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Synthesis and electrical studies of modified $PbTiO_3$ ceramics: $(Pb_{1-x}Ca_x)(Mn_{0\cdot05}W_{0\cdot05}Ti_{0\cdot90})O_3$

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Abstract. Modified ceramics $(Pb_{1-x}Ca_x)[(Mn_{0\cdot5}W_{0\cdot5})_{0\cdot10}Ti_{0\cdot90}]O_3$ have been fabricated for $x = 0$, 0·05, 0·10 and 0·15 by high temperature solid state reaction technique. XRD, SEM, DTA and electrical studies of the sample with $x = 0\cdot10$ have been performed. These studies show that the sample is homogeneous single phase perovskite type with tetragonal structure. The phase transition occurs at 330°C. Electrical behaviour of other samples have also been investigated as a function of frequency (1 kHz to 1 MHz) and temperature (26°C to 300°C). The samples with $x = 0\cdot05$ and 0·10 have low loss, low dielectric constant, and show negligible pyroelectric effect. The sample with $x = 0\cdot15$ has minimum values of ε and loss which are temperature independent up to about 200°C. It also shows good pyroelectric behaviour. Hence it may be of use in pyroelectric infrared sensors.

Keywords. Ferroelectrics; dielectric constant; pyroelectric coefficient.

1. Introduction

Lead titanate, $PbTiO_3$, in a number of modified forms, has dominated the field of low permittivity dielectrics since the discovery of its ferroelectric properties. $PbTiO_3$ has high Curie temperature (T_C) and low dielectric constant (ε) and has shown great promise as a stable material for device applications. In recent years several attempts have been made by various groups to develop new $PbTiO_3$ compositions with improved electrical properties (Yamashita *et al* 1981; Ichinose *et al* 1985; Deb 1988; Ichinose 1988; Mendiola *et al* 1989; Nadoliisky 1991; Sati and Prasad 1992; Prasad *et al* 1993). Ichinose *et al* (1985) investigated ceramics $(Pb_{1-x}Ca_x)[(Co_{0\cdot5}W_{0\cdot5})_{0\cdot04}Ti_{0\cdot96}]O_3$ obtained from modification of $PbTiO_3$ by partial substitutions of Pb with Ca, and Ti with Co as well as W. He studied this ceramic series for different values of x(0·04, 0·12, 0·18, 0·24, 0·28) and found that their structure is perovskite type tetragonal one. Their dielectric constants were in the range of 200 whereas the dielectric losses were of the order of 10^{-2}.

With the aim of getting suitable materials for device applications we have further studied such ceramics by replacing Co with Mn (Sati and Prasad 1992; Prasad *et al* 1993). Accordingly, in the present work, we report the synthesis and X-ray, SEM, DTA, dielectric and pyroelectric studies of the ceramic $(Pb_{1-x}Ca_x)[(Mn_{0\cdot5}W_{0\cdot5})_{0\cdot10}Ti_{0\cdot90}]O_3$ for $x = 0\cdot10$. For better understanding of electrical behaviour of these calcium modified $PbTiO_3$ materials we have also studied the dielectric and pyroelectric properties of the present system for $x = 0$, 0·05 and 0·15.

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2. Experimental procedure

Modified ceramics $(Pb_{1-x}Ca_x)[(Mn_{0.5}W_{0.5})_{0.10}Ti_{0.90}]O_3$ with $x = 0$, 0·05, 0·10 and 0·15 were prepared using high temperature solid state reaction technique. The constituent chemicals (AR grade), namely PbO, CaO, $MnCO_3$, WO_3 and TiO_2, were mixed in stoichiometric proportions and ground thoroughly for about 2 h. The materials were then heated at 980°C for 1 h in an alumina crucible. The preheated materials were ground again and then heated for another 4 h at 980°C. The calcined materials were reground and pressed into circular discs using polyvinyl alcohol as binder under a pressure of 6×10^7 kg m^{-2}. These pressed discs were sintered at 1050°C for 90 min.

The XRD scan was obtained with a Philips (PW 1710 – Holland) diffractometer using nickel filtered CuK_α radiation ($\lambda = 1.5418$ Å) in 2θ range from 10° to 70° at 2θ scanning rate of 2°/min. The surface morphology of the ceramic ($x = 0.10$) was examined using a Cambridge Stereoscan (S-180) scanning electron microscope. The density of these discs was determined by the Archimedes method.

Differential thermal analysis (DTA) was carried out on a self-recording differential thermal analyser of Stantan Red-Croft (STA-625 series) in air atmosphere from room temperature to 400°C at a heating rate of 10°C/min. Fired (at 400°C) silver paint was applied on both faces of pellets to serve as electrodes for dielectric measurements. The dielectric constant (ε) and corresponding loss factor ($\tan\delta$) of the specimens were measured as a function of frequency (1 kHz to 1 MHz) and temperature (26°C to 300°C) using LCR Hi-Tester (HIOKI 3530-Japan) and also with GR 1620 AP capacitance measuring assembly (USA). The results obtained by these two equipments were within 0·5% of each other. The pyroelectric current of the specimens were measured using direct measurement technique (Bayer and Roundy 1972) keeping the rate of change of temperature equal to 2°C/min for the unpoled samples.

3. Results and discussion

The XRD pattern (figure 1) analysis indicated that the specimen was of single phase tetragonal perovskite type structure. The lattice parameters were estimated using a

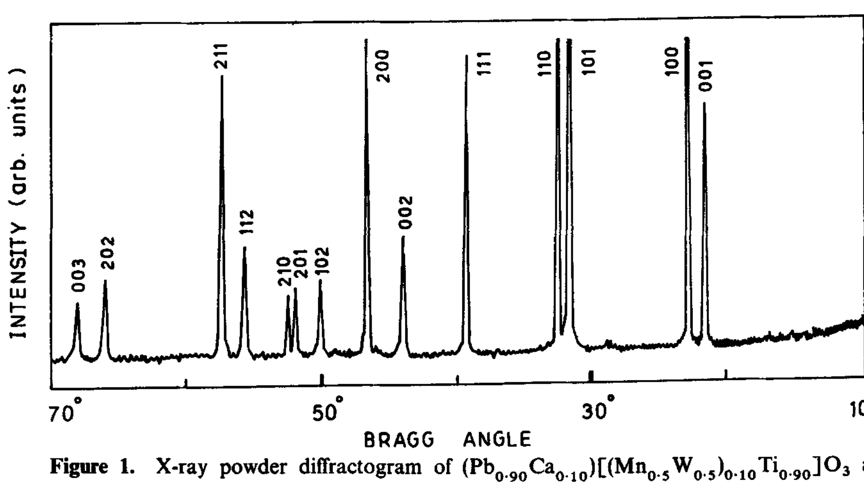

Figure 1. X-ray powder diffractogram of $(Pb_{0.90}Ca_{0.10})[(Mn_{0.5}W_{0.5})_{0.10}Ti_{0.90}]O_3$ at room temperature.

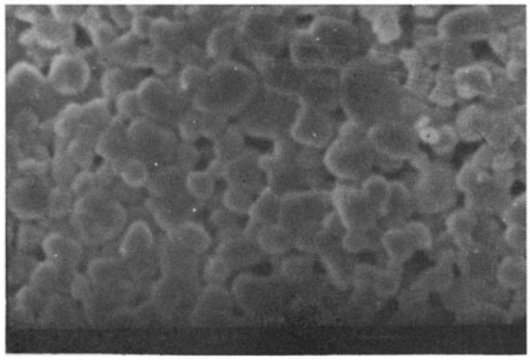

Figure 2. Scanning electron micrograph of $(Pb_{0.90}Ca_{0.10})[(Mn_{0.5}W_{0.5})_{0.10}Ti_{0.90}]O_3$ at room temperature.

standard least-squares refinement method using 14 (widely spread in θ) reflections of the powder diffraction profile, and are found to be $a = b = 3{\cdot}9001$ Å, $c = 4{\cdot}1190$ Å and tetragonal axial ratio $c/a = 1{\cdot}0535$. It is observed that the tetragonal axial ratio is smaller than 1·063, the value for pure $PbTiO_3$. This is in agreement with previous findings (Yamashita *et al* 1981; Prasad *et al* 1993). Single and sharp peaks of all the reflections clearly suggest the single phase nature of the compound. A good agreement between the calculated and observed *d* (interplanar spacing) values suggest that the lattice parameters reported above are correct.

The SEM at 3 μm magnification is shown in figure 2. The black regions represent low intensity of secondary electrons and white regions, the high intensity. The photograph suggests that the density of the material is quite good and all the particles are uniformly and homogeneously distributed. The experimentally determined density is also found to be 93% of the theoretical density. Grain size as obtained from SEM analysis is 2·8 μm.

The frequency dependence of ε and $\tan\delta$ (at 26°C) for $x = 0{\cdot}10$ is shown in figure 3. At low frequencies, both ε and $\tan\delta$ decrease with increase in frequency, and beyond 10^4 Hz both seem to be almost frequency independent. The temperature variation of ε and $\tan\delta$ (at 10 kHz) is shown in figure 4. As is typical of normal ferroelectrics, ε increases gradually with temperature below Curie temperature (T_C).

DTA was applied to detect the ferroelectric phase transition (T_C). For many materials DTA thermogram has been found not to be very sensitive for precise detection of the specific heat anomaly of ferroelectric phase transition (Bierlein and Sleight 1975; Pradhan and Choudhary 1987). The present system also seems to fall in this category (figure 5). However, we estimate the transition temperature for the present sample to be 330°C, observing a small anomaly (endothermic peak) in the thermogram.

We have further investigated ε and $\tan\delta$ as functions of frequency and temperature for $x = 0{\cdot}05$ and 0·15. This gives the effect of Ca content on ε and $\tan\delta$. Figures 3 and 4 show, respectively, the frequency (at 26°C) and temperature (at 10 kHz) dependence of ε and $\tan\delta$ for different x values. The curves have similar nature for different x. We see that as the percentage of Ca increases from 5 to 15 both ε and $\tan\delta$ decrease. These figures also show the behaviour of ε and $\tan\delta$ for $x = 0$, as determined by us, for the sake of comparison. All compositions ($x = 0{\cdot}05$, 0·10 and 0·15) have small ε and $\tan\delta$ values (figure 3). The minimum values of ε and $\tan\delta$, at 1 kHz and room

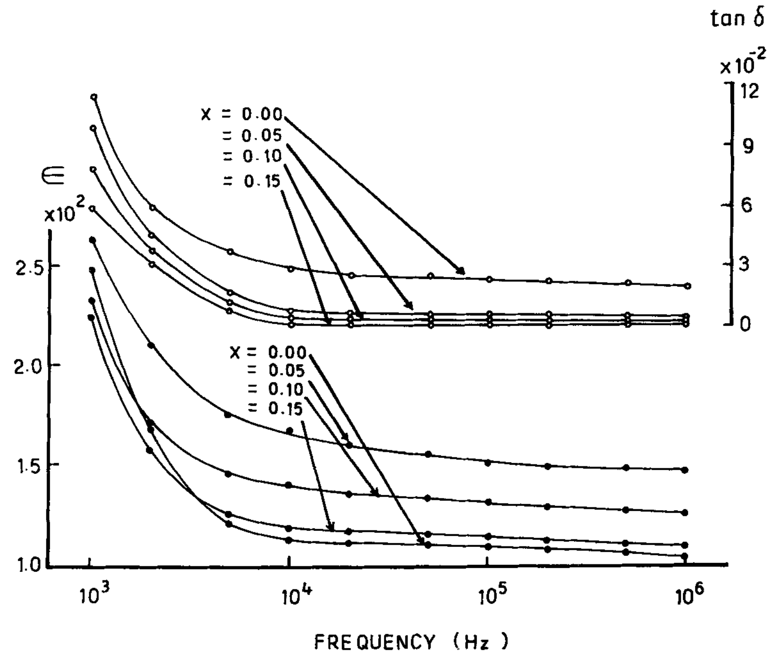

Figure 3. Frequency dependence of ε and $\tan\delta$ of $(Pb_{1-x}Ca_x)[(Mn_{0.5}W_{0.5})_{0.10}Ti_{0.90}]O_3$ at 26°C.

temperature, are 224·16 and $5{\cdot}88 \times 10^{-2}$, respectively. These minimum values occur for $x = 0{\cdot}15$ (figure 3).

Prasad *et al* (1993) investigated the electrical properties of Ca-modified $PbTiO_3$ ceramic $Pb_{1-x}Ca_xMn_{0.025}W_{0.025}Ti_{0.95}O_3$ for $x = 0{\cdot}05$, 0·15 and 0·30. Mendiola *et al* (1989) investigated the thermal behaviour of ε for the Ca-modified lead titanate $Pb_{1-x}Ca_x[Co_{0.5}W_{0.5}]_{0.04}Ti_{0.96}O_3$ for $x = 0{\cdot}24$, 0·30, 0·35 and 0·40 respectively, and Ichinose (1988) investigated it for x from 0·05 to 0·30.

The present results along with those of Prasad *et al* (1993), Mendiola *et al* (1989) and Ichinose (1988) clearly show that as the percentage of Ca increases up to about 20 ($x = 0{\cdot}20$) ε continues to decrease but increases thereafter with increase of Ca. On the other hand, the loss ($\tan\delta$) does not show any systematic dependence on Ca percentage. However, $\tan\delta$ is always small, of the order of 10^{-2}, which is of importance and is desirable for device applications. The dielectric loss in the material may be due to a scattering mechanism in which the scattering cross-section depends on the grain size and inter-grain spaces (Prasad *et al* 1993).

We find (figure 4) that ε and $\tan\delta$ for all the three compositions are temperature independent well beyond room temperature. For $x = 0{\cdot}15$ these are temperature independent up to 200°C. The findings of Prasad *et al* (1993) and Mendiola *et al* (1989) about thermal behaviour of ε for different x clearly demonstrate that as the percentage of Ca in the modified $PbTiO_3$ ceramics is increased the ferroelectric phase transition temperature (T_C) decreased.

Ueda (1972), while investigating the effects of modification of $PbTiO_3$ with BiO_3, MnO_2 and WO_3, found ε to be temperature independent over a large range (up to ≈ 300°C) with sharp transition peaks. Mendiola *et al* (1989) also found that the range

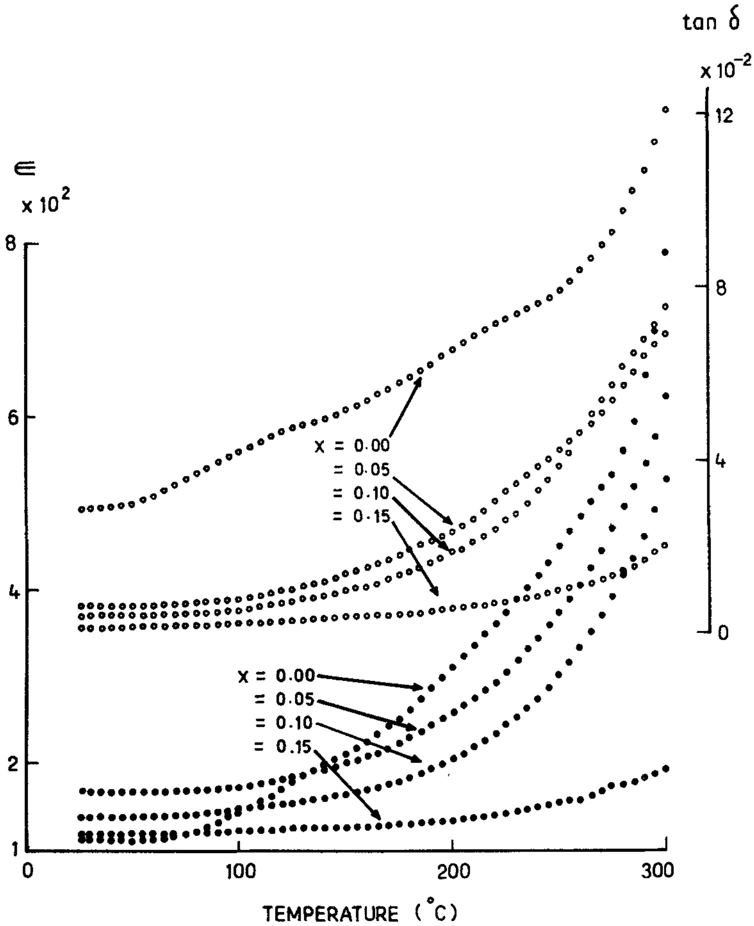

Figure 4. Temperature dependence of ε and $\tan\delta$ of $(Pb_{1-x}Ca_x)[(Mn_{0.5}W_{0.5})_{0.10}Ti_{0.90}]O_3$ at 10 kHz.

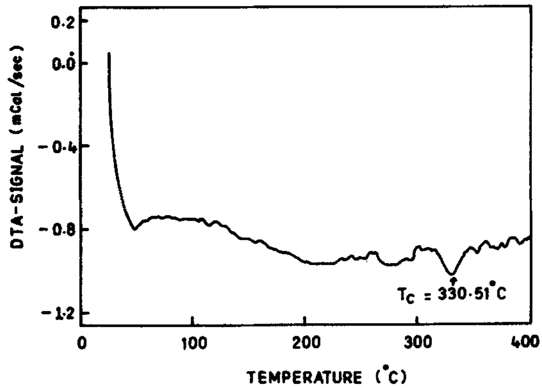

Figure 5. DTA thermogram of $(Pb_{0.90}Ca_{0.10})[(Mn_{0.5}W_{0.5})_{0.10}Ti_{0.90}]O_3$.

over which ε is temperature independent increases as the diffuseness of the peaks decreases.

Thus, the almost temperature independent dielectric behaviour in the range 25–300°C of the present sample for $x = 0.15$ may imply that the transition peak for this sample will be less diffuse compared to those for $x = 0.05$ and 0.10. The diffuseness in the transition peaks is a result of heterogeneities produced due to disorder caused by the introduction of Ca at Pb site.

The grain size in modified $PbTiO_3$ ceramics is the main factor which influences its electrical properties. The grain size is determined by the type and contents of the modifications. The small values of $\tan\delta$ and low ε may be due to diminishing stress between grains and large binding force at grain boundaries (Ueda 1972). It also seems that $\tan\delta$ is not sensitive to these factors whereas ε is. The decrease in ε up to $x \approx 0.20$ and its increase thereafter may imply that as x increases up to about 0.20, the stress between the grains diminishes and the binding force at the grain boundaries increases, and for x greater than 0.20 these trends reverse.

In addition, present ceramic with $x = 0.15$ also shows pyroelectric properties even without poling (pyroelectric coefficient $\Gamma = 0.96 \times 10^{-9}$ C/cm^2/°C). This Γ is found to be temperature independent from room temperature (26°C) up to 80°C. The samples with $x = 0.05$ and 0.10 did not show any detectable pyroelectric current. Thus, the ceramic $Pb_{0.85}Ca_{0.15}Mn_{0.05}W_{0.05}Ti_{0.90}O_3$ can be promising for device applications, specially for pyroelectric infrared sensors. The detailed pyroelectric investigations are under progress.

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