T$ modes belong to the ferroelectric tetragonal phase, and they are both corresponding to O–B–O bond bending vibration. The R_h belongs to the ferroelectric trigonal, and it corresponds to B–O bond stretching vibration. But the vibration mode of $A_1(3LO)$ is not observed at high-frequency. As can be seen from Table 2, when the annealing temperature increases, the E(2LO) and R_h modes move to high frequency, while the $E(3TO)_T$ and E(3LO) modes move to low frequency gradually. The changes of intensity of all vibration modes at high-frequency are given in Fig. 5.

It can be seen from Fig. 5, that the intensity of the $A_1(3TO)_T$ mode is gradually enhanced as the temperature is raised, but that of the E(2LO) and R_h modes falls. The $E(3TO)_T$ and E(3LO) modes are not changed disciplinary. The increase of the intensity of the $A_1(3TO)_T$ mode indicates that the amount of tetragonal cells increases with increasing annealing temperature. On the contrary, the amount of trigonal cells decreases as the R_h mode falls. So a conclusion can be drawn from this analysis that the trend of phase transition from trigonal to tetragonal is enhanced along with the annealing temperature. This is consistent with the result of IF analysis.

4. Conclusion

The Raman spectra of PZT films with the Zr/Ti ratio of 48/52 fabricated at different annealing temperatures are obtained. The location of vibration modes in IF and high-frequency are identified through Dat–Lab fitting. According to the Raman results at different annealing temperatures, the phase transition trends of PZT thin films are systematically analyzed. The conclusion is drawn from the analysis that the $P_{1.1}Z_{0.48}T_{0.52}$ thin films about 200 nm gradually turn from the trigonal phase into the tetragonal phase with increase of the annealing temperature.

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