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Investigations on Microstructural and Raman Scattering Properties of B_2O_3 Doped $Ba(Ti_{1-x}Zr_x)O_3$ Ceramics

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Abstract 0.5 wt. % B_2O_3–doped $Ba(Ti_{1-x}Zr_x)O_3$, (x=0-0.4) lead-free ceramics were synthesized using the solid-state reaction method by adopting the ball milling technique. The influence of the substitution content on crystallographic structure, phase transition, microstructure and sintering behavior of BT and BZT ceramics were investigated. XRD analysis at room temperature revealed a structural transformation from tetragonal to rhombohedral with enhancement of ZrO_2 content in the barium titanate matrix. The scanning electron microscope and energy-dispersive X-ray spectroscopy were used to investigate microstructure and surface morphology of the sintered samples. The evolution of the Raman spectra was studied for various compositions, and the spectroscopic signature of the corresponding phase was determined. Scanning Electron Microscope observations revealed enhanced microstructural uniformity and retarded grain growth with increasing Zr content.

Keywords $BaTiO_3$, Barium-titanate-zirconate, ceramics, Raman spectroscopy

1. Introduction

In recent years, $BaTiO_3$-based ceramics have received much attention from the scientific community in the process of searching for the lead-free ferroelectric materials [1]. Through chemical substitutions for A sites or B sites in $BaTiO_3$ ceramics, the different electrical properties can be acquired to meet our requirements for specific utilization. Among them, $Ba(Ti_{1-x}Zr_x)O_3$ (BZT) solid solution has attracted considerable attention for its special characteristics. Depending upon the composition, some of them exhibit a relaxor behavior whose characteristic depend upon the type of cationic substitution and to the substitution rate. For example, the replacement of $Ti^{4+}$by Zr^{4+}significantly changes the electrical and structural properties of $BaTiO_3$ (BT) [2]. The Zr atoms must be homogeneously integrated in the lattice structure throughout the material. Compositional fluctuations will lead to distribution of the phase transition temperature and hence to irreproducible and variable electromechanical properties. The presence of mechanical stress in the material also reduces the values of the property coefficients [3]. Many researchers have shown their interest in the solid solution system $Ba(Ti_{1-x}Zr_x)O_3$ with different concentrations of Ti and Zr [4-6]. Generally, optimization of the electrical properties of $BaTiO_3$ requires a high density and controlled microstructure. Many of the researches have been devoted to lowering the sintering temperatures of barium titanate based ceramics [7,8]. Many oxides such as Bi_2O_3, LiF, B_2O_3, SiO_2 and Al_2O_3 [9,10] have been used for the formation of the required liquid phase to enhance densification and grain growth in the BT based ceramics.

In this work Ba($Ti_{1-x}Zr_x$)O_3 ceramics were prepared by a solid-state reaction technique. Raman spectroscopy, X-ray and microstructural analyses were performed to study the effect of Zr substitution on 0.5 wt. % B_2O_3 dopedBa($Ti_{1-x}Zr_x$)O_3ceramics.

2. Experimental study

Ba($Ti_{1-x}Zr_x$)O_3(x=0-0.4) ceramic powders with 0.5 wt. % B_2O_3 substitution were prepared by solid state mixed oxide technique. The starting materials used were $BaCO_3$, ZrO_2, TiO_2 and B_2O_3 (all > 99.9% pure, Aldrich, USA). The stoichiometrically weighed amounts of these powders were milled by ball milling technique in isopropyl alcohol using ZrO_2 balls at 200 cycle/min for 24h and then dried in a Pyrex pan. The dried powders were calcined at 1000 °C for 2h. The calcined powders were crushed using planetary ball mill for a short duration, compacted by cold isostatic pressing at 150 MPa and then sintered at 1450°C/4h(at a ramp of 5°C/min.).

The crystal structure and phase purity of the samples were analyzed by powder X-ray diffraction (XRD) studies on Rigaku D/MAX/2200/PC diffractometer using Ni-filtered Cu-K_αX-rays of wavelength (λ)= 1.5408 Å. A Kaiser RAMANRXN1 Raman spectrometer was used for further investigation of phase composition of the $BaZr_xTi_{1-x}O_3$(x=0-0.4) microwave dielectric ceramics. The Raman scattering spectra of the ceramic samples were recorded using 785 nm Invictus laser light source, a low excitation power of 5 mW.The surface morphology and elemental analysis of the ceramics were examined by using a Field emission gun scanning electron microscope (FE-SEM, Tescan Mira3 XMU, Czechia) and Energy-dispersive X-ray spectroscopy(EDS, AZtec IE, U.K.) The FE-SEMsamples were examined by the secondary electron detector at an accelerating voltage of 15–20 kV.EDXS was used to determine their surface composition in a ≈0.01 mm^2 area, at source energy of 10 keV.

3. Results and Discussions

3.1. XRD analysis

The room-temperature X-ray diffraction patterns recorded for $BaTiO_3$ ceramics added with 0.5 wt% B_2O_3 sintered at 1450°C are shown in Fig.1.It is proven that all the ceramics with various Zr/Ti ratios are of perovskite crystal structure.The XRD studies do not show any phases related with either B_2O_3 which indicates the low content of the $B_2O_3$and the loss of B_2O_3 by evaporation from the structure or its presence as an amorphous phase.

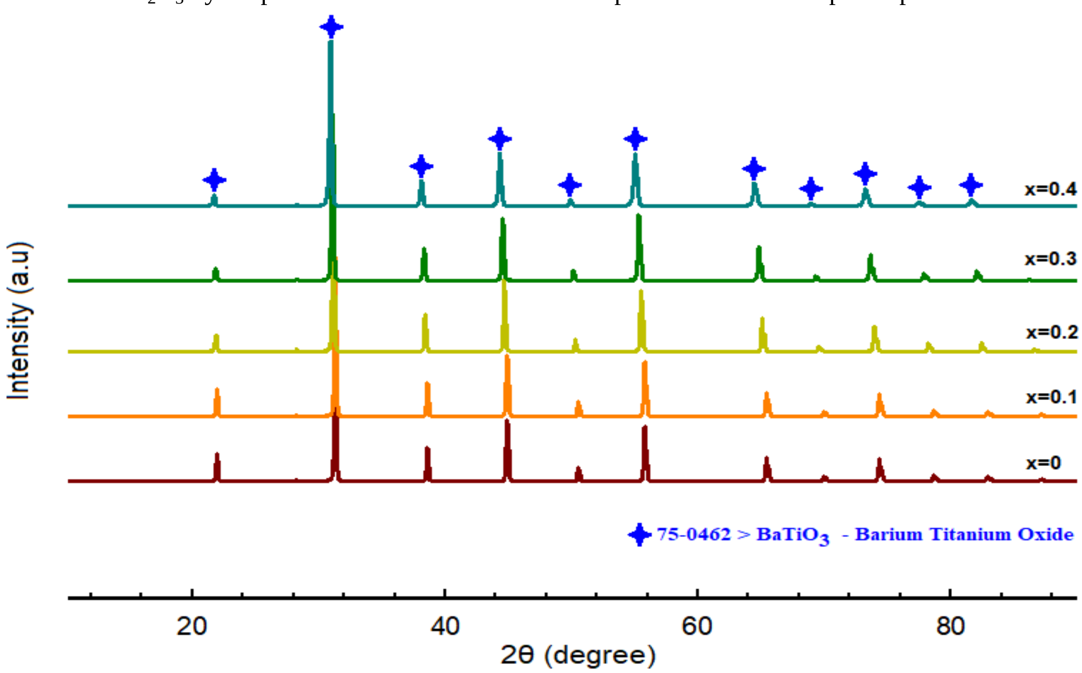

Figure 1: X-ray diffraction patterns of Ba($Ti_{1-x}Zr_x$)O_3 ceramics

3.2. SEM and EDXS analysis

The SEM micrographs and EDXS spectrums of $Ba(Ti_{1-x}Zr_x)O_3$(x=0-0.4) microwave dielectric ceramics with 0.5 wt.% B_2O_3 additionare shown in Fig.2 (a-f), respectively. ZrO_2 doped barium titanate based microwave dielectric ceramics without 0.5 wt. % B_2O_3 addition has been published in earlier work [6].SEM images reveal the powder structure and fine size of the milled BT-BZT powder.The pure BT sintered at 1450°C (Fig. 2(a)), had a relatively dense microstructure and the grain sizes were in a range of 7–7.5 μm.Compared with sample Fig.2(c)-Fig.2(d) and Fig. 2(e) can be sintered at 1450°C and the grain sizes were obviously decreased. It can be shown from the SEM images that the Zr modified BZT ceramics exhibit fine grain size and tetragonal structure to rhombohedral structural transformation [5].

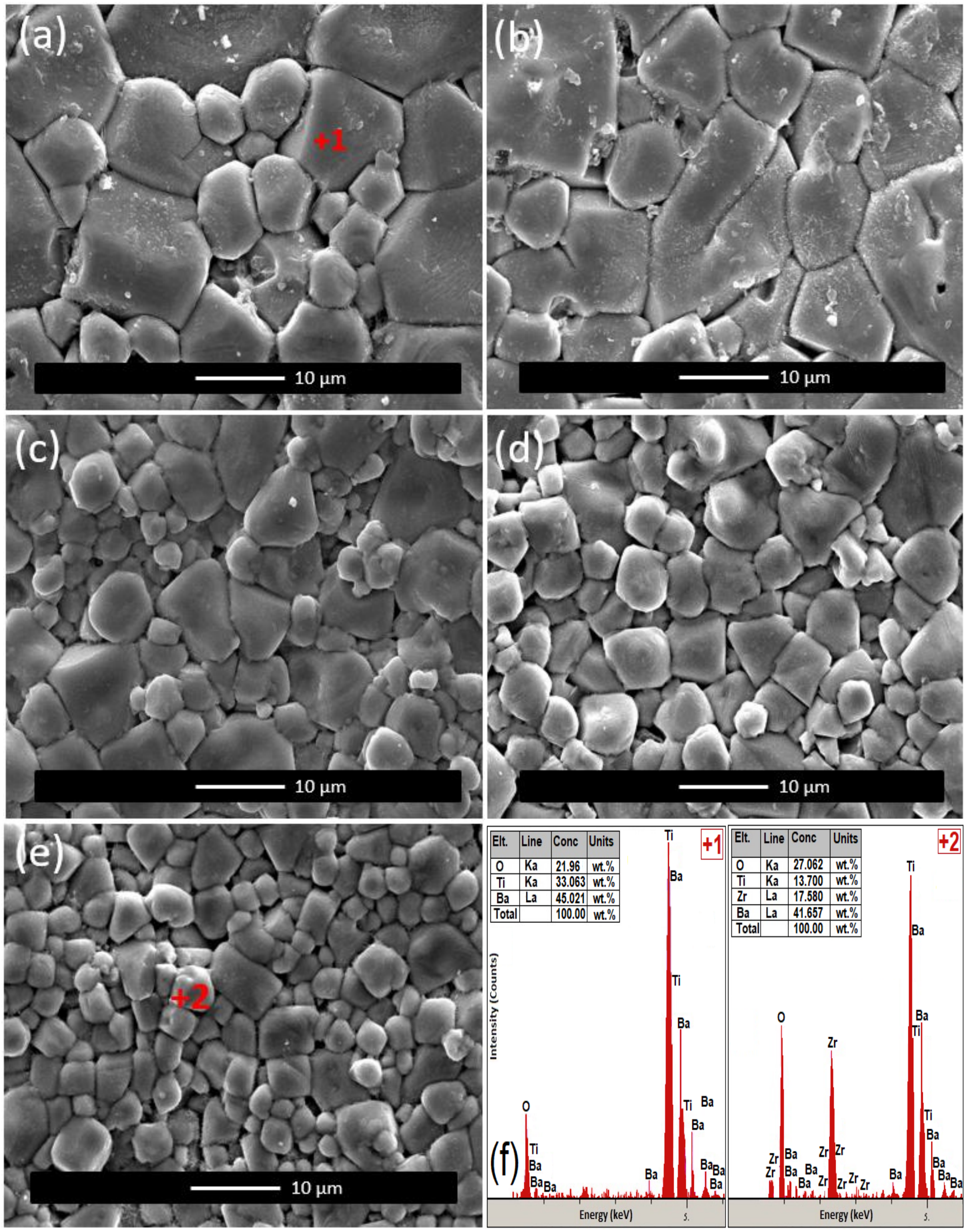

*Figure 2: SEM micrographs and EDS spectrum for $Ba(Ti_{1-x}Zr_x)O_3$ ceramics sintered at 1450 °C for 4h. a) x=0, b) x=0.1, c) x=0.2, d) x=0.3, e) x=0.4, f) (**+1**)$Ba(Ti_1)O_3$ – (**+2**)$Ba(Ti_{0.6}Zr_{0.4})O_3$.*

3.3. Raman spectroscopy

The evolution of the Raman spectra was studied for various compositions, and the spectroscopic signature of the corresponding phase was determined. The Raman spectra of $BaZr_xTi_{1-x}O_3$ ceramics with x = 0, 0.10, 0.20, 0.30 and 0.40 at room temperature are shown in Fig.3. Observed spectral features are numbered consecutively from 152 to 752, starting from the low-wavenumber region. Peaks at 302 cm^{-1}, 512 cm^{-1} and 712 cm^{-1} are found in all ferroelectric phases of BT based materials. Peaks at 280 cm^{-1} and 512 cm^{-1} have a dominant A_1(TO) character, as was proven in polycrystalline BT by polarization measurements [11,12] and the former is associated with polar Ti–O vibrations. The peak at 712 cm^{-1} is due to a bending and stretching of BO_6 octahedra and so has a mixed A_1 and E character [13,14] whereas peak at 302 $cm^{-1}$is the 'silent' mode [15].

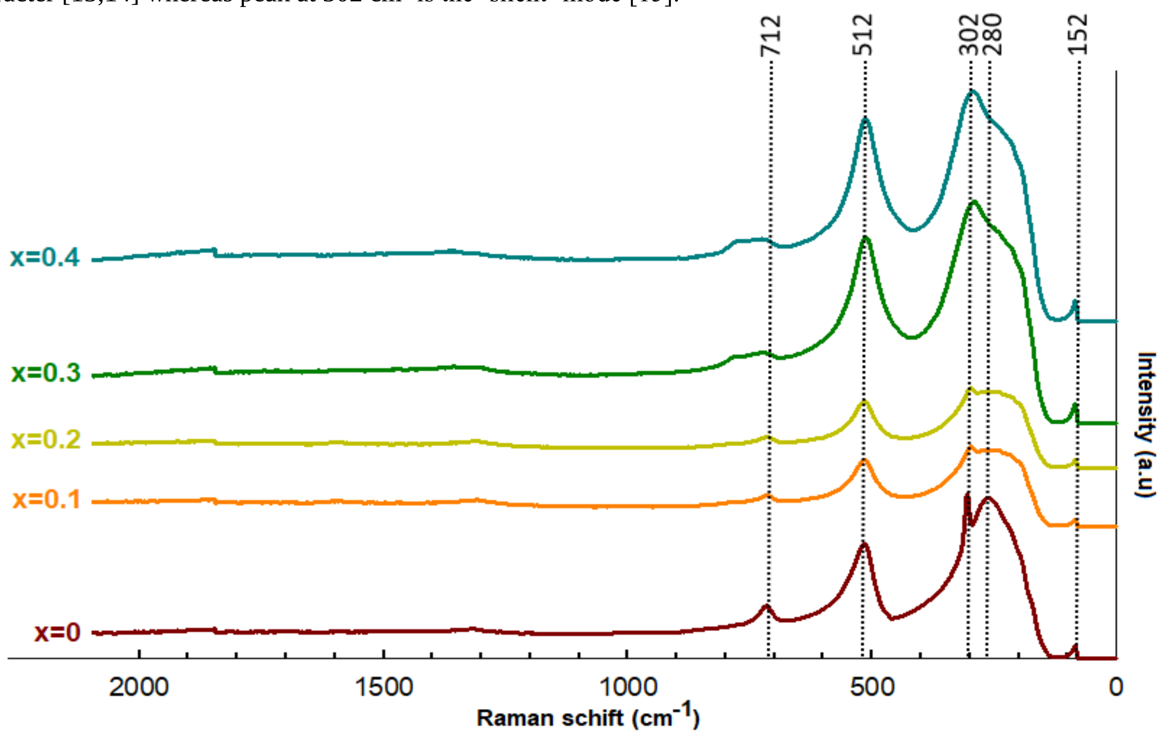

Figure 3: Raman spectra of $BaZr_xTi_{1-x}O_3$(x=0-0.4) microwave dielectric ceramics sintered at 1450 °C for 4h.

4. Conclusions

$Ba(Ti_{1-x}Zr_x)O_3$(x=0-0.4) solid solutions were prepared by the solid state reaction method. All the BT/BZT ceramics examined showed that there was a single-phased perovskite crystal structure after sintering at 1450°C for 4 hours. The crystalline structure and microstructure of BZT ceramics are strongly depended to the Zr content. The ZrO_2 causes an increase in the grain size of the BT ceramics at low concentration, but the increase in ZrO_2 content cause to decrease of the grain size of BZT ceramics. In conclusion, we have well characterized the phase transitions in BZT and some aspects of the BZT local atomic-scale structure of the $Ba(Ti_{1-x}Zr_x)O_3$(x=0-0.4) ceramics in sample regions where we have taken our Raman data.

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