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Preparation, characterization and sintering behaviour of $Ba_{1-x}Sr_xZro_3$ ($0 \leq x \leq 0.20$) by urea-nitrate combustion technique

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ABSTRACT

Strontium substituted barium zirconate $Ba_{1-x}Sr_xZrO_3$ (x = 0, 0.05, 0.10, 0.15 and 0.20) ceramics have been prepared by a urea-nitrate combustion technique, using barium nitrate, strontium nitrate and zirconium nitrate as oxidizers and urea as fuel at 500^{0}C in a pre-heated muffle furnace. The as- synthesized powders were heat treated at 800^{0}C for 6 h in order to get phase pure compounds. The heat treat powders were characterized by XRD, density, BET surface area and particle size measurements. The XRD pattern obtained on these powders showed the formation of cubic phase of $BaZrO_3$. Thin section of circular component of these powders was also made by uniaxial compression and were subjected to annealing at different temperatures from 900 to 1050^{0}C for 2 h. The surface morphology of the sintered components was studied by Scanning Electron Microscopy.

Key words: Perovskite oxides, combustion synthesis, characterization and sintering.

INTRODUCTION

Barium zirconate has a cubic perovskite structure and a high melting point of about 2600^{0}C. It is an important technological material and has found widespread applications in dielectrics and piezoelectric, electro-optic materials, catalysts and proton conductors[1-2]. It was discovered recently that $BaZrO_3$ does not react with the melt during the crystal growth of high Tc superconducting compound $YBa_2CU_3O_{7-\delta}$ [3-4]. Barium zirconate can be used as an inert crucible material either as bulk $BaZrO_3$ crucibles[4] or $BaZrO_3$ coated alumina crucibles[5].

Several techniques can be used to prepare advanced ceramic materials and the combustion synthesis route can be highlighted among them all[6]. Now a days, this method has been attracting increasing interest as a straightforward preparation process to produce homogeneous, very fine, crystalline and unagglomerated powders with good sintering behavior. It explores an exothermic, generally very fast and self-sustaining chemical reaction between the desired metal salts (nitrates, chlorides, sulfates) and a suitable organic fuel (such as glycine, urea), which is ignited at a temperature much lower than the actual phase formation temperature[7-13]. 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.

In this paper, we report the synthesis and characterization of strontium doped barium zirconate $Ba_{1-x}Sr_xZrO_3$(x = 0, 0.05, 0.10, 0.15 and 0.20) having a perovskite structure by urea-nitrate combustion method.

EXPERIMENTAL

In the urea-nitrate combustion method, fine particle of 'Sr' doped $BaZrO_3$ i.e. $Ba_{1-x}Sr_xZrO_3$ = 0, 0.05, 0.10, 0.15 and 0.20) materials were prepared by the combustion of the corresponding metal nitrate urea mixtures. In this process, barium nitrate, strontium nitrate and zirconium nitrate were used as oxidizers and urea was used as fuel. The stoichimetric 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 co-efficient 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[14]. Based on the propellant chemistry, the valence of C = +4, H = 1, divalent ions = +2, trivalent ions = 3 and so on, O = -2. The valence of nitrogen is considered to be zero. Based on these considerations Ba $(NO_3)_2$, Sr $(NO_3)_2$ and $ZrO(NO_3)_2$ 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 quartz crucible was then transferred to a muffle furnace preheated at 500°C, boils, froths, ignites and caches fire (temperature 1100 ± 100°C). 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. 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 taken for synthesis are indicated in Table 1. The following is the theoretical equation for producing parent oxide assuming complete combustion of the redox mixtures with urea as the fuel.

$$Ba(NO_3)_2 + ZrO(NO_3)_2 + 3.33NH_2CONH_2 \rightarrow BaZrO_3 + 3.33CO_2 + 3.66N_2 + 6.66\ H_2O \quad ...(1)$$

Calcinations of the as-synthesized samples was carried out in alumina crucibles at 800°C for 6 h in dry air atmosphere to remove

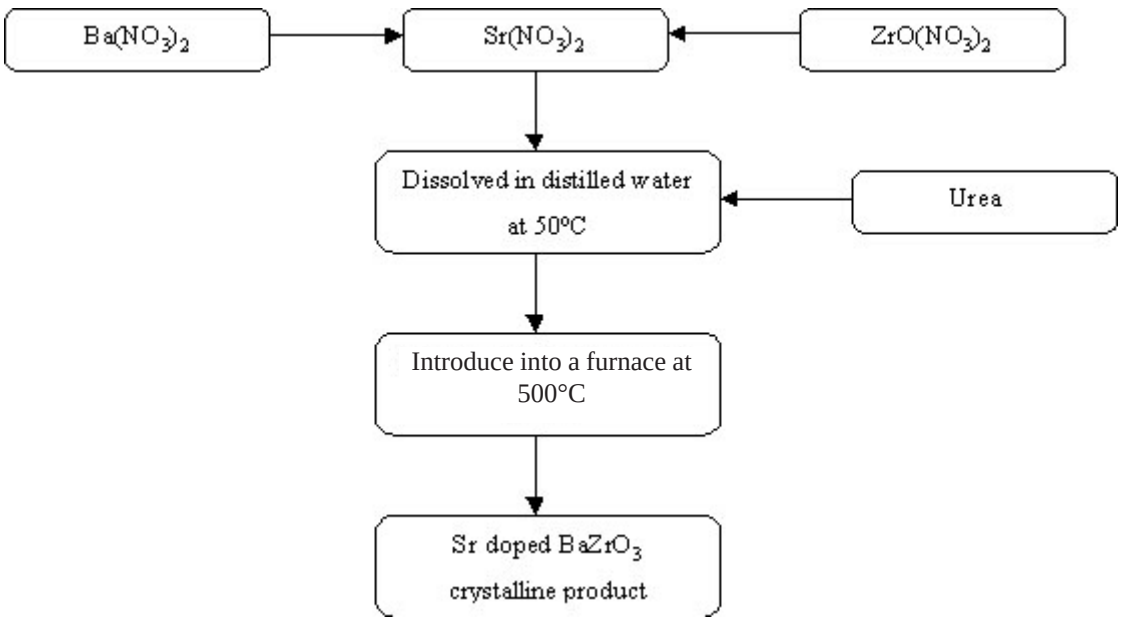

Fig. 1: Flow Chart to prepare 'Sr' doped with $BaZrO_3$ through Urea-nitrate combustion technique

deposited carbon and un-reacted organic residues and to get phase pure compound [15]. The calcinations of the as-synthesized powders show a significant weight loss for urea-nitrate synthesis. The weight loss in urea-nitrate synthesis was 9.97 to 33.07% for oxide powders. These data are indicated in Table 2. The combustion derived 'Sr' doped $BaZrO_3$ i.e. $Ba_{1-x}Sr_xZrO_3$ (x = 0, 0.05, 0.10, 0.15 and 0.20) powders were characterized by XRD, density, BET surface area, and particle size measurement. The XRD patterns of the heat-treated powders were obtained with a Philips type-PW1140/90 X-ray

Table 1: Amount of precursor materials taken for combustion synthesis of Sr' doped BaZrO3 Powder

Compositions	$Ba(NO_3)_2$ (g)	$Sr(NO_3)_2$ (g)	$ZrO(NO_3)_2$ (g)	Urea (g)	Yield (g)
$BaZrO_3$	14.519	-	12.846	11.109	16.235
$Ba_{0.95}Sr_{0.05}ZrO_3$	12.414	0.529	11.562	9.998	14.629
$Ba_{0.90}Sr_{0.10}ZrO_3$	11.76	1.058	11.562	9.998	11.8
$Ba_{0.85}Sr_{0.15}ZrO_3$	11.107	1.587	11.562	9.998	10.829
$Ba_{0.80}Sr_{0.20}ZrO_3$	10.454	2.116	11.562	9.998	15.947

Diffractometer, using cuka radiation. The powder density was measured by using a pychnometer with xylene as the medium.. Particle size of the heat treated powders was measured using Malvern Laser based particle size analyzer, Malvern Instrument Ltd, U.K. The surface area of the powders was measured using a Qauntasorb BET surface area analyzing instrument. The sintering behaviour of the circular pellets was studied in a temperature controlled programmable furnace between the temperature ranges from 900 to 1050°C. Surface morphology of the sintered components was studied using a scanning electron microscope (Steroscan model-360).

Table 2: Reduction in weight observed on 'Sr' doped $BaZrO_3$ perovskite powder during calcination at 800°C for 6 h

Compositions	W_i (g)	W_{ht} (g)	ΔW (%)
$BaZrO_3$	16.235	11.936	26.479
$Ba_{0.95}Sr_{0.05}ZrO_3$	14.629	9.791	33.071
$Ba_{0.90}Sr_{0.10}ZrO_3$	11.8	10.623	9.969
$Ba_{0.85}Sr_{0.15}ZrO_3$	10.829	9.717	10.269
$Ba_{0.80}Sr_{0.20}ZrO_3$	15.947	10.786	32.361

Wi=Initial Weight Wht - After heat treatment
ΔW-Reduction in weight

RESULTS AND DISCUSSION

XRD studies

The phase formation behaviour of the calcined powder $Ba_{1-x}Sr_xZrO_3$ (x = 0, 0.05, 0.10, 0.15 and 0.20) ceramics is revealed by XRD as shown Fig. 2. The XRD patterns show the formation of cubic strontium doped $BaZrO_3$ up to = x=0.20 The XRD pattern of the heated treated are matched with that of the parent compound $BaZrO_3$ (JCPDS No. 06-0399). One or two impurity peaks of $BaCO_3$ could also be identified. These impurity peaks, however gradually reduced with increase in dwell time at 800°C as well as with increase in calcinations temperature[16]. Lattice parameters were calculated

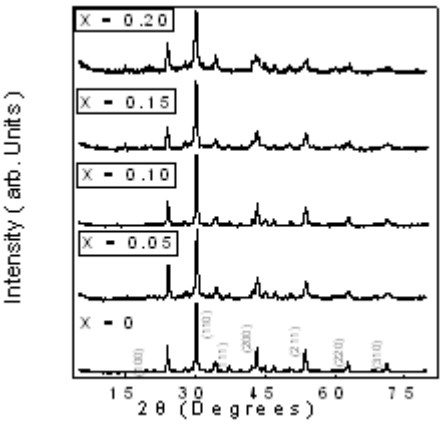

Fig. 2: XRD pattern obtained on Sr doped $BaZrO_3$ powder calcined at 800 °C for 6h

Table 3: XRD data obtained on 'Sr' doped $BaZrO_3$ powder calcined at 800°C for 6h

Properties	Standard XRD data for $BaZrO_3$ Powder JCPDS NO: 35-0739	Obtained XRD data $BaZrO_3$	$Ba_{0.95}Sr_{0.05}ZrO_3$	$Ba_{0.90}Sr_{0.10}ZrO_3$	$Ba_{0.85}Sr_{0.15}ZrO_3$	$Ba_{0.80}Sr_{0.20}ZrO_3$
Crystal Structure	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic
Unit cell parameter (A^0)	4.193	4.179	4.163	4.172	4.182	4.175
Unit cell Volume (A^0)	73.72	72.98	72.17	72.61	73.13	72.76
Theoretical density (g/cc)	6.229	6.291	6.291	6.21	6.109	6.084
Average Crystallite size (nm)	-	27.63	22.95	24.49	18.63	15.92

Table 4: Density and BET surface area measurements obtained on 'Sr' doped $BaZrO_3$ heat treated powder at 800°C for 6 h

Compositions	Bulk density g/cc	Tap density g/cc	Absolute density g/cc	Surface area (BET) m^2g^{-1}	Average particle size (from surface Area) µm
$BaZrO_3$	1.07	1.551	4.597	7.403	0.176
$Ba_{0.95}Sr_{0.05}ZrO_3$	0.85	1.134	3.921	16.686	0.092
$Ba_{0.90}Sr_{0.10}ZrO_3$	0.882	1.372	4.771	13.432	0.096
$Ba_{0.85}Sr_{0.15}ZrO_3$	0.84	1.176	3.746	11.38	0.141
$Ba_{0.80}Sr_{0.20}ZrO_3$	0.889	1.132	3.46	17.541	0.099

with a least square fitting method. The XRD data obtained on the heat treated powders are indicated in Table 3. The theoretical density has been calculated using the lattice parameters with[17]

$$D_{Th} = Z \frac{M}{NV} \quad ...(2)$$

Where, M (in atomic-weight units) is the mass of one unit of the chemical formula, Z is the number of such chemical units in one unit cell of the crystal, N is the Avogadro's number and V (in $Å^{-3}$) is the volume of the crystalline unit cell as determined by X-ray diffraction. The theoretical density computed is also found to be matched with parent compound $BaZrO_3$ (JCPDS 06-0399).

In a purely Ionic model the structural stability of a perovskite structure is given by the tolerance factor't'

$$t = r_A + r_o / \sqrt{2}(r_b + r_o) \quad ...(3)$$

Where r_A, r_B and r_O are the Ionic radii of an A-site cation, B-site cation and on oxygen ion respectively. For ideal structure't' is unity, although stable perovskite structures could exist for the values of 't' between 0.8 and 1.1. The tolerance factor for pure BZ is 1.17 and in the case of strontium doped BSZ also in the range from 1.16 to 1.14.

The powder densities such as, bulk density, tap density and absolute density (measured using

Table 5: Particle size measurement obtained on 'Sr' doped $BaZrO_3$ heat treated powder at 800°C for 6 h

Compositions	Cumulative under size (µm) 10%	50%	90%
$BaZrO_3$	0.21	4.41	16.37
$Ba_{0.95}Sr_{0.05}ZrO_3$	0.21	2.61	8.36
$Ba_{0.90}Sr_{0.10}ZrO_3$	0.2	2.18	10.91
$Ba_{0.85}Sr_{0.15}ZrO_3$	0.24	8.3	17.83
$Ba_{0.80}Sr_{0.20}ZrO_3$	0.24	7.16	17.45

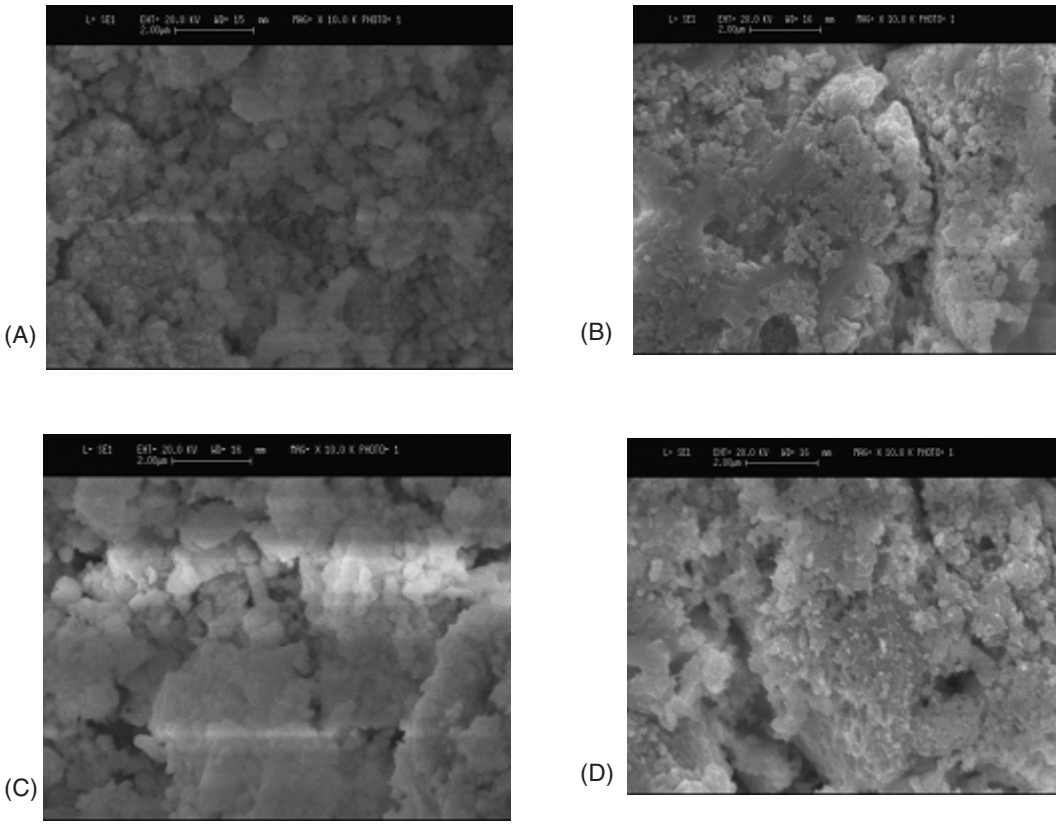

Fig. 3: SEM images of $Ba_{1-X}Sr_xZrO_3$ ceramics sintered at 1000°C for 2 h [(a) x = 0, (b) x = 0.05, (c) x = 0.10 and (d) x = 0.15]

pycnometer with xylene liquid) and BET surface area of the heat treated powders are shown in Table 4. The BET surface area values of all the heat treated powders are reported in the ranges from 7.4 to 17.5 m^2g^{-1}. The average particle size (D) of the oxide (assuming that the particles are spherical) was calculated the following formula[18,19].

$$D = 6/S\rho \quad ...(4)$$

Where 'S' is the surface area per unit weight in m^2/g and 'ñ' is the density of the particle in g/m^3. The values are indicated in Table 4. The particle characteristics of the heat treated powder 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 provides bounds between particle and substrate[20]. 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% PVA solution). They were uniaxially pressed into circular pellets of (12mm diameter, 1.5-2.00 mm thickness) at a pressure of 400 MPa. Initially, the binder content was removed by heating the pellet of 500°C for 30 minutes. Then, the binder burnt-out components were sintered in a controlled atmosphere from 900-1050°C for 2 h at a heating/cooling rate of 4°C and 5°C per minute. All composition could not be sintered to maximum density by urea-nitrate combustion route. In this route, all the compacts the increase in volume observed at 1000°C, which was due to the formation of inhomogeneous layer over the surface of the

compact, at this higher sintering temperature. Formation of additional layers at the surface of the compacts at higher annealing temperature reduce the densifying effect of the compacts. Higher firing temperature above 1600°C or longer soak time [21] or slow heating/cooling rate of 1°C per minute may be achieved a high density body after sintering (By solid state reaction method). The SEM images of Sr doped $BaZrO_3$ ceramics after sintering at 1000°C for 2 h are shown in Fig. 4 (a), (b), (c), (d) and (e). The grain sizes were found to be uniform for all the sintered compacts.

CONCLUSION

The urea-nitrate custion technique can be effectively used to the successful synthesis of 'Sr' doped $BaZrO_3$ at record low temperature (800^0C/ 6h) has been described. The BET surface area of the 'Sr' doped $BaZrO_3$ ceramic powders were ranges from $11.38 m^2g^{-1}$ to $17.54 m^2g^{-1.}$ The urea-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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