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Microwave dielectric properties of $Ba[Ti_{0.4}Ga_{0.3}Nb_{0.3(1-x)}Sb_{0.3x}]O_3$ perovskite ceramics

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ABSTRACT

The perovskite $Ba[Ti_{0.4}Ga_{0.3}Nb_{0.3(1-x)}Sb_{0.3x}]O_3$ ($x = 0$–1.00) solid solutions were synthesized by the conventional solid-state reaction method. The structures and microwave dielectric properties were investigated by X-ray and dielectric measurements. Their crystal structures transferred from the cubic to hexagonal one with increasing x. The oxygen octahedra distortions were described from the refinement data. It revealed that the negative and positive charge centers coincided at the origin in the corner-sharing octahedra, but they did not coincide with each other in the face-sharing ones. Two pairs of dipoles canceled in the face-sharing oxygen octahedra, which had an effect on lowering the dielectric constant (ε_r). The temperature coefficient of resonant frequency (τ_f) of ceramic at $x = 0.50$ was -1.1 ppm/°C. The hexagonal perovskite had much higher quality factor ($Q \times f$), nearer-zero τ_f, and lower ε_r than the cubic one. This was ascribed to the canceled dipoles and more shared oxygen ions in the face-sharing oxygen octahedra.

1. Introduction

ABO_3 perovskites have attracted considerable attentions for their superior electrical properties [1,2], such as ferroelectric, piezoelectric, and microwave dielectric properties. In the latter case, many cubic perovskites have been extensively studied [3–5] for their applications at microwave frequency. And the structure–composition–property relationships among them have been established. In recent years, some researches have been focused on the hexagonal perovskites for their interesting crystal structures and special physical properties [2,6]. But the formation mechanism of the hexagonal perovskites and the relationships between structures and properties are still not well clear.

Interestingly, some cation substitutions at "A" or "B" site in ABO_3 perovskites largely altered the crystal structures and the dielectric properties of the perovskite ceramics. For instance, in perovskite ceramic systems of $Ba[Ti_{1-x}(M_{0.5}W_{0.5})_x]O_3$ (M = Mg, Ni, Co, Zn) [7–10], their structures transferred from cubic to hexagonal and then to double cubic ones with increasing of the substitution amount (*i.e.*, x). And it was also found that the hexagonal perovskite had lower dielectric constant (ε_r), higher quality factor ($Q \times f$), and especially the near-zero temperature coefficient of resonant frequency (τ_f) than that of cubic one. In the case of M = Ni [8], the cubic phase of the perovskite ceramic was formed at $x = 0.40$, and its microwave dielectric properties were $\varepsilon_r = 71.2$, $Q \times f = 4800$ GHz, and $\tau f = +47.8$ ppm/°C, whereas the hexagonal one was formed at $x = 0.55$ and its microwave dielectric properties were $\varepsilon_r = 21.6$, $Q \times f = 38{,}400$ GHz, and $\tau_f = -7.8$ ppm/°C. The similar dielectric properties for samples M = Mg were also observed [7]. They were $\varepsilon_r = 31.2$, $Q \times f = 8200$ GHz, and $\tau_f = +125.5$ ppm/°C for the cubic phase at $x = 0.50$, whereas $\varepsilon_r = 13.1$, $Q \times f = 35{,}000$ GHz, and $\tau_f = -6.4$ ppm/°C for the hexagonal one at $x \approx 2/3$, which possessed better properties of $\varepsilon_r = 14.5$, $Q \times f = 107{,}000$ GHz, and $\tau_f = -7.6$ ppm/°C after slightly adjusting the chemical compositions and sintering processes. But the relationships between structures and microwave dielectric properties were still not well understood. It has been considered that the formation of the hexagonal perovskites and their high quality factors were ascribed to the B-site ordering [7,11]. However, the hexagonal structure was formed not only at $x \approx 2/3$, but also at other chemical compositions. For example, the $Ba[Ti_{1-x}(Zn_{0.5}W_{0.5})_x]O_3$ ceramic adopted hexagonal structure in the chemical composition region of $x = 0.55$–0.60. Therefore, there were other factors that also subtly determined their structures and properties.

Up to now, many hexagonal structures with the space group *P6₃/mmc* had been refined. The data about the bond lengths and angles found in literatures were listed in Table 1. The essential features of them can be observed. For the corner-sharing octahedra, the bond lengths of B1–O2 are equal, and the O–B1–O angles or the sum of the supplementary angles are equal to 180°. Whereas, for the face-sharing one, the bond lengths of B2–O1 are longer than B2–O2, and the O–B2–O bond angle deviations from 90° or 180° are large. The same features can be also observed in the

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Table 1
Bond lengths and angles in face- and corner-sharing octahedra for hexagonal perovskite with $P6_3/mmc$.

Chemical compounds	Face-sharing octahedra					Corner-sharing octahedra	
	B2–O1	B2–O2	O1-B2–O1	O2-B2–O1	O2-B2–O2	B1–O2	O2-B1–O2
$Ba_3CaTiWO_9$ [12]	2.040(7)	1.902(5)	–	–	–	2.213(6)	–
$Ba_3MgSb_2O_9$ [a] [13]	2.067(3)	1.918(2)	87.58(4)	–	–	2.098(2)	–
$Ba_3ZnSb_2O_9$ [a] [13]	2.062(1)	1.928(1)	86.98(7)	–	–	2.1049(9)	–
$Ba_2FeSbO_6{}^{1}$ [a] [14]	2.085(3)	1.950(4)	85.1	175.9(1)	–	2.011(3)	–
$Ba_2FeSbO_6{}^{2}$ [a] [14]	2.078(4)	1.954(3)	85.1	176.2(1)	–	2.012(3)	–
$Ba_2FeSbO_6{}^{3}$ [a] [14]	2.091(2)	1.950(3)	85.1	176.2(1)	–	2.019(2)	–
$Ba_2CoSbO_6{}^{3}$ [a] [14]	2.013(5)	1.948(6)	82.4	178.1(2)	–	2.007(4)	–
$Ba[Ti_{1-x}(Zn_{1/2}W_{1/2})_x]O_3$ ($x = 0.60$) [10]	2.0348	1.9469	78.674	166.754/91.132	97.568	2.0432	90.597/180/89.403
$Ba[Ti_{1-x}(Ni_{1/2}W_{1/2})_x]O_3$ ($x = 0.50$) [8]	2.0297 (12)	1.9336 (17)	79.91(11)	168.40(17)/ 91.24(11)	96.48(14)	2.0320(17)	90.14(10)/180/ 89.86 (13)

[a] Represents for ND; 1–3 represents for 97 K, 191 K, 295 K, respectively.

oxygen deficient hexagonal $BaTiO_3$ [15]. So, the oxygen octahedra distortions are different in the corner- and face-sharing octahedra, but few descriptions could be found about them.

The hexagonal $BaTi_{0.4}Ga_{0.3}Sb_{0.3}O_3$ and the cubic $BaTi_{0.4}Ga_{0.3}Nb_{0.3}O_3$ perovskite ceramics with opposite τ_f values were observed in our works. It is expected that the near-zero τ_f values could be obtained by substituting Sb for Nb in these material systems. In this work, the $Ba[Ti_{0.4}Ga_{0.3}Nb_{0.3(1-x)}Sb_{0.3x}]O_3$ ($x = 0$–1.00) perovskite ceramics were synthesized and the relationship between crystal structure and microwave dielectric properties was investigated. The oxygen octahedra distortions were described from the crystal structure refinement results and their effects on the microwave dielectric properties were discussed in detail.

2. Material and methods

The $Ba[Ti_{0.4}Ga_{0.3}Nb_{0.3(1-x)}Sb_{0.3x}]O_3$ ($x = 0$–1.00) ceramics were synthesized by the conventional solid-state reaction method. High-purity grade $BaCO_3$, Ga_2O_3, TiO_2, Sb_2O_3, and Nb_2O_5 powders (Sinopharm Chemical Reagent Co., Ltd., Beijing, China) were used as the starting materials. The powders were weighed in required molar ratios and milled for 4 h using a planetary mill, then drying and screening. The obtained powders were calcined at 1320 °C for 4 h. After milling, the powders were added with polyvinyl alcohol solution (5 wt%) as a binder. Then the powders were pressed into a cylinder with a diameter of 10 mm and a height of about 6 mm under an applied pressure of 200 MPa. Finally, the cylinders were preheated at 600 °C, and then sintered between 1350 °C and 1420 °C for 4 h in air.

The bulk densities of the sintered ceramics were measured by the Archimedes method. The crystal structures of these ceramics were determined by X-ray diffraction (XRD, Rigaku D/Max-2500, Tokyo, Japan). Rietveld refinements of the crystal structures in selected cases were carried out by the Fullprof program [16]. For structure refinement, XRD data were collected over the 2θ range 10–100°, with a step size of 0.02° and count-time of 0.5 s per step. The pattern was typically refined for the background, zero, scale factor, unit cell parameters, pseudo-Voigt profile function (U, V, W, X, and Y), and isothermal temperature factors (Biso). The cross-sections of the sintered ceramics were heat-etched and observed under scanning electron microscopy (SEM, JEOL JSM-6301F, Tokyo, Japan). The microwave dielectric properties of these ceramics were investigated by a HP8720ES network analyzer (Hewlett-Packard, Santa Rosa, CA). The dielectric constant was measured using the Hakki–Coleman post-resonator method [17] by exciting the TE_{011} resonant mode of the dielectric resonators using the electric probe of an antenna as suggested by Courtney [18]. The unloaded quality factors were measured using the TE_{011} mode in the cavity method [19]. All measurements were made in the frequency range of 5–9 GHz at room temperature. The temperature coefficients of resonant frequency (τ_f) were measured in the temperature range of 25–80 °C.

3. Results and discussion

XRD patterns of $Ba[Ti_{0.4}Ga_{0.3}Nb_{0.3(1-x)}Sb_{0.3x}]O_3$ ($x = 0$–1.00) ceramics sintered at 1400 °C are shown in Fig. 1. The XRD patterns for $x = 0$–0.10 were indexed as the cubic perovskite with the space group $Pm\bar{3}m$, according to the PDF card of 75-0215. A small amount of secondary phase, which was identified as $Ba_8Ti_3Nb_4O_{24}$, can be also observed. For $x = 0.40$–1.00, the patterns were indexed as hexagonal perovskite, with the space group $P6_3/mmc$, according to the PDF card of 89-8119. A small amount of secondary phase $BaSb_2O_6$ presented in the samples. And for $x = 0.20$–0.30, the ceramics were mixtures of cubic and hexagonal perovskites. It is noticed that, the chemical composition region of the diphase was narrow and the structure started to transfer at $x = 0.20$. This manifested that Sb had a great effect on the hexagonal phase formation in this system.

Fig. 2 illustrates the microstructure of $Ba[Ti_{0.4}Ga_{0.3}Nb_{0.3(1-x)}Sb_{0.3x}]O_3$ ceramics sintered at 1400 °C. It is clearly observed that the grains developed into round-like ones in both end members. The round-like grains imbedded into the plate-like ones was the typical morphology of these ceramics in the range of $x = 0.10$–0.90. The presence of the plate-like morphology may be correlated to the liquid sintering processes, which resulted by the

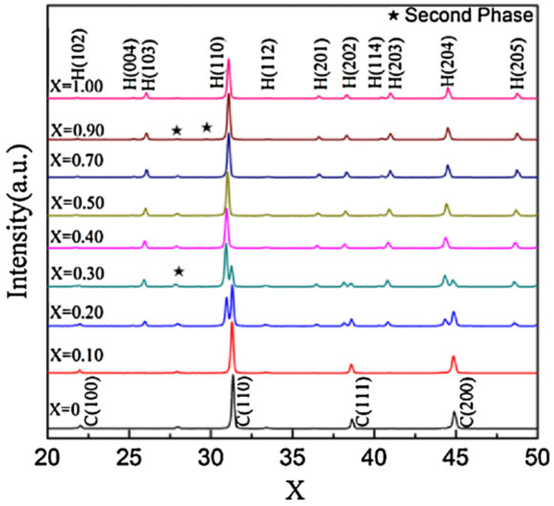

Fig. 1. Typical XRD patterns for ceramics $Ba[Ti_{0.4}Ga_{0.3}Nb_{0.3(1-x)}Sb_{0.3x}]O_3$ sintered at 1400 °C.