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Preparation, characterization and sintering behaviour of Sr doped $PbZrO_3$ powders by self-propagating combustion method

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The Sr doped $PbZrO_3$ ($Pb_{1-x}Sr_xZrO_3$; x=0, 0.05, 0.10, 0.15 and 0.20) ceramics have been prepared by glycine-nitrate self-propagating combustion technique. The ceramic powders have been heat treated at 800°C for 6 h in order to get phase pure compounds. The prepared powders are characterized by XRD, density and BET surface area measurements. The XRD patterns obtained on these powders show the formation of pure orthorhombic phase of $PbZrO_3$ without any impurities. Thin sections of circular components of these powders, made by uniaxial compression, are subjected to annealing at different temperatures in the range 900-1100°C for 2 h in order to throw light on their sintering behaviour. The surface morphology of the sintered components are studied by SEM.

Keywords: $Pb_{1-x}Sr_xZrO_3$ ceramics, Combustion synthesis, Characterization, Sintering

1 Introduction

Lead zirconate ($PbZrO_3$) is an antiferroelectric ceramic material. It is reported that $PbZrO_3$ has an orthorhombic crystal structure at room temperature. The dielectric constant of $PbZrO_3$ shows a sharp maximum at the phase transition from orthorhombic to cubic at the Curie point[1] near 230°C. It is reported that antiferroelectric (AFE) to ferroelectric transition (under the application of a strong electric field to the ceramics in the antiferroelectric state) leads to significant energy storage for *dc* field. This feature of $PbZrO_3$ makes it a candidate material for energy storage applications[2]. Several techniques can be used to prepare advanced ceramic materials and the glycine-nitrate combustion synthesis route can be highlighted among them all[3]. Preparation of lead zirconate by conventional process, that is, mixing and firing of the binary oxides (PbO and ZrO_2) requires use of high temperatures at which PbO volatility also becomes significant. It is reported that the full development of $PbZrO_3$ phase occurs after sintering at temperature above 1200°C for at least 2 h in controlled PbO atmospheres[4-6]. Lead zirconate was synthesized by a sol.gel method which necessitated the use of complex processing practices and strict control of many process parameters, such as *p*H of the solutions, temperature and concentrations of the cations. For the sol gel method, the calcination temperature to yield pure $PbZrO_3$ had reported to be as low as 700°C for 6 h of soaking time[7]. The phase formation temperature for pure $PbZrO_3$ by citrate route, was also reported to be in the vicinity of 700°C[8].

Recently combustion technique has been attracting, since it is as a straightforward preparation process to produce homogeneous very fine crystalline and un-agglomerated powders with good sintering behaviour. It explores an exothermic generally very fast and self-sub straining chemical reaction between the desired metal salts (nitrates) and suitable organic fuel (glycine) which is ignited at a temperature much lower than the actual phase formation temperature[9-16]. The key feature is that the heat required to drive the chemical reaction and accomplish the compound synthesis is supplied by the reaction itself and not by an external source. This process is safe, instantaneous and energy saving.

In this study, Sr doped $PbZrO_3$ ($Pb_{1-x}Sr_x$ ZrO_3; x=0, 0.05, 0.10, 0.15 and 0.20) is synthesized in the form of fine powders by glycine-nitrate combustion technique. The physical and thermal properties of the synthesized powders are systematically evaluated. The circular components of these materials are annealed at different temperatures (between 900-1100°C) in order to acquire information about their thermal properties such as densification factor, expansion and shrinkage among the adjoining cell components.

2 Experimental Details

In the glycine-nitrate combustion technique, fine particles of Sr doped $PbZrO_3$ i.e., $Pb_{1-x}Sr_xZrO_3$ (x=0, 0.05, 0.10, 0.15 and 0.20) materials were prepared by the combustion of the corresponding metal nitrates-glycine mixtures. In this process, high purity lead nitrate, strontium nitrate and zirconium nitrate (all from MERCK) were used as oxidizers and glycine (MERCK) was used as fuel. The stoichiometric compositions of the redox mixtures for the combustion were calculated using the total oxidizing (O) and reducing (F) valencies of the components which serve as the numerical coefficients for the stoichiometric balance, so that the equivalence ratio (i.e. O:F=1) is unity and the energy released by the combustion is maximum[17] . Based on the propellant chemistry, the valence of C = +4, H = 1, divalent ions = +2, trivalent ions= 3 and so on, and O = -2. The valance of nitrogen is considered to be zero. Based on these considerations $Pb(NO_3)_2$, $Sr(NO_3)_2$ and $ZrO(NO_3)_2$ will have an oxidizing valance of -10 and glycine will have a reducing valance of +9.

The appropriate stoichiometric quantities of the corresponding metal nitrates and an organic fuel (glycine) were weighed accurately, taken in a quartz crucible and dissolved in distilled water. The mixed solution was heated in a heating mantle up to boiling and self-ignition. The quartz crucible was then transferred to a muffle furnace preheated at 550°C, boils, froths, ignites and caches fire (temperature 1100±100ºC). At this higher temperature, the metal nitrates decompose to metal oxides of nitrogen and hence act as oxidizer for further combustion which leads to a voluminous, foamy combustion residue (yellow-coloured powder) within 5 min. The flame persisted for about 1 min. The foam was then lightly grounded in silica basin with porcelain pestle to obtain fine powders.

The procedure is explained in Fig. 1. The appropriate amounts of the reactants with glycine fuel taken for synthesis are indicated in Table 1. When glycine is the fuel the following reaction takes place and 1 mole of glycine gives 5 moles of gases.

$$2C_2NH_5O_2 + (9/2)\ O_2 \rightarrow N_2 + 4CO_2 + 5H_2O$$

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

$$Pb(NO_3)_2 + ZrO(NO_3)_2 + 2.22\ NH_2CH_2COOH \rightarrow PbZrO_3 + 4.44CO_2 + 3.11N_2 + 5.55\ H_2O$$

Calcination of the as-synthesized samples was carried out in alumina crucibles at 800°C for 6 h in a dry atmosphere to remove deposited carbon and un-reacted organic residues and to get phase pure compound[18]. The calcination of the as-synthesized powders implies a very significant weight loss for glycine-nitrate synthesis. The weight loss in glycine-nitrate synthesis was 2 to 4% for oxide powders. These data are indicated in Table 2. The combustion derived Sr doped $PbZrO_3$ i.e., $Pb_{1-x}Sr_xZrO_3$ (x=0, 0.05, 0.10, 0.15 and 0.20) powders were characterized by powder XRD, density, particle size analysis and BET surface area measurement. The XRD patterns of the heat-treated powders were obtained with a Philips type-PW 1140/90 X-ray Diffractometer, using CuK radiation. The powder density was measured by using a pycnometer with xylene as the medium. Particle size of the heat treated powders was measured using

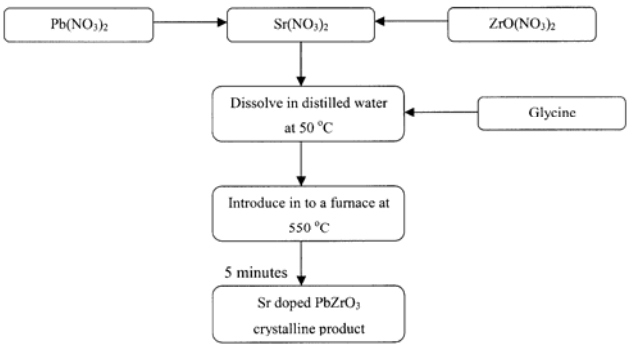

Fig. 1—Flow chart to prepare Sr doped with $PbZrO_3$ through glycine-nitrate combustion technique

Table 1—Amount of precursor materials taken for combustion synthesis of Sr doped with $PbZrO_3$ by glycine-nitrate route

Sample	$Pb(NO_3)_2$ (g)	$Sr(NO_3)_2$ (g)	$ZrO(NO_3)_2$ (g)	Glycine (g)	Yield (g)
$PbZrO_3$	16.56	--	11.562	8.331	9.265
$Pb_{0.95}Sr_{0.05}ZrO_3$(PSZ9505)	15.732	0.529	11.562	8.331	9.96
$Pb_{0.90}Sr_{0.10}ZrO_3$(PSZ9010)	14.904	1.058	11.562	8.331	10.14
$Pb_{0.85}Sr_{0.15}ZrO_3$(PSZ8515)	14.076	1.587	11.562	8.331	9.672
$Pb_{0.80}Sr_{0.20}ZrO_3$(PSZ8020)	13.248	2.116	11.562	8.331	9.868

Malvern particle size analyzer, Malvern Instrument Ltd, UK. The surface area of the powders was measured using a Quantasorb BET surface area analyzing instrument. The sintering behaviour of the circular pellets was studied in a temperature controlled programmable furnace between the temperature ranges of 900 to 1100°C. The accuracy in temperature measurement is ±1°C. Surface morphology of the sintered components was studied using a scanning electron microscope (Steroscan model-360).

3 Results and Discussion

3.1. XRD studies

The XRD patterns for the heat treated $Pb_{1-x}Sr_xZrO_3$ (x=0, 0.05, 0.10, 0.15 and 0.20) are shown in the Figs 2(a)-(e). All the peaks are very sharp showing the crystalline nature of the heat treated powders. The XRD pattern of the heat treated Sr doped $PbZrO_3$ powders is matched with standard data [JCPDS file for $PbZrO_3$ No: 35-0739]. From the XRD, it could be concluded that all Sr doped PbZrO3 had orthorhombic crystal structure. Lattice parameters were calculated with a least square fitting method. The lattice constants are in good agreement with the standard data [JCPDS files for $PbZrO_3$ No: 35-0739]. The crystalline sizes of the powders were calculated by Scherer's formula[19]. The crystalline sizes are in the range 29 to 40 nm. The XRD data obtained on the heat treated powders are given in Table 3.

Table 2—Reduction in weight obtained on Sr doped with $PbZrO_3$ ceramic powder during calcinations at 800°C for 6 h

Sample	W_i (g)	W_{ht} (g)	ΔW (%)
$PbZrO_3$	9.265	8.999	2.871
$Pb_{0.95}Sr_{0.05}ZrO_3$(PSZ9505)	9.96	9.652	3.092
$Pb_{0.90}Sr_{0.10}ZrO_3$(PSZ9010)	10.14	9.868	2.682
$Pb_{0.85}Sr_{0.15}ZrO_3$(PSZ8515)	9.672	9.373	3.091
$Pb_{0.80}Sr_{0.20}ZrO_3$(PSZ8020)	9.868	9.482	3.912

Wi–Initial weight, Wht–after heat treatment, W-Change (reduction) in weight

3.2. Particulate properties

The powder densities such as, bulk density, tap density and absolute density (measured using pycnometer with xylene liquid) and BET surface area of the heat treated powders are given in Table 4. The bulk density, tap density and absolute density of the powders were measured with accuracy of ± 0.05. The BET surface area values of all the heat treated powders are reported in the range of 1.5 to 3.3 m^2g^{-1} (accuracy of ± 0.05). The average particle size (D) of the oxide (assuming that the particles are spherical) was calculated using the following formula [20, 21]:

$$D = 6/S\rho$$

where S is the surface area per unit weight in m^2/g and ρ is the density of the particle in g/m^3. The values are

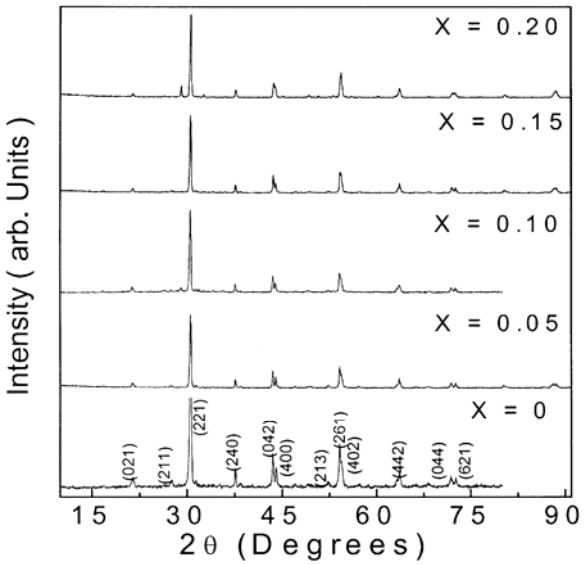

Fig. 2—XRD pattern obtained on Sr doped $PbZrO_3$ ($Pb_{1-x}Sr_xZrO_3$; x = 0, 0.05, 0.10, 0.15 and 0.20) ceramics

Table 3—XRD data obtained on Sr doped $PbZrO_3$ Powder synthesized by glycine-nitrate combustion technique

Properties	Standard XRD data for $PbZrO_3$ powder (JCPDS No.	Obtained XRD data				
		$PbZrO_3$	$Pb_{0.95}Sr_{0.05}ZrO_3$	$Pb_{0.90}Sr_{0.10}ZrO_3$	$Pb_{0.85}Sr_{0.15}ZrO_3$	$Pb_{0.80}Sr_{0.20}ZrO_3$
Crystal structure	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Unit cell parameter (Å)	a = 8.2318 b = 11.7764 c = 5.8816	a = 8.2316 b = 11.7790 c = 5.8885	a = 8.2408 b = 11.7723 c = 5.8736	a = 8.234 b = 11.7850 c = 5.8770	a = 8.2408 b = 11.7723 c = 5.874	a = 8.2408 b = 11.7723 c = 5.874
Unit cell volume $(Å)^3$	570.17	570.95	569.82	570.29	569.82	569.82
Theoretical density (g/cc)	8.071	8.059	7.936	7.79	7.657	7.518
Crystallite size (nm)	—	28.53	34.85	39.22	38.11	39.73

Table 4—Density and BET surface area measurements obtained on Sr doped $PbZrO_3$ powders

Samples	Bulk density g/cc (accuracy ±0.05)	Tap Density g/cc (accuracy ±0.05)	Absolute Density g/cc (accuracy±0.05)	Surface area (BET) m^2g^{-1}	Average Particle size (from surface area) μm
$PbZrO_3$	1.464	2.277	6.551	1.731 ±0.05	0.529
$Pb_{0.95}Sr_{0.05}ZrO_3$ (PSZ9505)	1.681	2.521	7.076	1.468 ±0.05	0.578
$Pb_{0.90}Sr_{0.10}ZrO_3$ (PSZ9010)	1.357	1.9	6.736	2.359 ±0.05	0.378
$Pb_{0.85}Sr_{0.15}ZrO_3$ (PSZ8515)	1.474	2.293	6.438	2.164 ±0.05	0.431
$Pb_{0.80}Sr_{0.20}ZrO_3$ (PSZ8020)	1.004	1.205	5.777	3.316 ±0.05	0.313

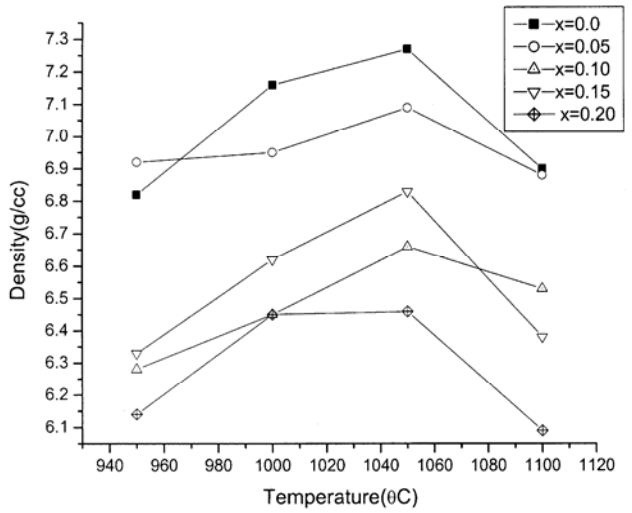

Fig. 3—Plot of density as a function of annealing temperature for Sr doped $PbZrO_3$ ($Pb_{1-x}Sr_xZrO_3$; x = 0, 0.05, 0.10, 0.15 and 0.20) ceramics

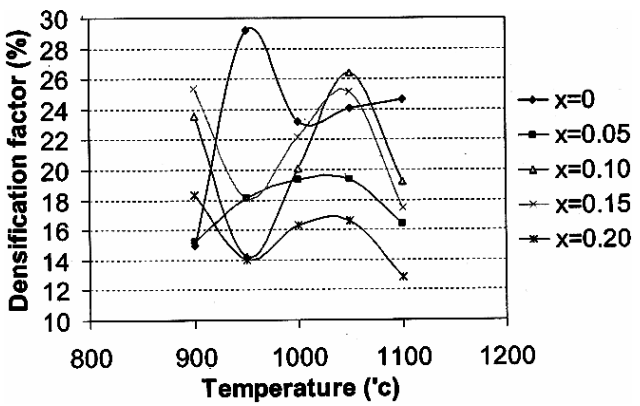

Fig. 4 (a)—The sintering behaviour pattern obtained on Sr doped $PbZrO_3$ ($Pb_{1-x}Sr_xZrO_3$; x = 0, 0.05, 0.10, 0.15 and 0.20) ceramics

given in Table 4. The above results indicated the fine particle characteristics of the synthesized powder. It is reported that the fine powder is, in general, preferred in processing of ceramic material as it tends to sinter more readily and can yield a finer grain size[22].

3.3. Sintering studies

In all processes, where powder particles are involved in the green body forming technique, the final possessing step requires sintering. The sintering process provides bonds between particles and substrate[23]. 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)]. They were uniaxially pressed into circular pellets of (12 mm diam, 2.0 mm thick) at a pressure of 150Mpa for 2 min duration. The prepared ceramic pellets were subjected to annealing in order to get useful information about their sintering behaviour. 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 to 1100°C for 2 h time duration at a heating/cooling rate of 5°C/min. Prior to annealing and after annealing, the physical parameters like, the shrinkage in volume and densification factor were calculated as a qualitative assessment of the powder compaction[24]. A plot of density as a function of sintering temperature is shown in Fig. 3. The density of the compact increased with increase in sintering temperature up to 1050°C as indicated[25]. It is found that beyond the temperature 1050°C, the density of all doped oxides is decreased due to the disjointing behaviour of ceramic particles above this temperature. This similar behaviour is also reported for Ba doped $PbZrO_3$[26]. The densification and shrinkage curves of Sr doped $PbZrO_3$ are shown in Figs 4 (a) and (b).

The SEM images of Sr doped $PbZrO_3$ ceramics (after sintering at 1050°C for 2 h) are shown in Figs 5 (a)-(e). It has been observed that the particles were closely packed at their sintering temperature of 1050°C. There has been found a small change in the grain sizes for all the sintered compacts (around 2

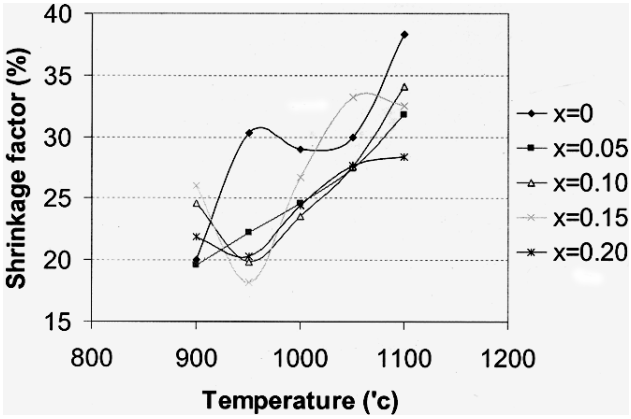

Fig. 4 (b)—The percentage shrinkage in volume of Sr doped $PbZrO_3$ ($Pb_{1-x}Sr_xZrO_3$; x = 0, 0.05, 0.10, 0.15 and 0.20) ceramics

μm). From the above results, it is found that the $PbZrO_3$ ceramics may be sintered at 1050°C for 2 h effectively.

4 Conclusions

The glycine-nitrate combustion technique can be effectively used for the preparation of lead zirconate ceramics for transducer / energy storage applications. It is reported that the fine powders of Sr doped $PbZrO_3$ resulted in good sintering characteristics (below 1050°C). The glycine-nitrate combustion technique is safe and it seems to be a promising technique for synthesizing oxide ceramics in a cost effective manner.

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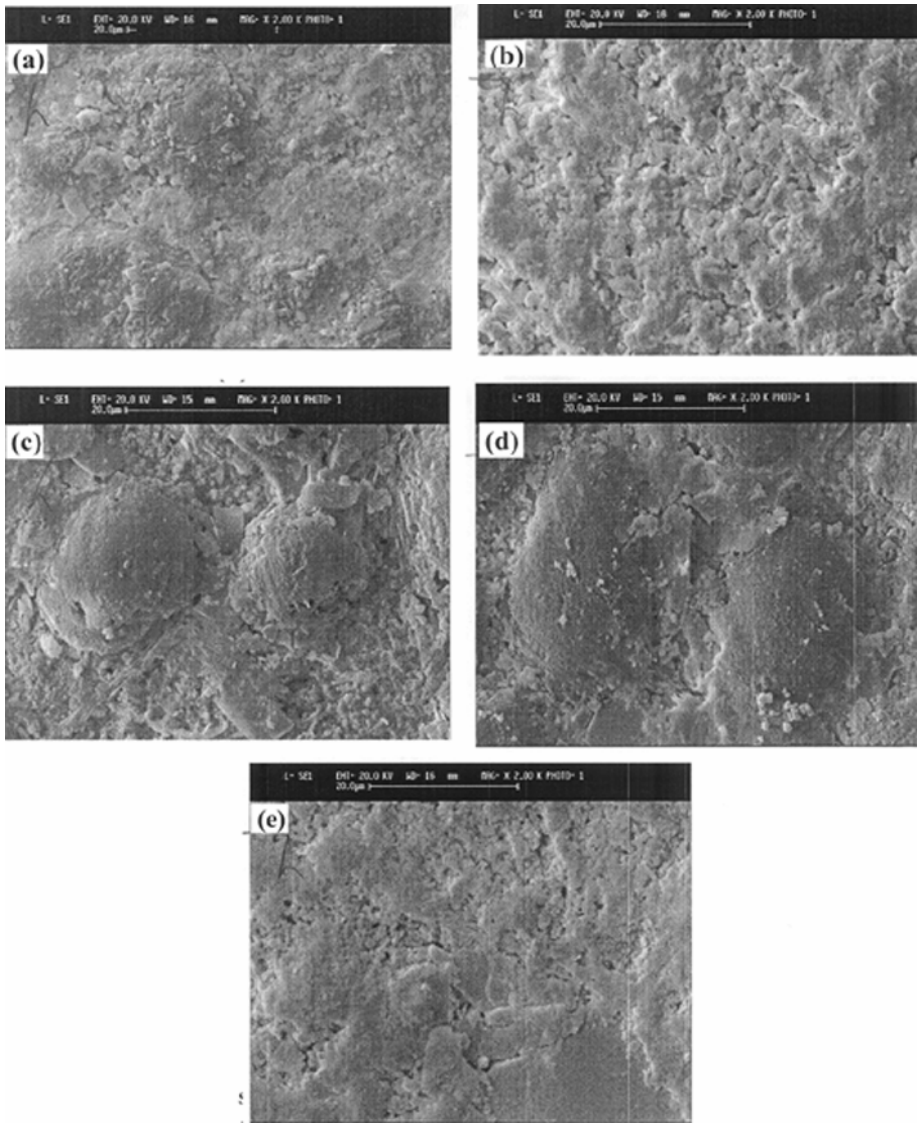

Fig. 5—SEM images of $Pb_{1-X}Sr_xZrO_3$ ceramics sintered at 1050ºC for 2h : (a) x = 0, (b) x = 0.05, (c) x = 0.10, (d) x = 0.15 & (e) x = 0.20

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