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Dielectric and piezoelectric properties of lanthanum-modified $0.55Pb(Sc_{1/2}Ta_{1/2})O_3$–$0.45PbTiO_3$ ceramics

H. Liu [a,c,*], J.F. Wang [b], J.Y. Wang [a], H.D. Jiang [a], X.B. Hu [a], H.M. Dong [b]

[a] *State Key Laboratory of Crystal Materials, Shandong University, 250100, Jinan, Shandong, People's Republic of China*
[b] *Department of Physics, Shandong University, 250100, Jinan, Shandong, People's Republic of China*
[c] *Department of Inorganic Materials, Shandong Institute of Light Industry, 250100, Jinan, Shandong, People's Republic of China*

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Abstract

The effects of lanthanum addition and annealing (900°C, 8 h) on the Curie temperature, dielectric and piezoelectric properties of lanthanum-modified $Pb_{(1-x)}La_x(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$ ceramics (La-doped PSTT) ($x=0.005$, 0.01, 0.02, 0.03) were investigated. It was found that annealing and the addition of lanthanum can significantly modify all these properties. For the compositions where $x=0.005$ and $x=0.01$, many 'abnormal' phenomena, which are different from other compositions and other systems, were found. X-ray diffraction (XRD) and scanning electron microscope (SEM) study were performed to investigate the crystalline structure and the microstructure of PSTT ceramics. They revealed that the dielectric and piezoelectric properties of La-doped PSTT strongly depend on the amount and the location of La ions in the samples. A model describing the diffusion of La ions in PSTT during sintering and annealing is proposed. The model agreed well with the XRD analysis results, and explained the effect of La doping on the properties of PSTT.

Keywords: Dielectric properties; La-doping; $Pb(Sc,Ta)O_3$–$PbTiO_3$; Perovskites; Piezoelectric properties

1. Introduction

The solid solution $(1-x)[Pb(Sc_{1/2}Ta_{1/2})O_3]$–$xPbTiO_3$ (PSTT) has been widely investigated[1–7] because of its many unique characteristics. It was found that $0.55Pb(Sc_{1/2}Ta_{1/2})O_3$–$0.45PbTiO_3$ possesses excellent piezoelectric and pyroelectric properties. The effect of adding lanthanum, which can improve the properties of ferroelectric materials, has been studied in the $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$[9–11] and $PbZrO_3$–$PbTiO_3$ systems.[11] Recently, the effect of lanthanum addition on order-disorder transition in $Pb(Fe_{1/3}Nb_{2/3})O_3$ (PFN) and $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST) has been studied by Yoshihiro Fujii et al.[9] However, the lanthanum content in this system was very high (5 and 10 at.%). Until now, no study has been published on lanthanum addition to the $Pb(Sc_{1/2}Ta_{1/2})O_3$– $PbTiO_3$ system. This study investigates the dependence of dielectric and piezoelectric properties, phase constitution, and microstructure on the lanthanum content of La-modified $0.55Pb(Sc_{1/2}Ta_{1/2})$–$0.45PbTiO_3$ ceramics.

2. Experimental procedure

2.1. Sample preparation

Polycrystalline ceramic samples of $Pb_{(1-x)}La_x(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$, with different compositions (as shown in Table 1), were prepared by solid state reaction using appropriate amounts of reagent grade materials of PbO (99.99%), La_2O_3 (99.99%), Sc_2O_3 (99.27%), Ta_2O_5 (99.99%) and TiO_2 (>99.99%) (Shanghai Chemical Regent Company). The perovskite phase of La-doped PSTT was synthesized by columbite precursor method[13] in order to avoid the growth of undesirable cubic pyrochlore phase. The starting materials, Sc_2O_3 and Ta_2O_5, were batched and milled by planetary mill for 6 h (agate mill ball and polyvinyl fluoride pot, alcohol as the milling media). After drying, the mixture was calcined in an aluminum oxide crucible at 1400°C for 4 h. X-ray diffraction indicated that the phase of the batched

* Corresponding author.
E-mail address: hongliu@icm.sdu.edu.cn (H. Liu).

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Table 1
Dielectric and piezoelectric properties of $Pb_{(1-x)}La_x(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$ ceramics before and after annealing

$Pb_{(1-x)}La_x(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$		$x=0$	$x=0.005$	$x=0.01$	$x=0.02$	$x=0.03$
Piezoelectric strain coefficient d_{33} (pC/N)	Unannealed	278	380	400	350	160
	Annealed	350	460	471	533	370
Free permittivity $\varepsilon_{33Troom}/\varepsilon_0$	Unannealed	1580	2190	2490	2670	3070
	Annealed	1850	824	1700	2390	3230
Piezoelectric voltage coefficient g_{33} (mVm/N)	Unannealed	19.2	19.6	18.1	14.8	5.9
	Annealed	21.4	63.1	31.3	25.2	12.7
Curie temperature (measured) (°C)	Unannealed	211	222	207	170	143
	Annealed	225	240	218	188	160
Curie temperature (calculated) (°C)	Unannealed	209.5	224.0	207.8	173.5	147.0
	Annealed	227.1	240.3	217.0	190.7	160.4
Curie–Weiss constant C'	Unannealed	12 653 878	3 287 503	2 1123 38	5 614 114	14 554 729
	Annealed	5 950 604	6 467 350	7 044 556	5 125 413	74 319 481
Diffuseness exponent γ	Unannealed	1.78994	1.48792	1.50931	1.61891	1.79066
	Annealed	1.65317	1.79828	1.57570	1.61882	1.99072

materials was pure columbite ($ScTaO_4$). PbO, $ScTaO_4$, TiO_2 and La_2O_3 were combined according to the compositions in Table 1 and milled for 6 h using the method mentioned above. The mixture was pressed into pellets with 20 mm in diameter and calcined in an aluminum oxide crucible at 900°C for 1.5 h to synthesize the perovskite powder. An additional amount of 1 wt.% PbO was added to each composition to compensate for PbO loss during calcining and sintering. The perovskite powder was further milled for 4 h and then pressed into pellets with 12 mm in diameter and 1.2 mm in thickness by adding 2 wt.% polyvinyl alcohol (PVA) solution binder. The pellets were heated to 500°C for 60 min and to 800°C for 30 min to remove the binder.

Pellets of all compositions were buried in ZrO_2 fine powder, covered with an aluminum oxide crucible without any PbO atmosphere, and sintered at 1390–1420°C for 30 min During sintering, the samples were buried in fine ZrO_2 powder and sealed by covered aluminum oxide crucible. For each composition, a certain number of the sintered samples were annealed at 900°C for 8 h to investigate the effect of annealing on the properties of such compositions. Before and after sintering and annealing, each sample was weighted to measure the weight loss.

2.2. Measurements

The density of the samples was measured by Archimedes method. X-ray diffraction was carried out on a 12 kW (Cu K_α) using a Philips APD1700 to determine the crystalline structure for all the compositions before and after annealing. The theoretical density of the samples was calculated from the result of XRD. For carrying out the scanning electron microscope (SEM) study, before and after annealing, the fracture surface of sintered samples for all the compositions were polished and thermally etched at 1200°C for 20 min. Both surfaces of all the samples were polished and pasted with silver electrodes. Dielectric property measurements were carried out using a LF impedance analyzer (HP-4193A) at 10 kHz. For piezoelectric measurements, the samples were poled by applying a DC field of 3 kV/mm for 30 min in silicone oil at 150°C (the samples for which $x=0.03$ was polarized at 120°C, because of its lower Curie temperature, $T_c=143$°C). As soon as the polarization was performed, the piezoelectric coefficient, d_{33}, of polarized samples was measured by a quasi-static d_{33} meter (ZJ-2, Acoustic Institute, Chinese Academy of Science). The principle of quasi-measurement of d_{33} is referred to an American National Standard.[19] The corresponding piezoelectric voltage coefficient, g_{33}, was subsequently calculated by the relationship ($g_{33}=d_{33}/\varepsilon_{33}$, where ε_{33} is free permittivity).

3. Results and discussion

3.1. Dielectric properties

Figs. 1–5 show the temperature dependence of the dielectric constant and dielectric loss target for different La-doped $Pb_{(1-x)}La_x(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$ ceramics with $x=0$, 0.005, 0.01, 0.02 and 0.03 sintered at 1400°C for 30 min before and after annealing. From these figures, it can be seen that the dielectric peaks for all the compositions have different curve shapes before and after annealing. The compositions of undoped and highly doped ($x=0.02$ and $x=0.03$) PSTT have the typical character of relaxor-type ferroelectric materials, that is, the dielectric peaks become sharper and higher and the Curie temperature becomes higher after

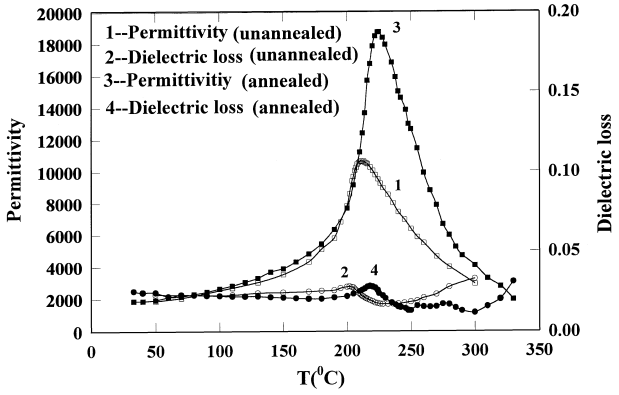

Fig. 1. Permittivity and dielectric loss vs. temperature for annealed and unannealed $Pb(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$ ceramics ($f=10$ KHz).

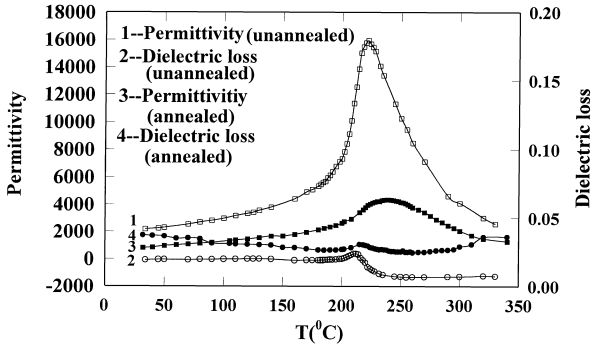

Fig. 2. Permittivity and dielectric loss vs. temperature for annealed and unannealed $Pb_{0.995}La_{0.005}(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$ ceramics ($f=10$ KHz).

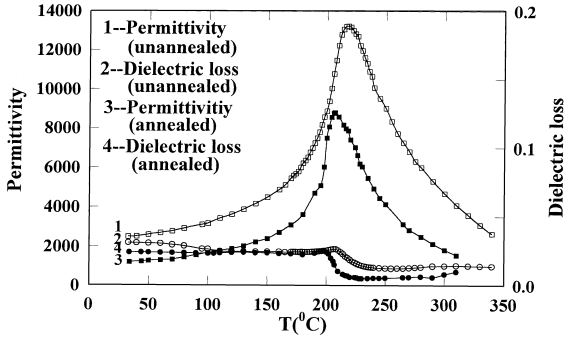

Fig. 3. Permittivity and dielectric loss vs. temperature for annealed and unannealed $Pb_{0.99}La_{0.01}(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$ ceramics ($f=10$ KHz).

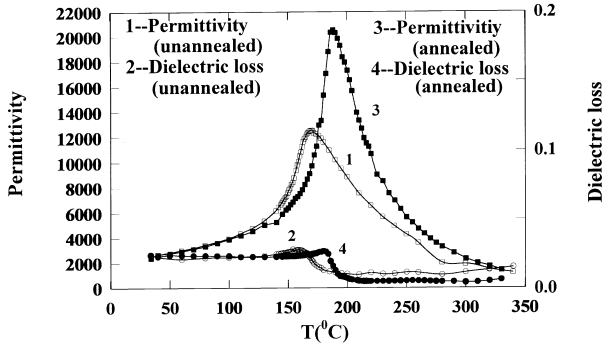

Fig. 4. Permittivity and dielectric loss vs. temperature for annealed and unannealed $Pb_{0.98}La_{0.02}(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$ ceramics ($f=10$ KHz).

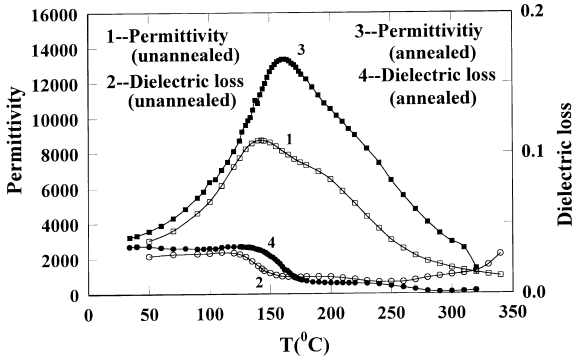

Fig. 5. Permittivity and dielectric loss vs. temperature for annealed and unannealed $Pb_{0.97}La_{0.03}(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$ ceramics ($f=10$ KHz).

annealing at 900°C for 4 h, as reported by Setter and Cross[3] and Zhili[4] in pure $Pb(Sc_{1/2}Ta_{1/2})O_3$ ceramics. Their result are attributed to such phenomena that a transition from disordered state to ordered state after annealing takes place. For the compositions where $x=0.005$ and 0.01, it has been found that the dielectric peaks for the annealed samples became lower and broader than the corresponding peaks for the unannealed ones. This phenomenon has never been reported in other papers and can not be explained by the transition of the order degree of lattice. From these figures, it can also be seen that the dielectric peak for as-sintered doped PSTT sample becomes lower and broader with increasing La-content. This phenomenon is consistent with the results of investigation of Yoshiro Fujii et al.[12] in La-doped $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST)ceramics. In their study, the dielectric peaks significantly broaden with increasing La-content (doped content was 5 and 10 at.%), and all the peaks for doped PSTs were broader and lower than those for undoped ones. Another interesting observation in this study was that the peaks for unannealed La-doped PSTTs were even sharper and higher than those for undoped PSTT for both lower doping compositions ($x=0.005$ and 0.01). Therefore, when the La-content is very small, La-doped PSTTs exhibit some novel properties unlike other doped ones and other doped systems,[9,10] which cannot be explained by the existing theories.

Yoshiro Fujii et al.[12] believed that the broadening of the dielectric constant peak of La-doped PST for differ-

ent La-contents occurs because La-ions only enter the lattice of the ordered domains rather than undergo the transition of order degree. Their group proved that La content only slightly changed the order parameter in this system, which could not affect the shape of dielectric peaks seriously. Fang et al.[11] obtain a similar result in La-doped $PbZrO_3$–$PbTiO_3$ (PZT). Their work agreed that non-homogeneity of chemical composition and imbalance of charges occurred between the ordered and disordered domains, because La-cations entered the lattice of the disordered domains and caused non-stoichiometry in such domains, therefore, the dielectric constant peak broadened for La-doped PST or PZT. In our study, the experimental results for the compositions where $x=0.02$ and 0.03 could be adequately explained by their theory; however, it was difficult to explain the phenomena found in the compositions where $x=0.005$ and 0.01. We can hypothesize a model in which La ions are concentrated in the grain boundaries primarily during the sintering process, and diffused to the ordered domains with the rising of temperature or during higher temperature annealing. If the La-content was much higher, the diffusion rate would be very high. Therefore, the La ions could enter the lattice of the ordered domains much faster, as Yoshiro Fujii et al.[12] explained, and the dielectric constant peaks of such compositions for as-sintered samples would be broader and lower than those of the undoped PSTT. After higher temperature annealing, the La-cations further diffused into the disordered domains, restoring the homogeneity of La constituent and the balance of charges between the ordered and disordered domains, which caused the peak to become sharper and higher. In addition, the dielectric constant peak was influenced by the percentage of perovskite in the samples as will be discussed below. If the La content was less than 0.01 at.% in La-doped PSTT, the diffusion rate of the La-ions would be very low. Therefore, most of La-ions were still in the grain boundaries during the sintering process, compared with undoped PSTT, the vaporization of PbO was much lower, and the pyrochlore phase grew much slowly. Without the effect of cubic pyrochlore, the dielectric peaks for such compositions were even higher and sharper than that of non-doped PSTT. This had been proved by the results of X-ray diffraction as will be shown below. After annealing for longer time, the La-ions diffused preferably to the lattice of ordered domains, the dielectric peak for such composition became broader and lower than that of unannealed one, since the non-homogeneity of La content and imbalance of charges occurred between the ordered and disordered domains.

The dependence of the Curie temperatures of $Pb_{(1-x)}La_x(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$ ceramics on La content for annealed and unannealed samples is shown in Fig. 6. It can be seen from the figure that the effect of La-doping is to shift the Curie temperature downward

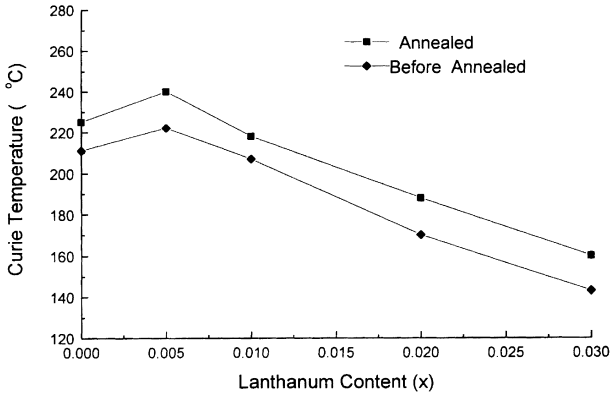

Fig. 6. Curie temperatures vs. lanthanum contents for annealed and unannealed $Pb_{(1-x)}La_x(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$ ceramics.

by about 26°C/at.%, similar to the result for the La-doped PMN-PT ceramics studied by Kim et al.[8] (in their study, La-doping shifted the Curie temperature downward by about 25°C/at.%). But for the composition where $x=0.005$, the Curie temperature changes in an abnormal way, that is, unlike other La-doped compositions, its Curie temperature (either before or after annealing) was even slightly higher than the undoped PSTT, as shown in Fig. 6. This peculiar behavior of the Curie temperature will be explained below by the results of X-ray diffraction. After annealing, the Curie temperatures for all the compositions were about 15°C higher than those of the unannealed samples. The shifting of the Curie temperatures after annealing at 900°C for 8 h was mainly caused by the improvement of order degree of ceramics.[14] In our study, we did not examine the order degree of the samples.

The Curie temperature, T_m, and Curie–Weiss constants, C', as well as the critical exponent, γ, was calculated by following formula suggested by Uchino and Nomura.[15]

$$1/\varepsilon - 1/\varepsilon_m = C'(T - T_m)^{\gamma}$$

Where, the notations ε_m and T_m refer to the maximum dielectric constant and the corresponding temperature (i.e. the averaged Curie temperature) of relaxor ferroelectrics, C' is Curie–Weiss constant of relaxor ferroelectrics, γ is critical exponent. The calculation was done by iterative computation and then fitted by method of minimum squares. The results of calculation are shown in Table 1. All the calculated Curie temperatures are closed to the measured values.

3.2. Piezoelectric properties

The piezoelectric properties of $Pb_{(1-x)}La_x(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$ ceramics are shown in Table 1. The piezoelectric properties vary significantly with increasing La content. In the investigation of La-modified

PMN–PT made by Tai-Bor Wu et al.,[9] the piezoelectric strain coefficient d_{33} increased constantly as the La content increased from 1 to 3 at.%. In our study, the dependence of d_{33} on La content for $Pb_{(1-x)}La_x(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$ ceramics is different from their work. The d_{33} values of those compositions with low La contents increase with the increasing the addition of La, reach a maximum, and then finally decrease. From Table 1, the d_{33} values increase significantly for all the compositions after annealing. The dependence of d_{33} on the La content for the annealed samples was the same as those for the unannealed one. However, the La cantent corresponding to the maximum d_{33} is different, i.e. for $x=0.01$, 400 pC/N for the unannealed sample, whereas for $x=0.02$, $d_{33}=533$ pC/N for the annealed sample. The piezoelectric behavior can be partly explained by the results of X-ray diffraction (XRD) and SEM.

3.3. Phase analysis

Figs. 7 and 8 show a series of XRD patterns of $Pb_{(1-x)}La_x(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$ ceramics with $x=0$, 0.005, 0.01, 0.02, 0.03 before and after annealing. Table 2 shows the crystal systems and the volume fractions of pyrochlore in such compositions before and after annealing. The crystalline system has been identified as rhombohedral or tetragonal based on the diffraction pattern exhibiting a single or double 200 peak, respectively. The ratio of related intensities of the (222) pyrochlore peak (I_{pyro}) and the (110) perovskite PSTT peak was used to determine the volume fraction of pyrochlore present, as given by Eq. 1:

$$\text{Pyrochlore phase}(\%) = I_{(222)\text{Pyro}} \times 100/(I_{(222)\text{Pyro}} + I_{(110)\text{Perov}}) \quad (1)$$

From the XRD patterns of undoped PSTT ceramics shown in Figs. 7 and 8, it can be determined[18] that the crystalline structure of the unannealed sample is rhombohedral perovskite with 9.09% cubic pyrochlore, and that of the annealed sample is tetragonal perovskite with 13.75% pyrochlore. For the undoped PSTT, it is difficult for grain boundary phase to form around the ceramic grains during sintering due to the small amount of impurity. Therefore, PbO easily vaporizes in the samples at higher temperature during sintering according to the following reaction.

$$8Pb(Sc_{1/2}Ta_{1/2})O_3 \rightarrow 5PbO\uparrow + Pb_3Ta_4O_{13} + Sc_2O_3 \quad (2)$$

The weight loss of all the undoped samples after sintering is consistent with the above reaction. So, the composition of the sintered sample shifts to the PT in

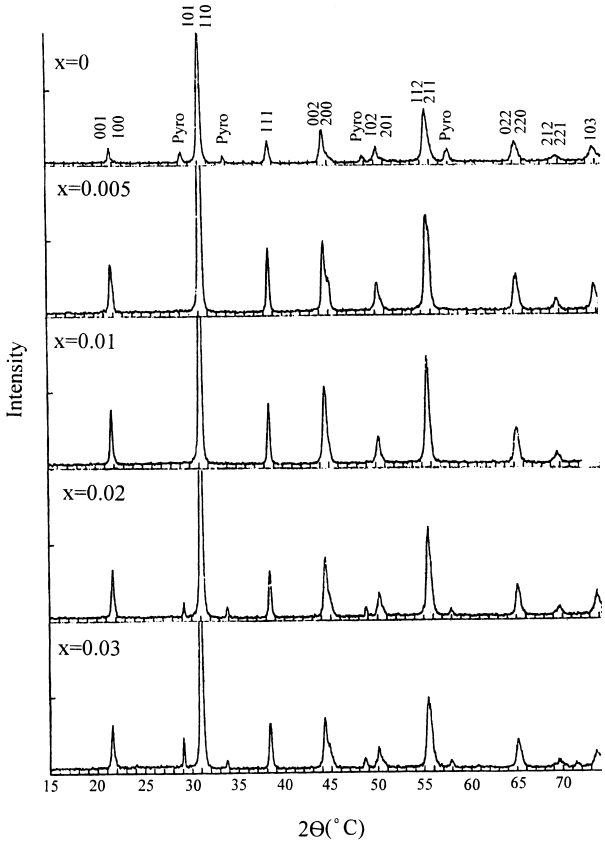

Fig. 7. XRD patterns of unannealed $Pb_{(1-x)}La_x(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$ ceramics.

the phase diagram of the PST–PT binary system. In the XRD pattern of the undoped PSTT sample before annealing, the 200 peak ($d=2.030$–2.040) is single but obviously broadening at the base, suggesting the presence of a small amount of tetragonal phase in the sample. After annealing, PbO concentration further decreases with its vaporization; therefore the amount of pyrochlore phase is higher than that of the unannealed one, and the percentage of PST further decreases. Therefore, the pattern of the annealed PSTT shows a double 200 peak. The piezoelectric properties of tetragonal perovskite ceramics are generally considered to be better than those of rhombohedral ones.[6]

The XRD patterns of La-doped PSTT are different from those of the undoped one. When La-content is very small, such as $x=0.005$ and 0.01, pyrochlore peaks can not be observed in the XRD patterns either before or after annealing. As the La-content increases, the pyrochlore peaks in the XRD patterns appear and become higher for the as-sintered samples. It must be noted that after annealing, the pyrochlore peaks of highly doped PSTT surprisingly disappears, unlike that in the undoped PSTT case.

The results of XRD for doped PSTT can be adequately explained by the location and diffusing of La-ions in PSTT during sintering and annealing as dis-

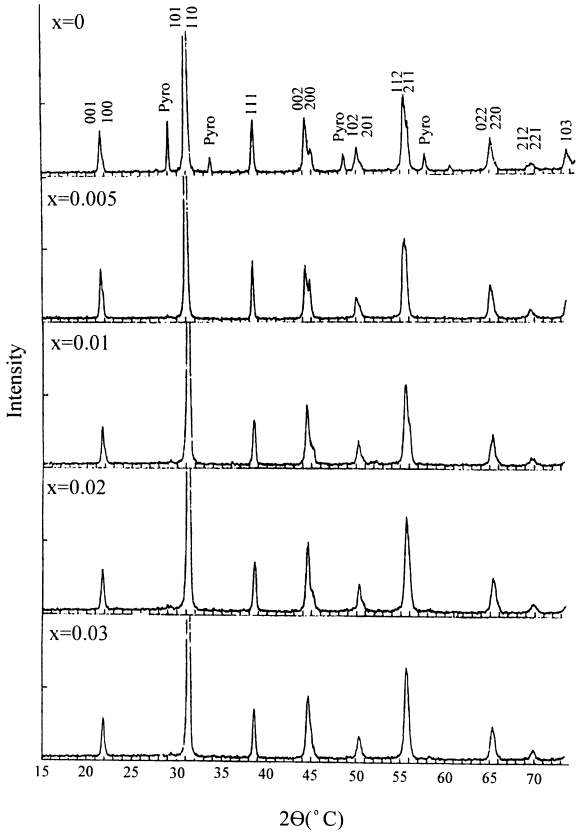

Fig. 8. XRD patterns of annealed $Pb_{(1-x)}La_x(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$ ceramics.

cussed earlier. As an impurity, those La-ions, which do not enter the perovskite lattice after synthesis, can enhance the formation of phase boundaries and thus increase the density of ceramics so as to prevent the vaporization of PbO during sintering. Because many La-ions remain in grain boundaries after sintering, the number of 'A' site ions in the $Pb_{(1-x)}La_x(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$ lattice are less than the number they should be; therefore, there would be a certain amount of vacancies in the lattice to keep the balance of charges. When La-content is very small, such as $x=0.005$ and 0.01, the perovskite structure can be kept by the formation of vacancies, and the ceramics are composed of pure perovskite without any cubic pyrochlore. There are two reasons to explain why the piezoelectric properties for the compositions where $x=0.005$ and 0.01 are better than those of the undoped PSTT. One is that the phase for such compositions is the pure perovskite; the other is that there were many vacancies in the lattice, which play an important role in improving the piezoelectric activity.[4,5] At higher La-concentrations, such as $x=0.02$ and 0.03, although vacancies still exist in the samples, the balance of charges could not be kept by depending only on vacancy formation, and a serious shortage of 'A' site ions should cause the following reaction:

$$8Pb(Sc_{1/2}Ta_{1/2})O_3 - 5PbO \rightarrow Pb_3Ta_4O_{13} + 2Sc_2O_3 \quad (3)$$

Table 2
The crystalline structure of $Pb_{(1-x)}La_x(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$ ceramics before and after annealing

$Pb_{(1-x)}La_x(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$			$x=0$	$x=0.005$	$x=0.01$	$x=0.02$	$x=0.03$
Measurement density (g/cm^3)		Unannealed	8.186	8.174	8.156	8.076	8.056
Theoretical density (g/cm^3)		Unannealed	8.245	8.546	8.327	8.345	8.121
		Annealed	8.501	8.444	8.581	8.357	8.407
Measurement density (g/cm^3)		Unannealed	8.186	8.174	8.156	8.076	8.056
Relative density (%)		Unannealed	99.30	91.59	97.95	96.78	98.62%
Crystalline type		Unannealed	Rhombohedral (200 broadening)	Tetragonal	Rhombohedral	Rhombohedral	Rhombohedral
		Annealed	Tetragonal	Tetragonal	Tetragonal	Rhombohedral (200 broadening)	Rhombohedral
Lattice parameter	a (Å)	Unannealed	4.1064	4.019	4.0705	4.0648	4.0911
	c (Å)			4.0720			
	α		90°40′		90°22′	90°21′	90°19′
	a (Å)	Annealed	4.0259	4.037	4.0096	4.0629	4.0519
	c (Å)		4.0823	4.0848	4.0706		
	α					90°22′	90°16′
Pyrochlore content (vol. %)		Unannealed	9.09	0	0	4.83	9.61
		Annealed	13.75	0	0	0	0

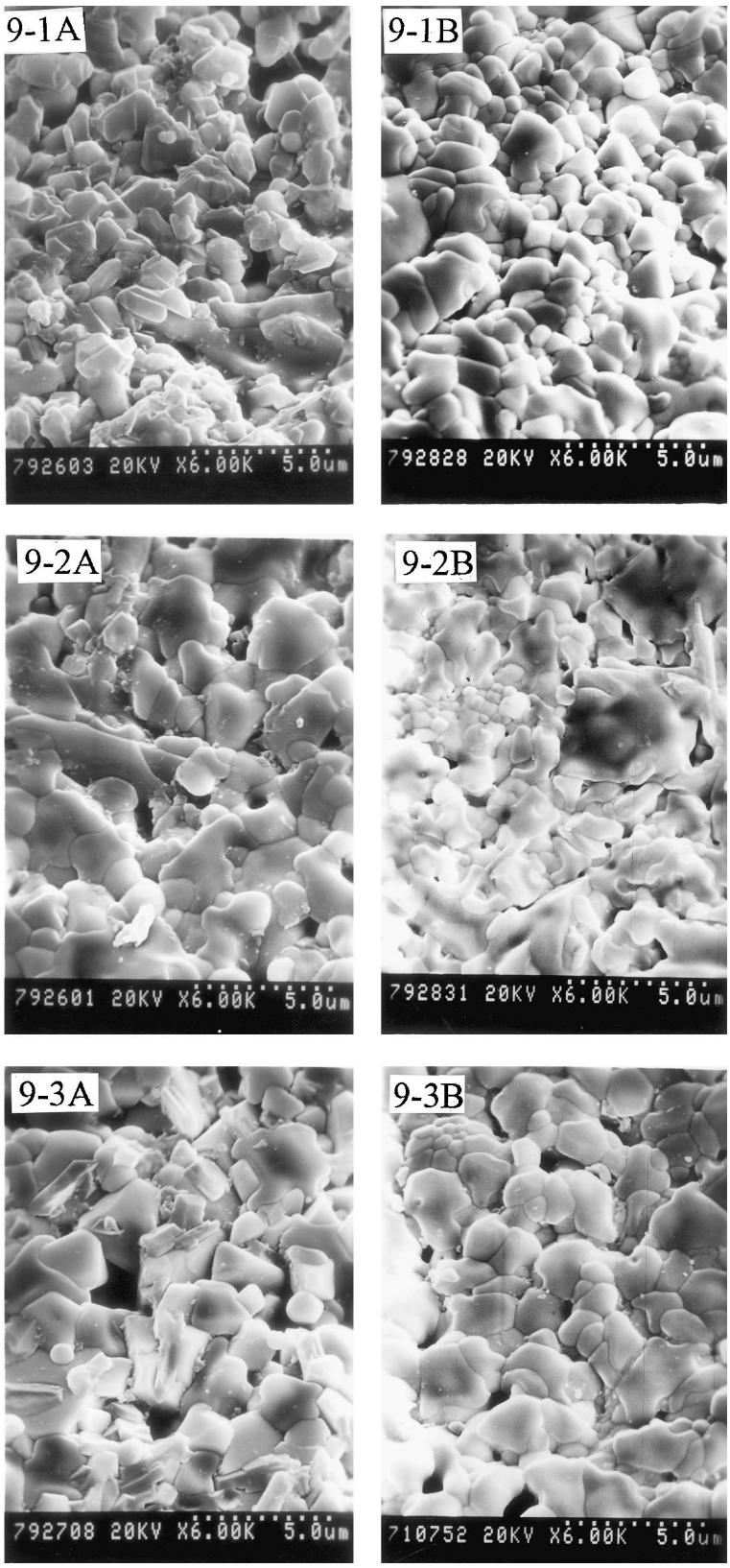

Fig. 9. SEM images of polished fracture surface of annealed and unannealed $Pb_{(1-x)}La_x(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$ ceramics 9-1A $x=0$, unannealed; 9-1B $x=0$, annealed 9-2A $x=0.005$, unannealed; 9-2B $x=0.005$, annealed 9-3A $x=0.01$, unannealed; 9-3B $x=0.01$, annealed 9-4A $x=0.02$, unannealed; 9-4B $x=0.02$, annealed 9-5A $x=0.03$, unannealed; 9-5B $x=0.03$, annealed (*continued on next page*).

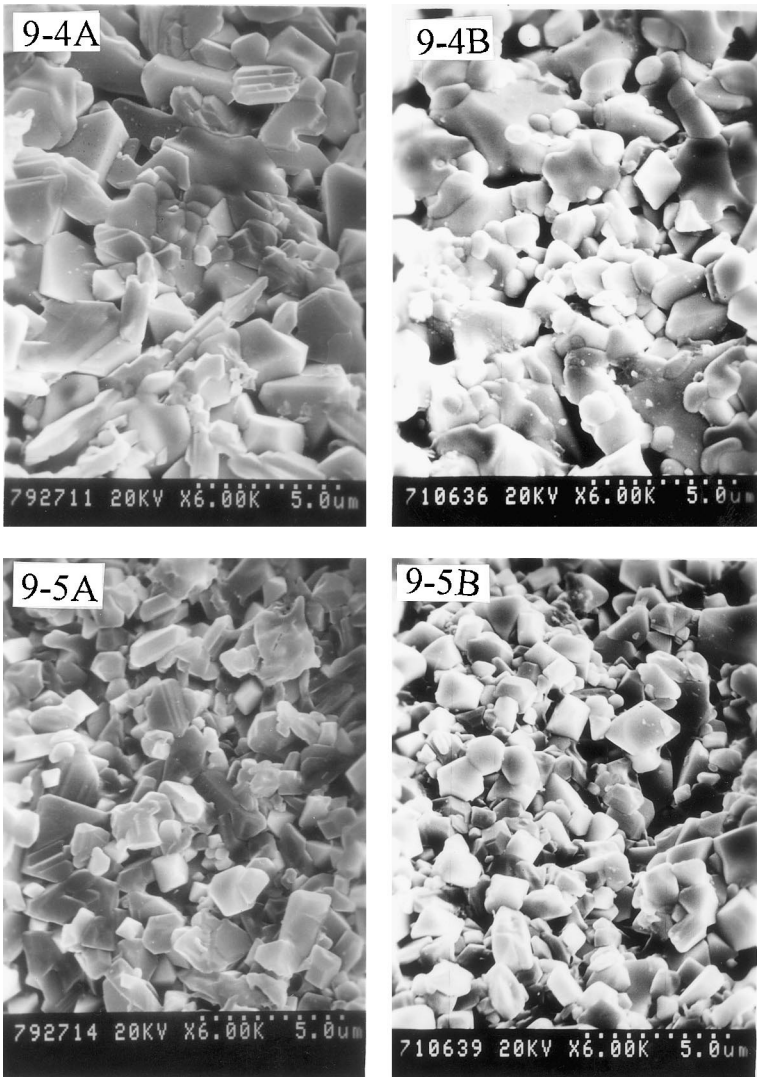

Fig. 9. (*continued*).

Therefore, pyrochlore peaks can be found in the patterns of the compositions where $x=0.02$ and 0.03. Because of the cubic pyrochlore phase in our samples, the d_{33} of the compositions where $x=0.02$ and 0.03 are lower than those of the composition where $x=0.005$ and 0.01.

According to our assumption, the La-ions existing in the grain boundaries can diffuse to the grain lattice during sintering and annealing at higher temperature for a long time, because La-ion diffusion coefficient[16] in perovskite $BaTiO_3$ is only as low as about 10^{-12} cm^2 s^{-1}. During annealing, most of the La-ions diffuse to the grains where certain amount of pyrochlore phase exists and causes the following reaction:

$$2Pb_3Ta_4O_{13} + 4Sc_2O_3 + 5La_2O_3 \rightarrow 6Pb(Sc_{1/2}Ta_{1/2})O_3 - 10La\square_{1/2}(Sc_{1/2}Ta_{1/2})O_3 + 5/2O_2 \quad (4)$$

The slight loss of all the La-doped PSTT samples is consistent with reactions (3) and (4). By this reaction, the pyrochlore and Sc_2O_3 generated from reaction (3) and La ions diffusing from grain boundaries transform into the composite perovskite lattices during annealing. Therefore, the crystalline phase of the annealed samples for the compositions where $x=0.02$ and 0.03 was the pure perovskite. For this reason, the piezoelectric properties of the annealed doped PSTTs are better than those of the unannealed ones are.

In addition, from the XRD patterns of all the samples, it can be concluded that the crystalline structure of all the doped PSTT samples transform from tetragonal to rhombohedral with increasing La content. The effect of La doping on the PSTT crystalline structure is different from the effect of Nb doping on the $Pb(Mg_{1/3}Nb_{2/3})$–$PbZrO_3$–$PbTiO_3$ (PMN–PZ–PT) ternary system which was studied by Shaw et al.[17] and on PSTT studied

by our group. So far, no satisfactory explanation for the transformation of the structure has been suggested.

The measured and the theoretical, as well as the relative densities of samples, for all the compositions are shown in Table 2. The relative densities for all the samples are greater than 90%, which is suitable for piezoelectric use. The samples for $x=0$ and 0.03 are greater than that of other compositions because of the presence of pyrochlore phase whose density is 8.59, which is greater than the densities of PSTTs for all the compositions.

3.4. Microstructure study

SEM images of polished and thermally etched fracture surfaces of $Pb_{(1-x)}La_x(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$ ceramics with $x=0$, 0.005, 0.01, 0.02, 0.03 before and after annealing are shown in Fig. 9. The average grain sizes measured on the SEM pictures of these specimens are shown in Fig. 10. Gupta and Viehland[7] proved that the La-modification of $Pb(Mg_{1/3}Nb_{2/3})$–$PbTiO_3$ ceramics was resulted in a significant decrease in the grain size for La-contents of 0, 5 and 10 at.%. In our study, the behavior of the grain size with increasing La-content is the same as that of La-doped PMNT, but the grain size for the composition where $x=0.005$ is much larger than that of undoped PSTT for the as-sintered samples. The grains of the undoped PSTT are smaller than those of the doped ones because of the formation of the second phase (pyrochlore) in undoped samples, as proved by the XRD study. At lower values of La-content, the grains grow faster than in undoped PSTT, because of the effect of grain boundary phase and vacancies in the grains; therefore, the grain size of such composition becomes much larger. As the La-content increases, the grain size of La-doped PSTT decreases because of the emergence and growth of pyrochlore during sintering. Since the piezoelectric properties of ceramics can be improved with increasing grain size, SEM result can be regarded as another explanation of the variation of d_{33} with increasing La-content in $Pb_{(1-x)}La_x(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$ ceramics.

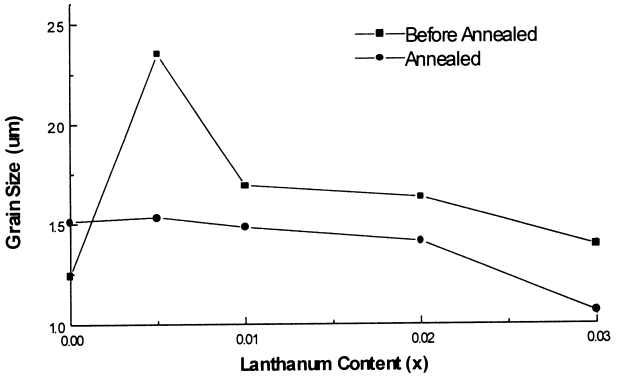

Fig. 10. The average grain size vs. La contents for annealed and unannealed $Pb_{(1-x)}La_x(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$ ceramics.

After annealing, the grain size of undoped PSTT increases. The grain size of all the annealed La-doped PSTT ceramics decreases significantly, which is different from any other perovskites. The reason of this discrepancy is still unclear.

4. Conclusion

The dielectric and piezoelectric properties and the structural evolution as well as the microstructure of $Pb_{(1-x)}La_x(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$ for the compositions where $x=0$, 0.005, 0.01, 0.02, 0.03 were investigated.

The addition of lanthanum modified the dielectric properties, Curie temperature, and piezoelectric properties of PSTT significantly. The dielectric constant peaks of La doped PSTT broadened with increasing La content. But for $x=0.005$, the dielectric peak of the doped PSTT was sharper and higher than that of the undoped PSTT. A sharp dielectric peak of La doped PSTT was obtained after long time annealing (900°C, 8 h), but for the composition $x=0.005$, the peak became dramatically lower and broader than that of the unannealed one. The effect of lanthanum doping was usually to reduce the Curie temperature, approximately 26°C/at.%, but for the composition where $x=0.005$, T_c became higher slightly than that of undoped PSTT. Annealing can shift the Curie temperatures of all the samples to higher temperature. The piezoelectric strain coefficient d_{33} of $Pb_{(1-x)}La_x(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$ ceramics before and after annealing vary with La content. The value of d_{33} increases with increasing La-dopant; reaches a maximum, and then decreases. The maximum value of d_{33} is 400 pC/N for $x=0.01$ before annealing and 533 pC/N for $x=0.005$ after annealing. The annealing process can improve the piezoelectric properties of all the samples significantly.

The crystalline structure of La doped PSTT is affected by the La-content and annealing. When the La-content is low, the crystal of $Pb_{(1-x)}La_x(Sc_{1/2}Ta_{1/2})_{0.55}Ti_{0.45}O_3$ ceramic has the tetragonal perovskite structure. At higher La-content, the crystalline structure of La-doped PSTT transforms to rhombohedral. After annealing, the crystal structure of all the compositions transforms from rhombohedral to tetragonal. As the La-content increases before annealing, the pyrochlore phase appears and increases in sample; but it disappears dramatically after the annealing for all the doped compositions. The microstructure study confirmed that the grain size of La-doped PSTT is larger than the undoped PSTT when the La-content is very low; it decreases with increasing La content. The grain size of the sample is influenced by the grain boundary and vacancy in the perovskite lattice as well as the presence of second phase, pyrochlore.

An important result of our work is that PSTT with a small amount of La-dopant possesses the best piezoelectric properties, which results from the percentage of perovskite, crystal structure, grain size, and lattice defect, and related to the location and diffusion of La-cations during sintering and annealing.

A model for the location and diffusion of La-ion in La-doped PSTT during sintering and annealing is proposed. It is thought that most of the La ions in PSTT do not enter the lattice after perovskite synthesis, but concentrate in the grain boundary in the initial stage of sintering, and enter the ordered domains in a sample, and then diffuse to the disordered domains. This model can explain most of our experimental results.

Acknowledgements

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