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The influence of Cd doping on the surface acoustic wave properties of Sm-modified $PbTiO_3$ ceramics

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Abstract

The Sm-modified lead titanate ceramics with a composition of $(Pb_{0.85-x}Cd_xSm_{0.1})(Ti_{0.98}Mn_{0.02})O_3$; $x=0.01$–0.08 were prepared by conventional mixed-oxide method. Dielectric and piezoelectric properties of these doped ceramics were measured at room temperature. Microstructural and phase content analyses have been carried out using SEM and XRD. The Curie point versus the amount of Cd composition was also investigated. Surface acoustic wave (SAW) properties, including phase velocity, electromechanical coupling coefficient and temperature coefficient of frequency, were measured. The experiments successfully showed that Cd additive is helpful to obtain higher phase velocity and high electromechanical coupling coefficient, and improve the temperature coefficient of frequency (TCF). In addition, it also reduces the sintering temperature of processing. The SAW properties of our samples (V_p, IL, k^2, and TCF) compare well to the commercially-made PZT and PT samples.

Keywords: Composites; Dielectric properties; (Pb,Cd,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 °C and low dielectric constant of about 200 °C, which make them more attractive for higher temperature and higher 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 these 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 ($k_t \gg k_p$). These substitutions of Pb by Sm in $PbTiO_3$ 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 surface acoustic wave (SAW) devices and piezoelectric transducer.

On the other hand, it is known that the sintering temperature of piezoelectric ceramics is usually above 1250 °C by using conventional oxide-mixed method. Normally, doping with low melting oxides could reduce the sintering temperature of ceramics, and many researchers have shown that Cd (the melting point is 321 °C) dopants could help reducing the sintering temperature of the Pb-based piezoelectric ceramics.[8–11] Those researchers suggested that the Cd^{2+} ion could replace Pb^{2+} ion in the A site and that Cd^{2+} ions could combine with other additives to form a liquid phase which is helpful in reducing the sintering temperature. However, the influence of Cd dopants on the piezoelectric and dielectric characteristics of the $PbTiO_3$-based ceramics for high frequency and high temperature applications has hardly been investigated.

Since 1967, the applications of piezoelectric ceramics for SAW devices have been investigated.[12–18] The

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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.

In our previous paper,[19] we have successfully demonstrated that Cd dopants not only effectively reduce the sintering temperature but also keep good piezoelectric anisotropy and dielectric properties of the Sm-modified $PbTiO_3$ ceramics. In this paper, we continue our research and prepare $(Pb_{0.85-x}Cd_xSm_{0.1})(Ti_{0.98}Mn_{0.02})O_3$ ($x=0.01$–0.08) system to investigate the surface acoustic wave properties.

2. Experimental

2.1. Sample preparation

The conventional ceramic procedure was used to prepare the sample. Raw materials, PbO, TiO_2, Sm_2O_3, CdO and MnO_2 powders (>99.0% purity), were wet-mixed by ball milling method for 6 h. The $(Pb_{0.85-x}Cd_xSm_{0.1})(Ti_{0.98}Mn_{0.02})O_3$, $x=0.01$–0.08, powders were calcined at 900 °C for 2 h, and excess PbO (~5 wt.%) was added to counteract the volatilization of Pb during firing. The powders were dried and milled with 8 wt.% of a PVA solution. Then, the powders were pressed into plates with dimension; $20\times20\times1$ mm^3, for SAW measurements, and discs of 12 mm diameter and 1 mm thickness, for bulk measurements, using a pressure of 25 MPa. Specimens were then sintered at a heating rate of 10 °C/min at 1150 °C for 2 h. A Pb-rich atmosphere using $PbTiO_3$ powder was maintained 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 porosity ratio was calculated from the equation:

$$p = \frac{D_x - D_a}{D_x} \times 100\%$$

where D_x and D_a are the theoretical and experimental density, respectively. The bulk densities of the sintered bodies were measured by the Archimedes method. Phase content analyses for the sintered bodies were performed using an X-ray diffraction (XRD, Rigaku D/MAX2 500) and microstructures were observed using a scanning electron microscope (SEM, Hitachi S4100). The mean grain size of each sample was obtained from the observation of the SEM micrographs by the line intercept method using several different images. In order to measure the electrical properties, the samples were coated with silver paste on both sides, 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 silicone oil for 15 min. The piezoelectric properties were calculated from the standard resonance measurement method.[20] The Curie point was observed 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 fmish 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 $V_p = f_0 \times \lambda$, where f_0 is center frequency and λ is the wavelength. The experimental k^2 was obtained from the equation:[21]

$$k^2 = \left(\frac{\pi}{4N}\cdot\frac{G_a}{B}\right)_{f=f_0},$$

where N is the number of IDT fingers, and G_a and B are radiation resistance and susceptance, respectively. The temperature coefficient of resonant frequency, TCF, was determined from measurements of the shift of center frequency at temperature from 25 to 80 °C, using the following equation

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

3. Results and discussion

3.1. XRD analysis and microstructure

Fig. 1 shows the bulk density as a function of the amount of Cd content. The density decreased slightly

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

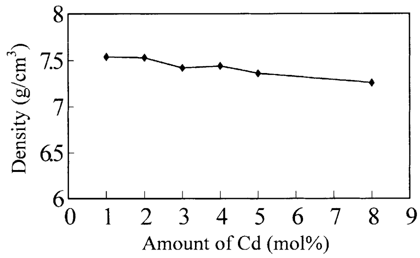

Fig. 1. Dependence of the bulk density on the amount of Cd content.

with increasing Cd substitutions. The X-ray diffraction patterns of $(Pb_{0.85-x}Cd_xSm_{0.1})(Ti_{0.98}Mn_{0.02})O_3$ ceramics are shown in Fig. 2, in which the Pb is systematically substituted for Cd on the A-site. The X-ray analyses indicated that the $PbTiO_3$ and Cd-doped $PbTiO_3$ ceramics have major peaks at (101), and all of them correspond to the tetragonal phase of the perovskite-like structure. There is no obvious difference of X-ray diffraction patterns between $PbTiO_3$ and Cd-doped $PbTiO_3$ samples. In addition, the porosity ratios of the samples are about 3%. The SEM images of Sm-modified $PbTiO_3$ ceramics doped and undoped with Cd are shown in Fig. 3. The Cd-doped and undoped samples were sintered at 1150 and 1200 °C, respectively. It shows that the samples are very dense, and grain size of the Cd = 2 mol% doped sample sintered at 1150 °C is similar to that of undoped sample sintered at 1200 °C. Fig. 4 shows the dependence of grain size on the Cd content. The Cd dopant was found to increase the grain growth correspondingly. According to Ref. 8, we assumed that the grains have grown and become more uniform by the liquid-phase sintering.

3.2. Dielectric and piezoelectric properties

The dielectric and piezoelectric properties of our samples are shown in Table 2. The experimental results show that, at room temperature, the dielectric constant increases slightly with the Cd content. The loss factors of all samples changed little and are smaller than 9×10^{-3}. The results of the thickness coupling factors (k_t) indicate that k_t value increases at first and reaches the maximum value of 0.562 at Cd = 3 mol% as the Cd additive increases. It is obvious that k_t values for $x = 0.02$–0.04 are larger than 0.55. The k_p value is about 0.04–0.05 as Cd content changed. The thickness frequency constant (N_t) and planar frequency constant (N_p) of the studied samples changed little as Cd content increases and their values are about 2050 and 2750 Hz m, respectively.

Fig. 5 shows the dielectric constant as a function of temperature measured at 1 kHz for $x = 0.02$, 0.04 and 0.08. The Curie–Weiss behavior in the curves is well observed for all samples. The Curie point (T_c) reduces from 330 °C ($x = 0.02$) to 295 °C ($x = 0.08$) by doping with up to 8 mol% Cd, and the peak value of dielectric constant decrease and the peak width increase with the increasing Cd content. Other researchers have reported similar results for increase of peak width with increasing

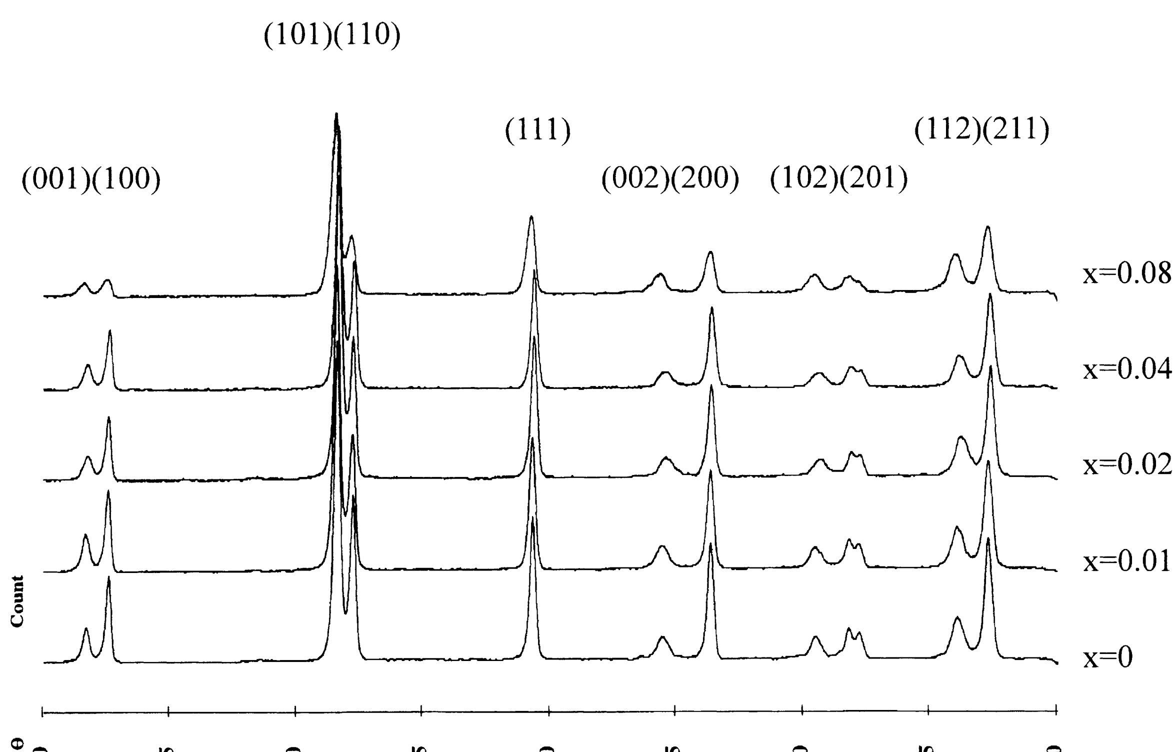

Fig. 2. The XRD patterns of $(Pb_{0.85-x}Cd_xSm_{0.1})(Ti_{0.98}Mn_{0.02})O_3$ samples.

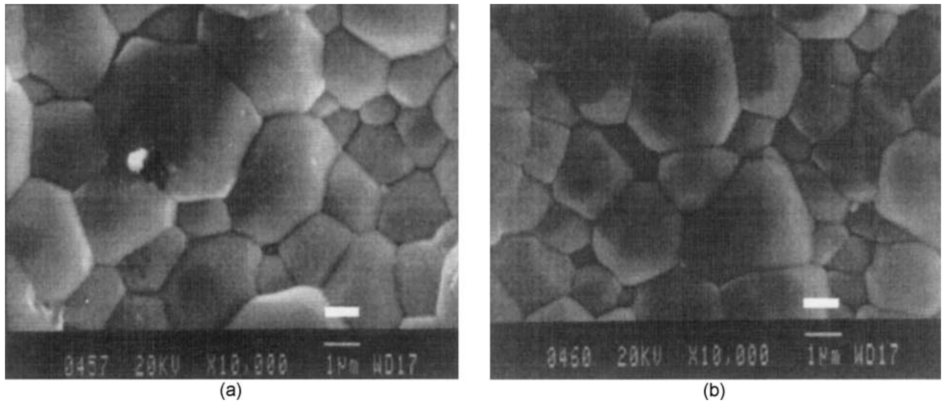

Fig. 3. SEM photographs of (a) $(Pb_{0.85}Sm_{0.1})(Ti_{0.98}Mn_{0.02})O_3$ (sintered at 1200 °C for 2 h) and (b) Cd = 2 mol% (sintered at 1150 °C for 2 h).

La content.[22] The inset of Fig. 5 shows the effect of Cd content on the temperature of the maximum permittivity. It indicates a linear decrease in T_c at the rate of 6 °C per mol% as the Cd amount increases.

3.3. Surface acoustic wave properties

Fig. 6 shows the frequency response of the SAW device as Cd = 0.08 with impedance matching. The center frequency is 32.99 MHz and it leads to a phase velocity of 2639 m/s; the insertion loss is about 14.33 dB. The phase velocity as a function of the amount of Cd content is shown in Fig. 7. It shows that the phase velocity increases with the increasing Cd additives from 2551 to 2639 m/s. The phase velocities of our samples are higher than the commercial Pb-based ceramics shown in Table 3 and are potentially good material for high-frequency applications. Fig. 8 shows the electromechanical coupling coefficient (k^2) of the SAW devices

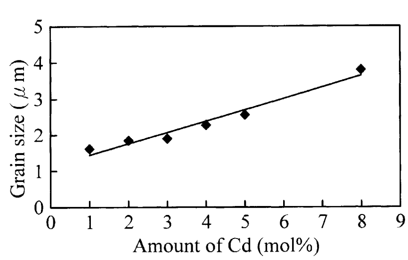

Fig. 4. Dependence of the grain size on the amount of Cd content.

Table 2
The dielectric and piezoelectric properties of bulk samples

x	ε_r	tan δ	k_t	k_p	N_t (Hz m)	N_p (Hz m)
0.01	212	9×10^{-3}	0.54	0.042	2091	2757
0.02	221	8×10^{-3}	0.557	0.036	2056	2762
0.03	220	7×10^{-3}	0.562	0.041	2003	2736
0.04	222	8×10^{-3}	0.55	0.044	2037	2750
0.05	218	7.5×10^{-3}	0.544	0.047	2068	2788
0.08	226	8×10^{-3}	0.532	0.048	2069	2816

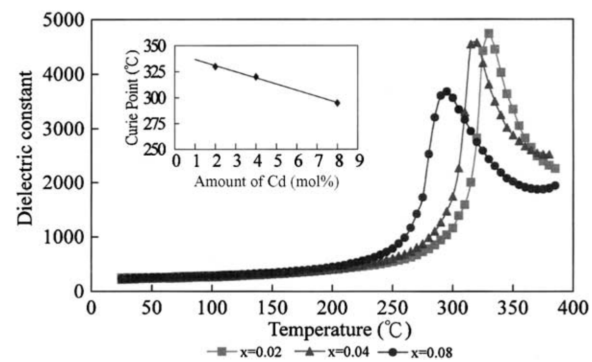

Fig. 5. Dielectric constant of $(Pb_{0.85-x}Cd_xSm_{0.1})(Ti_{0.98}Mn_{0.02})O_3$ as a function of temperature at 1 kHz for $x = 0.02$, 0.04 and 0.08. Inset shows effect of Cd content on the Curie point.

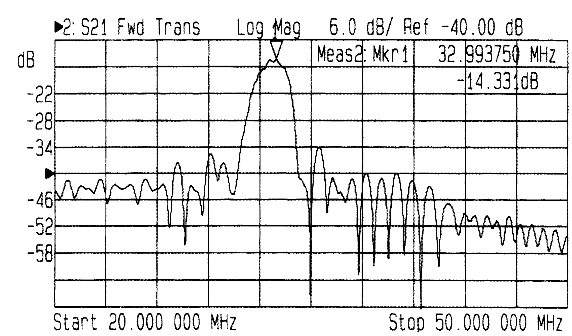

Fig. 6. Frequency response of the SAW device for $x = 0.08$ with impedance matching.

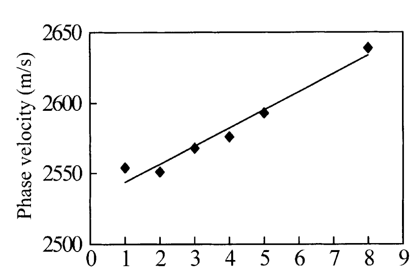

Fig. 7. Dependence of the phase velocity on the amount of Cd content.

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	13
(Pb,$Cd_{0.04}$,Sm)(Ti,Mn)O_3	2576	*3.05*	−14.5	Our sample
(Pb,$Cd_{0.08}$,Sm)(Ti,Mn)O_3	*2639*	2.41	−14.3	Our sample

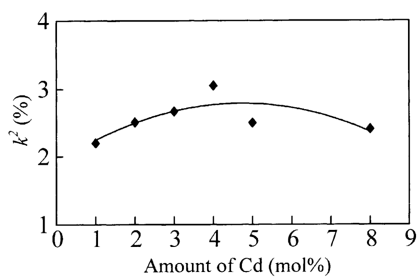

Fig. 8. Dependence of the electromechanical coupling coefficient on the amount of Cd content.

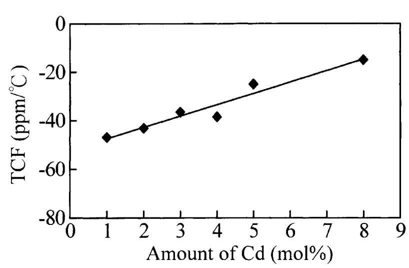

Fig. 9. Dependence of the temperature coefficient of frequency on the amount of Cd content.

versus the amount of Cd additives. The k^2 value increases at first and reaches the maximum value of 3.05% as Cd = 4 mol%, and then decreases again. Fig. 9 shows the temperature coefficient of frequency (TCF) of the SAW device as a function of Cd additives. As expected, it is obvious that, the Cd-doped piezoelectric substrates have negative TCF values, and its absolute values decrease correspondingly with the increasing Cd content. In other words, the Cd content improve the temperature coefficient of frequency of the SAW devices from −47 to −15 ppm/°C.

4. Conclusions

Generally speaking, the sintering temperature of Sm-modified $PbTiO_3$ ceramic is about 1250 °C using powders issued from conventional oxide-mixed method. Addition of Cd lowers the sintering temperature to 1150 °C and consequently reduces Pb volatilization. The addition of Cd cannot only effectively reduce the sintering temperature but also keep good piezoelectric and dielectric properties of the Sm-modified $PbTiO_3$ ceramics. Also, the measured thickness electromechanical coupling coefficients, k_t, are larger than 0.55 for Cd = 2–14 mol%.

According to the experimental results, Cd additives are helpful improving the temperature coefficient of frequency of the SAW devices and increasing the phase velocity and electromechanical coupling coefficient, whereas the propagation losses of our devices are about 14–15 dB. The Cd = 8 mol% doped sample showed the following data: $\rho = 7.26$ g/cm^3, $V_p = 2639$ m/s, $k^2 = 2.41\%$ and TCF = −15.1 ppm/°C. The Cd-doped modified lead titanate ceramics have high electromechanical coupling coefficient and small temperature coefficient of frequency that make them suitable for broad-band SAW filter and SAW gas sensor applications.

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