Piezoelectric characteristics of spray dried PLZT ceramics modified by sodium

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Lead zirconate titanate [Pb (Zr, Ti)O_3] ceramics modified with lanthanum (PLZT) have been studied by numerous investigators in order to modify the properties of the materials for wide applications in various piezoelectric, electrooptic, ultrasonic, and underwater devices along with actuators, sensors, and smart devices in different fields of science and technology [1–5]. It is well known that the electromechanical properties of PZT depend strongly on additives [6] as well as the morphotropic phase boundary [7]. It has been reported that the electromechanical properties of PZT ceramics could be enhanced by substitution of La^{3+} on the basis of easy domain wall motion taking place due to the formation of A-site vacancies [8]. In addition, it has also been reported that La^{3+} additives influence poling efficiency and consequently the piezoelectric activities of the pure PZT ceramics. (Pb, La) (Zr, Ti)O_3 [PLZT] with 2 at.% La^+ and Zr/Ti ratio 53/47, being in the vicinity of morphotropic phase boundary (MPB), has shown better dielectric and piezoelectric properties. Much work has been reported on PLZT for dielectric and piezoelectric applications but work on the effect of addition of alkali ions Na^+ at A-site of PZT along with La^{3+} (PLNZT) near MPB has rarely been reported. The present investigation was, therefore, undertaken to study the role of Na^+ ions on the dielectric and piezoelectric properties of PLZT prepared with spray drying technique.

Powders of PLZT and Na^+-doped PLZT (PLNZT) of the following compositions were prepared by spray drying the composite nitrate solutions of the constituents:

PLZT: $Pb_{0.97}La_{0.02}[\ ]_{0.01}(Zr_{0.53}Ti_{0.4})O_3$

PLNZT: $Pb_{0.98}(La_{1-x/3}Na_x)_{0.02}(Zr_{0.53}Ti_{0.47})_{0.9950}O_3$

where $x = 0.0, 0.5, 1.0, 1.5, 2.0, 2.5$.

Analytical grade $Pb(NO_3)_2$, $ZrOCl_2{\cdot}8H_2O$, $TiCl_4$, $NaNO_3$, and $La(NO_3)_3{\cdot}6H_2O$ were used as primary raw materials. Lead and lanthanum nitrates were further purified by precipitating their aqueous solutions as hydroxide and then dissolving them in dilute HNO_3. Chlorides of zirconium and titanium (after crystallization in HCl) were converted separately into their nitrates by precipitating their aqueous solutions as hydroxides using NH_4OH as precipitating agent and redissolving the chloride-free hydroxides in dil. HNO_3. $NaNO_3$ was, however, used as such without further purification. Nitrates of Pb, Zr, Ti, La, and Na, taken in appropriate ratio, were spray dried using Eyela Mini Spray dryer, Japan (model SD-1) to get the desired PLZT and PLNZT powders. The spray dried nitrate powders were calcined at 800 °C for 6 hr and pressed into the circular disks of 10-mm diameter and 2-mm thickness at 150 MPa using hydraulic press and 2 wt% PVA binder which was burnt out during sintering at 1100 °C for 3 hr. To prevent PbO loss during high-temperature sintering, an equilibrium PbO vapor pressure was established using $PbZrO_3$ powder. The sintered disk were lapped and electroded with fired silver paste. The dielectric constant (ε) and tangent loss ($\tan\delta$) were measured at different temperatures from 120 to 400 °C at 10 kHz. The disks were polarized using a high dc field of 30 kV/cm for 15 min at 100 °C in a silicon bath. The electromechanical properties of individual pellets were measured using IRE standard [9].

The measured values of dielectric constant (ε), tangent loss ($\tan\delta$) (both as a function of variation of temperatures), transition temperature T_c (°C), diffusivity (γ), Gaussian diffuseness "δg," electromechanical coupling factor (K_p), and piezoelectric strain coefficient (d_{33}) at different atomic % of Na^+ additives in PLZT (2/53/47) are listed in Table I.

Addition of Na^+ in PLZT causes significant changes on electrical and electromechanical properties (Table I). The dielectric constant (ε), $\tan\delta$, Gaussion diffuseness (δ_g) increase with the addition of Na^+ atomic % and show a peak at 1.5 at.% of Na^+ except γ, which peaks at 1.0 at.% of Na^+ whereas transition temperature (T_c)

TABLE I Measured values of ε, $\tan\delta$, T_c (°C), γ, δg, K_p, and d_{33} at different atomic % of Na^+ additives in PLZT

Sl. no.	Na^+ (at.%)	ε_{max}	$\tan\delta$	T_c (°C)	γ	δg	K_p	d_{33} ($\times 10^{-12}$ C/N)
1	0.0	7450	0.052	210	1.50	64.6	0.50	290
2	0.5	7500	0.046	225	1.60	70.3	0.51	285
3	1.0	7598	0.042	240	1.75	68.3	0.53	298
4	1.5	7690	0.048	255	1.63	81.9	0.59	312
5	2.0	7300	0.037	275	1.44	77	0.43	276
6	2.5	7050	0.034	285	1.38	66.4	0.41	260

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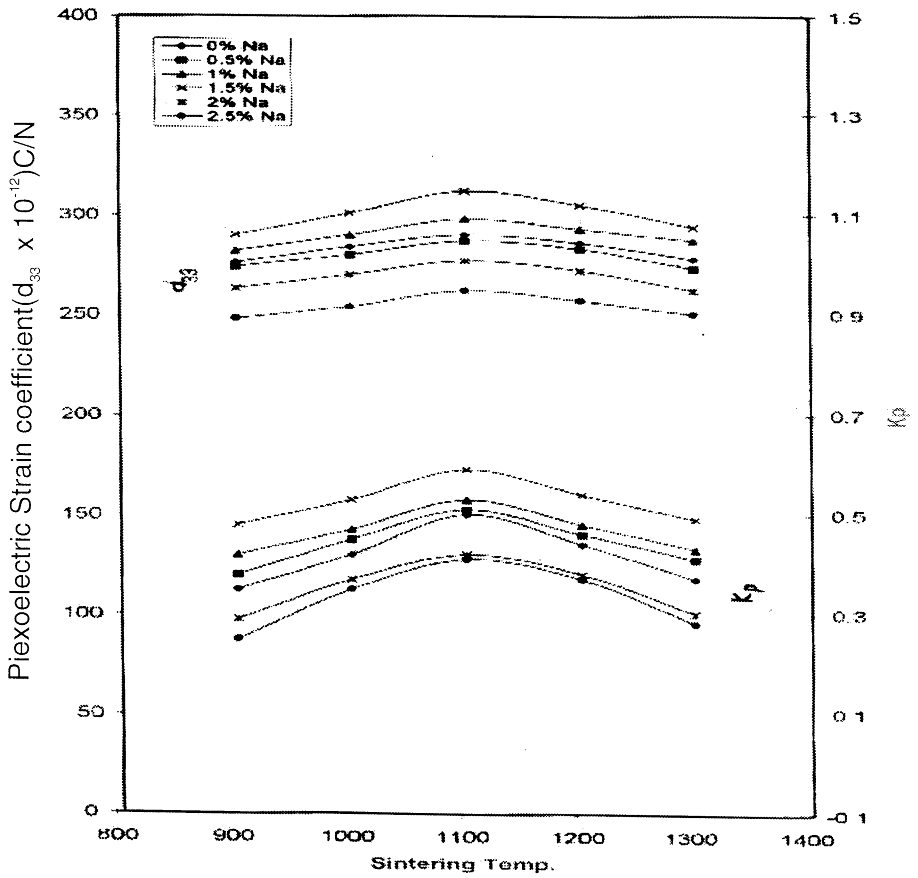

Figure 1 Variation of 'd_{33}' and 'K_p' of PLZT (0% Na) and PLNZT as a function of sintering temperature.

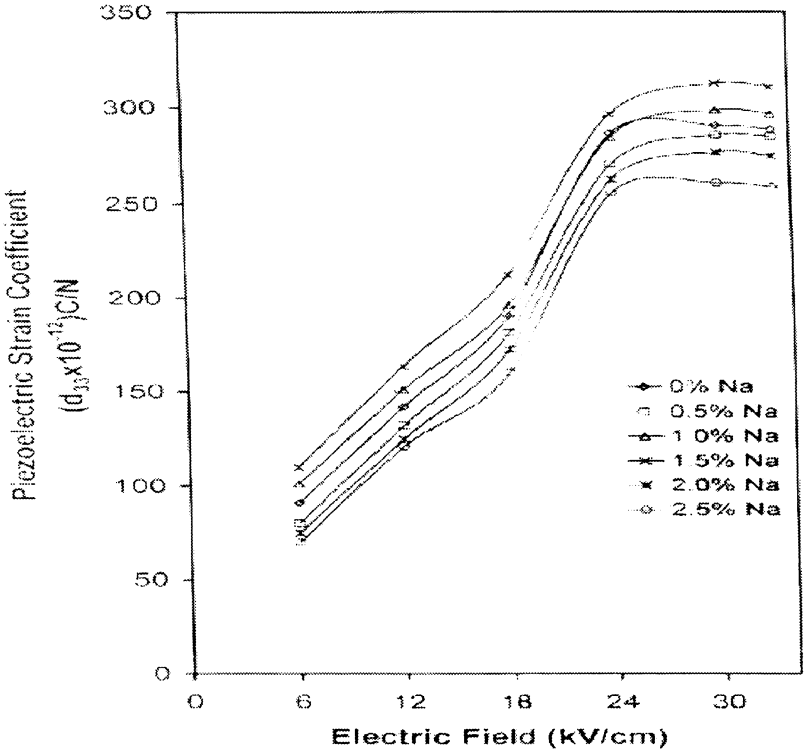

Figure 2 Variation of 'd_{33}' of PLZT (0% Na) and PLNZT as a function of poling field.

increases continuously with increase in Na^+ concentrations. Similar results were observed in the case of K-modified PLZT [10]. The electromechanical coupling factor (K_p) and piezoelectric strain coefficient (d_{33}) also peak at 1.5 at.% of Na^+. This may be attributed to the fact that lattice vibrations also increase with increase in temperature and the interaction between the increase/decrease of vacancies created by La^{3+}/Na^+ ions doping may be responsible for the change in the ε-value and the corresponding K_p and d_{33} values. These values going to its maximum for 1.5 at.% Na^+ doping in PLZT may be the result of the fact that predominance of vacancies (created by La^{3+} ions) reduces beyond the 1.5 at.% Na^+ addition.

Fig. 1 shows variation of piezoelectric strain coefficient d_{33} and electromechanical coupling factor K_p with sintering temperatures of PLZT (0% Na) and PLNZT ceramics. It is obvious (Fig. 1) that the sintering temperature of 1100 °C is the most suitable temperature for the pellets to get the maximum value of d_{33} and K_p. This is due to the fact that beyond 1100 °C agglomeration of particles starts taking place with the consequent increase of porosity of the ceramics [1, 11–12].

The variation of piezoelectric stain coefficient with poling (high dc) field for PLZT (0% Na) and PLNZT for various concentrations of Na^+ is shown in Fig. 2. It is observed that the d_{33} value increases with the increase of applied dc field and it shows peaks at 30 kV/cm for all Na^+ concentrations. This is due to the increase in the mobility of ferroelectric domain walls with increases of dc field and at 30 kV/cm, polarizability comes to a saturation point [13]. Thus, it can be concluded that lead lanthanum zirconate titanate (PLZT) ceramics added to sodium ions may find special applications in piezoelectric, ultrasonic, and underwater transducer devices.

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