



Novel X7R BaTiO₃ ceramics co-doped with La³⁺ and Ca²⁺ ions



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ABSTRACT

(Ba_{1-x}La_x)(Ti_{1-x/2}Ca_{x/2})O₃ (0.03 ≤ x ≤ 0.06) (BLTC) ceramics were prepared using a mixed oxides method. The structure, microstructure, and dielectric properties of BLTC were investigated by X-ray diffraction, Raman spectroscopy, scanning electron microscopy, atomic force microscope, and dielectric measurements. Both symmetric (200) XRD peak indicative of cubicity and sharp 308 cm⁻¹ Raman band indicative of tetragonality are characteristics of pseudo-cubic symmetry of BLTC. The unit cell volume of BLTC increased linearly with x, satisfying Vegard's law. A strong "Raman charge effect" appeared at 836 cm⁻¹ because of the aliovalent double substitution in BLTC. The x = 0.03 sample because of its higher permittivity (ε' = ~2000) and lower loss (tan δ < 0.04) is a novel dielectric for X7R applications. The formation of La_{Ba}^{II} - Ca_{Ti}^{IV} - La_{Ba}^{II} defect complexes was responsible for the dielectric-temperature stability of BLTC.

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1. Introduction

In the dielectric field of BaTiO₃-based ceramic materials, the two typical dielectric specifications named by the Electronic Industry Association (EIA) are Y5V (-82% ≤ (ε' - ε'_{RT})/ε'_{RT} ≤ +22% in a temperature range -30 to 85 °C) and X7R (|(ε' - ε'_{RT})/ε'_{RT}| ≤ 15% in a range -55 to 125 °C). They represent room-temperature high-ε (i.e., high-k) behavior and dielectric-temperature stability, respectively. It is well known that the Curie temperature (T_C) of BaTiO₃ is approximately 125 °C, at which a clear cubic-tetragonal phase transition occurs, accompanied by a very sharp dielectric peak (ε' ~ 10,000) [1,2]. This phase transition belongs to a first-order phase transition (FPT) [3]. In most cases, when BaTiO₃ is doped with different types of ions, its T_C generally shifts toward low temperature, and with increasing doping levels, this sharp dielectric peak gradually becomes vague, forming so-called diffuse phase transition (DPT) [3]. Because the reduplicative orientations by TiO₆ octahedron constitute the skeleton of the BaTiO₃ perovskite structure and Ba ions are located on the interstitial space of the TiO₆ skeleton [4], the substitution of dopants at the Ti site compared to the Ba site will induce a larger lattice deformation, which can cause a stronger broadening of the permittivity maximum (ε'_m) associated with DPT. The Y5V specification needs DPT to occur as far as possible in the vicinity of room temperature. This requires that the solid solution limit of dopants at the Ti site in the BaTiO₃ lattice is sufficiently high to enable the ε'_m to shift to room temperature.

The ionic radius of dopants is a critical factor contributing to DPT. The radii of some ions versus coordinate number (CN) are listed in Table 1 [5]. Three types of Ti-site dopants such as Sn⁴⁺ (0.69 Å), Zr⁴⁺ (0.72 Å), and Ce⁴⁺ (0.87 Å), are illustrated to focus on the relationship between the ionic size of dopants and DPT. These three dopants have higher Ti-site solid solubility because of their high ability to maintaining the lattice electroneutrality [3,6–8]. One found that with an increase in ionic radius, the sintering temperature needs to be elevated continuously so that the doping ions gain enough energy to enter the Ti site of the BO₆ octahedrons skeleton, and that the phase transition becomes more diffused, as observed for Ce⁴⁺-doped BaTiO₃ [8]. Although these BaTiO₃-based ceramics might meet Y5V or Z5U (-56% ≤ (ε' - ε'_{RT})/ε'_{RT} ≤ +22% in a range 10–85 °C) specifications [3,6–8], they cannot reach the X7R specification. One probably imagines that with increasing the size of Ti-site doping ions, a continuous trend of the ε'_m smoothness would be going on, accompanied by an evolution from Y5V-type high-ε behavior to X7R-type dielectric-temperature stability.

However, it is difficult to find an ideal Ti-site tetravalent dopant whose ionic radius is greater than Ce⁴⁺. In recent years, Zhang et al. proposed Ti-site Ca²⁺ (1.00 Å) as a potential dopant for applications of a higher dielectric specification X8R (|(ε' - ε'_{RT})/ε'_{RT}| ≤ 15% in a range -55 to -155 °C) [9]. The much larger ionic size of Ca²⁺ (1.00 Å) compared to Ti⁴⁺ (0.605 Å) results in a lower Ti-site solid solution limit of x = ~0.04 for Ba(Ti_{1-x}Ca_x)O_{3-x} with DPT at T_C = 44 °C, and the sintering temperature had to be elevated to a higher temperature of 1500 °C [9]. Even so, researchers cannot achieve the Y5V specification for Ba(Ti_{1-x}Ca_x)O_{3-x}. This is probably

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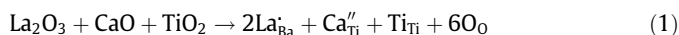
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Table 1
Ionic radii versus coordinate number (CN).

Ion	CN	r (Å)
Ba ²⁺	12	1.61
Ti ⁴⁺	6	0.605
La ³⁺	12	1.36
Ca ²⁺	12	1.34
Ca ²⁺	6	1.00
Ce ⁴⁺	6	0.87
Zr ⁴⁺	6	0.72
Sn ⁴⁺	6	0.69

attributed to the presence of oxygen vacancies caused by the aliovalent substitution of Ca²⁺ at the Ti site.

In this work, our purpose is to incorporate much larger Ca²⁺ ions completely into the Ti site by means of Ba-site codopant in BaTiO₃, to achieve a more diffused phase transition and further to expect X7R-type dielectric-temperature stability. La³⁺ donor (an ion with a higher valence than the host Ba²⁺ ion) and Ca²⁺ acceptor (an ion with a lower valence than the host Ti⁴⁺ ion) are used as codopants at the Ba- and Ti-sites in BaTiO₃, respectively, to develop (Ba_{1-x}La_x)(Ti_{1-x/2}Ca_{x/2})O₃ ceramics, for the three considerations: (1) On the site substitution, Ca²⁺ is generally applied as the Ba-site dopant [10–13]. Even in the case of (Ba + Ca)/Ti = 1, however, Ca-doped BaTiO₃ prepared by the mixed oxide route has a feature of the double substitution [14,15]. La ions are known to be substituted exclusively for the Ba site as La³⁺ [16–19]. La³⁺ donor might compel Ca²⁺ as an acceptor to enter the Ti site and then improve the solid solubility of Ca²⁺ at the Ti site. (2) For Ba(Ti_{1-x}Ca_x)O_{3-x}, Ca²⁺ in place of Ti⁴⁺ inevitably induces oxygen vacancies [9,20,21]. The presence of mobile oxygen vacancies is apt to cause electrical conduction and ferroelectric aging. Incorporation of La³⁺ into the Ba site in Ba(Ti_{1-x}Ca_x)O_{3-x} is likely to result not only in reduction of oxygen vacancies and dielectric loss, but also in significant lowering of the sintering temperature by means of the formation of La_{Ba}[•] – Ca_{Ti}^{••} – La_{Ba}[•] defect complexes described in Eq. (1), where the Kröger–Vink defect notation [22] is used and the charge equilibrium is equivalent to the host cations, meeting the lattice electroneutrality.



The probable reasons that the formation of defect complexes would lower the sintering temperature are that, a complementary ionic radii relation between ($R_{\text{La}} + R_{\text{Ca}}$) and ($R_{\text{Ba}} + R_{\text{Ti}}$) (Table 1) is beneficial to the incorporation of La_{Ba}[•] – Ca_{Ti}^{••} – La_{Ba}[•] defect complex as a corporate entity into the perovskite grains, which could surmount the potential barrier of the much larger Ca²⁺ ions entering the Ti site. Meanwhile, at a lower temperature of 1350 °C, La³⁺ ions may induce Ti vacancies [17], which can compel Ca²⁺ ions to enter the Ti site and accelerate diffusion of Ca²⁺ ions into the perovskite grains.

(3) For BaTiO₃ ceramics with the double substitution, La³⁺ at the Ba site may play a role in raising dielectric permittivity and further broadening of the ϵ'_m [23–26].

In this article, we report the results of a comprehensive study of (Ba_{1-x}La_x)(Ti_{1-x/2}Ca_{x/2})O₃ (BLTC) solid solution materials. The effect of La/Ca co-doping on structure, microstructure, and dielectric properties are reported. Novel X7R-type dielectric-temperature stability can be realized at a low doping level of $x = 0.03$. Further, there are two advantages of BLTC materials over the conventional X7R BaTiO₃-based materials with core-shell structure [27–29]: (1) the control of preparation conditions of BLTC compared to core-shell ceramics is easier; and (2) the X8R specification with higher dielectric-temperature stability can be achieved by La/Ca co-doping at a higher doping level of $x = 0.06$.

2. Experimental procedures

Ceramic raw materials were reagent-grade BaCO₃, La₂O₃, TiO₂, and CaCO₃ powders. The ceramics were prepared according to the nominal formula (Ba_{1-x}La_x)(Ti_{1-x/2}Ca_{x/2})O₃ ($x = 0.03, 0.04, 0.05, 0.06$) (BLTC) using a mixed oxides method described elsewhere [22]. The stoichiometric mixture in accordance with the above formula was carefully mixed. The schedules of calcination, forming (PVA aqueous solution was added as a binder for forming process) and final sintering were at 1100 °C for 5 h in air, 200 MPa for 2 min, and at 1400 °C for 12 h in air, respectively. For the final sintering, the heating rate was 100 °C/h; the samples were cooled to 1000 °C at a rate of –200 °C/h and then furnace-cooled to room temperature. In addition, BaTiO₃ ceramic was prepared at 1300 °C for analysis on lattice deformation of BLTC.

Powder X-ray diffraction (XRD), using a DX-2700 X-ray diffractometer (Dandong Haoyuan Inc.), was used for structural measurements and as an indication of phase purity. Lattice parameters and unit cell volume of BLTC were calculated by MS Modeling (Accelrys, Inc.) using Rietveld refinement in Reflex Package and Cu K α radiation ($\lambda = 1.540562$ Å). Raman spectroscopy was carried out using a LabRAM XploRA Raman spectrometer (Horiba Jobin Yvon) with a 532 nm laser. A Linkam-600 heating and cooling stage was equipped for temperature-dependent Raman measurements. Microstructural properties were determined using a JSM-6490 scanning electron microscope (SEM) (JEOL) operated at 25 kV and using a CSPM-5000 atomic force microscope (AFM) (Beyuan Nano-instruments Co.). Scanning was carried out in contact mode AFM with a W-type silicon cantilever and the scanning frequency was set at 1.5 Hz. The surfaces of BLTC samples were polished and thermally-etched for observation of microstructure. Temperature dependences of the dielectric permittivity and loss were measured at 1 kHz using a RCL meter (Fluke PM6306).

3. Results

XRD patterns of BLTC are shown in Fig. 1. All the BLTC ceramics exhibited a single-phase perovskite structure (Fig. 1(a)). There is no indication of any secondary phase separating out. The structures of BLTC were determined as pseudo-cubic, as marked by a symmetric (200) peak (Fig. 1(b)). The larger FWHM (full width of half maximum) values ($\geq 0.27^\circ$) in BLTC compared to that in BaTiO₃ (0.15°) implied a larger lattice deformation existing in each BLTC sample. The lattice deformation was smallest for $x = 0.05$ (FWHM = 0.27°) and largest for $x = 0.03$ (FWHM = 0.38°) among all the BLTC ceramics.

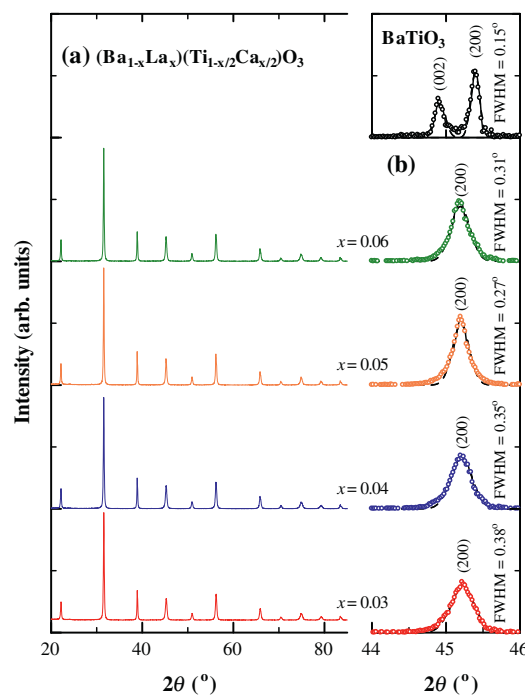


Fig. 1. XRD patterns of (a) (Ba_{1-x}La_x)(Ti_{1-x/2}Ca_{x/2})O₃ (BLTC) ceramics ($x = 0.03$ – 0.06). (b) Gaussian-fitting to the XRD peaks in the vicinity of 45° for BLTC and BaTiO₃. FWHM denotes the full width of half maximum of the peak at $\sim 45^\circ$.

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