Influence of Cr Valence State on Dielectric-Temperature Stability of Barium Titanate Ceramics

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Abstract. For Barium Titanate Ceramics doped with the trivalent and hexavalent chromium oxides, the influence of Cr valence state on dielectric-temperature stability was investigated with Atomic force microscopy, X-ray diffraction, Raman spectroscopy, and dielectric measurements. The application of the trivalent Cr_2O_3 dopant can give rise to a temperature-stable X7R specification and a lower dielectric loss (< 0.02) when the sample was prepared at 1240 ºC, but the dielectric permittivity is lower (~600); Cr ions exist predominantly as Cr^{4+} and slightly as Cr^{3+}. Increasing sintering temperature will destroy the core-shell structure of the samples. The application of the hexavalent CrO_3 dopant can not produce a temperature-stable X7R ceramic; Cr ions exist as Cr^{4+} and Cr^{5+}. Cr^{5+} can not enter the perovskite lattice owing to the valence mismatching.

Introduction

The development on temperature-stable $BaTiO_3$-based dielectrics is now a research hot owing to its friendliness to the environment and application in multilayer ceramic capacitors (MLCCs) meeting EIA (Electronic Industries Association) X7R specification (±15% from 55 to 125 ºC). A famous temperature-stable dielectric is Nb-Co system [1-3] with a core-shell mode, in which a fine grain has a ferroelectric $BaTiO_3$ core, a paramagnetic Nb-Co-rich coating surface layer (shell), and a transition region between the two formers. The transition metal Mn is often used [4] owing to its variable-valence advantage of high ability to conduct electron trapping and increasing insulating [5-7]. Cr, which is adjacent to Mn in atomic number, is also a transition metal element, with more multiple valence state from +2 to +6. However, no report is available as yet on the influence of Cr valence on dielectric-temperature stability of $BaTiO_3$ doped with different types of chromium oxides. In this work, Cr_2O_3 with Cr^{3+} and CrO_3 with Cr^{6+} were chosen as $BaTiO_3$ dopants to prepare core-shell structured ceramics. The influence of Cr valence on dielectric-temperature stability was studied.

Table 1 Symbols and information of the ceramic samples

Sample	Dopant	Content	Sintering Temperature (ºC)
C31	Cr_2O_3	0.02	1240
C61	CrO_3	0.02	1240
C32	CrO_3	0.02	1280
C62	Cr_2O_3	0.02	1280

Experimental Procedure

The starting materials were $BaCO_3$ (99.4 %), TiO_2 (99.5 %), and AR-grade Cr_2O_3 and CrO_3. Ceramic powders, with the nominal compositions $(1-x) BaTiO_3 + x BaCO_3 + x/2 Cr_2O_3$ and $(1-x) BaTiO_3 + x BaCO_3 + x CrO_3$ (x = 0.02), were prepared using a conventional cold-pressing ceramic

technique. The symbols and information of the ceramic samples are listed in Table 1. After mixing (agate ball-mill, water) and calcining (1100 ºC, 2 h) the initial mixtures, they were fine-milled (agate ball-mill, water). The dried powder mixed with a PVA aqueous solution was pressed into disklike pellets of 12 mm diameter, and then sintered at 1240 ºC and 1280 ºC for 2 h in air, respectively.

Atomic force microscopy (AFM) images were recorded in ambient environment using a CSPM-5000 scanning probe microscope system (Beyuan Nano-instruments Co., China) to scan the surface morphology of all the samples. Scanning was carried out in contact mode AFM with a W-type silicon cantilever. The scanning frequency was set at 1.5 Hz.

Room-temperature powder XRD data were collected between $20° \leq 2\theta \leq 100°$ in steps of 0.02° using a DX-2700 X-ray diffractometer (Dandong Fangyuan Inc., China). Lattice parameters and unit cell volume were calculated by MS Modeling (Accelrys, Inc.) using Cu Kα1 radiation (λ = 1.540562 Å).

The surfaces of polished ceramic disks (0.8 mm in thickness) were sputtered with thin Au atoms and then pasted with silver to form electrodes for dielectric measurements. Temperature dependence of dielectric constant was measured with a weak 1 kHz ac electric field using a RCL meter (Fluke PM6306, USA).

Raman spectra (RS) were measured on a polished ceramic disc using a LabRAM XploRA Raman spectrometer (Horiba Jobin Yvon, French), with a 532 nm laser focused on a spot of about 3 nm in diameter.

Results and discussion

AFM micrographs of the polished ceramics are shown in Fig. 1. C31 and C32 adopting Cr_2O_3 dopants are the two samples prepared at 1240 ºC and 1280 ºC, respectively. Their average grain size is 375 nm and 400 nm, respectively. While C61 (1240 ºC) and C62 (1280 ºC) adopting CrO_3 dopants reach 425 nm and 445 nm, respectively. It can be seen that the grain size growth caused by the dopant change in Cr valence state (~50 nm) is half that caused by sintering temperature (~25 nm).

Powder XRD patterns for the samples are shown in Fig. 2. All the samples exhibit a typical perovskite structure. The tetragonal $BaTiO_3$ generally shows well separate (002) and (200) peaks [8], which is characteristic of tetragonality. However, it can be seen from Fig. 2 inset that the two peaks of our samples are much less separate as compared to $BaTiO_3$, which implies that chromium oxide has been coated on the $BaTiO_3$ grains to form a paramagnetic shell, but the shell is so thin that the ferroelectric phase is mainly detected by XRD. Therefore the samples show a tetragonal feature.
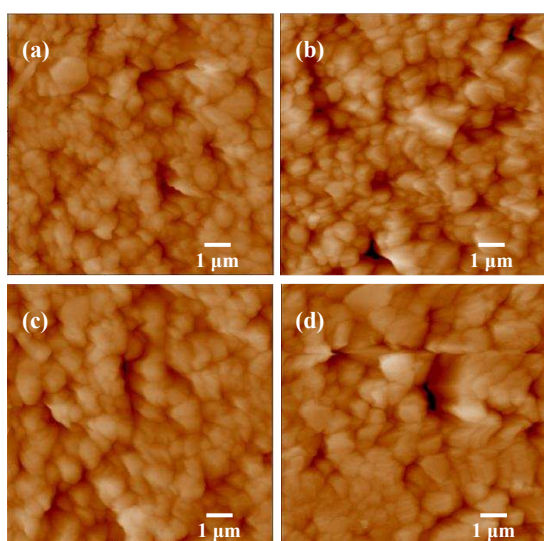

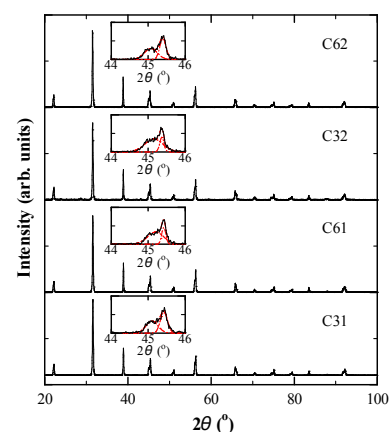Fig. 1. AFM micrographs of the polished ceramics, (a) C31; (b) C61; (c) C32; (d) C62.

Fig. 2. XRD patterns for C31, C32, C61, and C62. The inset depicts Gaussian fit to the peak in the vicinity of 45° for each sample.

The plot of unit cell volume (V_0) versus sintering temperature for the samples is shown in Fig. 3. Cr is known to be substituted for Ti site due to its ionic size [Cr^{3+} (0.615 Å), Cr^{4+} (0.55 Å), Cr^{5+} (0.49 Å)] approaching to Ti^{4+} (0.605 Å) and far smaller than Ba^{2+} (1.61 Å) [9]. Even if CrO_3 dopant was adopted, Cr^{6+} can not exist in the perovskite lattice or surface owing to valence mismatching. The same Cr^{2+} mismatching as Cr^{6+} is tenable if Cr_2O_3 dopant was adopted. Cr valence state in our samples exists in the three forms of Cr^{3+}, Cr^{4+}, and Cr^{5+}. The increase of V_0 with increasing sintering temperature illustrates the change from Cr^{4+} to Cr^{3+}.

It has been reported that in air-sintered ceramics chromium is incorporated with valence states 3+ and 4+ and the valence states 4+ predominates when Cr_2O_3 is chosen as dopant [10,11]. Thus, V_0 of C31 and C32 is less than that of $BaTiO_3$ ($V_0 = 64.41$ Å^3, from JCPDS No. 5-626) when Cr ions are incorporated into the $BaTiO_3$ grains.

V_0 of the samples doped with CrO_3 is greater relative to Cr_2O_3 (Fig. 3). This is an unexpected phenomenon because Cr^{6+} ion is far less than Cr^{3+} one. In order to clarify the abnormality, Raman scattering was carried out.
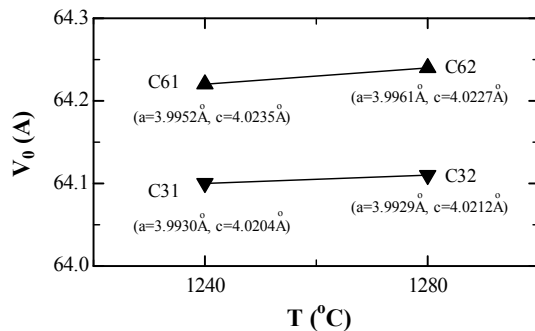

Fig. 3. Plot of unit cell volume (V_0) versus sintering temperature for C31, C61, C32, and C62. Lattice parameters of each sample are listed in this figure.
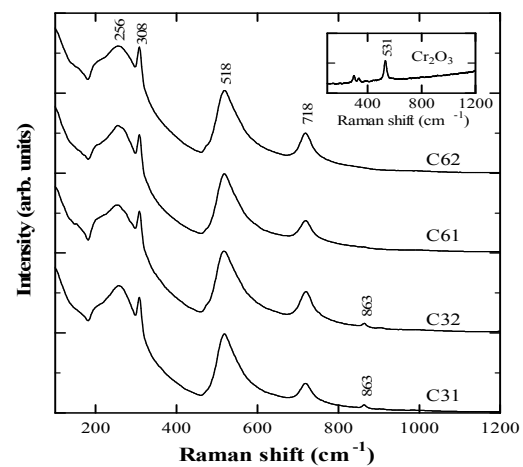

Fig. 4. Raman spectra of C31, C61, C32, and C62. Raman spectrum is shown in the inset for comparison.

Raman spectra of the samples are shown in Fig. 4. All the samples exhibit typical ferroelectric $BaTiO_3$ feature, i.e., the four commonly-reported phonon modes peaking at ~250 cm^{-1} [A_1], ~520 cm^{-1} [A_1], ~305 cm^{-1} [$B_1 + E$], and ~720 cm^{-1} [$A_1 + E$]. For C31 and C32, a new band peaking at 863 cm^{-1} appears. It is reported that either isovalent substitution of trivalent rare earth ions at A site [8,12-14] or aliovalent substitution of Nb^{5+} [15] or Ca^{2+} at B site [16] in $BaTiO_3$ can cause a ~840 cm^{-1} band, which may be attributed to an internal deformation of the BO_6 octahedron caused by the charge difference of different types of ions at equivalent sites in $BaTiO_3$ [8]. Based on these results, it can be considered that the 863 cm^{-1} band in C31 and C32 is attributed to a vibrating mode caused by a certain amount of Cr^{3+} ions incorporated into the surface layer of perovskite grains, because the main Raman peak of Cr_2O_3 (Fig. 4 inset) appears at 531 cm^{-1} and its intensity is one-tenth with respect to the perovskite phase. Therefore, the 863 cm^{-1} band is not associated with Cr_2O_3 dopant. It can be considered that Cr_2O_3 dopant is incorporated into the perovskite grains or coated on the surface layer of grains.No band peaking at 863 cm^{-1} was observed in C61 and C62. Muzur indicated that Cr^{6+} are oxidized into Cr^{4+} and Cr^{5+} for oxidized sample when Cr^{6+} ions are chosen as the dopant of $BaTiO_3$ [17]. The XRD results indicate that V_0 of the samples doped with CrO_3 (Cr^{6+}) is greater relative to Cr_2O_3 (Cr^{3+}) (Fig. 3). This fact implies that only a small amount of Cr^{4+} ions are incorporated into the perovskite grains or coated on the surface layer of grains when CrO_3 dopant was adopted. Cr^{5+} exists in the surface layer of grains because the 863 cm^{-1} band associated with incorporation of Cr^{5+} (or Cr^{3+}) into the lattice of grains was not observed.

Temperature dependences of dielectric permittivity (ε') and loss ($\tan\delta$) for the samples prepared at 1240 and 1280 ºC are shown in Fig. 5 and Fig. 6, respectively. A marked feature is that dielectric loss in the X7R temperature range is quite low (< 0.02) for Cr_2O_3 dopant, while the samples show a higher $\tan\delta$ especially in the high-temperature region when CrO_3 dopant is adopted.
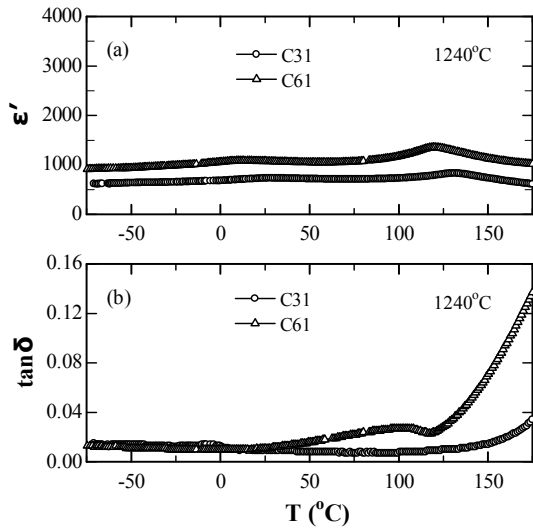

Fig. 5. Temperature dependences of (a) dielectric permittivity (ε') and (b) loss ($\tan\delta$) for C31 and C61 prepared at 1240 ºC.
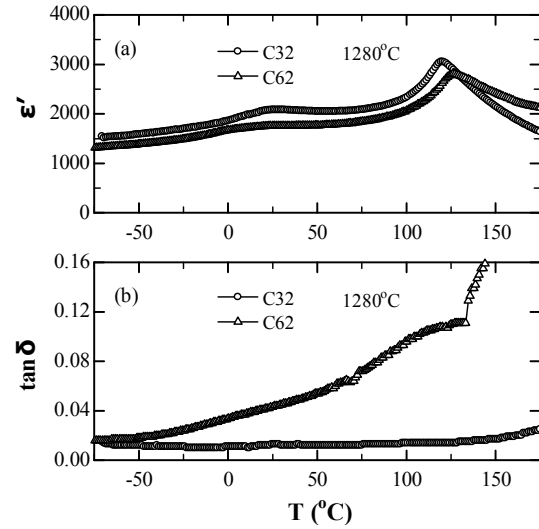
Fig. 6. Temperature dependences of (a) dielectric permittivity (ε') and (b) loss ($\tan\delta$) for C31 and C61 prepared at 1280 ºC.

When CrO_3 dopant is adopted, the samples can not meet the X7R specification at the two sintering temperatures. Only C31 prepared at 1240 ºC shows a flat dielectric X7R stability. However, ε' is lower (~600). With increasing sintering temperature to 1280 ºC, ε' of the samples increases rapidly, but the dielectric peak near the $BaTiO_3$ tetragonal-cubic phase transition point T_C (~125 ºC) can not be suppressed and a broader orthorhombic-tetragonal phase transition peak appears around room-temperature, leading to temperature-unstable dielectric behavior. Based on this fact, it can be inferred that increasing sintering temperature will lead to the intense incorporation of Cr ions into the lattice of the $BaTiO_3$ grains, which leads to reduction of the surface layer of grains with the core-shell structure.

Conclusions

Cr_2O_3- and CrO_3-doped Barium Titanate Ceramics prepared at 1240 and 1280 ºC were investigated. The application of trivalent chromium oxide Cr_2O_3 at 1240 ºC can lead to a temperature-stable X7R specification and lower dielectric loss (< 0.02), but dielectric permittivity is lower (~600); Cr ions exist in predominant Cr^{4+} and a small amount of Cr^{3+}. Increasing sintering temperature will destroy core-shell structure and lead to more Cr^{3+} ions into the lattice. The application of hexavalent CrO_3 dopant can not produce a temperature-stable X7R ceramic; Cr ions exist in Cr^{4+} and Cr^{5+}. Cr^{5+} can not enter the perovskite lattice owing to valence mismatching, which is demonstrated by XRD and Raman results.

Acknowledgements

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