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Structural and microwave dielectric properties of $Ba_{5-x}La_xTi_xNb_{4-x}O_{15}$ ceramics

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Abstract The structural and microwave dielectric properties of $Ba_{5-x}La_xTi_xNb_{4-x}O_{15}$ ($1 \le x \le 3$) was investigated. The single phase with $A_5B_4O_{15}$-type cation-deficient hexagonal perovskite structure was obtained over the whole composition range. These ceramics have high dielectric constant up to 56, high quality factors ($Q \times f$) up to 35,000, and low temperature coefficient of resonant frequencies (τ_f) in the range +69 to −3 ppm °C^{-1}. The dielectric constants and τ_f of these ceramics gradually decrease parallel to an increase in B-site bond valence with increasing La and Ti content.

Keywords Dielectrics · Dielectric resonators · Microwave ceramics · Hexagonal perovskites

1 Introduction

Recent progress in microwave telecommunication and satellite broadcasting has demanded the need for good quality ceramics dielectric resonators (DR). The important characteristics required for a DR are high dielectric constant (>25) for miniaturization, high quality factor (Q>2000) for selectivity and low temperature coefficient of resonant frequency (τ_f <±20 ppm) for stability. Several DR materials such as $Ba(Zn_{1/3}Ta_{2/3})O_3$, $BaTi_4O_9$, $Ba_2Ti_9O_{20}$, (Zr,Sn) TiO_4, and $Ba_{6-3x}RE_{8+2x}Ti_{18}O_{54}$ (RE=Nd, Sm, La) systems have been investigated for practical application [1, 2]. Still, the search for new materials having those properties is in rapid progress owing to the drive for further system miniaturization and improved filtering capabilities [3, 4]. Recently, some $A_5B_4O_{15}$ type cation-deficient hexagonal perovskites such as $Ba_5Nb_4O_{15}$, $Ba_{5-x}Sr_xNb_4O_{15}$, $Ba_5Ta_4O_{15}$, and $MLa_4Ti_4O_{15}$ (M= Ba, Sr, and Ca) were characterized by high dielectric constant up to 54, high quality factors with $Q \times f$ up to 50,215 GHz, and low τ_f in the range −25 to + 78 ppm/°C [5–10]. Among them the $Ba_5Nb_4O_{15}$ is reported to have a dielectric constant of 42 and τ_f of 78 ppm/°C, while $BaLa_4Ti_4O_{15}$ has a dielectric constant of 43 and τ_f of −17 ppm/°C [5]. However, there is no report on any other La-contained $A_5B_4O_{15}$ type cation-deficient perovskites in the $BaO–La_2O_3–TiO_2–Nb_2O_5$ system, and the effect of La substitution for Ba on the microwave dielectric properties of $Ba_5Nb_4O_{15}$ has not yet been investigated. In the present paper, we report the preparation, characterization, and dielectric properties of the cation-deficient hexagonal perovskites $Ba_{5-x}La_xTi_xNb_{4-x}O_{15}$ (x=1, 1.5, 2, 3), for the first time.

2 Experimental

The ceramics were prepared through the solid-state ceramics route. High-purity raw powders $BaCO_3$ (99.9%), La_2O_3 (99.99%), TiO_2 (>99.95%), and Nb_2O_5 (99.9%); all chemicals used were from Aldrich Chemical. The powders were weighed according to the stoichiometry of $Ba_{5-x}La_xTi_xNb_{4-x}O_{15}$ (x=1, 1.5, 2, 3) and ball-milled in distilled water medium for 12 h in a plastic bottle using zirconia balls. The

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Table 1 The unit cell parameters and tolerance factor of $Ba_{5-x}La_xTi_xNb_{4-x}O_{15}$.

Samples	a (Å)	c (Å)	V (Å^3)	Tolerance factor	Relative density (%)
x=1	5.7292	11.7053	332.63	1.0306	97.1
x=1.5	5.6969	11.6664	327.90	1.0239	96.2
x=2	5.6697	11.6277	323.70	1.0174	96.8
x=3	5.6154	11.5109	314.34	1.0043	97.5

wet mixtures were dried and calcined in the range 1,200 °C for 4 h, then ground and again calcined at 1,380~1,400 °C for 4 h. The calcined powders were thoroughly reground and mixed with 5% solution of polyvinyl alcohol (PVA) as a binder. The slurries were then dried, ground, and then pressed into cylindrical disks of different thickness in the range 5~7 mm and 11 mm in diameter under a pressure of 150 MPa. The green pellets were sintered at different temperatures in the range of 1,450~1,520 °C for 3 h. The sintering temperatures were optimized for maximum density. The sintered samples were polished and the bulk densities were measured using the Archimedes method. The phase purity of the sintered samples were studied by X-ray diffraction (XRD) using a Rigaku D/MAX-RB X-ray diffractometer using CuKα radiation (λ=0.15406 nm). The fracture surface morphology of the ceramics was studied using a JSM-5610LV scanning electron microscope (SEM).

The microwave dielectric properties such as dielectric constant and Q were measured using an Agilent 8722ET network analyzer; the dielectric constant was calculated using TE_{011} mode under the end-shortened condition using the method suggested by Hakki and Coleman and modified by Courtney [11, 12]. The τ_f was measured by noting the temperature variation of the TE_{011} resonance in the temperature range 25–85 °C.

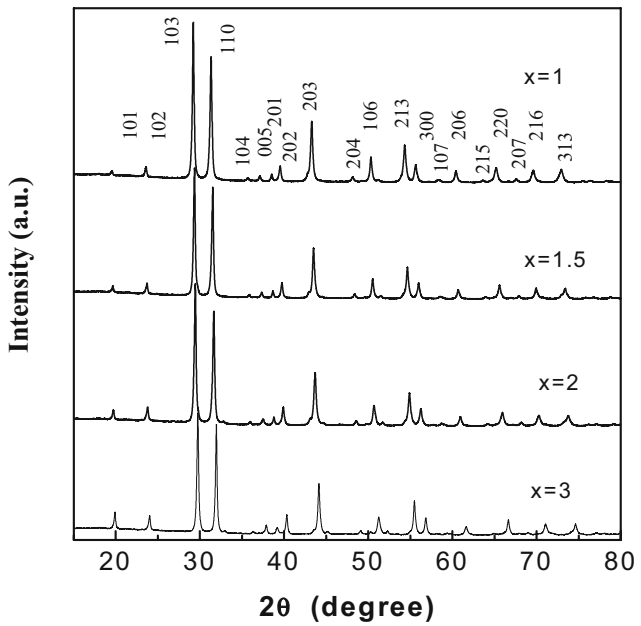

Fig. 1 XRD patterns of $Ba_{5-x}La_xTi_xNb_{4-x}O_{15}$ ceramics

3 Results and discussion

The $Ba_{5-x}La_xTi_xNb_{4-x}O_{15}$ (x=1, 1.5, 2, 3) ceramics were sintered into dense bodies. The relative densities of the sintered samples are given in Table 1. The ceramics show densities in the range of 96~98 % of their theoretical densities. The XRD patterns obtained using CuK_α radiation are shown in Fig. 1. The patterns are similar and match with the one reported for $Ba_5Nb_4O_{15}$ by Galasso *et al.* (JCPDS file No.14-28) [13]. The unit cell parameters of the ceramics refined by the least-squares method are listed in Table 1.

Those compounds crystallize in a cation-deficient hexagonal $A_5B_4O_{15}$ perovskite structure where Ba and La ions

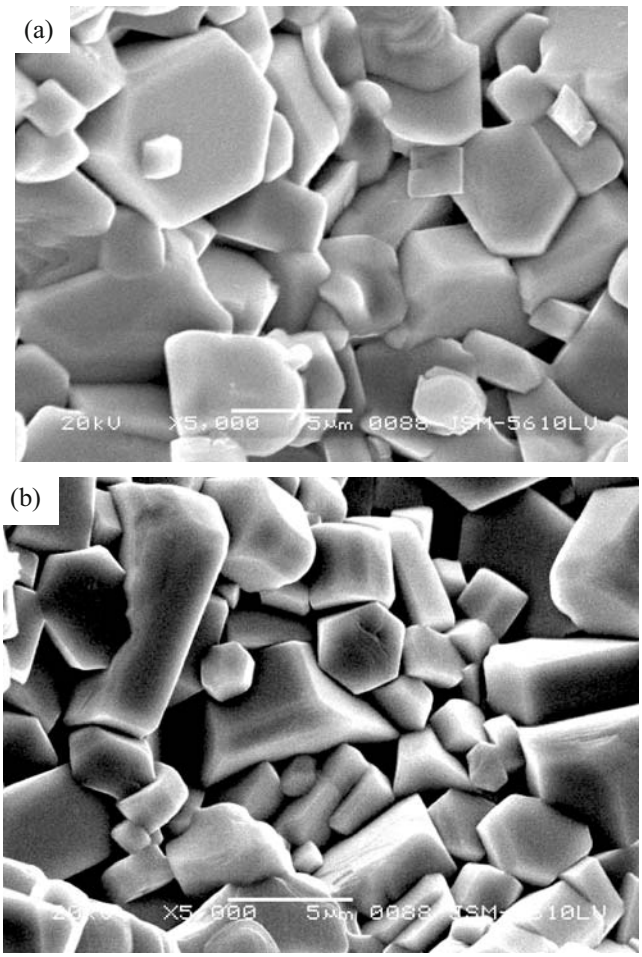

Fig. 2 SEM micrographs of (a) $Ba_3La_2Ti_2Nb_2O_{15}$ and (b) $Ba_2La_3Ti_3NbO_{15}$

Table 2 Microwave dielectric properties of $Ba_{5-x}La_xTi_xNb_{4-x}O_{15}$.

Composition	ε_r	Q	f (GHz)	$Q\times f$ (GHz)	τ_f (ppm °C^{-1})
$Ba_4LaTiNb_3O_{15}$	56.3	3,650	4.6402	16,936	+69
$Ba_{3.5}La_{1.5}Ti_{1.5}Nb_{2.5}O_{15}$	54.2	5,050	4.8721	24,604	+45
$Ba_3La_2Ti_2Nb_2O_{15}$	49.8	5,890	5.9894	35,277	+8
$Ba_2La_3Ti_3NbO_{15}$	47.1	4,760	6.0746	28,912	−3

occupy the A sites with coordination numbers of 12, and Nb and Ti ions disorderly occupy the B sites with coordination numbers of 6. The crystal structure can be described as consisting of identical perovskite-like blocks, four-corner-sharing BO_6 octahedra thick, separated by layers of vacant octahedral [14]. The unit-cell parameters, volumes, and tolerance factor of $Ba_{5-x}La_xTi_xNb_{4-x}O_{15}$ slightly decrease with increasing La and Ti content, as Shannon's effective ionic radius [15] of La^{3+} (1.36 Å) is smaller than that of Ba^{2+} (1.61 Å) at the A site and the radius of Ti^{4+} (0.605 Å) is smaller than that of Nb^{5+} (0.64 Å) at the B site.

Figure 2 shows the typical SEM micrographs of $Ba_3La_2Ti_2Nb_2O_{15}$ and $Ba_2La_3Ti_3NbO_{15}$. The microstructure indicates a monophase constitution with uniformly hexagonal packed grains in the range of 3~10 μm size for both $Ba_3La_2Ti_2Nb_2O_{15}$ and $Ba_2La_3Ti_3NbO_{15}$.

The microwave dielectric properties of $Ba_{5-x}La_xTi_xNb_{4-x}O_{15}$ were measured under TE_{011} mode, shown in Table 2. They exhibit high ε_r in the range 56.3~47.1 and high quality factors with $Q\times f$ in the range 16,936~35,277 GHz. $Ba_3La_2Ti_2Nb_2O_{15}$ and $Ba_2La_3Ti_3NbO_{15}$ may be suitable for practical application as dielectric resonators due to their smaller τ_f close to zero. It is found that ε_r gradually decrease from 56.3 to 47.1 with increasing content of La and Ti ions. Generally, the dielectric constant of the single-phase ceramics with high relative density is known to be largely dependent on the ionic polarizability (α) of cations and oxygen at the microwave frequency [16–18]. According to the ionic polarizabilities of cations reported by Shannon [19], the theoretical molecular ionic polarizabilities of these perovskites obtained from the additive rule decrease with increasing contents of La and Ti because the values of the ionic polarizabilities of Ba^{2+} (6.40 Å^3) and Nb^{5+}(3.97 Å^3) are larger than those of La^{3+} (6.07 Å^3) and Ti^{4+} (2.93 Å^3). Thus, the dielectric constants of these perovskites decrease with increasing content of La and Ti.

Moreover, the τ_f of these four ceramics also decreases from +69 ppm °C^{-1} to −3 ppm °C^{-1}, with increasing content of La and Ti ions. It has been reported that the τ_f could be effectively evaluated by the B-site bond valence in the perovskite-related structure [16]. The numerical the valences (V_i) of B-site ions in these crystal structures were determined by the bond valence sum, calculated using Brown's method [21] (in Eqs. 1 and 2).

$$S_{ij} = \exp\left(R_0 - R_{ij}\right)/B \tag{1}$$

$$V_i = \sum_j S_{ij}, \tag{2}$$

where R_0 and B are known as the bond valence parameters of various cations and a constant value (0.37 Å), respectively, and then R_{ij} means the interatomic distance between cations i and j. In this paper, R_{ij} is the mean bond length of B–O. For the case of hexagonal perovskite, d_{B-O} was defined as half of the cube root on the cell volume per formula. The B-site bond valence (V_{Nb}, V_{Ti}) values of these perovskite ceramics are listed in Table 3.

It is clear that the B-site bond valances of these ceramics gradually increase, in contrast to the decreases in τ_f and unit-cell volumes, with increasing content of La and Ti ions. Too high values probably reflect the fact that all interatomic distances are averaged data, and good resolution would be obtained from neutron diffraction measurement. This result is similar to previous results in $A_6B_5O_{18}$-type cation-deficient perovskites [21] and some complex perovskites such as $Ca_{1-x}Sm_{2x/3}TiO_3$ and $Pb_{0.45}Ca_{0.55}Fe_{0.5}(Nb_{1-x}Ta_x)_{0.5}O_3$ [16–18]. Therefore, the τ_f might be controlled with the increase of B-site bond valences in $A_5B_4O_{15}$ cation-deficient perovskites in the $BaO–La_2O_3–TiO_2–Nb_2O_5$ system, Further, a near-zero τ_f might be achieved in the ceramics of intermediate compositions between $Ba_3La_2Ti_2Nb_2O_{15}$ and $Ba_2La_3Ti_3NbO_{15}$, and this work is in progress.

Table 3 B-site bond valance of $Ba_{5-x}La_xTi_xNb_{4-x}O_{15}$.

Composition	R_{Nb} (Å)	R_{Ti} (Å)	$R_{B\text{-}O}$ (Å)	V_{Nb}	V_{Ti}	$V_{unit\text{-}cell}$ (Å^3)
$Ba_4LaTiNb_3O_{15}$	1.911	1.815	2.0259	4.40	3.39	332.63
$Ba_{3.5}La_{1.5}Ti_{1.5}Nb_{2.5}O_{15}$	1.911	1.815	2.0163	4.51	3.48	327.90
$Ba_3La_2Ti_2Nb_2O_{15}$	1.911	1.815	2.0076	4.62	3.57	323.70
$Ba_2La_3Ti_3NbO_{15}$	1.911	1.815	1.9881	4.87	3.75	314.34

4 Conclusion

$Ba_{5-x}La_xTi_xNb_{4-x}O_{15}$ have been synthesized and identified as $A_5B_4O_{15}$ type cation-deficient hexagonal perovskites. These ceramics exhibit high dielectric constants in the range 56.3~47.1, high quality factors with $Q \times f$ value in the range 16,939~35,227 GHz, and low τ_f in the range of +69~−3 ppm $°C^{-1}$. The dielectric constant and τ_f of these ceramics gradually decrease parallel to an increase in B-site bond valence with increasing La and Ti content, and this suggests the potential for microwave application of the present materials.

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