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Microwave dielectric properties of $Ba_4LaTiNb_{3-x}Ta_xO_{15}$ ceramics

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Abstract High dielectric constant and low loss ceramics in the system $Ba_4LaTiNb_{3-x}Ta_xO_{15}$ ($x = 0$–3) have been prepared by conventional solid-state ceramic route. $Ba_4LaTiNb_{3-x}Ta_xO_{15}$ solid solutions adopted $A_5B_4O_{15}$ cation-deficient hexagonal perovskite structure for all compositions. The materials were characterized at microwave frequencies. They show a linear variation of dielectric properties with the value of x. Their dielectric constant varies from 53.1 to 42.3, quality factor $Q_u \times f$ from 18,790 to 28,070 GHz and temperature variation of resonant frequency from +94.3 to +33.1 ppm/°C as the value of x increases.

1 Introduction

The recent advances in the telecommunication systems have led to an increasing attention on microwave ceramic dielectric resonators (DRs) [1]. DRs are extensively used in microwave devices like filters, oscillators and Dielectric Resonator Antennas. To meet the requirements for use in such wide applications, the materials should possess stringent properties like (a) high dielectric constant (ε_r) for miniaturization, (b) high unloaded quality factor (Q_u) or low dielectric loss for better selectivity and (c) low temperature coefficient of resonant frequency (τ_f) for frequency stability. Although several 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 reported for practical applications [1–2], active research is still going on for new ceramics due to the great demand for a variety of materials with varying dielectric constants [3–9].

Recently Sebastian and Vineis et al. reported the microwave dielectric properties of some $A_5B_4O_{15}$ type cation-deficient hexagonal perovskites such as $Ba_5Nb_4O_{15}$, $Ba_{5-x}Sr_xNb_4O_{15}$, and $MLa_4Ti_4O_{15}$ (M = Ba, Sr and Ca) [10–15]. More recently, we also investigated the microwave dielectric properties of A site and B sites co-substituted $Ba_5Nb_4O_{15}$ ceramics such as $Ba_4LaMNb_3O_{15}$ (M = Ti, Sn), $Ba_3Ln_2Ti_2Nb_2O_{15}$ and $Ba_2Ln_3Ti_3NbO_{15}$ (Ln = La, Nd) [16–18]. Among those compounds, $Ba_4LaTiNb_3O_{15}$ was characterized by high dielectric constant of 52, high quality factors with $Q_u \times f$ of 15,652 GHz, but its τ_f value (+93 ppm $°C^{-1}$) is too large and precludes its application as DRs [16]. Since many studies have reported that the substitutions of Nb with Ta to form solid solutions might reduce the value of τ_f and improve the properties of microwave dielectric ceramics such as $Ca_5Nb_{2-x}Ta_xTiO_{12}$, $GdTiNb_{1-x}Ta_xO_6$ $A_5Nb_xTa_{4-x}O_{15}$ (A = Ba, Sr) and $Mg_4Nb_{2-x}Ta_xO_9$ [14, 19–21]. In the present study, the preparation, characterization and microwave dielectric properties of $Ba_4LaTiNb_{3-x}Ta_xO_{15}$ ($x = 0$–3) ceramics were investigated.

2 Experimental

The ceramic resonators in the system $Ba_4LaTiNb_{3-x}Ta_xO_{15}$ ($x = 0$, 1, 2 and 3) were prepared by the conventional

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solid-state ceramic route. High purity raw powders $BaCO_3$ (99.9%), La_2O_3 (99.99%), TiO_2 (>99.95%), Ta_2O_5 (99.9%) and Nb_2O_5 (99.9%) were used as the starting materials. Stoichiometric amounts of the powders were weighed and ball milled using zirconia balls in plastic containers. $Ba_4LaTiNb_{3-x}Ta_xO_{15}$ was calcined at 1,300 °C for 8 h. The calcined powders were ground well and mixed with 5 wt.% solution of PVA as the binder. The powders were then uniaxially pressed into cylindrical disks with 11 mm diameter and 7 mm height under a pressure of 300 MPa. The samples were fired at 600 °C for 2 h to remove the organic binder and then sintered in the range 1,400–1,520 °C for different durations. The sintered sample was typically annealed at 1380 °C for 2 h to minimize the reduction of titanium ions.

The sintered samples were well polished and their bulk density was calculated by Archimedes method. The crystal structure and phase purity of the samples were studied using a Rigaku D/MAX-RB X-ray diffractometer using CuKα radiation (λ = 0.154060 nm). The surface morphology of the samples was examined using a JSM-6380LV scanning electron microscope (SEM). The microwave dielectric properties were measured using an Agilent 8722ET network analyzer. The dielectric constant was measured by the dielectric post resonator method suggested by Hakki and Coleman and modified by Courtney [22, 23]. The resonator was placed between two gold-coated copper metallic plates, and microwave energy was coupled through E-field probes to excite various resonant modes. Among the various resonant modes, the TE_{011} mode was selected for the measurements. The τ_f was measured by noting the temperature variation of the TE_{011} resonance in the temperature range 15–85 °C.

3 Results and discussion

The room temperature XRD patterns recorded for the $Ba_4LaTiNb_{3-x}Ta_xO_{15}$ (x = 0–3) ceramics using CuK_α radiation are shown in Fig. 1. The patterns are similar and match with JCPDS file No.56-400 of $Ba_4LaTiNb_3O_{15}$. All of the peaks were indexed and there was no evidence of any second phases(s) present. The system $Ba_4LaTiNb_{3-x}Ta_xO_{15}$ crystallizes in a cation-deficient hexagonal $A_5B_4O_{15}$ perovskite structure where the large Ba and La ions occupy the A sites with coordination numbers of 12, and Ti and Nb/Ta ions occupy the B sites with coordination numbers of 6 [16]. The solid solutions of $Ba_4LaTiNb_{3-x}Ta_xO_{15}$ are easily formed for all x values since the Shannon's effective ionic radii (0.64 Å) [24] and charge are the same for Nb^{5+} and Ta^{5+} ions.

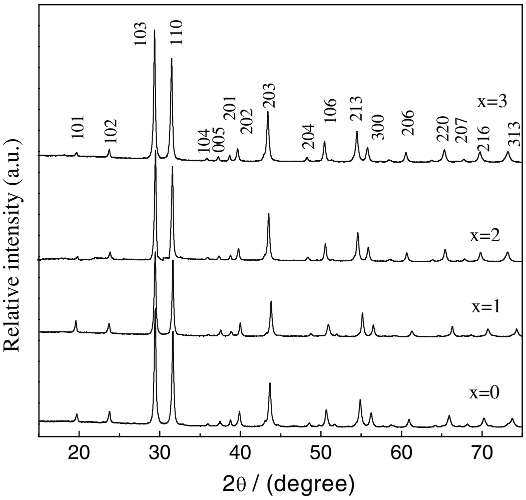

Fig. 1 XRD pattern of $Ba_4LaTiNb_{3-x}Ta_xO_{15}$ ceramics

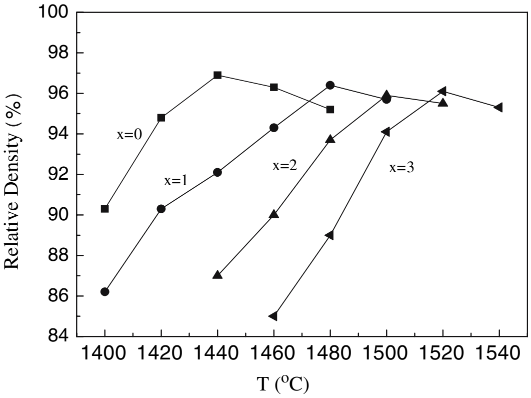

Fig. 2 The variation of relative density of $Ba_4LaTiNb_{3-x}Ta_xO_{15}$ ceramics as a function of the sintering temperature

Figure 2 demonstrates the relative density of $Ba_4LaTiNb_{3-x}Ta_xO_{15}$ ceramics as a function of sintering temperature, through which the optimized sintering temperature of the solid solutions can be determined at 1,440, 1,480, 1,500 and 1,520 °C for the compositions of x = 0, 1, 2 and 3, respectively. It clearly reveals that the maximum densities for all the samples could reach >95% of the theoretical X-ray density. The microstructure of the ceramics with maximum densities was characterized using SEM and no apparent difference with composition was observed. Figure 3 shows the typical SEM micrographs of the surface recorded for two end members $Ba_4LaTiNb_3O_{15}$ and $Ba_4LaTiTa_3O_{15}$. The both ceramics have a close microstructure with low porosity, and the packed plate-like grains are in the size range of 2–12 µm for both ceramics.

Under optimum sintering conditions, the microwave dielectric properties of the solid solution phases $Ba_4LaTiNb_{3-x}Ta_xO_{15}$ (x = 0, 1, 2 and 3) are given in Table 1. $Ba_4LaTiTa_3O_{15}$ and $Ba_4LaTiNb_3O_{15}$ both show high quality factors with $Q_u \times f$ values of 28,070 and 18,790 GHz. $Ba_4LaTiTa_3O_{15}$ has a comparatively lower ε_r of 42.3 and τ_f of + 33.1 ppm/°C than $Ba_4LaTiNb_3O_{15}$, which has ε_r of 53.1 and τ_f of +94.3 ppm/°C. The influence of Ta substitution for

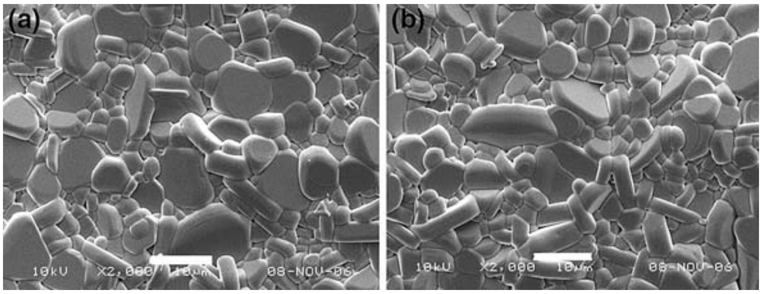

Fig. 3 SEM micrographs of (**a**) $Ba_4LaTiNb_3O_{15}$ and (**b**) $Ba_4LaTiTa_3O_{15}$ ceramics

Table 1 Microwave dielectric properties of $Ba_4LaTiNb_{3-x}Ta_xO_{15}$

x	Sintering temperature (°C)	Density (%)	ε_r	$Q_u \times f$ (GHz)	τ_f (ppm/°C)
0	1,440	96.1	53.1	18,790	+94.3
1	1,480	95.9	49.5	24,150	+75.2
2	1,500	96.3	45.3	25,070	+52.5
3	1,520	95.7	42.3	28,070	+33.1

Nb on the dielectric constants and quality factors as a function of compositions x are shown in Fig. 4. The dielectric constant linearly decreased as x increased while the unloaded quality factors $Q_u \times f$ increased with the value of x. This result is similar to those of $Ca_5Nb_{2-x}Ta_xTiO_{12}$ (x = 0–2) [19] and $Mg_4Nb_{2-x}Ta_xO_9$ (x = 0–2) [21]. Ratheesh et al. [25] has suggested larger short-range interaction parameter in O–Ta–O bond as the cause of lower dielectric constant and lower dielectric loss for tantalum compounds than the niobium compounds. The temperature coefficients of resonant frequency (τ_f) also linearly decreased with increasing Ta content from x = 0 to x = 3 (see Fig. 5), which is similar to those of $Ca_5Nb_{2-x}Ta_xTiO_{12}$ (x = 0–2) [19] and $Ba_5Nb_xTa_{4-x}O_{15}$ (x = 0–4) [14].

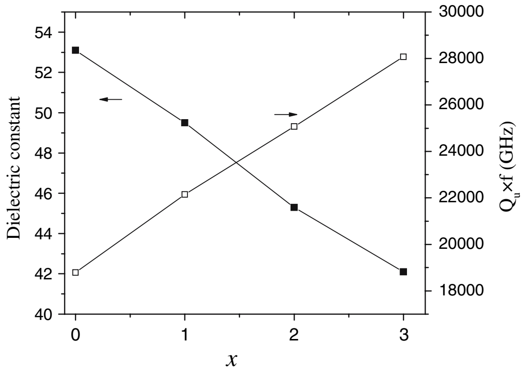

Fig. 4 Variations of dielectric constant and Q × f of $Ba_4LaTiNb_{3-x}Ta_xO_{15}$ ceramics with x

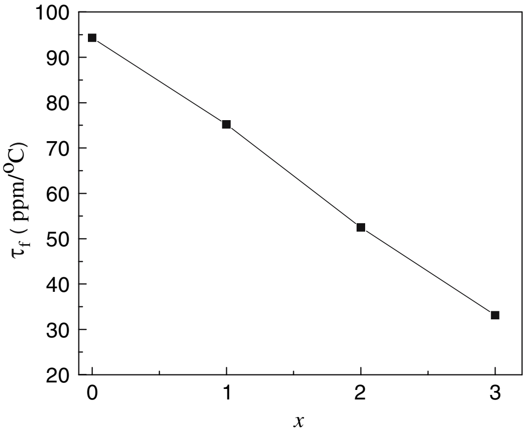

Fig. 5 Variations of τ_f of $Ba_4LaTiNb_{3-x}Ta_xO_{15}$ ceramics with x

4 Conclusions

The $Ba_4LaTiNb_{3-x}Ta_xO_{15}$ (x = 0–3) has been prepared as single-phase materials by the conventional solid-state ceramic route. The optimum sintering temperature of $Ba_4LaTiNb_{3-x}Ta_xO_{15}$ ceramics increased with increasing x values and ranged from 1,440 to 1,520 °C. The microwave dielectric properties of $Ba_4LaTiNb_{3-x}Ta_xO_{15}$ ceramics show a linear variation between that of the end members for all compositions. These ceramics exhibit high ε_r ranged from 53.1 to 42.3, low τ_f value from +93.4 to +33.1 ppm/°C, and high quality factor with $Q_u \times f$ value from 18,790 to 28,070 GHz with increasing x values.

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