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Synthesis and sintering behaviour of 'Strontium' substituted $PbZrO_3$ by urea-nitrate combustion technique

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ABSTRACT

Strontium substituted Lead zirconate ($Pb_{1-X}Sr_XZrO_3$ (x = 0, 0.05, 0.10, 0.15 and 0.20) ceramics have been synthesized by a novel method called urea-nitrate self-propagating combustion technique, using lead nitrates, strontium nitrates, zirconium nitrates as. oxidizer and urea's as fuel at 550°C in preheated muffle furnace. The as-synthesized ceramic powder was heat treated at 800°C for 6h in order to get phase pure compounds. The prepared powder were characterized by XRD, FTIR, density, particle size analysis and BET surface and measurements. The XRD patterns obtained on these powders showed the formation of pure orthorhombic phase of PbZrO3 without any impurities. Thin sections of circular components of these powders were also made by uniaxial compression and were subject ed to annealing at different temperatures ranging 900°C to 1050°C for 2 h in order to throw light on their sintering behavior. The surface morphology of the sintered components was studied by SEM.

Key words: $Pb_{1-X}Sr_XZrO_3$, ceramics, combustion synthesis, characterization, sintered components.

INTRODUCTION

Lead zirconate (PZ) is a typical antiferroelectric (AFE) material at room temperature[1-2], from which the ferroelectric (FE) state can be induced when subjected to a sufficiently large electric field. It has been extensively studied because of its unique pyroelectric, electrooptical[3-4] and piezoelectric properties[5-9], which are required for many application in electronic and microelectronic[10-11]. Lead zirconate is also a candidate material for energy storage applications12.

Several techniques can be used to prepare advanced ceramic materials and the urea-nitrate combustion technique can be highlighted among them all[13], Preparation of lead zirconate by concentional 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[14-16]. 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 pH of the solution, temperature and concentrations of the cations. For the sol. Gel method, the calcinations temperature to yield pure $PbOZrO_3$ had reported to be as low as 700°C for h of soaking time[17]. The phase formation temperature for pure $PbOZrO_3$ by citrate route was also reported to be in the vicinity of 700°C[18].

Recently combustion technique has been attracting, since it is as a straightforward preparations process to produce homogeneous very fine crystalline and un-agglomerated powders with good sintering behavior. It explores and exothermic generally very fast and self-sub straining chemical reaction between the desired metal salts (nitrates) and suitable organic fuel (urea) which is ignited at a temperature much lower than the actual phase formation temperature[19-25]. 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 external source. This process is safe, instantaneous and energy saving.

In, this present work, a novel urea-nitrate self-propagating combustion technique has been used for the preparation of 'Sr') substituted $PbOZrO_3$ ($Pb_{1-X}Sr_XZrO_3$ (x = 0, 0.05, 0.10, 0.15 and 0.20) in the form of fine powders. The physical and thermal properties of the synthesized powders were systematically evaluated. When the circular components of these materials area annealed at different temperatures (between 900-1050°C) in order to acquire information about their thermal properties such as densification factor, expansion and shrinkage among the adjoining cell components.

EXPERIMENTAL

The starting materials used in the present work included; a high purity lead zirconate (>99% Merck), strontium nitrate (>99% Merck), zirconium nitrate (>99% Merck) and Urea (>99% Merck). In the urea-nitrate combustion technique, fine particles of 'Sr' substituted $PbOZrO_3$ ie. ($Pb_{1-X}Sr_XZr0_3$ (x = 0, 0.05, 0.10, 0.15 and 0.20) materials were prepared by the combustion of the corresponding metal nitrates-urea mixtures. In this process, Lead nitrate, strontium nitrate and zirconium nitrate were used as oxidizers and urea was used as fuel. The stoichiometric composition 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 stroichometric balance, so that the equivalence ratio (i.e.O:F=1) is unity and the energy released by the combustion is maxiumum[26]. Based on the propellant chemistry, the valence of C=+4,=+1, divalent ions = +2, trivalent ions = +3 and so on, and O = -2 valance of Nitrogen is considered to be zero. Based on these considerations Pb $(NO_3)_2$, $Sr(NO_3)_2$, $ZrO(NO_3)_2$ will have an oxidizing valance of –10 and urea will have a reducing valance of +6.

The appropriate stoichiometric quantities of the corresponding metal nitrates and an organic fuel (urea) were weighed accurately, taken in a quartz crucible and dissolved in distilled water. The mixed solution was heated in heating mantle up to boiling and self-ignition. The quarth crucible was then transferred to a muffle furnace preheated at 550°C, boils, froths, ignites and caches fire (temperature 1100±100°C). At this higher temperature the metal nitrates decompose of metal oxides of nitrogen and hence act as oxidizer for further combustion residue in less than 5 minutes. The flame persisted for about 1 minute. The foam was then lightly grounded in silica basin with porcelain pestle to obtain fine powders. The procedure is explained in the schematic Fig.1. The appropriate amounts of the reactants with urea fuel are indicated in Table 1.

Table 1: Amount of precursor materials taken for combustion synthesis of 'Sr' doped $PbZrO_3$ by urea-nitrate combustion technique

S. No.	Sample	$Pb(NO_3)_2$ (gm)	$Sr(NO_3)_2$ (gm)	$Zro(NO_3)_2$ (gm)	Urea (gm)	Yield (gm)
1.	$PbZrO_3$	13.248	-	9.249	7.99	11.572
2.	$Pb_{0.95}Sr_{0.005}ZrO_3$(PSZ9505)	12.732	0.529	11.562	9.998	14.457
3.	$Pb_{0.90}Sr_{0.010}ZrO_3$(PSZ9010)	14.904	0.528	11.562	9.998	14.289
4.	$Pb_{0.85}Sr_{0.015}ZrO_3$(PSZ8515)	14.076	1.587	11.562	9.998	14.119
5.	$Pb_{0.80}Sr_{0.020}ZrO_3$(PSZ8020)	13.248	2.116	11.562	9.998	13.853

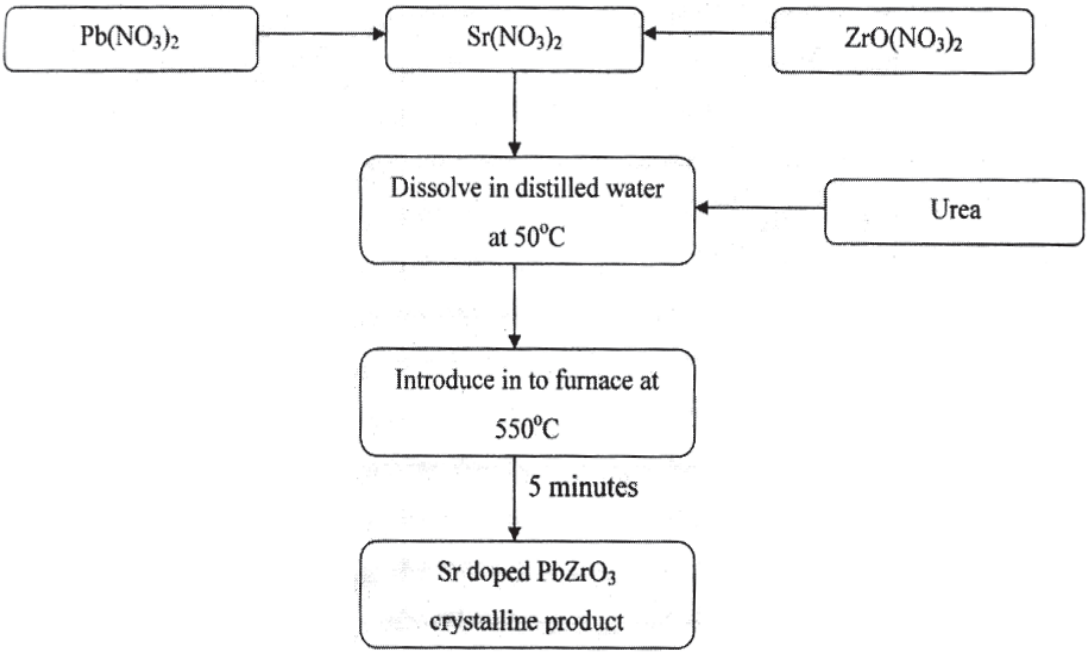

Fig. 1: Flow chart to prepare 'Sr' doped with $PbZrO_3$ through Urea-nitrate combustion technique

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

$$Pb(NO_3)_2 + ZrO(NO_3)_2 + 3.33\ NH_2CONH_2 \rightarrow PbZrO_3 + 3.33\ CO_2 + 3.66N_2 + 6.66\ H_2O \quad \ldots(1)$$

Calcinations of the as-synthesized samples was carried out in alumina crucible at 800°C for 6 h in dry atmosphere to remove deposited carbon and unreacted organic residues and to get phase pure compounds[27]. The calcinations of the as-synthesized powders imply a significant weight loss for urea-nitrate synthesis. The weight loss in urea-nitrate synthesis was 1.7 to 5.7% for oxide powders. These data area indicated in Table 2. The combustion derived 'Sr' doped $PbOZrO_3$ ie. $(Pb_{1-x}Sr_xZrO_3$ (x = 0, 0.05, 0.10, 0.15 and 0.20) powders were characterized by powder XRD, Density, particle size analysis, Fourier Transform IR spectroscopy [FTIR], and BET surface are measurement. The XRD patterns of the heat-treated powders were obtained with a Philips Type-PW 1140/90 X-ray Diffractometer, using cula radiation. Lattice parameters were calculated with a least square fitting method. The average crystalline sizes of the powders were calculated by Schere's formula. The powder density was measure by using a pycnometer with xylene as the medium. Perkin-Elmer paragon 500 FTIR spectrometer was employed to record the IR spectra of the heat powder in the range of 4000-400/cm^{-1}. Particle size of the heat-treated powders was measured using Malvern Laser based particle size analyzer. Malvern instruments Ltd, UL. The surface area of the powders was measured using a Quantasorb BET surface area analyzing instruments. The sintering behavior of the circular pallets was studied in temperature controlled programmable furnace between the temperature ranges of 900-1050°C. Surface morphology of the sintered components was studied using a scanning electron microscope (SEM), Stereoscan model - 360.

RESULTS AND DISCUSSION

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 Fig.2. All the peaks area very sharp showing the crystalline nature of the heat treated powders. The XRD pattern of the heat-treated 'Sr' doped $PbOZrO_3$ powders and matched with standard data [JCPDS file for $PbOZrO_3$ No: 35-0739]. From the XRD, it could be concluded that all 'Sr' doped $PbOZrO_3$ had orthorhombic crystal structure. Lattice parameters were calculated with a least square fittings method. The lattice constants are in good agreement with the standard data [JCPDS file for $PbOZrO_3$ No: 35-0739]. The average crystalline sizes of the powders were calculated by Sherer's formula[28]. The XRD data obtained on the heat treated powders are indicated in Table 3.

FTIR studies

The FTIR spectra 'Sr' doped $PbOZrO_3$ ie. ($Pb_{1-X}Sr_XZrO_3$ (x = 0, 0.05, 0.10, 0.15 and 0.20) are shown in the Fig. 3. The FTIR spectra of lead zicronate and strontium substituted lead zirconate powders in all composition have almost similar characteristics peaks are observed. The peak appeared at 571.35cm^{-1} in PSZ9505, 403.92cm^{-1} in PSZ85.515, 561.76cm^{-1} in PSZ8020 samples are due to the presence of metal-oxygen bonds in the

Table 2: Reduction in weight obtained or 'Sr' doped wiht $PbZrO_3$ Oxide powder during Calcinations at 800°C/6h by Urea-nitrate combustion synthesis

S. No.	Sample	W_i (g)	W_{ht}(g)	ΔW (%)
1.	$PbZrO_3$	11.572	11.144	3.699
2.	$Pb_{0.95}Sr_{0.005}ZrO_3$(PSZ9505)	14.457	14.188	1.861
3.	$Pb_{0.90}Sr_{0.010}ZrO_3$(PSZ9010)	14.289	13.739	3.849
4.	$Pb_{0.85}Sr_{0.015}ZrO_3$(PSZ8515)	14.119	13.313	5.709
5.	$Pb_{0.80}Sr_{0.020}ZrO_3$(PSZ8020)	13.853	13.618	1.696

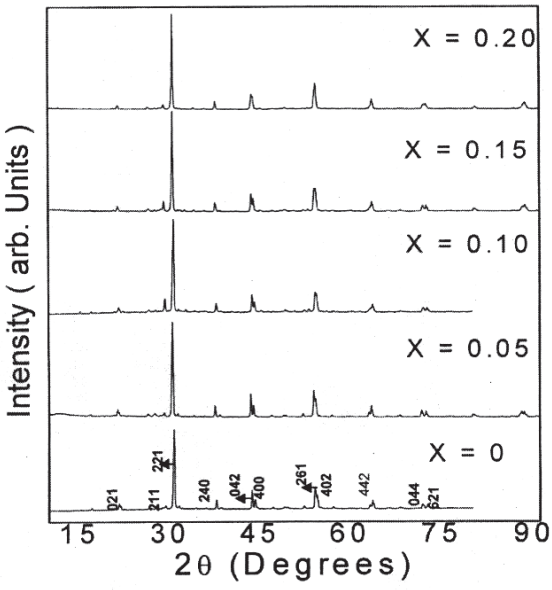

Fig. 2: XRD pattern obtained on 'Sr' doped $PbZrO_3$ ($Pb_{1-x}Sr_xZrO_3$ (X=0,0.05, 0.10, 0.15 and 0.20)) ceramic powder calcined at 800°C/16h

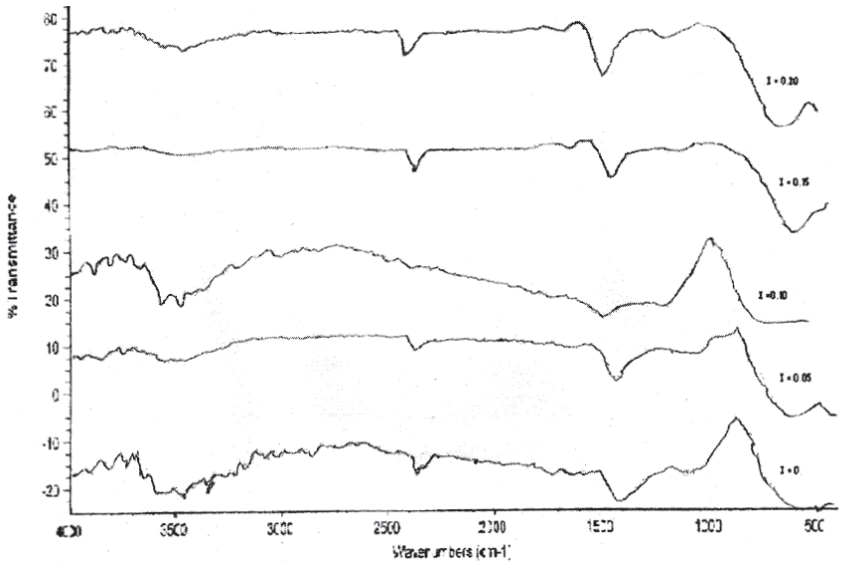

Fig. 3: FTIR spectrum obtained on 'Sr' doped $PbZrO_3$ ($Pb_{1-x}Sr_xZrO_3$ (X=0,0.05, 0.10, 0.15 and 0.20)) ceramic powder calcined at 800°C/16h

Table 3: XRD data obtained or Sr doped $PbZrO_3$ Powder synthesized by Urea-nitrate combustion technique

S. No.	Properties	Standard XRD Data for $PbZrO_3$ powder[JCPDS No. 35-0739]	Obtained XRD data				
			$PbZrO_3$ ZrO_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
1.	Crystal structure	Orthorhombic	Orthorh-ombic	Orthorh-ombic	Orthorh-ombic	Orthorh-ombic	Orthorh-ombic
2.	Unit cell parameter (A)	a = 8.232 b = 11.756 c = 5.882	a = 8.237 b = 11.775 c = 8.875	a = 8.326 b = 11.776 c = 5.8820	a = 8.237 b = 11.775 c = 5.879	a = 8.241 b = 11.775 c = 5.874	a = 8.237 b = 11.775 c = 5.89
3.	Unit cell Volume (A)	570.17	570.12	570.46	570.18	569.82	570.18
4.	Theoretical Density (g/cc)	8.071	8.071	7.927	7.791	7.657	7.513
5.	Average Crystalline size(nm)	-	31.99	34.39	32.97	38.17	42.35

The values are indicated in Table 4. The above results indicated the fine particle characteristic 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[33]. The particle characteristic of the powders obtained from particle size distribution analysis is indicated in Table 5.

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 bonds between particles and substrate[34]. The combustion derived product was mixed with a biding agent (4% polyvinyl alcohol (PV A) solution). They were uniaxially pressed into circular pellets of (12mm diameter, 1.5-2.0mm thickness) at a pressure of 150 MPa for 2 minutes duration. The prepared ceramic pellets were subjected to annealing in order to get useful information about their sintering behavior. Initially,

Table 4: Density and BET suface area measurements obtained on Sr doped $PbZrO_3$ powders

Samples	Bulk density g/cc	Top density g/cc	Absolute density g/cc	Surface area (BET) mg-1	Average Particle (from surface area)µm
$PbZrO_3$ 1.563	2.501	7.012	1.535	0.557	
$Pb_{0.95}Sr_{0.005}ZrO_3$(PSZ9505)	1.684	2.481	6.505	1.422	0.649
$Pb_{0.90}Sr_{0.010}ZrO_3$(PSZ9010)	1.520	1.901	6.782	1.381	0.641
$Pb_{0.85}Sr_{0.015}ZrO_3$(PSZ8515)	1.608	2.010	6.676	1.522	0.591
$Pb_{0.80}Sr_{0.020}ZrO_3$(PSZ8020)	1.540	2.155	6.028	1.525	0.653

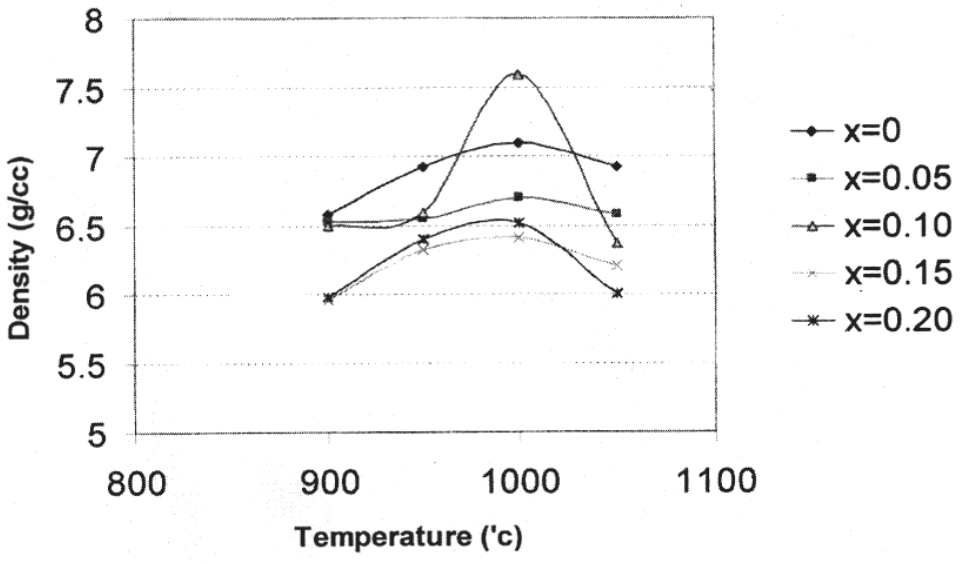

Fig. 4: Plot of density as a function of annealing temperature for 'Sr' doped $PbZrO_3$ ($Pb_{1-x}Sr_xZrO_3$ (X=0,0.05, 0.10, 0.15 and 0.20)) ceramic

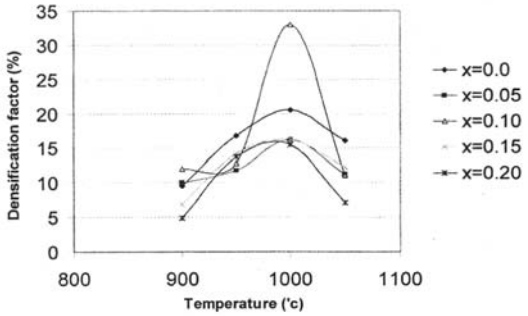

Fig. 5(a): The sintering behavior patern obtained on 'Sr' doped $PbZrO_3$ ($Pb_{1-x}Sr_xZrO_3$ (X=0,0.05, 0.10, 0.15 and 0.20)) ceramic

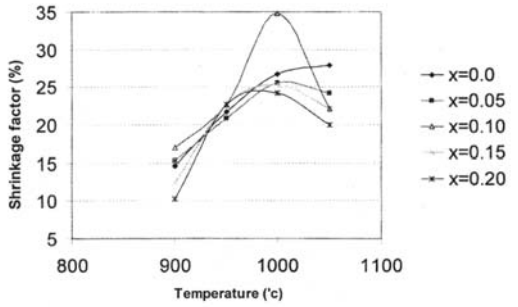

Fig. 5(b): The percentage shrinkage in volume of 'Sr' doped $PbZrO_3$ ($Pb_{1-x}Sr_xZrO_3$ (X=0,0.05, 0.10, 0.15 and 0.20)) ceramics

solid structure. The peak appeared at 34.17.92 cm^{-1}, 3456.17cm^{-1}, 3449.87cm^{-1}, 3445.99cm^{-1}, are corresponding to PZ, PSZ9505, PSZ9010, PSZ8020 samples are attributed to the presence of moisture in the samples[29]. Also the peaks observed at 2365.09cm^{-1} in PZ, 2359.42cm^{-1} in PSZ9505, 2353.95cm^{-1} in PSZ9010, 2353.99cm^{-1} in PSZ8020 are due to the presence in CO_2[30]. This indicate that their structural similarity of the samples. Most of the peaks appeared in PZ and Sr doped PZ are comparable with each other with lattice variation in their absorption wavelengths, which conformed the similarity in their structural properties. The structural similarity is also confirmed by XRD for all the stable orthorhombic structural geometry.

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 area shown in Table 4. The BET surface area values of all the heat treated powders are similar to each other, 1.4 to 1.5m^2g^{-1}. The average particle size (D) of the oxide (assuming that the particles are spherical) was calculated the following formula[31-32].

$$D=6/S\rho \quad \ldots(2)$$

Where, S is the surface area per unit weight in m^2/g and ρ is the density of the particle in g/m3.

Table 5: Particle size measurement of 'Sr' doped $PbZrO_3$ heat treated powders

S. No.	Sample	Cumculative under size (μm)		
		(10%)	(50%)	(90%)
1.	$PbZrO_3$(PZ)	0.18	0.42	8.84
2.	$Pb_{0.95}Sr_{0.005}ZrO_3$(PSZ9505)	0.25	11.01	26.70
3.	$Pb_{0.90}Sr_{0.010}ZrO_3$(PSZ9010)	0.22	3.75	14.03
4.	$Pb_{0.85}Sr_{0.015}ZrO_3$(PSZ8515)	0.19	0.75	10.91
5.	$Pb_{0.80}Sr_{0.020}ZrO_3$(PSZ8020)	0.18	0.58	10.44

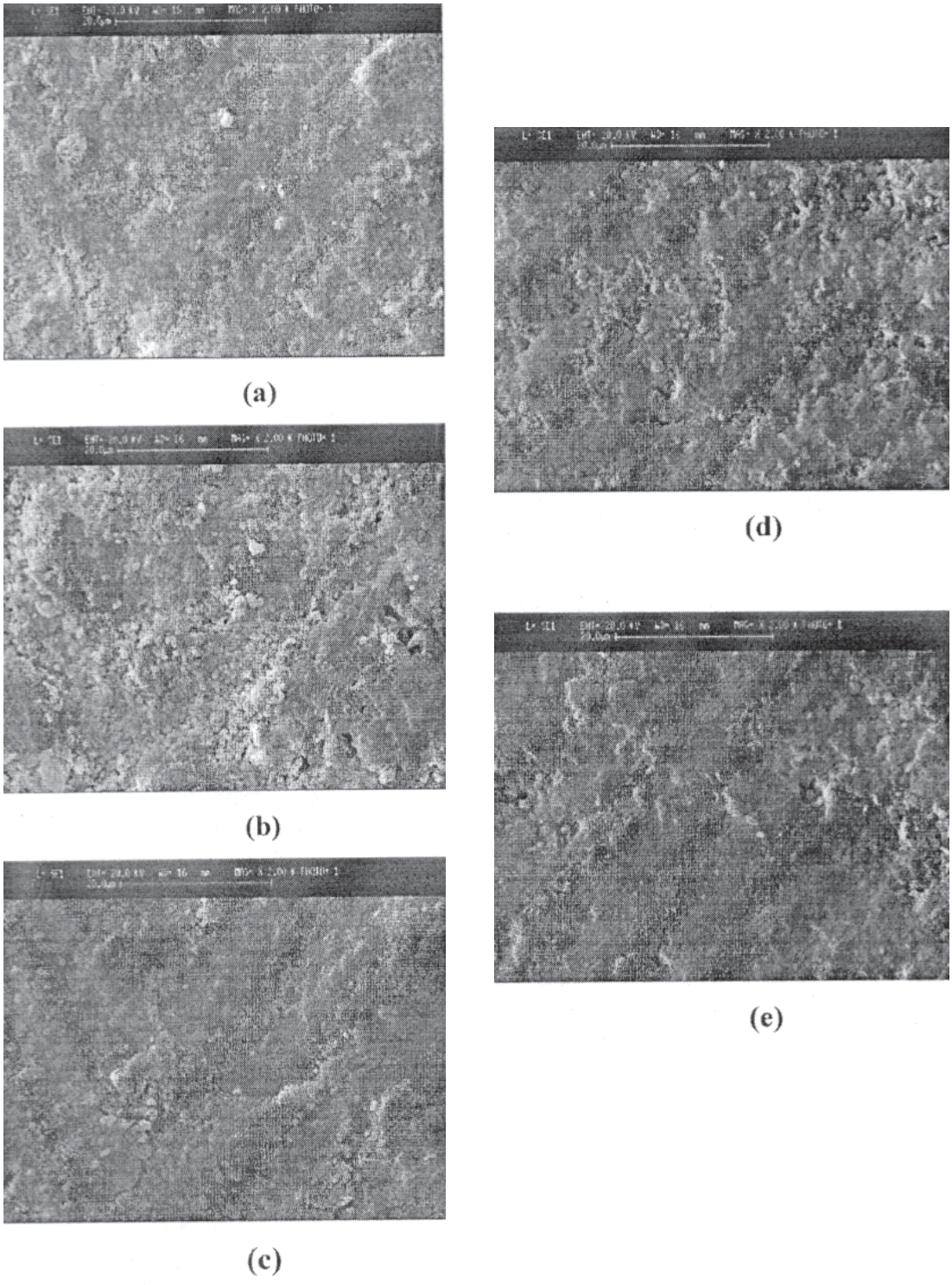

Fig. 6: SEM images of $Pb_{1-x}Sr_xZrO_3$ ceramics sintered at 1000°C for 2 h [(a) x = 0, (b) x = 0.05, (c) x = 0.10 and (d) x = 0.15]

the binder content was removed by heating the pellet at 700° for 30 minutes. Then the binder burnt-out components were sintered in controlled atmosphere from 900°to 1050°C for 2h time duration at a heating/ cooling rate or 5°C/minute. Prior to annealing and after annealing the physical parameters like, the shrinkage in volume and densification factor were calculated as qualitative assessment of the powder compaction[35]. A plot of density as a function of sintering temperature is shown in Fig. 4. The density of the compact increased with increase in sintering temperature up to 1000°C as indicated[36]. It is found that beyond the temperature 1000°C, the density of all doped oxides is decreased due to the disjointing. The densification and shrinkage curves of Sr doped $PbZrO_3$ are shown in Fig.5 (a and b).

The SEM image of Sr doped $PbZrO_3$ ceramics (after sintered at 1000°C) for 2 h) are shown in Fig.6. (a, b, c and d). They showed that the particles were closely packed at their singering temperature of 1000°C. The grains sizes were found to be uniform for all the sintered compact (around 2μm). From the above results, it is found that the $PbZrO_3$ ceramics may be sintered at 1000°C for 2h effectively).

CONCLUSION

The urea-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 powder for Sr doped $PbZrO_3$ resulted in good sintering characteristics (below 1000°C). The urea nitrate combustion technique is safe and it seems to be promising technique for synthesizing oxide ceramics in a cost effective manner.

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