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The piezoelectric and dielectric properties of Ca-additive Sm-modified $PbTiO_3$ ceramics intended for surface acoustic wave devices

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Abstract

Sm-modified lead titanate ceramics with a composition of $(Pb_{0.88-x}Ca_xSm_{0.08})(Ti_{0.98}Mn_{0.02})O_3$; $x=0.11\sim0.17$ were prepared by conventional mixed-oxide method. The dielectric and piezoelectric properties of these doped ceramics were measured at room temperature. Microstructural and compositional analyses have been carried out using SEM and XRD. The Curie point (T_c) was studied by measuring the dielectric behavior as a function of temperature. The experiments successfully showed that Ca additive not only reduce the lattice anisotropy but is also helpful in providing a higher thickness electromechanical coupling coefficient, k_t (>0.57), than that of conventional $PbTiO_3$ based ceramics while still keeping a small planar electromechanical coupling coefficient, k_p. In addition, the Ca additive produced a higher phase velocity and high electromechanical coupling coefficient. The SAW properties of our samples (V_p and k^2) are better than those of commercially-made PZT and PT samples.

Keywords: Composites; Dielectric properties; (Pb,Ca,Sm)(Ti,Mn)O_3; $PbTiO_3$; Piezoelectric properties; Surface acoustic wave devices; X-ray methods

1. Introduction

In recent years, lead titanate ($PbTiO_3$) ceramics have attracted attention due to their high Curie temperature of 490° and low dielectric constant of about 200, which make them more attractive for high-temperature and high-frequency transducer applications than PZT ceramic.[1,2] However, pure lead titanate ceramics are difficult to sinter because of their large lattice anisotropy (c/a $=1.064$). On cooling through the Curie temperature, the large anisotropy causes the ceramic to become fragile. In addition, it is difficult to pole the ceramics as a result of their low resistivity (10^7–10^8 Ω·cm).

By substitution of isovalent (Ca^{2+}, Ba^{2+}, Cd^{2+}...etc) or off-valent (Sm^{3+}, Gd^{3+},Y^{3+}...etc) ions into the Pb^{2+} sites, the lattice anisotropy is reduced,[3–7] and the samples become more dense. These modified $PbTiO_3$ ceramics will result in a relatively large thickness electromechanical coupling coefficient, k_t, and a small planar electromechanical coefficient, k_p. In other words, the electromechanical coupling factor for thickness vibration k_t will be much larger than that for planar extensional vibration k_p ($k_t>>k_p$). The addition of Ca or Sm into $PbTiO_3$ results in a higher k_t/k_p ratio compared with PZT ceramics. This property makes it possible for $PbTiO_3$ based ceramics to be used for high-frequency applications such as SAW (Surface Acoustic Wave) devices and piezoelectric transducer.

Since the 1970s, the applications of piezoelectric ceramics for SAW devices have been investigated.[8–14] The modified lead titanate piezoelectric ceramics have potential for SAW device applications due to the ability to modify the composition to achieve a desirable combination of properties, such as high surface phase velocity and high electromechanical coupling coefficient. However, the use of piezoelectric ceramics in SAW devices has been limited by the high propagation loss at high frequency compared to single crystal materials.

Many researchers reported that $(Pb_{0.85}Sm_{0.1})(Ti_{0.98}Mn_{0.02})O_3$ ceramics shows exceptionally large electromechanical anisotropy.[15–18] In this paper, we prepare

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$(Pb_{0.88-x}Ca_xSm_{0.08})(Ti_{0.98}Mn_{0.02})O_3$ ($x=0.11$–0.17) system with additional doping with Ca to investigate the dielectric, piezoelectric and SAW properties.

2. Experimental procedure

2.1. Sample preparation

A conventional ceramics preparation procedure was used to prepare the sample. Raw materials were mixed using pure reagent PbO, TiO_2, Sm_2O_3, $CaCO_3$ and MnO_2 powders (>99.0% purity). The materials $(Pb_{0.88-x}Ca_xSm_{0.08})(Ti_{0.98}Mn_{0.02})O_3$, $x=0.11$–0.17, were calcined at 900 °C for 2 h, and excess PbO was added to counteract the volatilization of PbO during firing, then followed by pulverization. The powders were then dried and milled with 8 wt.% of a 5% PVA solution. Then, the powders were pressed into plates with dimensions; $20\times20\times1$ mm^3, for SAW measurements, and discs of 12 mm diameter and 1 mm thickness, for bulk measurements, using a pressure of 25 kg/g^2. Specimens were then sintered isothermally at a heating rate of 10 °C/min at 1200 °C for 2 h. A PbO rich atmosphere using $PbTiO_3$ powders was maintained with $PbTiO_3$ powder to minimize the lead loss during sintering.

2.2. Measurements

Five samples were used in each experiment to check the errors. The error in each experiment is very small (within ±1%), so we repeat the experiment and average the results. The bulk densities of the sintered bodies were measured by the Archimedes method. The mean grain size was obtained from the observation of the scanning electron micrograph (SEM) by the line intercept method. In order to measure the electrical properties, silver paste was coated to form electrodes on both sides of the sample, then subsequently fired at 600 °C for 25 min. After that, the samples were poled with an electric field up to 5 kV/mm at 150 °C in silicon oil for 15 min. The dielectric and piezoelectric properties were measured by using an impedance analyzer (HP4194A). The piezoelectric properties were calculated from the resonance measurement method.[19] The piezoelectric d_{33} coefficient was measured with a Berlincourt d_{33}-meter. The compositional analyses and lattice parameters for the sintered bodies were determined using an X-ray diffraction (XRD) and microstructures were observed using a scanning electron microscope (SEM). The Curie temperature was calculated by measuring the dielectric behavior as a function of temperature using an impedance analyzer (HP4192).

In order to measure the SAW properties, the plates were polished to a mirror finish on one side with surface roughness below 0.1 μm. Then, aluminum electrode patterns, 0.3 μm thick in the form of interdigital transducers (IDTs), were applied onto the polished surface using the lift-off photolithographic process. The IDT pattern parameters are shown in Table 1. The IDT pattern of 20 μm width leads to a wavelength of 80 μm.

The frequency response of SAW device was measured by using a network analyzer (HP 8714ES). The experimental phase velocity was obtained from the equation $v=f_0\times\lambda$, where f_0 is center frequency and λ is the wavelength. The experimental k^2 was obtained from the equation[20] $k^2=\left(\frac{\pi}{4N}\cdot\frac{Ga}{B}\right)_{f=f_0}$, where N is the number of IDT fingers, and Ga and B are radiation resistance and susceptance, respectively. The temperature coefficient of frequency, TCF was determined from measurements of the shift of center frequency at temperature from 25 to 80 °C, using the following equation

$$TCF=\frac{1}{f_{0(25\,^\circ C)}}\cdot\frac{f_{0(80^\circ C)}-f_{0(25^\circ C)}}{(80-25)}.$$

3. Results and discussion

3.1. XRD analysis and microstructure

Fig. 1 shows the bulk density as a function of the amount of Ca. The density decreased with increasing Ca substitutions. The X-ray diffraction patterns of $(Pb_{0.88-x}Ca_xSm_{0.08})(Ti_{0.98}Mn_{0.02})O_3$ ceramics are shown in Fig. 2. The X-ray analyses indicated that the $PbTiO_3$ and Ca-doped $PbTiO_3$ ceramics have major peaks at (101), and all of them belong to the tetragonal phase. The differences of X-ray diffraction patterns between the $PbTiO_3$ and Ca-doped $PbTiO_3$ are not obvious except that the peak of (002) and (200) (around $2\theta=45^\circ$) move toward each other as Ca doping increases. Fig. 3 shows the lattice anisotropy of samples versus

Table 1
IDT parameters of the SAW device

Electrode finger pairs	15.5
Electrode width	20 μm
Wavelength	80 μm
Electrode overlap	4 mm
Delay-line distance	1.6 mm

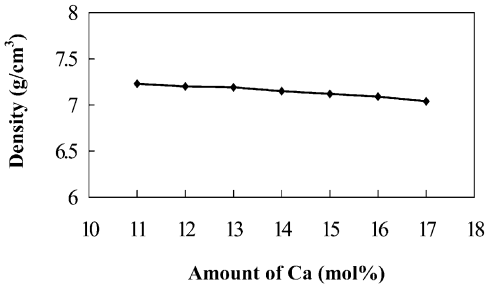

Fig. 1. Dependence of the bulk density on the amount of Ca additives.

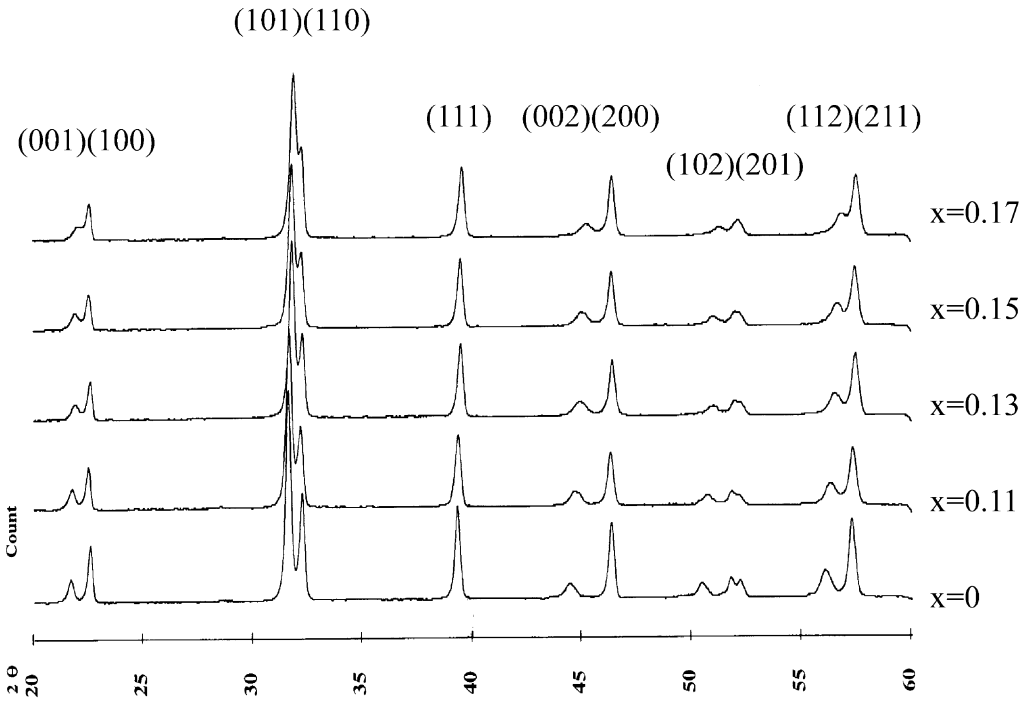

Fig. 2. XRD patterns of $(Pb_{0.88-x}Ca_xSm_{0.08})(Ti_{0.98}Mn_{0.02})O_3$ samples.

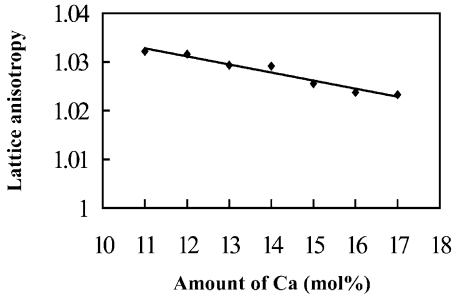

Fig. 3. Dependence of the lattice anisotropy on the amount of Ca additives.

the amount of Ca, respectively. The lattice anisotropy (c/a) decreases with increasing Ca additive. It is due to the lattice constant c-axis (002) decreases with increasing Ca additive, while the a-axis (200) changes little. This will assist the modified lead titanate ceramics in the sintering process. The SEM patterns of the Sm-modified $PbTiO_3$ ceramics doped and undoped with Ca are shown in Fig. 4, and both of them are very dense. The average grain size of all Ca-doped samples is about 1.2 μm.

3.2. Piezoelectric properties

The results of the thickness coupling factors are shown in Fig. 5. As Ca additive increases, the k_t value increases at first and reaches its maximum value of 0.574 at Ca = 13 mol%. It is obvious that the k_t value for $x = 0.13$–0.15 is larger than 0.55, which is higher than previously reported data for Sm-modified lead titanate in Table 2. The k_p values of all samples are about 0.04–0.05 as Ca changes, and the minimum value occurs as Ca = 13 mol%. The planar (N_p) and thickness (N_t) frequency constant increase slightly with the increasing Ca additives, and their values are about 2850 and 2050 Hz-m, respectively. The piezoelectric d_{33} coefficient as a function of the amount of Ca additives is shown in Fig. 6. It shows that d_{33} increases with the increase of the amount of Ca dopants. Their values are larger than 80 pC/N for $x = 0.13$–0.17, and the maximum value is 89 pC/N as Ca = 15 mol%.

3.3. Dielectric properties

Fig. 7 shows the dielectric constant of all samples versus the amount of Ca, respectively. It shows that the dielectric constant increase correspondingly with the increase of amount of Ca, while the loss factor changed little around 7×10^{-3}.

Fig. 8 shows the temperature dependence of the relative dielectric constant (ε_r) measured at 1 kHz for the samples $x = 0.11$, 0.13, 0.15 and 0.17. The Curie–Weiss behavior in the curves is well observed for all samples. It shows that the Curie point (T_c) decreases correspondingly with the increasing Ca additives from 298 °C($x = 0.11$) to 247 °C($x = 0.17$). This is related to the decreased lattice anisotropy with the increasing Ca additives.

3.4. Surface acoustic wave properties

Fig. 9 shows the frequency response of the SAW device at Ca = 11 mol% with impedance matching. The

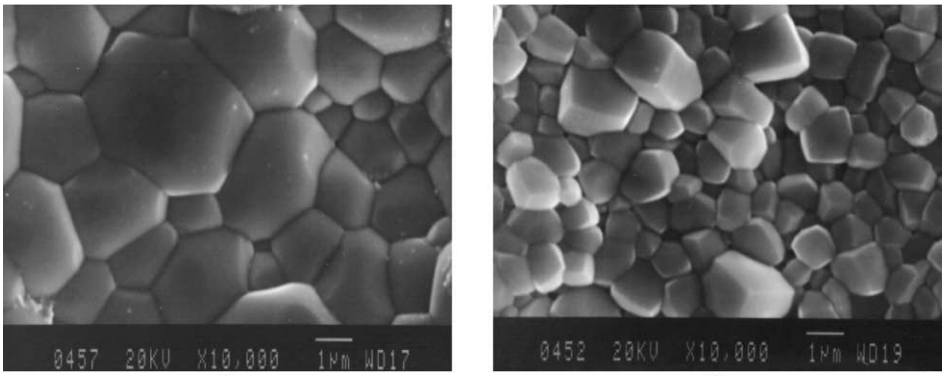

Fig. 4. SEM photographs of (a) $(Pb_{0.85}Sm_{0.1})(Ti_{0.98}Mn_{0.02})O_3$ (b) $(Pb_{0.75}Ca_{0.13}Sm_{0.08})(Ti_{0.98}Mn_{0.02})O_3$ samples sintered at 1200 °C for 2 h. (bar = 2 μm).

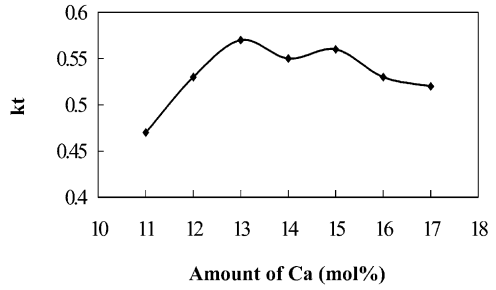

Fig. 5. Dependence of the thickness coupling factor amount of Ca additives.

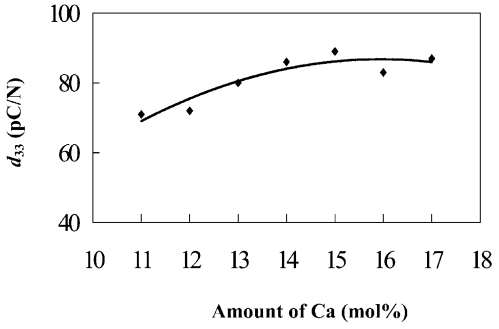

Fig. 6. Dependence of the piezoelectric d_{33} coefficient on the amount of Ca additives.

Table 2
The study of sintering temperature, k_t and k_p in different $PbTiO_3$-based system

Compositions	Sintering Temperature (°C)	k_t	k_p	Reference
$(Pb,Ca)(Co,W)TiO_3$	1200	0.52	0.05–0.2	[2]
$(Pb,Sr)(Co,W)TiO_3$	1200	0.45	0.1–0.2	[2]
$(Pb,Ba)(Co,W)TiO_3$	1200	0.36	0.1–0.2	[2]
$(Pb,Sm)(Ti,Mn)O_3$	1240–1280	0.5	0.03–0.05	[3,15–17]
$(Pb,La)(Ti,Mn)O_3$	1280	0.47	0.09	[3]
$(Pb,Nd)(Ti,Mn)O_3$	1280	0.46	0.065	[3]
$(Pb,Gd)(Ti,Mn)O_3$	1280	0.49	0.05	[3]
$(Pb,Ca_{0.13},Sm)(Ti,Mn)O_3$	1200	0.574	0.045	Our sample

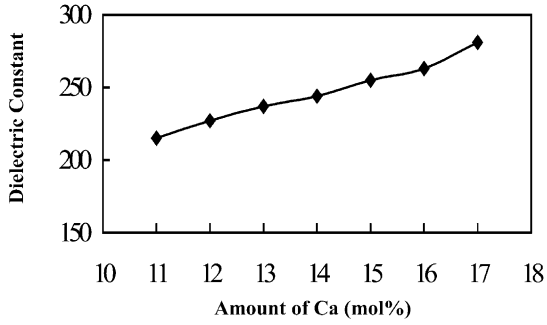

Fig. 7. Dependence of the dielectric constant on the amount of Ca additives.

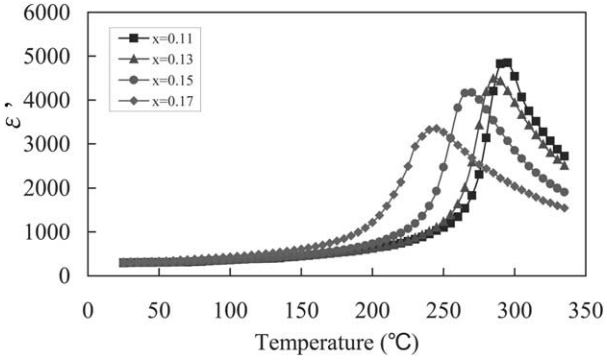

Fig. 8. Real value of the dielectric constant, ε′, as a function of the temperature at 1 kHz for Ca additives $x = 0.11$, 0.13, 0.15, and 0.17.

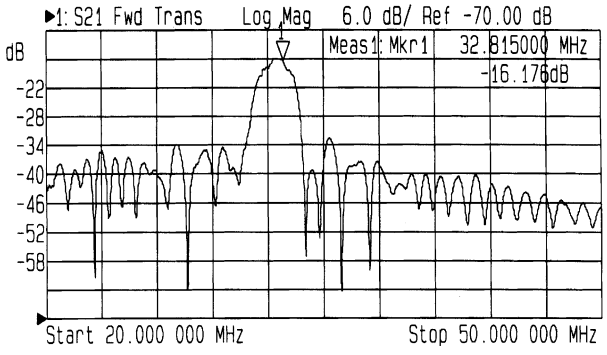

Fig. 9. Frequency response of the SAW device for $x = 0.11$ with impedance matching.

center frequency of the device is 32.815 MHz, leading to a phase velocity of 2625 m/s; the insertion loss is about 16 dB. The phase velocities of all devices are about 2600–2700 m/s with increasing Ca additive, and the maximum value is 2710 m/s as Ca = 13 mol%. The phase velocities of our samples are higher than those of commercial Pb-based ceramics is shown in Table 3 and are suitable for high-frequency applications. Fig. 10 shows the electromechanical coupling coefficient (k^2) of the SAW devices versus the amount of Ca additive. The k^2 value increases at first and reaches the maximum value of 3.81% as Ca = 13mol% with increasing Ca dopant, then falls. Fig. 11 shows the temperature coefficient of frequency (TCF) of the SAW device as a function of Ca additive. It is obvious that the Ca doped piezoelectric substrates have negative TCF values and their absolute values increase correspondingly with increasing Ca additive.

Table 3
The study of phase velocity (V_p), k^2 and IL in different Pb-based system

Composition	V_p (m/s)	k^2 (%)	*IL* (dB)	Reference
PZT-4	2210	1.81	>20	[8]
Pz24	2238	1.91	−22.5	[12,13]
Pz26	2075	2.73	−16.7	[12,13]
Pz27	2016	3.95	−13.8	[12,13]
Pz28	2028	1.69	−21.4	[12,13]
Pz34	2510	1.65		[12]
$(Pb,La,Sm)(Ti,Mn)O_3$	2555	2.12	−30.0	[12]
$(Pb,Ca_{0.13},Sm)(Ti,Mn)O_3$	2710	3.81	−16.1	Our sample

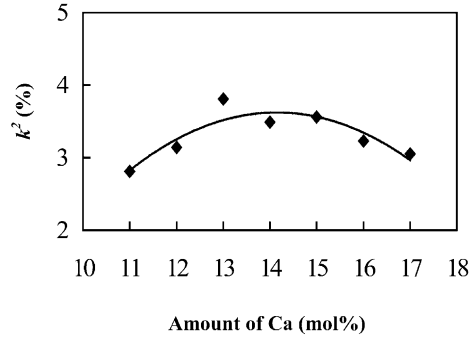

Fig. 10. Dependence of the electromechanical coupling coefficient (k^2) on the amount of Ca additives.

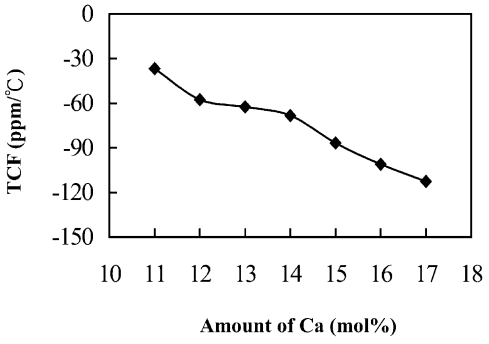

Fig. 11. Dependence of the temperature coefficient of frequency on the amount of Ca additives.

4. Conclusions

The addition of Ca and Sm simultaneously not only reduces the lattice anisotropy (c/a), but also maintains the good dielectric and piezoelectric anisotropy properties of the modified $PbTiO_3$ ceramics. The reduction of lattice anisotropy makes the Ca-doped samples not so fragile during the sintering process. The measured thickness electromechanical coupling coefficients, k_t, are larger than 0.55 for Ca = 13–15 mol%. The loss factors of the studied samples are smaller than 7×10^{-3}, and the dielectric constant is about 250. The Curie points of the studied samples are larger than 240 °C.

Modified lead titanate piezoelectric ceramics are potential substrates for SAW devices, owing to their high electromechanical coupling coefficient, low cost and possibility to adjust composition and obtain a small temperature coefficient of frequency. But the main disadvantage for SAW applications is their high propagation losses.

According to the experimental results, Ca additives are helpful in increasing the phase velocity and electromechanical coupling coefficient of the SAW devices. The insertion losses are about 15–20 dB. For the Ca = 13 mol% doped sample gave, there were the following data: $\rho = 7.19$ g/cm^3, $k_t = 0.574$, $V_p = 2710$ m/s, $k^2 = 3.81\%$ and $TCF = -62.4$ ppm/°C. The Ca-doped modified lead titanate ceramics have high electromechanical coupling coefficients that make them suitable for broad-band SAW filter and SAW gas sensor applications.

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