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Dielectric and Piezoelectric Behaviour of Spray Dried $\text{Pb}_{1-3x/2}\text{Sm}_x(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ Ceramic System

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Abstract: Powders of polycrystalline sample of PZT modified by Sm with composition $\text{Pb}_{1-3x/2}\text{Sm}_x(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ (PSZT) with $x = 0.0, 0.5, 1.5$ and 2.5 , ceramics were synthesized by spray drying technique. The DTA-TGA and XRD studies were used to characterize the compound synthesized. The powders were calcined at 800°C . The sample was crystallized into rhombohedral phase as revealed by XRD studies. The calcined samples were palletized and sintered at $900, 1000$ and 1100°C . SEM was used for microstructure evaluation which showed the spherical and homogeneous grains. The grain size increases with increase in sintering temperatures. The sintered pellets were electroded and cooled slowly for all their electrical measurements. The dielectric constant (ϵ) and tangent loss ($\tan\delta$) of the compound were studied at different temperatures at 10 kHz frequency and at room temperature with different frequencies. The PZT sample modified with $x = 1.5$ shows maximum ϵ -value. The electromechanical properties d_{33} and K_p were measured with these electroded samples after poling. The maximum values of d_{33} and K_p were found for the samples polled at 33 kV cm^{-1} .

Key words: Dielectric, piezoelectric, PZT, samarium, spray drying

INTRODUCTION

Perovskite oxide $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ (called PZT) have potential applications in non-volatile ferroelectric random access memories and its ferroelectric properties are of great importance for both device applications and fundamental studies^[1,2]. It is well known that PZT ceramics are widely used for a variety of applications because of their excellent electrical and electromechanical properties. These properties of PZT ceramics can be improved considerably by addition of certain trivalent and/or pentavalent impurity ions into the PZT lattice. A large number of studies have been carried out on PZT ceramics modified by trivalent ions, lanthanum^[3-6], which create A-site lattice vacancies and hence facilitate domain wall motion^[7].

It has also been reported that trivalent rare earths substitute for the Pb^{2+} site of PZT, maintaining the stoichiometry and also enhancing its properties^[5,8-10]. It has been reported that the effect of Sm^{3+} doping is similar to that of La^{3+} in lead zirconate titanate ceramics^[11]. Some of the dielectric and piezoelectric properties have been reported for few compositions of Sm^{3+} doped PZT (i.e., PSZT)^[12] and it was found that dielectric constant of these materials is lower than PLZT. However, the hydrostatic piezoelectric figure of merit, of PSZT is

considerably higher than that of PLZT^[13]. In spite of these studies meagre information is available regarding various dielectric and electromechanical parameters at different levels of Sm^{3+} doped PZT close to Morphotropic Phase Boundary (MPB). In the present investigation, we study the effect of Sm^{3+} addition to PZT at $\text{Zr}/\text{Ti} = 53/47$ ratio close to MPB on various dielectric and piezoelectric properties.

MATERIALS AND METHODS

Ceramic samples of $\text{Pb}_{1-3x/2}\text{Sm}_x(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ (PSZT) with $x=0.0, 0.5, 1.5$ and 2.5 were prepared by spray drying technique. The DTA-TGA records of these spray dried powders were done to know the decomposition pattern as well as solid state reaction characteristics leading to the formation of PZT solid solution. The spray dried nitrate powders were calcined at 800°C for 6 h. XRD pattern of $x=1.5$ powder sample was recorded using $\text{Co K}\alpha$ radiation at room temperature with scanning rate 2° per minute. The calcined powders were mixed thoroughly with 2% PVA binder and palletized into circular discs of diameter 10 mm using hydraulic press at a pressure of 150 MPa for 5 min. PVA binders were removed during sintering the pellets at 1100°C for 4 h. To prevent lead loss during sintering, lead rich atmosphere was established using PbZrO_3 powder.

The sintered pellets were polished to make both their faces parallel and electroded with high purity silver paste. In order to dry the paste pellets were kept in a furnace at 150°C for 2 h and cooled slowly for their electrical measurements such as dielectric constant (ϵ) and dielectric loss ($\tan\delta$). ' ϵ ' and ' $\tan\delta$ ' were measured at different frequencies and at temperatures. Microstructure of the freshly polished surfaces of sintered pellets with a thin layer of graphite coating were observed using SEM (JEOL JSM-840 model of M/s. JEOL Ltd. Japan). The electroded pellets (with silver paste) were poled in silicon oil bath at 100°C by applying a DC field of 30 kV cm⁻¹ for 15 min. Electromechanical parameters of individual pellets were measured using IRE standard^[14].

RESULTS AND DISCUSSION

Figure 1 shows XRD pattern of complex PSZT calcined at 800°C. The diffraction peaks of the powder samples are sharp and unsplit indicating good homogeneity and crystallization of the materials. The PSZT compound was crystallized in rhombohedral phase as determined by using observed d-values of strong, medium and low intensity reflections over a wide range of Bragg's angle.

The scanning electron micrographs of PSZT (x = 1.5) pellets sintered at 900, 1000 and 1100°C are shown in Fig. 2a-c. The grain size range of PSZT samples sintered

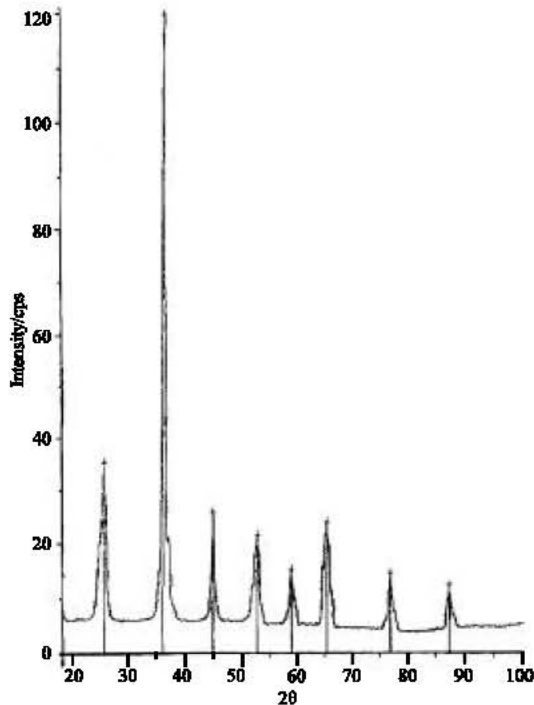


Fig. 1: XRD pattern of PSZT (53/47) modified with 1.5 atomic % of Sm³⁺ (Co K α) i.e. PSZT

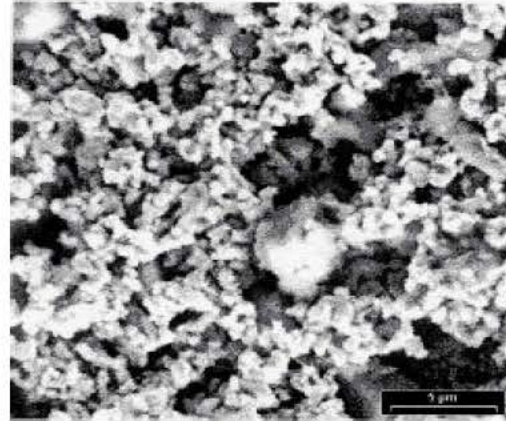


Fig. 2a: SEM of Pb (Zr_{0.53} Ti_{0.47}) O₃ modified with 1.5 atomic % of Sm₃₊ sintered at 900°C

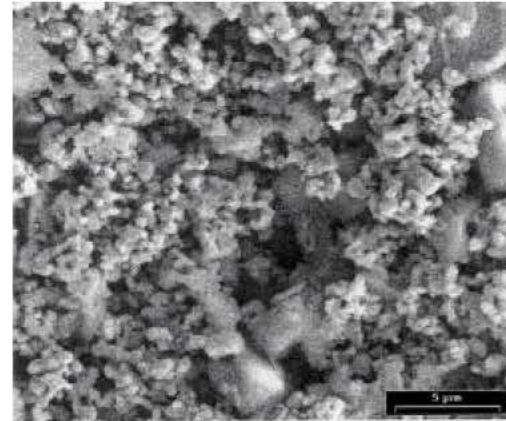


Fig. 2b: SEM of Pb (Zr_{0.53} Ti_{0.47}) O₃ modified with 1.5 atomic % of Sm₃₊ sintered at 1000°C

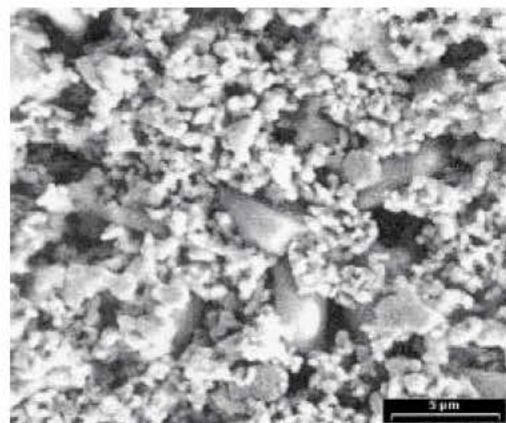


Fig. 2c: SEM of Pb (Zr_{0.53} Ti_{0.47}) O₃ modified with 1.5 atomic % of Sm₃₊ sintered at 1100°C

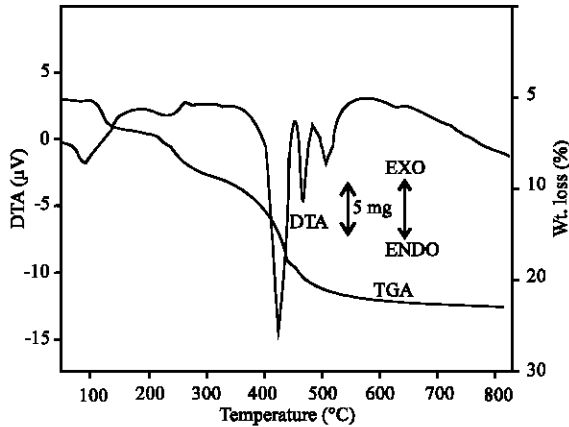


Fig. 3: DTA-TGA plots of PSZT (x=1.5)

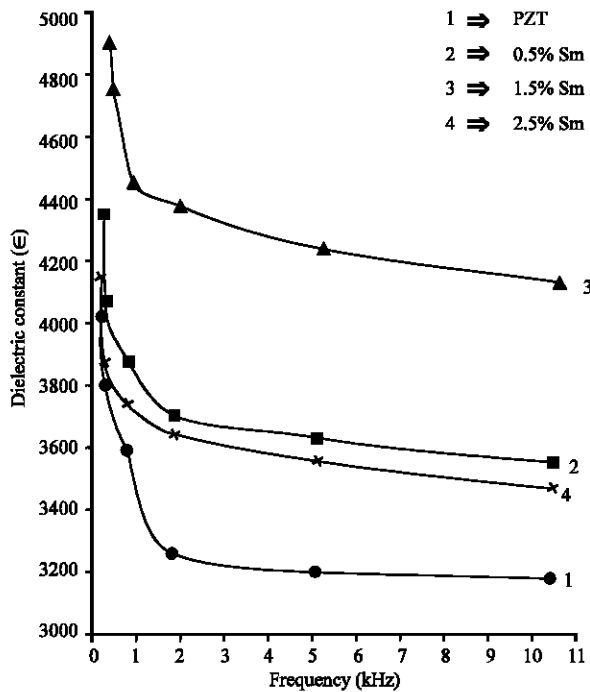


Fig. 4: Variation of dielectric constant (ϵ) of PSZT as a function of frequency

at 900, 1000 and 1100°C are 0.81-2.16, 0.83-2.17 and 0.84-2.21 μm , respectively. From Fig. 2, it is obvious that grains are spherical and uniform with a grain size range of 0.83-2.18 μm on average as measured by SEM. It is clear from data that grain size increases with increasing sintering temperatures and agglomeration of grains takes place beyond 1100°C.

Figure 3 shows the DTA- TGA plots of PSZT (x=1.5) power from room temperature to 800°C. The weight loss occurs in three steps and gets completed at $\sim 578^\circ\text{C}$ after which there is no weight loss as indicated by TGA curve (Fig. 3). In first stage loss, endothermic peaks observe at

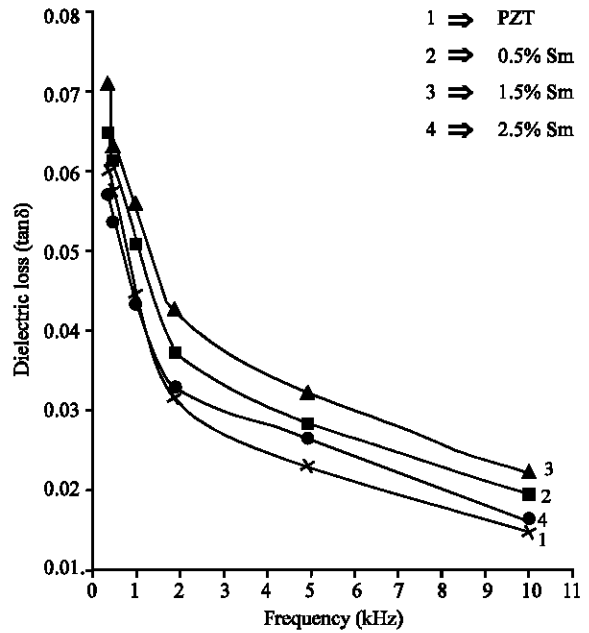


Fig. 5: Variation of dielectric loss ($\tan\delta$) of PSZT as a function of frequency

around 100°C in the DTA curve is due to the removal of water molecules as indicated by TGA curve. A small exothermic peak observe at around 250°C in second stage loss is due to result of simultaneous decomposition of both $\text{ZrO}(\text{NO}_3)_2$ and $\text{Ti}(\text{NO}_3)_4$. A third and final weight loss with three prominent endothermic peaks may be attributed to the multiple decomposition of $\text{Pb}(\text{NO}_3)_2$ [15].

From Fig. 4 and 5 it is clear that, both ' ϵ ' and ' $\tan\delta$ ' decrease with increase in frequency and becomes frequency independent at higher frequency regions exhibiting normal characteristics of ferroelectric materials. It is also observed that for all frequencies ' ϵ ' and ' $\tan\delta$ ' increase with increasing concentration level of Sm^{3+} upto 1.5 atomic % and then it starts decreasing for further increase in Sm^{3+} concentrations.

Figure 6 and 7 show variation of ' ϵ ' and ' $\tan\delta$ ' of PZT and PSZT, respectively as a function of temperatures at 10 kHz. Curie temperature for PZT (Fig. 3), found at $T_c=340^\circ\text{C}$, decreases to 280°C on addition of 0.5 atomic % of Sm^{3+} and the decrease gets reduced with further increase in Sm -concentrations upto 1.5 atomic %.

T_c is found to be 300 and 320°C for PZT modified with 1.5 atomic % and 2.5 atomic % of Sm^{3+} , respectively. It has also been observed that ' ϵ ' of PZT modified with 1.5 atomic % of Sm^{3+} increases by 3.63% in comparison to unmodified PZT. The $\tan\delta$ of PZT modified with 1.5 atomic % Sm^{3+} is 0.038 at $T_c=240^\circ\text{C}$ and that of pure PZT, 0.5 and 2.5 atomic % Sm^{3+} modified PZT is

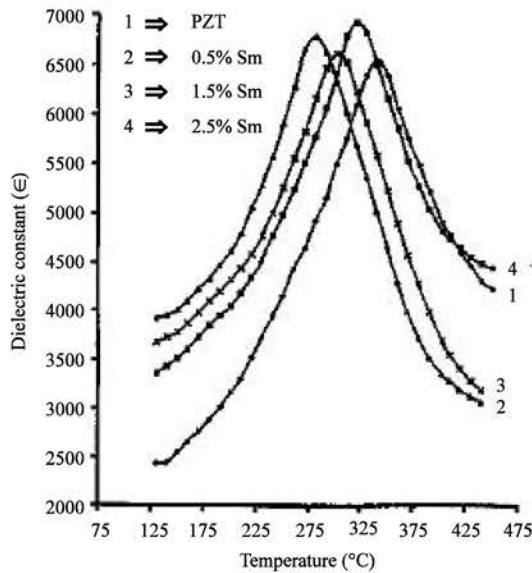


Fig. 6: Variation of dielectric constant (ϵ) of PSZT as a function of temperature

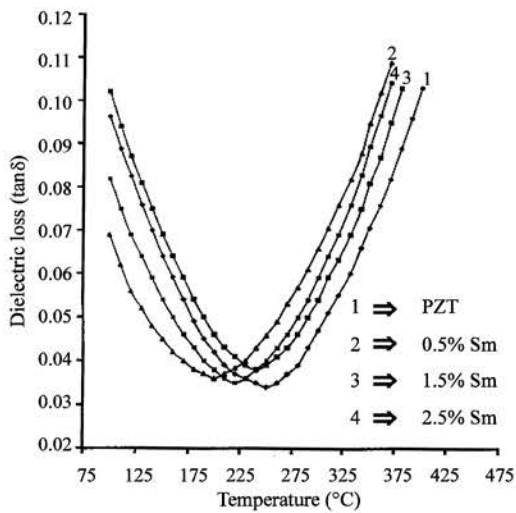


Fig. 7: Variation of dielectric loss ($\tan\delta$) of PSZT as a function of temperature

found to be 0.034, 0.036 and 0.035 at T_c of 250, 200 and 220°C, respectively. This increase or decrease in $\tan\delta$ is related with spontaneous, electronic, ionic, electronic-ionic relaxation polarisation. It is well known that tangent loss is minimum at a temperature, when time of relaxation of polarisation processes approximately coincides with the period of alternating field acting upon the dielectric. If the temperature is such that the relaxation time of polarisation processes considerably exceeds the half period of the applied field, then the thermal motion of the ferroelectric domain walls be less intensive and the

dielectric loss will decrease. If the temperature rises in such a way that the relaxation time of polarisation processes is considerably smaller than the half period of the applied field, the thermal motion of the ferroelectric domains grows and, hence the dielectric loss increases. In the case of PSZT, after certain temperature, relaxation time of polarisation process seems to become considerably smaller than the half period of the applied field and the thermal motion of the ferroelectric domains grows and hence the dielectric loss starts to increase upto that particular temperature where the relaxation time of polarisation process was greater than the half period of the applied field.

The piezoelectric strain co-efficient ' d_{33} ' and electromechanical coupling factor ' K_p ' of unmodified (or pure) PZT at 33 kV cm^{-1} are $163 \times 10^{-12} \text{ C/N}$ and 0.41, respectively. These values are found to be maximum for 1.5 atomic % Sm^{3+} doped PZT the values being $167 \times 10^{-12} \text{ C/N}$ and 0.48, respectively. Thus ' d_{33} ' of 1.5 atomic % Sm^{3+} doped PZT increases by 4.38% and its k_p increases by 17.07% in comparison to pure PZT. It is observed that the value of d_{33} increases with the increase in applied DC field and found to be maximum at 30 kV cm^{-1} . This is due to the fact that the mobility of ferroelectric domain wall increases with increase in DC field and polarisability comes to saturation point at 33 kV cm^{-1} .

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