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Defect chemistry of a high-k ‘Y5V’ $(Ba_{0.95}Eu_{0.05})TiO_3$ ceramic

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Abstract

The influence of the sintering temperature (T_s) on the structure, dielectric and valence-state properties of $(Ba_{1-x}Eu_x)TiO_3$ ($x=0.05$) ceramics was investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), electron paramagnetic resonance (EPR), Raman spectroscopy, and dielectric temperature measurements. An increase in T_s can increase the solubility limit of Eu in $BaTiO_3$. When the T_s was increased to 1450 °C, a high-k ‘Y5V’ ($\varepsilon'_{RT}=8500$) ceramic (C-BE5T) with a single-phase cubic structure was obtained. The dielectric peak shifted rapidly toward lower temperatures with increasing T_s at a rate of -0.46 °C/K. A symmetric (200) XRD peak, exaggerated grain growth (5.6 μm), a mixed valence of Eu^{2+}/Eu^{3+}, an asymmetric main Raman band at 2494 cm^{-1} and a weak sharp band at 1516 cm^{-1} in the high-wavenumber region are characteristics of cubic symmetry of C-BE5T. The formation of a solid solution of C-BE5T and defect chemistry are discussed.

Keywords: A. Powders: solid state reaction and Sintering; B. Defects; C. Dielectric properties; D. BaTiO3 and titanates

1. Introduction

Europium-doped barium titanate ($BaTiO_3$) ceramics or powders have drawn a great deal of attention because of their luminescence properties [1–4]. In 2005, however, a low-porosity, highly-insulating, dielectric-ageing-resistant, and fine-grained $(Ba_{1-x}Eu_x)Ti_{1-x/8}O_3$ ($x=0.05$) ceramic that exhibited dielectric-temperature stability in a lower temperature range of -100 to 50 °C was obtained, accompanied by the appearance of a secondary phase, $Eu_2Ti_2O_7$, which was formed due to the solubility limit of $x=0.03$ at a powder sintering temperature of 1300 °C [5]. Since then, the valence state and site occupation of Eu ions in the $BaTiO_3$ lattice and the dielectric properties associated with different charge-compensation mechanisms have been successively investigated [6–10]. Europium may occupy Ba sites as Eu^{3+} [6–8] or as mixed Eu^{3+}/Eu^{2+} [6,9], or may occupy both Ba and Ti sites as Eu^{3+} [9,10]. Eu has been reported to prefer Ba sites to Ti sites but can transfer from Ba sites to Ti sites depending on the Ba/Ti ratio [10]. Electron paramagnetic resonance (EPR) investigations suggested that a self-compensation mode with the amphoteric behavior of Eu ions can occur in $(Ba_{1-x/2}Eu_{x/2})(Ti_{1-x/2}Eu_{x/2})O_3$ ($x=0.05$) and results in no reduction of Eu^{3+} to Eu^{2+} occurring [9]. For $(Ba_{1-x}Eu_x)TiO_3$ ceramics prepared via a solid-state method, however, no evidence for the valence change of Eu^{3+} to Eu^{2+} was provided [8]. Eu-doped $BaTiO_3$ generally exhibits a tetragonal structure and its dielectric peak cannot reach room temperature because of the solubility limit of $x=0.03$ [5]. A single-phase and high-k ‘Y5V’ $(Ba_{1-x}Eu_x)TiO_3$ ($x\leq 0.05$) has not been reported to date. (*Note*: Y5V specification: $-82\% \leq (\varepsilon' - \varepsilon'_{RT})/\varepsilon'_{RT} \leq +22\%$ in a temperature range of -30 to 85 °C)

In this work, $(Ba_{1-x}Eu_x)TiO_3$ ($x=0.05$) ceramics were prepared at different sintering temperatures (T_s) using a cold-pressing ceramic technique. Our objective is to increase the T_s to increase the solubility limit of Eu in $BaTiO_3$ to obtain a single-phase cubic ceramic and realize a high-k Y5V behavior. The structural, dielectric and valence-state properties of the

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cubic $(Ba_{1-x}Eu_x)TiO_3$ ceramic were investigated using XRD, SEM, ESR, Raman spectroscopy, and dielectric measurements to elucidate the solid solution formation and the defect chemistry. The high-wavenumber Raman and EPR spectra in the cubic phase showed novel features.

2. Experimental procedures

$(Ba_{1-x}Eu_x)TiO_3$ ($x=0.05$) ceramics (abbreviated BE5T) were prepared using a cold-pressing ceramic technique described elsewhere [5]. The final sintering conditions were chosen as 1200, 1250, 1300, 1350, 1400, and 1450 °C for 3 h. $Eu_2Ti_2O_7$ and Eu_2O_3 ceramics were prepared at 1300 °C under the same route as that used for BE5T for Raman scattering analyses and comparison. Powder X-ray diffraction (XRD) measurements were performed between $20° \leq 2\theta \leq 100°$ in steps of 0.02° using a DX-2700 X-ray diffractometer (Dandong Haoyuan Inc.). Lattice parameters and unit cell volume were calculated by MS Modeling software package (Accelrys Inc.) using Cu Kα1 radiation ($\lambda=1.540562$ Å). Scanning electric microscopy (SEM) images were obtained using a JSM-6490 SEM (JEOL) operated at 25 kV. The temperature dependence of the dielectric permittivity and loss was measured from −75 to 200 °C with a weak 1 kHz ac electric field using an RCL meter (Fluke PM6306). Electron paramagnetic resonance (EPR) spectra were measured at an X-band frequency of 9.148 GHz from 25 to 150 °C in the sweep range of 50–550 mT using a JES-RE3X spectrometer (JEOL) equipped with a Mn^{2+} standard marker. The gyromagnetic values (g values) were calculated in terms of the third and fourth lines of the Mn^{2+} standard sextet marker ($g_3=2.0327$ and $g_4=1.9810$). Raman spectra of the ceramic powders were measured at room temperature using a LabRAM XploRA Raman spectrometer (Horiba Jobin Yvon), with a 532 nm laser focused on a spot of approximately 3–5 μm in diameter. The Raman spectrometer was equipped with a Linkam-600 heating and cooling stage for temperature-dependent Raman measurements from −150 to 180 °C.

3. Results

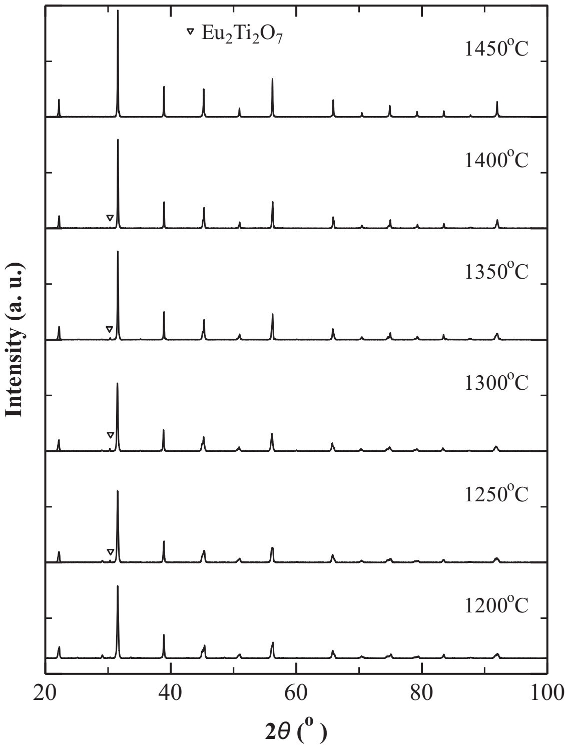

Fig. 1. XRD patterns of BE5T ceramics prepared at different sintering temperatures ($T_s=1250$–1450 °C).

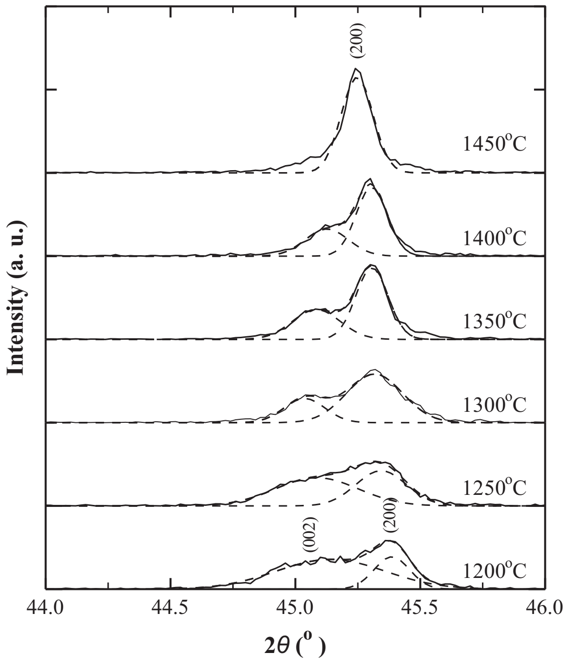

Fig. 2. Gaussian fitting of the XRD peaks in the vicinity of 45° in Fig. 1.

Powder XRD patterns of all the BE5T ceramics sintered at different sintering temperatures (T_s) are shown in Fig. 1. The main perovskite phase was formed at each T_s. When the T_s was less than 1400 °C, a small amount of a second phase separated from the main tetragonal perovskite phase. A pyrochlore phase, $Eu_2Ti_2O_7$ (JCPDS: no. 23-1072), appeared at $T_s=1250$ °C and the quantity of this phase gradually decreased with increasing T_s. For the main tetragonal perovskite phase, the separate (002) and (200) peaks shift toward each as T_s is increased, as shown in Fig. 2. This shift indicates a decrease in tetragonality. When the T_s was increased to 1450 °C, the $Eu_2Ti_2O_7$ phase disappeared and a single-phase ceramic formed, with a symmetric (200) peak characteristic of a cubic structure. The unit-cell volume (V_0) of the cubic BE5T sample (called C-BE5T in the following) was determined to be 64.31 Å^3, which is significantly less than the V_0 (65.50 Å^3) of the cubic $BaTiO_3$ (JCPDS: no. 31–174). C-BE5T can therefore be considered as a sufficient incorporation of Eu ions into Ba sites in the $BaTiO_3$ lattice; otherwise, an expansion of the crystal cells would be observed if Eu entered the Ti sites