

Mechanical and electrical properties of PZT ceramics (Zr:Ti = 0.40:0.60) related to Nd³⁺ Addition

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Abstract

Single phase lead zirconate titanate (PZT) of tetragonal structure (Zr:Ti = 0.40:0.60) was modified using a trivalent rare earth additive Nd₂O₃. The samples having composition Pb_{1-(3x/2)}Nd_x(Zr_{0.40}Ti_{0.60})O₃ was prepared by solid state route. The Nd content in the samples was varied from 0–4 mol %. The effect of Nd³⁺ additive on mechanical and electrical properties of PZT ceramics has been studied. It was observed that Nd addition results in enhancement of fracture toughness (K_{IC}) and Vicker's hardness (H_v) in the samples. Nd addition also results in substantial increase in dielectric constant and d_{33} piezo coefficient of PZT ceramics. The maximum value of K_{IC} obtained is 2.05 Mpa^{1/2}. Also the peak value of 680 for dielectric constant and a d_{33} of 240 pC N⁻¹ is obtained for the same composition. Both the mechanical and electrical properties seem to peak at 2% Nd³⁺ addition, which makes this composition attractive for actuator and other high power ultrasonic transducer applications. The increase in mechanical properties has been attributed the increased tetragonality (c/a ratio) and increase in sintered density with Nd addition. It seems that the ferroelastic domain switching is the main contributor to toughening in these ceramics. The increased tetragonality with Nd addition results in more work done in domain switching and, hence, enhanced toughness. The increase in electrical properties with Nd addition has been attributed to reduction in oxygen vacancies in the samples. The X-ray and the sintered density results also suggest that at 2 mol % Nd addition, Nd is reaching its solubility limit in PZT system. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: PZT ceramics; Nd³⁺; fracture toughness; Vicker's hardness

1. Introduction

Lead zirconate titanate (PZT) ceramics are commercially the most important piezoelectric materials because of their superior properties and also because of the ability of tailoring their properties, either by changing the composition or by doping them with different ions. PZT ceramics are known to be simultaneously ferroelectric–ferroelastic [1,2] materials. The mechanical properties of PZT ceramics are of considerable importance in the design of transducers and other piezoelectric devices. Many of the applications of these ceramics involve electrical or thermally induced stresses as well as mechanical loads induced due to vibrations that may result in mechanical failure and consequent

dielectric breakdown of the devices. Also, PZT ceramics are increasingly being used in load-bearing applications, such as actuators. Thus, understanding the mechanical properties of ferroelectric ceramics in general, and PZT in particular, have become important, as not only do they depend on general microstructural features such as grain size, porosity, and flaw size distribution as is the case for other ceramics but also on additional factors such as domain effect [3–5], poling field direction [6], internal stresses [7], crystallographic phases [8], and chemical stoichiometry [8–10]. Also, the study of the mechanical properties of electronic ceramics has received much less attention as compared to their electrical or other ‘active’ properties.

PZT occurs as a series of solid solutions of PbZrO₃ with PbTiO₃, and exists in various crystal structures [11]. It has been observed [8,12] that there is a substantial dependence of fracture toughness on the Zr/Ti ratio in the samples. The fracture toughness passes through a

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series of maxima and minima with a distinct minima in K_{IC} ($\approx 1.25 \text{ Mpa m}^{1/2}$) at the morphotropic phase boundary. As there is a need for enhancing the mechanical properties of PZT ceramics without compromising their piezoelectric properties, so we have studied the PZT composition in the tetragonal region modified with a trivalent additive (Nd). This paper reports the preparation and characterization of mechanical and electrical properties of Nd modified PZT. The study was done with a aim of obtaining PZT ceramic material with improved mechanical properties without much compromising on their piezoelectric properties.

1.1. Experimental procedure

Lead zirconate titanate with the composition $\text{Pb}_{1-(3x/2)}\text{Nd}_x(\text{Zr}_{0.40}\text{Ti}_{0.60})\text{O}_3$ were prepared. The Nd composition was chosen to be 0.01, 0.015, 0.02, 0.03, and 0.04. Also for comparison $\text{Pb}(\text{Zr}_{0.40}\text{Ti}_{0.60})\text{O}_3$ was also prepared. Our formulation was based on the assumption that Nd^{3+} predominantly goes to the A site (Pb^{2+}). Weighed amounts of PbO , ZrO_2 , TiO_2 (Aldrich), and Nd_2O_3 (Indian Rare Earth, Kerala) powders were mixed and wet ball-milled in triple distilled water using ZrO_2 balls in a poly-propylene jar for 5 h. The dried powder was crushed and calcined in a closed Al_2O_3 crucible at a temperature of 850°C for 2 h. The calcined powder was crushed in an agate mortar pestle and sieved using a 100-mesh sieve. This sieved powder was mixed with a 4 w/t % PVA solution to give 1 w/t % PVA as binder in the dried powder, and then pelletized

in a steel die into pellets of 12.5 mm ϕ and 3.5 mm height using a uniaxial pressure of $\approx 560 \text{ MPa}$. Binder removal was carried out by heating the pellets to 600°C and holding there for 3 h. The pellets were subsequently sintered at 1200°C for 2 h in a closed crucible, using $\text{PZ} + 10\% \text{ PbO}$ atmosphere powder. The density of the sintered pellets was measured using the Archimedes' principle after polishing and cleaning the pellets followed by drying the pellets at 110°C for 4 h. X-ray diffraction was carried out on sintered pellets using a Rigaku X-ray diffractometer with $\text{Cu-K}\alpha$ radiation. Fracture toughness was measured on mirror polished pellets using indentation technique. For this, samples were polished to a mirror finish using 3 and 1 μm diamond paste successively. They were then cleaned using acetone. The samples were then indented in a Vicker's microhardness tester (Leitz Model 2002, Germany) 10 N load. Six–eight indentations were carried out on each sample at each load. The K_{IC} was measured using the formula [13]

$$K_{IC} = 0.0726 P C^{-3/2}$$

where, P is the load in Newtons and $2C$ is the total crack length, which is equal to the sum of the lengths of the crack on both the sides of the indent and the diagonal length. The hardness was measured at 4.9 N using the formula [14]

$$H_v = 0.47 P/a^2$$

where, P is the load in Newtons and a is half the average diagonal length.

Hewlett Packard impedance analyzer (HP 4192A) was used to measure the dielectric properties. For the measurement of d_{33} strain coefficient, samples were polished and electroded and corona poled with a corona voltage of 7 kV at a current of 50 μA at 100°C for 15 min. The strain coefficient d_{33} was measured using a Pennebaker (model 8000) d_{33} meter.

2. Results and discussion

Fig. 1 shows the variation in the sintered density with Nd_2O_3 addition. The density increases with increasing amount of Nd till it peaks at $\approx 2\%$ Nd and then decreases. In PZT ceramics, the oxygen vacancies are the slowest moving species and control the rate of densification in these materials [15,16]. As Nd^{3+} is having a ionic radii of 1.04 Å, which is relatively close to that of Pb^{2+} (1.32 Å) so it seems that Nd^{3+} in all probability goes mostly to A (Pb) site in the perovskite (ABO_3) PZT system. This is also in agreement with the results obtained by other researchers [17,18] that Nd^{3+} in all probability goes to A site in the PZT lattice. The charge compensation will occur by creation of vacancies at A site and also can occur by decrease in the

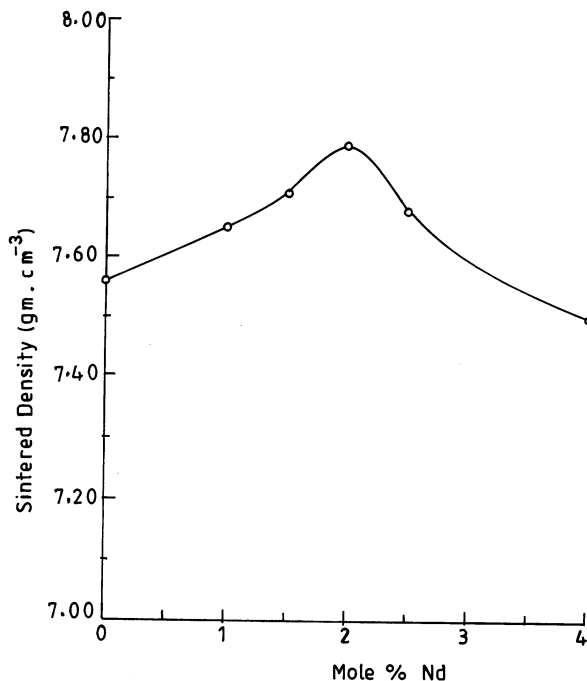


Fig. 1. Effect of Nd modification on sintered density of PZT ceramics.

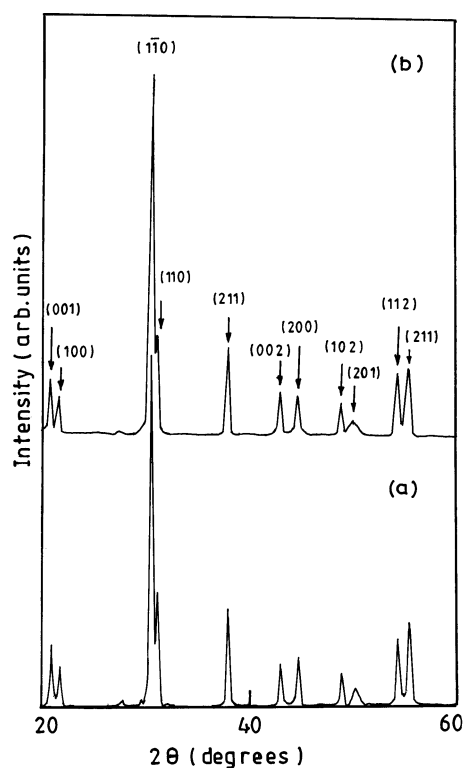


Fig. 2. X-ray diffractograms showing samples having a tetragonal phase for (a) PZT and (b) 2 mol % Nd modified PZT.

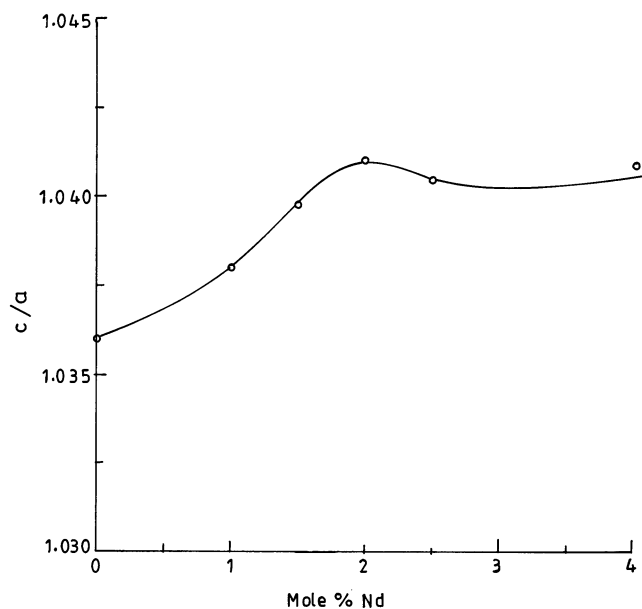


Fig. 3. Variation of tetragonality (c/a ratio) with Nd content in PZT.

number of oxygen vacancies already present in PZT system due to Pb evaporation [19,20]. Thus it seems that increasing Nd addition leads to decreasing oxygen vacancies which enhances densification rate. The decrease in density above 2% may be attributed to the reason that Nd had reached its solid solubility limit in

PZT solid solution and is now getting precipitated at grain boundaries, thus resulting in grain boundary pinning. Precipitation of rare earth's in PZT system at around 2 mol % addition has also been observed by other researchers [21,22].

Fig. 2 shows the typical X-ray diffractograms of 0 and 2% Nd modified PZT samples. The X-ray diffractograms show that samples are in pure tetragonal phase. Similar results are observed for other compositions also. This is in agreement with the PZT phase diagram [11].

The variation of c/a ratio of PZT system with Nd addition is shown in Fig. 3. The c/a ratio increases with addition of Nd up to 2% and subsequently becomes nearly constant. The tetragonality results support our above conclusion that Nd addition leads to decrease in oxygen vacancies, as it is known that oxygen vacancies lead to shrinking of unit cell size of PZT system [23]. The c/a ratio becoming nearly constant for samples

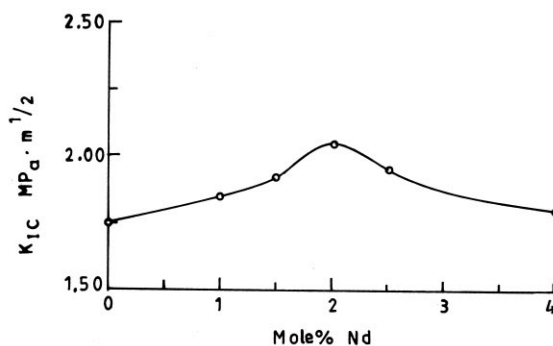


Fig. 4. Indentation fracture toughness K_{IC} vs. Nd content in PZT ceramics. The indentation was carried out at 10 N.

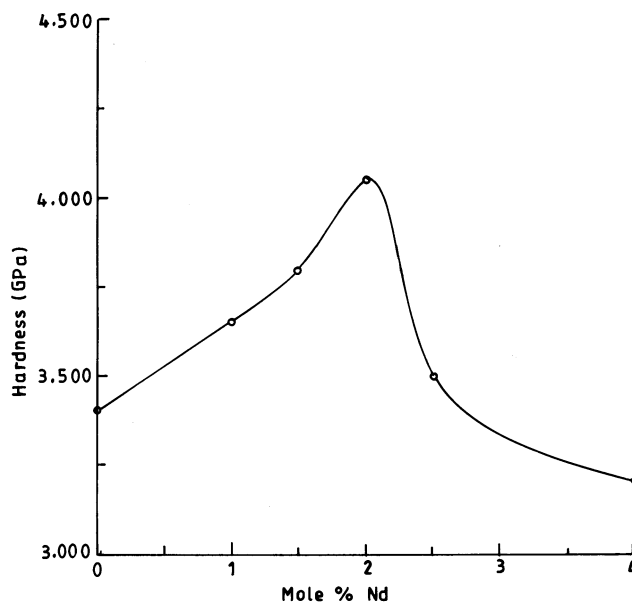


Fig. 5. Vicker's hardness vs. Nd content in PZT ceramics at 4.9 N load.

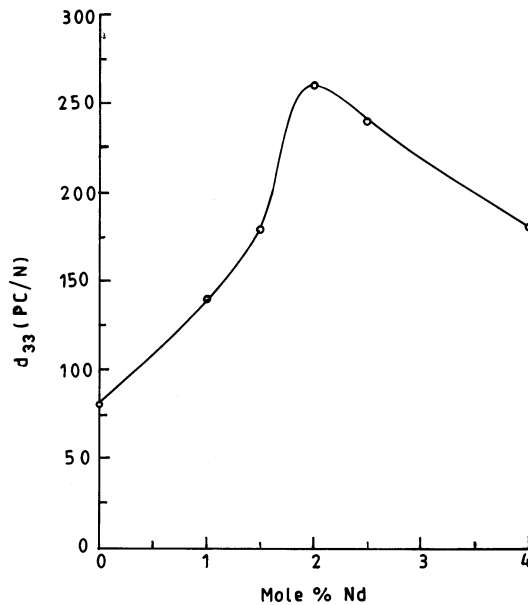


Fig. 6. Strain coefficient d_{33} vs. Nd content in PZT.

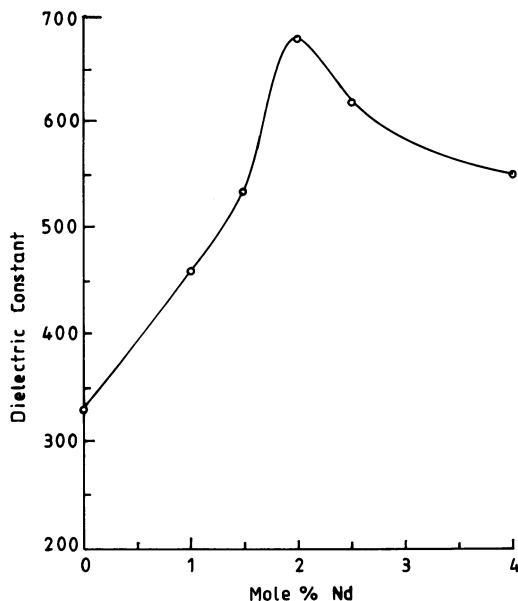


Fig. 7. Variation of dielectric constant with Nd content in PZT ceramics.

containing Nd > 2 mol %, further support that Nd reaches its solid solubility limit at ≈ 2 mol %. It seems that the precipitation of this second phase is less than the detection limit of X-ray.

Fig. 4 shows the variation of indentation fracture toughness K_{IC} of PZT ceramics with Nd content. It is seen from the figure that K_{IC} increases with Nd addition and reaches a maximum value of $2.05 \text{ Nm}^{-3/2}$ in samples containing 2 mol % Nd. It is also observed that the K_{IC} decreases on further addition of Nd. The peak value of K_{IC} obtained is $\approx 60\%$ higher than the re-

ported values for the PZT samples prepared at morphotropic phase boundary [8]. It is observed that K_{IC} shows nearly the same behavior as c/a (Fig. 3) up to 2 mol % Nd. We believe that the domain switching is the main contributor to toughening in our samples. The increased tetragonality (c/a) with Nd addition implies greater strain and hence the work done in domain switching. The increase in K_{IC} with tetragonality has also been reported by Okazaki et al. in PLZT system [24]. Domain switching as a toughening mechanism in PZT ceramics have also been reported by others [3–5]. When a ferroelectric ceramic is cooled below the Curie temperature, each grain of the ceramic breaks into domains to minimize the stresses accompanying the transformation. Domains are oriented randomly, consistent with the requirement of minimizing the stresses. Phonka et al. [10,12] recognized that PZT ceramics being simultaneously ferroelastic the domain can switch their direction under the stress field of the crack and give rise to energy absorption. Some correlation with the sintered density can also be seen as decrease in K_{IC} above 2% Nd may be due to the increased porosity in the samples.

The variation of Vicker's hardness with Nd content in PZT samples is shown in Fig. 5. The hardness also increases with Nd addition and also shows a peak at 2% Nd containing PZT samples. There seems to be a closer correlation of hardness with sintered density. The decreasing porosity at the grain boundaries leads to enhanced grain boundary strength which leads to higher hardness. The correlation of hardness with density has also been observed earlier [25].

The variation of d_{33} strain coefficient and dielectric constant ϵ_r with Nd content in PZT is shown in Fig. 6 and Fig. 7, respectively. It is observed that Nd modification has also enhanced the values of dielectric constant and piezoelectric strain coefficient d_{33} of PZT significantly. With higher values of fracture toughness and hardness as compared to other rare earth doped PZT and reasonable values of dielectric constant and piezo coefficient, Nd modified PZT show a promising materials as actuators. As our samples are in the tetragonal reason so the domains are difficult to orient which leads to poor values of piezo coefficient and dielectric constant in the virgin samples. Moreover, they may also have their domains clamped due to oxygen vacancies present in the samples. Now it is known that oxygen vacancies are the main cause of wall domain clamping [23]. This will lead to lowering of dielectric constant and the saturation polarization. As discussed above that Nd doping leads to reduction in oxygen vacancies thus it seems that reduction in oxygen vacancies with Nd addition enhances the d_{33} and dielectric constant. The fall in the values over 2% Nd may be due to the precipitation of non-ferroelectric second phase at

the grain boundaries as the Nd seems to reach its solubility limit.

3. Conclusions

Lead zirconate titanate of tetragonal structure modified with a rare earth additive Nd_2O_3 have been prepared using solid state route. It has been observed that Nd modification results in enhanced fracture toughness K_{IC} and hardness of PZT ceramics. It is also observed that Nd modification has also substantially enhanced the dielectric constant and piezo strain coefficient d_{33} of these ceramics. A K_{IC} of $2.05 \text{ M Nm}^{-3/2}$, dielectric constant of 680 and d_{33} of 240 pC N^{-1} is obtained for 2 mol % Nd modified PZT. With higher values of fracture toughness and hardness as compared to other rare earth doped PZT and reasonable values of dielectric constant and piezo coefficient Nd modified PZT show a promising materials as actuators and other high power ultrasonic transducer devices.

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