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Synthesis and characterization of A-site deficient rare-earth doped $BaZr_xTi_{1-x}O_3$ perovskite-type compounds

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ABSTRACT

A-site deficient rare-earth doped $BaZr_xTi_{1-x}O_3$ (BZT) ceramics were prepared from a soft-chemistry route and by solid-state reaction (SSR). Perovskite-like single-phase diagrams for the $BaTiO_3$–$La_{2/3}TiO_3$–$BaZrO_3$ system were constructed for each method of synthesis. Infrared spectroscopy on $(Ba_{1-y}La_{2y/3})Zr_xTi_{1-x}O_3$ solid solution revealed a dramatic stress on the M–O (M = Ti, Zr) bonds due to the combined effect of A-site vacancies and the lower ionic radius of La^{3+} than that of Ba^{2+}. A relationship between the M–O stretching vibration (υ) and the tolerance factor (t) was determined. $(Ba_{1-y}Ln_{2y/3})Zr_{0.09}Ti_{0.91}O_3$ (Ln = La, Pr, Nd) samples synthesized by SSR were selected for detailed studies. X-ray diffraction data were refined by the Rietveld method. Scanning electron microscopy on sintered compacts detected abnormal crystal growth and grain sizes in the range of about 1 µm up to 10 µm when the dopant concentration is 6.7 at. %. Impedance measurements exhibited that ferroelectric to paraelectric phase-transition temperature shifted to lower values as increasing rare-earth content. $(Ba_{1-y}Ln_{2y/3})Zr_{0.09}Ti_{0.91}O_3$ system showed a diffuse phase transition with a relaxor-like ferroelectric behaviour. Furthermore, the dielectric constant was enhanced with respect to non-doped BZT system.

1. Introduction

$BaZr_xTi_{1-x}O_3$ (BZT) ceramics are interesting materials for being used as dielectrics in commercial capacitor applications. They present high dielectric constant, high voltage resistance, composition-dependent Curie temperature and exhibit better temperature stability than $Ba_{1-x}Sr_xTiO_3$ in the paraelectric state [1–4].

Impurity-doping in BZT electroceramics has become also a common way to improve the material performance [5–7]. BZT-based tunable ferroelectric materials with moderate dielectric constant and low dielectric loss have been obtained by manipulating the doping amount of suitable rare-earth ions up to 4% [8]. In this way, recent studies of rare-earth doping on $(Ba_{1-x}Ln_x)Zr_{0.2}Ti_{0.8-x/4}O_3$ (Ln = La, Sm, Eu, Dy, Y) ceramics have demonstrated the effects of different ionic radius rare-earth elements on the dielectric properties and relaxor behaviour of BZT ceramics for potential applications as tuneable ceramic capacitors and tuneable microwave devices [9].

Nevertheless, reported works related to the A-site vacancy defect compensation model on rare-earth doped BZT ceramics are even scarcely investigated. Therefore, the focus of our investigation is set to the $(Ba_{1-y}Ln_{2y/3})Zr_xTi_{1-x}O_3$ system (Ln = La, Nd, Pr), where the effect of Ln-substitution for Ba-ion can be expressed by Kröger–Vink notation as

$$BaO + Ln_2O_3 \rightarrow Ba_{Ba} + 2Ln^{\bullet}_{Ba} + V''_{Ba} + 4O_O. \tag{1}$$

Eq. (1) implies that for every two Ln^{3+} ions positioned in the A-site, one cationic vacancy (V''_{Ba}) is necessary for charge neutrality in the perovskite structure. Obviously, the number of vacancies increases with increasing Ln^{3+} content.

The main purpose of this research is the synthesis and characterization of A-site deficient rare-earth doped $BaZr_xTi_{1-x}O_3$ (BZT) ceramics as a kind of suitable tunable dielectric materials for tunable ceramic capacitors and microwave device applications. In the present work, we have constructed perovskite-like single-phase diagrams for the $BaTiO_3$–$BaZrO_3$–$La_{2/3}TiO_3$ system. Samples were obtained from two different methods of synthesis. Lanthanum-doping influence on MO_6-perovskite (M = Ti, Zr) octahedra has been analyzed for $(Ba_{1-y}La_{2y/3})Zr_xTi_{1-x}O_3$ compounds. Microstructural analysis and dielectric characterization of the $(Ba_{1-y}Ln_{2y/3})Zr_{0.09}Ti_{0.91}O_3$ (Ln = La, Pr, Nd) solid solution have been performed for compounds obtained by solid-state reaction.

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2. Experimental procedure

2.1. Synthesis

$(Ba_{1-y}Ln_{2y/3})Zr_xTi_{1-x}O_3$ (Ln = La, Pr, Nd) solid solutions were prepared from two different routes of synthesis: the oxalate–peroxide method (O–P) [10] and solid-state reaction method (SSR) [11]. The starting materials used for the O–P method were $Ba(NO_3)_2$ (Probus QP), $La(NO_3)_3.6H_2O$ (Panreac 99.0%), Pr_6O_{11} (Aldrich 99.9%), Nd_2O_5 (Aldrich 99.9%), $TiOCl_2$ (Millennium Chemicals 99.5%), $ZrOCl_2.8H_2O$ (Fluka 95%), H_2O_2 30% (Panreac 99.9%) and $(NH_4)_2C_2O_4.H_2O$ (Panreac QP). The O–P method required two precursors, A and B. A-precursor was prepared by mixing a solution that contains the titanium oxychloride and zirconium oxychloride in nitric acid (4 M) with and aqueous solution of barium nitrate and the corresponding lanthanide nitrate. Pr_6O_{11} and Nd_2O_5 oxides were previously attacked with warm (1:1) nitric acid. B-precursor was prepared by mixing the aqueous solution of ammonium oxalate with ammonia solution (5 M) in order to obtain a pH of 9. The amount of ammonium oxalate in relation to the number of metallic ions in the reaction was fixed at 0.5. The A-precursor was added dropwise to the B-precursor at room temperature with constant stirring and pH was kept constant by the addition of aqueous ammonia. The precipitate was filtered, washed, dried and calcined for 5 h at 1000 °C in air on platinum vessels.

For the SSR method, the starting materials used were $BaCO_3$ (Aldrich 99%), La_2O_3 (Fluka 99.9%), Pr_6O_{11} (Aldrich 99.9%), Nd_2O_5 (Aldrich 99.9%), TiO_2 (Aldrich 99.9%) and ZrO_2 (Aldrich 99.0%). Oxides were dried overnight at 900 °C to drive off CO_2 prior to weighing. Pre-treated oxides and the barium carbonate were mixed in the desired proportions in an agate mortar with acetone and dried at 100 °C for 2 h. After grinding, samples were pressed uniaxially (500 MPa) into pellets and placed in platinum vessels. The pellets were calcined at 1200 °C for 12 h, repelleted and calcined at 1350 °C for 15 h. A final treatment was carried out at 1400 °C for 15 h.

2.2. Characterization

The phase identification were exercised using X-ray diffraction (XRD) measurements with a Siemens D-500 diffractometer in reflection mode with Cu-Kα radiation at room temperature, at 0.05° steps and a scanning rate of 1°/min. Cell parameters of single-phase perovskites were refined by the Rietveld method using the Win-PLOTR Fullprof program [12]. Chemical composition was determined by the inductive coupled plasma (ICP) method, using a Perkin Elmer OPTIMA 3200 RL spectrometer. Infrared (IR) data were recorded on an FTIR Thermo Nicolet IMPACT 400 spectrophotometer, using transparent KBr pellets. Particle morphology was observed by scanning electron microscopy (SEM) with a JEOL JSM-840 microscope. For dielectric measurements, samples were pressed uniaxially (300 MPa) into pellets of 5.0–6.0 mm in diameter and 0.9–1.1 mm in thickness. All compacts were sintered at 1450 °C for 3 h in air and quenched at room temperature. Gold electrodes were painted on both sides of the discs. Experimental setup for dielectric measurements was placed in a closed loop cold-finger cryogenic systems. Dielectric response from 50 K up to 350 K was measured using Agilent 4294A impedance analyzer at frequencies from 100 Hz to 1 MHz. The densities of ceramic samples were measured by the Archimedes method.

3. Results and discussion

The range of compositions for obtaining the $(Ba_{1-y}La_{2y/3})Zr_xTi_{1-x}O_3$ solid solution as single-phase was established from the $BaTiO_3$–$BaZrO_3$–$La_{2/3}TiO_3$ system. The corresponding phase diagrams for each method of synthesis employed were constructed from the XRD patterns and ICP data (Fig. 1).

Two distinct areas were found in these triangles: a coloured region of perovskite-like solid solutions and a mixed-phase region. The range of solubility for compounds obtained by solid-state reaction was slightly lower than those obtained by the O–P method, and remarkably lower than it reported for the $(Sr_{1-y}La_{2y/3})Zr_xTi_{1-x}O_3$ system [13]. These results are related to the effect of the method of synthesis employed and justified in terms of the favourable lower A-site ionic radii difference between strontium and lanthanum ($\Delta r_{Sr-La} = 0.08$ Å) than barium and lanthanum ($\Delta r_{Ba-La} = 0.25$ Å) in the perovskite structure. Non single-phase compounds showed the $La_2Zr_2O_7$ (JCPDS 71-2363) oxide as the main impurity. Other major impurities were $BaTiO_3$ (JCPDS 75-0211), $La_{2/3}TiO_3$ (JCPDS 26-0827) and $Ba_6Ti_{17}O_{40}$ (JCPDS 72-0135) for compounds synthesized by the O–P method ($y > 0.20$); and $BaTiO_3$ (JCPDS 75-0211), $BaLa_2Ti_4O_{12}$ (JCPDS 43-0117) and $La_4Ti_9O_{24}$ (JCPDS 36-0137) for compounds synthesized by SSR method ($y \geq 0.20$).

The influence of La^{3+} ions on MO_6-perovskite octahedra of the $(Ba_{1-y}La_{2y/3})Zr_xTi_{1-x}O_3$ system was studied by infrared spectroscopy [14]. IR spectra for compounds obtained from the O–P method are shown in Fig. 2. Similar behaviour was observed for SSR method.

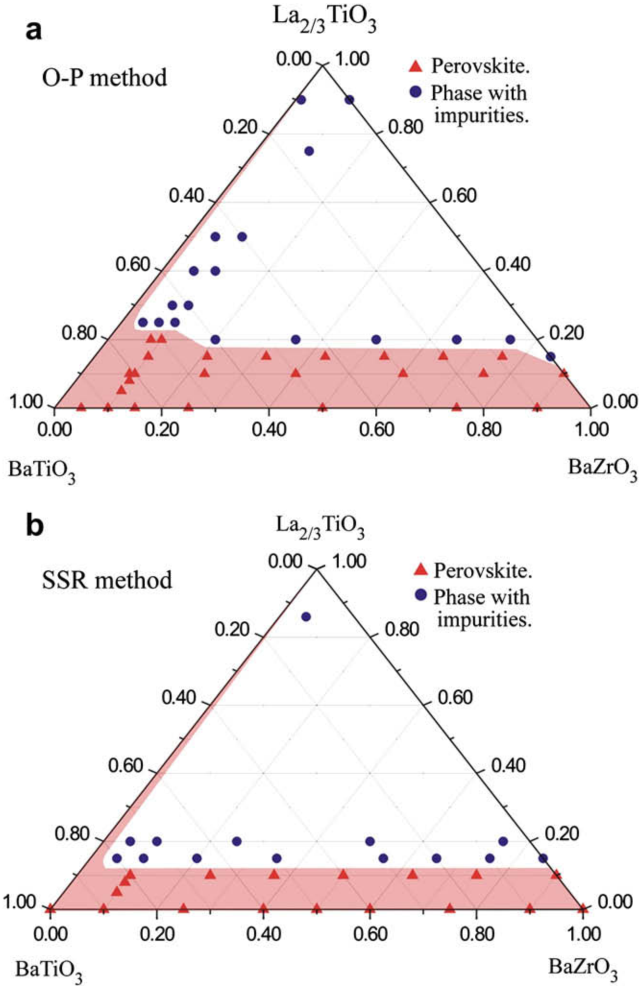

Fig. 1. Phase diagrams for $(Ba_{1-y}La_{2y/3})Zr_xTi_{1-x}O_3$ system synthesized by a) the O–P method at 1000 °C and b) SSR at 1400 °C.