On the structural and electrical properties of modified PbTiO_3 ceramics[†]

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Abstract. Ceramics $(\text{Pb}_{0.75}\text{Ca}_{0.25})[(\text{Ni}_{1/2}\text{W}_{1/2})_y\text{Ti}_{1-y}]\text{O}_3$ for $y = 0.05, 0.10, 0.15$ and 0.30 have been prepared using high temperature solid state reaction method. X-ray analyses show that these materials are of single-phase perovskite type tetragonal structure. To solve inaccuracy in finding para-ferroelectric phase transition temperature $T_c(\epsilon_{\max})$, we have carried out the analyses of the data using a computer program. The role of Ni and W as modifiers on structural and electrical (dielectric and pyroelectric) properties is discussed in terms of the usefulness of these materials. Results indicate that ceramic $\text{Pb}_{0.75}\text{Ca}_{0.25}\text{Ni}_{0.025}\text{W}_{0.025}\text{Ti}_{0.95}\text{O}_3$ is a good candidate for pyroelectric applications.

Keywords. Ferroelectrics; dielectric constant; pyroelectric coefficient; diffuse phase transition; lead titanate ceramics.

1. Introduction

Pyroelectric infrared sensor has the advantage of wavelength independent sensitivity at room temperature operation. Thus it is expected to provide various thermal detectors for the object at near room temperature which can find their use in various fields such as industrial robots, diagnosis, environmental observation, etc. Lead titanate (PbTiO_3 ; ABO_3 type) is a suitable material for pyroelectric infrared sensor, because it has a large pyroelectric coefficient, γ and small dielectric constant, ϵ . Therefore it has a large figure of merit. PbTiO_3 has also small temperature coefficient of ϵ and γ over a considerable range of working temperature because of its high Curie temperature T_c .

$(\text{Pb}_{1-x}\text{Ca}_x)[(\text{M}_{1/2}\text{W}_{1/2})_y\text{Ti}_{1-y}]\text{O}_3$ ceramics, prepared by replacing a part of Pb^{2+} by Ca^{2+} and Ti^{4+} by $\text{M}(\equiv \text{Co}^{2+}$ (Ichinose 1985; Mendiola *et al* 1989; Nadoliisky *et al* 1991), Mn^{2+} (Prasad *et al* 1993a, b, 1994a) or Ni^{2+} (Prasad *et al* 1994b, 1995b)) and W^{6+} from PbTiO_3 , is expected to be an excellent pyroelectric material because it is possible to control its T_c by changing the concentration of the substituents at Pb or Ti sites.

The phase transition of ferroelectric ceramics is smeared as a consequence of chemical composition, microstructure and sintering processes. The transition region extends over some tens of degrees around the temperature of maximum $\epsilon(\epsilon_{\max})$. The electrical polarization, P_r , is continuously decreasing with temperature and it is difficult to determine, with accuracy, the temperature for $P_r = 0$.

In classical perovskite type ferroelectrics, the anomalies which take place at a ferro-paraelectric phase transition are generally described by the susceptibility, χ , and the

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order parameter, P , by the expression:

$$\chi_{ij}^{-1} = \chi_0^{-1} + \sum g_{ijkl} P_k P_l. \quad (1)$$

The coupling constant g_{ijkl} describes the breaking of symmetry by the phase transition (Krisch *et al* 1986; Jimenez *et al* 1987).

However, there is a set of anomalies in the behaviour of some perovskite type ferroelectrics with a diffuse phase transition (DPT) which are difficult to explain on the basis of classical theories of ferroelectrics (Jimenez *et al* 1987). Above the transition temperature, parameters such as refractive index (Burns and Dacol 1985), specific heat (Fouskova *et al* 1981), thermal expansion (Kirsch *et al* 1986), etc deviate from their normal behaviour in a temperature interval of some tens of degrees above T_c . These anomalies have been explained by Burns and Dacol (1985) assuming the existence of local polarization which disappears at temperature much higher than T_c .

The maxima of dielectric constant in DPTs are not well defined. It is thus experimentally difficult to know, with accuracy, the temperature of the ferro-paraelectric phase transition, T_c . In the paraelectric phase, dielectric constant behaves as;

$$\varepsilon^{-1} = \varepsilon_{\max}^{-1} + A(T - T_c)^\Gamma, \quad (2)$$

where Γ is the diffusivity parameter—a measure of broadness in DPT, varies between 1. normal Curie-Weiss type and 2. typical diffuse transition type (Kuwata *et al* 1982; Alemany *et al* 1987) and A is a constant.

In this report we have studied the role of Ni and W as a modifier on structural and electrical (dielectric and pyroelectric) properties of $(\text{Pb}_{0.75}\text{Ca}_{0.25})[(\text{Ni}_{1/2}\text{W}_{1/2})_y\text{Ti}_{1-y}]\text{O}_3$ ceramics for $y = 0.05, 0.10, 0.15$ and 0.30 . Computer fitting has been done in order to obtain the value of T_c using $\varepsilon(T)$ data, which gives the best agreement between experimental and expression (2). Also, the experimental results of dielectric constant, in the present ceramics, has been discussed by means of Burns and Dacol's assumptions.

2. Experimental

The stoichiometric mixtures of $(\text{Pb}_{0.75}\text{Ca}_{0.25})[(\text{Ni}_{1/2}\text{W}_{1/2})_y\text{Ti}_{1-y}]\text{O}_3$ for $y = 0.05, 0.10, 0.15$ and 0.30 were prepared through the process shown in figure 1, starting from high purity (99.9%) oxides. The obtained material is dried and thermally treated at 1020°C for 4h. From these materials a set of thin pellets of 12.5 mm diameter and 1.5 mm height were prepared under isostatic pressure of $6 \times 10^7 \text{ Kg m}^{-2}$. Once pressed, the pellets were fired at 1100°C and times between 0.5 h to 4h. The synthesis process were monitored by XRD-technique.

For preliminary structural studies, X-ray diffractograms (XRD) were recorded at room temperature by X-ray diffractometer PHILIPS (PW 1710-Holland) using nickel filtered $\text{CuK}\alpha$ -radiation ($\lambda = 1.5418 \text{ \AA}$) at a scanning rate of $2^\circ(2\theta)/\text{min}$. The angular range 2θ covered was 10° – 70° . To measure ε and loss ($\tan\delta$) of the compounds, air drying silver paint was applied on both the large faces of the samples to serve as electrodes. Measurements of ε and $\tan\delta$ were carried out as a function of temperature (26°C – 300°C) with a.c. field of 10 KHz frequency using LCR Hi-Tester (HIOKI-Japan) and with GenRad 1620 AP Capacitance measuring assembly, USA. The temperature of

Figure 1. Flow chart for preparation of the materials.

the samples was varied at intervals of $2^\circ\text{C}/\text{min}$ using a furnace built for this purpose and a temperature controller (Indotherm 401D). The temperature was measured with a chromel-alumel thermocouple (accuracy $\pm 0.25\%$). To overcome the moisture effect on the electrical properties, the samples were preheated to 100°C to evaporate the moisture and then cooled to room temperature and then experiments were carried out. Differential scanning calorimeter (DSC) curve was obtained by a computer-controlled differential scanning calorimeter (Model DSC-4) of Perkin-Elmer, USA. The experiments were carried out between room temperature (26°C) to 450°C in nitrogen atmosphere at a heating rate of $20^\circ\text{C}/\text{min}$. Alumina crucibles were used in the experiment.

3. Fitting procedure

To solve the inaccuracy in finding T_c ($\epsilon_{\max}$) we first took T_c as the mean value of the temperature at the extrema (extended on a 10°C interval, where ϵ had an apparently constant value) of the interval and fitted to expression (2) by the method of least squares. Also, in order to optimize the regression coefficient R^2 between (2) and experimental data, we took values of T_c in a $\pm 4^\circ\text{C}$ interval around the previous mean value. The optimized results are shown in table 1.

Table 1. Statistical analysis for diffuse phase transition and some materials parameters.

y	c/a	ϵ_{RT}	ϵ_{max}	$\tan\delta$ ($\times 10^3$)	$T_c(^{\circ}C)$	Γ	No. of points	Regr. coeff. (R^2)
0.05	1.045	166	4751	3.0	253	1.21	59	0.9967
0.10	1.041	181	2987	3.8	241	1.28	80	0.9928
0.15	1.037	192	1648	5.0	233	1.43	84	0.9979
0.30	1.032	209	753	6.7	197	1.52	102	0.9987

Figure 2. Variation of densification (%) with sintering time (h) for $Pb_{0.75}Ca_{0.25}Ni_{0.025}W_{0.025}Ti_{0.95}O_3$ at $1100^{\circ}C$.

4. Results and discussion

Figure 2 shows the densification of the pellets as a function of sintering time for $Pb_{0.75}Ca_{0.25}Ni_{0.025}W_{0.025}Ti_{0.95}O_3$ ceramic. The first part of the isothermal curve (0.5 to 1.5h) can be explained on the basis of the consideration that the sintering mechanisms dominate the process and a recovery of densification is observed. For higher times a degradation of the ceramic takes place. 96% theoretical density is achieved for the ceramics sintered at $1100^{\circ}C$ for 1.5h. The sintered density decreases due to the evaporation of PbO as the sintering time increases.

All samples are found to have single phase perovskite-type tetragonal structure ($c/a < 1.063$) from the XRD analyses. Also, with the increment in Ni and W content, c/a decreases (table 1).

Figure 3 shows the temperature dependence of ϵ for the present ceramics. As typical of normal ferroelectrics, ϵ increases gradually with increment in temperature up to T_c and then decreases. A distinct deviation from Curie-Weiss law in paraelectric phase, can be observed in figures 3 and 4, and follows expression (2). To see if the transition has a diffusive character, computer fitting, to expression (2), has been done. We found $\Gamma > 1$ for all cases (table 1), which confirms the diffusive character of phase transition

Figure 3. Temperature variation of ϵ of $(\text{Pb}_{0.75}\text{Ca}_{0.25})[(\text{Ni}_{1/2}\text{W}_{1/2})_{1-y}\text{Ti}_{1-y}]\text{O}_3$ at 10 kHz.

(del Olmo *et al* 1987). This may be due to the presence of more than one cation in the sublattice, that should produce some kind of heterogeneities (Mendiola *et al* 1989; Prasad *et al* 1995a). The behaviour of ϵ with temperature above T_c may be due to the electrical conductivity of the materials that modifies the value of the capacitance as the temperature increases.

We find that with the increment in Ni and W content T_c decreases, ϵ_{RT} increases (inset figure 3) while dielectric peak ($\epsilon_{\max}$) decreases and shifts towards lower temperature side and $\epsilon-T$ curve flattens (figure 3). The decrease in $\epsilon_{\max}$ implies that the substitution of Ni and W ions reduces the dipole moment of the lattice and lowers the peak dielectric constant. Temperature coefficient of dielectric constant is defined as $T_{C\epsilon} = (\epsilon_T - \epsilon_{RT}) / \epsilon_{RT} \times 100$ (Halliyal *et al* 1987; Prasad *et al* 1995a). A very small variation in $T_{C\epsilon}$ with temperature has been found over a considerable range of working temperature which is very much desirable for pyroelectric application. $T_{C\epsilon}|_{100^\circ\text{C}} = 4.22\%$ has been found for $y = 0.05$ which is also clear from figure 3 that ϵ seems almost independent of temperature up to 100°C . In all the materials, $\tan\delta$ was found to be $\sim 10^{-2}$. The low $\tan\delta$ of this

Figure 4. Temperature variation of dielectric stiffness ($1/\epsilon$) and pyroelectric coefficient (γ) of $\text{Pb}_{0.75}\text{Ca}_{0.25}\text{Ni}_{0.025}\text{W}_{0.025}\text{Ti}_{0.95}\text{O}_3$.

Figure 5. Variation of T_c and ϵ_{RT} with axial ratio (c/a).

kind can be advantageous when improved detectivity is required. By taking reciprocal of ϵ (figure 4) the T_0 (Curie-Weiss point) temperature is extrapolated. It is found that $T_0 < T_c$ for all materials, which confirms the phase transition to be of the first order. Linear fitting of the results allow us to obtain the Curie-Weiss constant C . The value of C has been estimated to be $\sim 10^{50}\text{K}$ for the present specimens.

Assuming that the ferroelectricity in the present materials is only due to dipolar contribution, then we have

$$\epsilon = \frac{T - C}{T - T_c}, \quad (3)$$

where $C = 2N\mu^2/9\epsilon_0 k_B$, $T_c = N\mu^2/9\epsilon_0 k_B$, N is the number of molecules per unit volume, k_B the Boltzmann constant and μ the permanent dipole moment. Thus, as

$T \rightarrow T_C$, from (3) $\varepsilon \rightarrow \infty$. This divergence is called 'polarization catastrophe'. From this it follows that at $T < T_C$ there should be spontaneous polarization and material should be ferroelectric. Further, we have $C = 2T_C$. But experimental results show that $C \gg 2T_C$ and are of the order of 10^5 K. Hence, ferroelectricity in the present modified PbTiO_3 ceramics is not just be due to permanent dipole moments but significant contribution must come from relative displacement of all B–O ions in a cooperative manner (Harada *et al* 1970; Srivastava and Srinivasan 1991). This happens due to hybridization between the B (Ti 3d states) cation and O (2p states) that essentially weakens the short-range repulsions and allow the ferroelectric transition (Cohen 1992).

The relation between T_C and ε_{RT} with axial ratio (c/a) is shown in figure 5. The curve for T_C shows a positive slope. The results indicated the lowering of T_C and increase in ε_{RT} with the decrease of tetragonal distortion (Prasad *et al* 1995b). This can be explained on the basis that the delicate balance of short-range forces (favouring the non-polar cubic phase) and long-range Coulomb forces (favouring the ferroelectric state) makes the transition sensitive to defects (substitutions) that modify the short-range interactions and to carriers (e.g. photoelectrons) that screen the long-range field (Cohen 1992).

Pyroelectric currents in the unpoled state were measured using direct measurement technique (Bayer and Roundy 1972). Only the ceramic for $y = 0.05$ exhibited pyroelectric effect. The γ is found to be almost temperature independent from room temperature to 100°C (figure 4) which is essential for pyroelectric applications. The value of pyroelectric coefficient at room temperature has been found to be

$$\gamma_{\text{RT}} (= I_{\text{PE}}/A(dT/dt)) = 2.32 \times 10^{-9} \text{ C cm}^{-2} \text{ K}^{-1};$$

where I_{PE} and A are the pyroelectric current and surface area of the sample respectively. The appropriate 'figures of merit' for application of interest $F_1 (= \gamma/\rho C_p)$, $F_v (= \gamma/\rho C_p \varepsilon)$ and $F_D (= \gamma/\rho C_p \sqrt{\varepsilon \tan \delta})$, where C_p is specific heat (Prasad *et al* 1995b) were calculated. The values of which are, respectively, 9.10×10^{-10} , 3.98×10^{-12} and 4.74×10^{-10} . Reasonably high values of figures of merit make $\text{Pb}_{0.75}\text{Ca}_{0.25}\text{Ni}_{0.025}\text{W}_{0.025}\text{Ti}_{0.95}\text{O}_3$ ceramic promising for pyroelectric device applications. Moreover, these materials have reproducible properties, they are suitable for mass production and these oxide ceramics are easy to make in the form of thin specimens for efficient pyroelectric detection; and it may not be necessary to pole these materials after fabrication.

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