

Self-propagating combustion synthesis of $\text{Pb}_{1-x}\text{Sr}_x\text{ZrO}_3$ ($0 \leq x \leq 0.20$) ceramics and their dielectric properties

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Abstract. Lead strontium zirconate, $\text{Pb}_{1-x}\text{Sr}_x\text{ZrO}_3$ ($0 \leq x \leq 0.20$) ceramics, were prepared by novel glycine-nitrate self-propagating combustion technique. The crystal structure of the ceramics was investigated as a function of composition via X-ray diffraction (XRD). The XRD patterns obtained on these powders showed the formation of pure orthorhombic phase of lead strontium zirconate without impurities and all the compounds retained the orthorhombic structure. The samples were sintered at 900–1100°C for 2 h. It has been observed that the dielectric constant decreases with increase in strontium content (100 kHz). In all compositions, dielectric constant showed a peak at transition temperature and the magnitude of the peak was found to decrease with strontium doping level.

Keywords. Lead strontium zirconate; combustion technique; dielectric properties.

1. Introduction

Lead zirconate (PbZrO_3) is a well known antiferroelectric material and its dielectric properties, crystal structure and phase diagram have been extensively investigated (Jona and Shirane 1957; Fushimi and Ikeda 1967; Scott and Burns 1972). PbZrO_3 is an ABO_3 -type perovskite and its dielectric constant shows a sharp maximum at the phase transition from antiferroelectric to paraelectric which is associated with orthorhombic to cubic structural phase transition at the Curie point near 230°C (Jaffe *et al* 1971). Phase transition between the antiferroelectric (AFE) and ferroelectric (FE) phases of pure and compositionally modified PbZrO_3 has attracted considerable attention in recent years (Kanno *et al* 1995; Park *et al* 1997; Yamakawa *et al* 1997; Yoon *et al* 1997; Harrad *et al* 1998). This transition can be induced by varying the temperature (Shirane 1952; Yoon *et al* 1997), electric field (Pan *et al* 1989a, b; Ujma *et al* 1992; Park *et al* 1997; Yoon *et al* 1997) or hydrostatic pressure (Berlincourt *et al* 1963; Pokharel and Pandey 2000). The electric field induced AFE to FE transition in these materials can give rise to longitudinal strains as high as 0.85% making them potentially useful for high displacement electromechanical actuator applications (Pan *et al* 1989a, b; Park *et al* 1997). Similarly, the pressure induced reverse transition (FE to AFE) in poled specimens can supply high instantaneous cur-

rents with considerable potential for application in energy conversion device (Berlincourt *et al* 1963). The structure of AFE phase is orthorhombic [A_o] with eight formula units in the unit cell, whereas the FE phase has a rhombohedral structure [F_R] possibly with two formula units (Pokharel *et al* 1999b). The F_R phase transforms into a paraelectric cubic (P_C) phase on heating above 231°C (Goulpeau 1967; Handerek *et al* 1981a). The relative stability of AFE and FE phases may be altered through chemical substitutions like Ba^{2+} , Sr^{2+} and Ca^{2+} at the Pb^{2+} site and Ti^{4+} at the Zr^{4+} site (Krainik 1958; Jaffe *et al* 1971; Nedelec *et al* 1992; Kato *et al* 1993; Yoon *et al* 1997; Gachigi *et al* 1998; Harrad *et al* 1998).

It is reported that the properties of PbZrO_3 can be improved by adding Ba ions into the Pb sites of PbZrO_3 (Shirane 1952; Yoon *et al* 1997; Pokharel *et al* 1999a; Pokharel and Pandey 2000). Many authors have reported that as the Ba ion concentration in $\text{Pb}_{1-x}\text{Ba}_x\text{ZrO}_3$ increases, the Curie temperature of $\text{Pb}_{1-x}\text{Ba}_x\text{ZrO}_3$ shifts towards lower temperature (Roberts *et al* 1950, 1981; Shirane 1952). The AFE to FE switching can occur (Yoon *et al* 1997; Shirane and Hoshino 1954) even at room temperature in $(\text{Pb}_{0.95}\text{Ba}_{0.05})\text{ZrO}_3$, whereas it requires much higher temperature in pure PbZrO_3 (Shirane *et al* 1951; Handerek *et al* 1981b). However, there is no report about the dielectric studies of Sr substituted PbZrO_3 by glycine-nitrate combustion synthesis.

Advanced ceramic materials can be prepared by using a variety of techniques, among which combustion technique is an important one and possesses several advan-

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tages over others. In recent times, this method has received much attention because of its simple and rapid preparation process which yields homogeneous, fine and agglomeration free crystalline powders. This method is based on the rapid exothermic and self-sustaining chemical reaction between the desired metal salts and an organic fuel. The key advantage is that the thermal energy required for the reaction to occur is provided by the reaction itself and not by an external source (Rao 1993).

This paper presents the structural, sintering temperature, relative density, and dielectric properties of strontium-doped PZ ceramics prepared via glycine–nitrate self-propagating combustion technique.

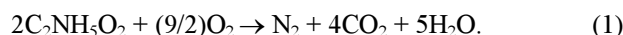
2. Experimental

Polycrystalline powders of $\text{Pb}_{1-x}\text{Sr}_x\text{ZrO}_3$ where $x = 0.0, 0.05, 0.10, 0.15$ and 0.20 were prepared by a novel method called glycine–nitrate self-propagating combustion technique. High purity lead nitrate, strontium nitrate, zirconium nitrate were used as oxidizers and glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) was used as fuel. The stoichiometric composition of the redox mixtures for the combustion were calculated using the total oxidizing (O) and reducing (F) valences of the components which served as the numerical coefficients for the stoichiometric balance, so that the equivalence ratio (i.e. $O/F = 1$) was unity and the energy released by the combustion was maximum (Jain and Adiga 1981). Based on the considerations of the combustion chemistry, $\text{Pb}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$ and $\text{ZrO}(\text{NO}_3)_2$ had an oxidizing valence of -10 and glycine had a reducing valence of $+9$.

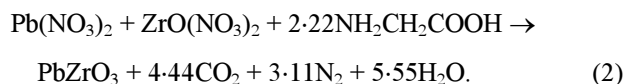
The stoichiometric quantities of the corresponding metal nitrates and the organic fuel (glycine) were weighed accurately, taken in a quartz crucible and dissolved in distilled water. The quartz crucible was then transferred to a muffle furnace preheated at 550°C where it boiled, frothed,

ignited and caught fire (temperature rise up to $1100 \pm 100^\circ\text{C}$). At these high temperatures, the metal nitrates decomposed to metal oxides of nitrogen and hence acted as oxidizer for further combustion which led to a voluminous, foamy combustion residue (yellow-coloured powder) within 5 min. The flame persisted for about one min. The foam was then lightly grounded in silica basin with porcelain pestle to obtain fine powders.

The procedure is explained in figure 1. When glycine is the fuel, the following reaction takes place where one mole of glycine gives five moles of gases



The following is the theoretical equation for producing parent oxide assuming complete combustion of the redox mixtures with glycine as the fuel



Calcination of the as-synthesized samples was carried out in alumina crucibles at 800°C for 6 h in dry air atmosphere to remove deposited carbon and un-reacted organic residues and to get phase pure compound (Hatchell *et al* 1999). The calcination of the as-synthesized powders showed a very significant weight loss for glycine–nitrate synthesis. The weight loss in glycine–nitrate synthesis was 2 to 4% for oxide powders. The combustion derived ‘Sr’ doped PbZrO_3 , i.e. $\text{Pb}_{1-x}\text{Sr}_x\text{ZrO}_3$ ($x = 0, 0.05, 0.10, 0.15$ and 0.20) powders, were characterized by powder XRD. The XRD patterns of the heat-treated powders were recorded using a Philips Type-PW 1140/90 X-ray diffractometer, using $\text{CuK}\alpha$ radiation. The combustion derived product was crushed and pulverized in an agate mortar into fine powders. The calcined powders were mixed with a binding agent (4% polyvinyl alcohol (PVA) solution) and were uniaxially pressed into circular pellets of 12 mm diameter, 1.5–2 mm thickness at a pressure of 150 MPa for about 2 min. The samples were placed in an alumina crucible and were buried in PbZrO_3 powder to minimize the lead loss during sintering. Initially, the binder content was removed by heating the pellet at 700°C for 30 min. Then, the binder burnt-out components were sintered in a controlled atmosphere from 900 – 1100°C for 2 h time duration at a heating/cooling rate of 5°C per min. The density of the sintered specimens was determined by Archimedes method. For electrical measurements, the polished surfaces of the samples were sputtered with gold and their silver leads were attached with silver paste and baked at 100°C for 15 min. The capacitance measurements were carried out in the 100 Hz to 10 MHz frequency range as a function of temperature (room temperature to 300°C) using HP4194A impedance analyser at a signal strength of 0.5 Vrms. The dielectric constant was evaluated by taking the dimensions of the samples into consideration.

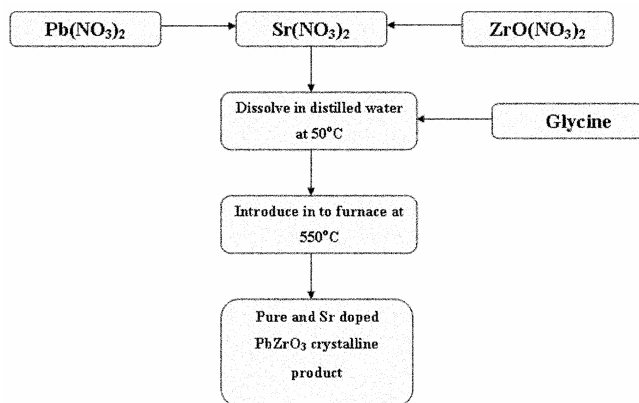


Figure 1. Flow chart to prepare pure and Sr-doped PbZrO_3 through glycine–nitrate combustion technique.

3. Results and discussion

3.1 X-ray structural analysis

The X-ray powder diffraction (XRD) patterns obtained for the calcined powders of various compositions in $Pb_{1-x}Sr_xZrO_3$ (where $x = 0, 0.05, 0.10, 0.15$ and 0.20) are shown in figure 2. All the peaks are very sharp showing the crystalline nature of the heat treated powders. The XRD patterns of the 'Sr' doped $PbZrO_3$ powders are well matched with that of the parent compound, $PbZrO_3$ (JCPDS 35-0739). Other than the perovskite phase, no secondary phase was observed for the whole range of compositions. This shows that by adopting this type of combustion method, phase pure and well crystalline powders of perovskite materials can be prepared in a short duration. Considering the fact that the peak splitting between (400) and (042) has not vanished until 20 mol% substitution, the structure of $Pb_{1-x}Sr_xZrO_3$ has not changed from orthorhombic for all compositions, which was also confirmed by the lattice constant measurements of this system.

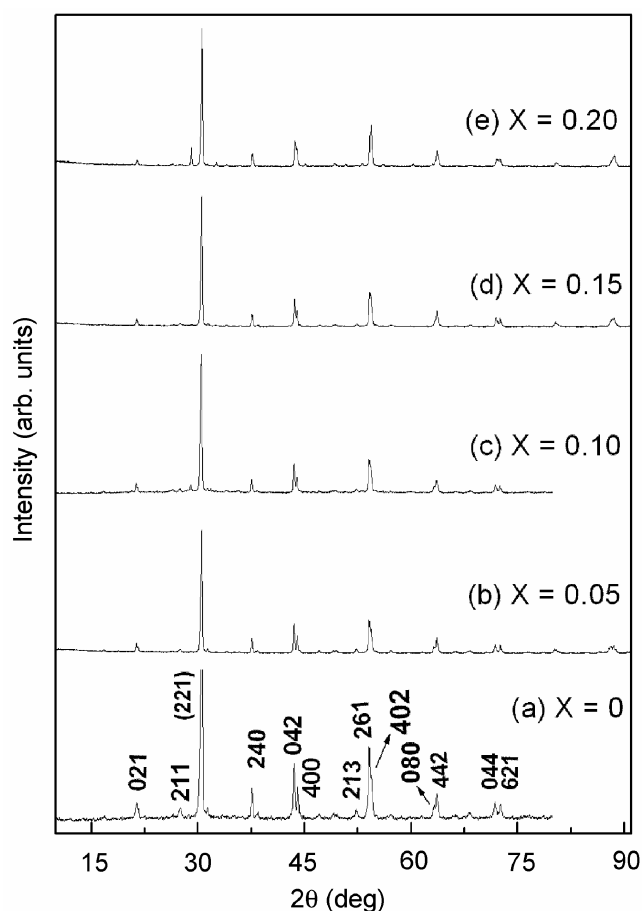


Figure 2. XRD pattern obtained on 'Sr' doped $PbZrO_3$ ($Pb_{1-x}Sr_xZrO_3$ ($x = 0, 0.05, 0.10, 0.15$ and 0.20)) ceramics.

3.2 Sintering behaviour

For different sintering temperatures, the relative densities of the sintered $Pb_{1-x}Sr_xZrO_3$ ceramics were measured. The relative densities of the samples are in the range of 89–94%. It is possible that volatilization of PbO during firing is the main reason for the failure in preparing dense ceramics over this composition range (Krainik 1958;

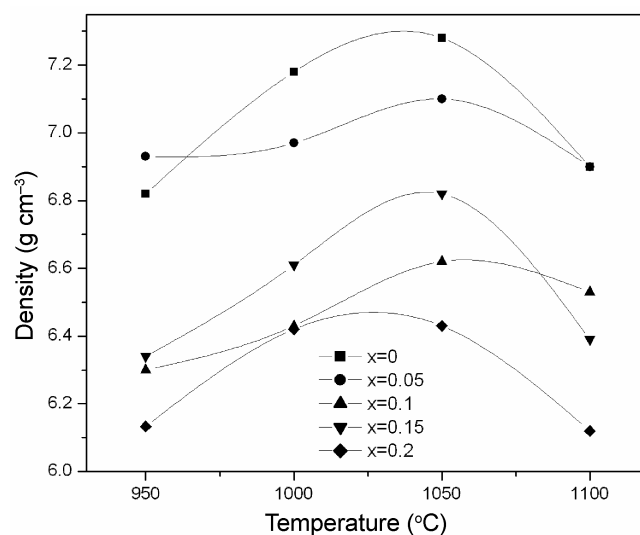


Figure 3. Variation of absolute density as a function of sintering temperature for various compositions.

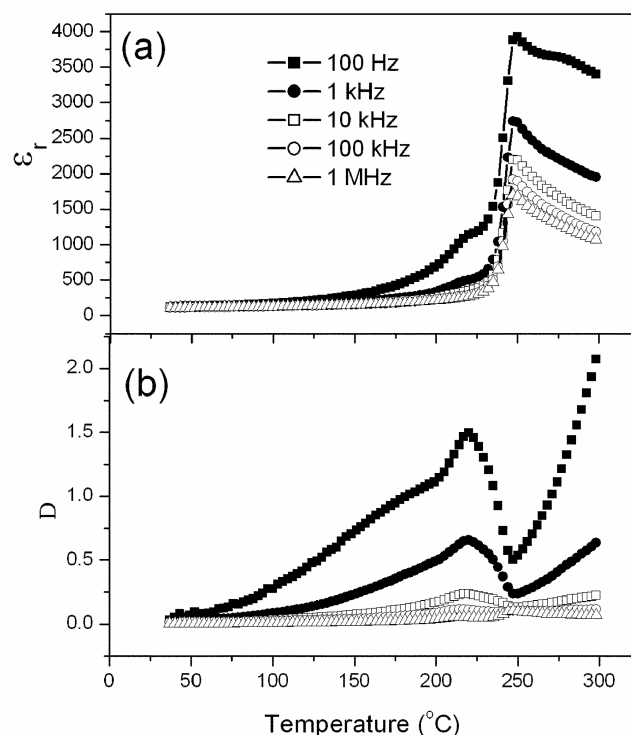


Figure 4. Variation of (a) dielectric constant and (b) loss as a function of temperature for the pure $PbZrO_3$.

Kato *et al* 1993; Gachigi *et al* 1998; Jaffe *et al* 1971; Nedelec *et al* 1992). A plot of density as a function of sintering temperature is shown in figure 3. The density of the compact increased with increase in sintering temperature up to 1050°C as indicated by Gaukler *et al* (1994). It is found that beyond the temperature of 1050°C the densities of all doped oxides decreased due to the disjoining behaviour of ceramic particles above this temperature. This similar behaviour is also reported for 'Ba' doped PbZrO₃ (Pokharel *et al* 1999a).

3.3 Dielectric studies

The dielectric properties of pure and strontium-doped ceramics prepared from combustion synthesized powders were studied. Figure 4(a) shows the variation of dielectric constant (ϵ_r) as a function of temperature at various frequencies for undoped PZ sample.

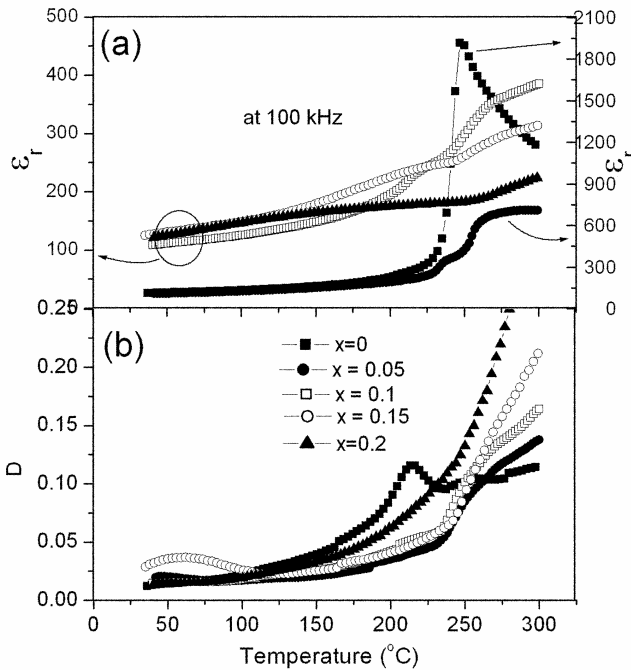


Figure 5. Variation of (a) dielectric constant and (b) loss as a function of temperature for the various compositions at 100 kHz.

Table 1. Dielectric properties of Pb_{1-x}Sr_xZrO₃ ($x = 0, 0.05, 0.10, 0.15$ and 0.20) ceramics.

Composition (x)	T_{c1} (°C)	T_{c2} (°C)	ϵ_r (at T_{c2})
0	247	—	1980
0.05	278	236	668
0.1	269	217	349
0.15	299	224	313
0.2	299	182	223

It can be seen that the dielectric constant exhibits a sharp phase transition at 247°C (Curie temperature, T_{c1}) and the phase transition temperature was found to be same for all the frequencies. This transition is attributed to the antiferroelectric to paraelectric phase transition. In conventional sintered lead zirconate ceramics the Curie temperature was found to be ~230°C and in the present case there is slight deviation from that, which may be because of the different syntheses routes adopted. So this shows that antiferroelectric lead zirconate can be prepared easily by combustion technique without any deterioration in the dielectric properties. The value of dielectric constant at room temperature and the phase transition temperature is about 120 and 1900, respectively which is comparable to that of the ceramic by conventional solid state reaction route. The variation of the dielectric loss (D) as a function of temperature is shown in figure 4(b) and it showed a peak at 220°C for all the frequencies (100 Hz–1 MHz).

Figure 5(a and b) shows the variation of ϵ_r and D as a function of temperature (at 100 kHz) for the strontium-doped lead zirconate of different compositions. The strontium-doped samples showed another anomaly at temperatures (T_{c2}) lower than the antiferroelectric to paraelectric transition. The transition temperatures for all the compounds and transitions are listed in table 1. Similar behaviour was observed in the conventionally prepared ceramic which was attributed to the presence of another antiferroelectric phase in the strontium-doped sample and the dielectric anomaly was attributed to antiferroelectric to antiferroelectric phase transition (Shirane 1952). So the ceramics prepared by combustion synthesis also behaves in a similar way as that of the conventionally prepared ceramic. The peak value of the dielectric constant at the Curie point decreases rapidly with increasing Sr concentration which is because of the doping of bigger strontium ions in place of the smaller lead ions.

4. Conclusions

For the first time, antiferroelectric PbZrO₃ was synthesized by a rapid glycine–nitrate self propagating combustion method. The effect of strontium doping on the structural and dielectric properties of PbZrO₃ was studied. All compositions in this study were single phasic perovskite with orthorhombic structure. The dielectric properties were found to be same as that of the ceramics prepared by conventional routes.

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