Preparation and microwave dielectric properties of a new $A_4B_3O_{12}$-type cation-deficient perovskite $BaLa_3Ti_2NbO_{12}$

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The dramatic advances during the last two decades in the microwave integrated circuit technology have brought a revolution in telecommunication and satellite broadcasting system. Dielectric resonators (DRs) provide significant advantages in terms of compactness, light weight, temperature stability, and relatively low cost in the production of high frequency devices. The important characteristics required for a DR are high dielectric constant (ε_r>25) for miniaturization, high quality factor (Q>2000) for selectivity and low temperature coefficient of resonant frequency ($\tau_f < \pm 20$ ppm) for stability. Although 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, and La) systems have been investigated for practical application [1, 2], the drive for further system miniaturization and improved filtering capabilities requires the development of new materials with higher dielectric constant and lower losses [3–8]. Recently, the microwave dielectric properties of some $A_nB_{n-1}O_{3n}$ (n=5, 6, 7 and 8) cation-deficient hexagonal perovskites such as $A_5B_4O_{15}$ (A = Ba, Sr; B = Nb, Ta), $MLa_4Ti_4O_{15}$ (M = Ba, Sr, and Ca), $M_2La_4Ti_5O_{18}$, $Ba_7Ti_2Nb_4O_{21}$ and $Ba_8Ti_3Nb_4O_{24}$ have been reported [9–19]. These ceramics are characterized by high dielectric constant up to 56, high quality factors with Qf up to 88000 GHz. However, there is no report so far on the microwave dielectric properties of any $A_4B_3O_{12}$-type cation-deficient hexagonal perovskites, then it is worthwhile to investigate whether $A_4B_3O_{12}$ perovskites might have equivalent or superior properties. In the present paper, we report the synthesis, characterization and dielectric properties of a new $A_4B_3O_{12}$-type cation-deficient perovskite, $BaLa_3Ti_2NbO_{12}$, for the first time.

Polycrystalline sample of $BaLa_3Ti_2NbO_{12}$ was prepared using high temperature solid-state reaction techniques. The stoichiometric mixtures of the high purity powders of $BaCO_3$ (99.9%), La_2O_3 (99.99%), TiO_2 (>99.95%) and Nb_2O_5 (99.9%), were weighed and ball milled in distilled water medium for 12 hr in a plastic bottle using zirconia balls. The wet mixture was dried and calcined in the range 1200 °C for 4 hr, then ground and again calcined at 1300 °C for 4 hr. The calcined powders were thoroughly reground and mixed with 5% solution of polyvinyl alcohol (PVA) as a binder. The slurry was then dried, ground and then pressed into cylindrical disks of different thickness in the range 5∼6 mm and 11 mm in diameter under a pressure of 300 MPa. The green compacts were initially fired at a rate of 3 °C/min up to 600 °C and then at a rate of 6 °C/min to the sintering temperature. An intermediate soaking at 600 °C for 2 hr was given to expel the binder. The optimized sintering temperature was 1460 °C for $BaLa_3Ti_2NbO_{12}$. The sintering was carried out for a duration of 6 hr. The sintered sample was typically annealed at 1400 °C for 4 hr to minimize the reduction of titanium ions.

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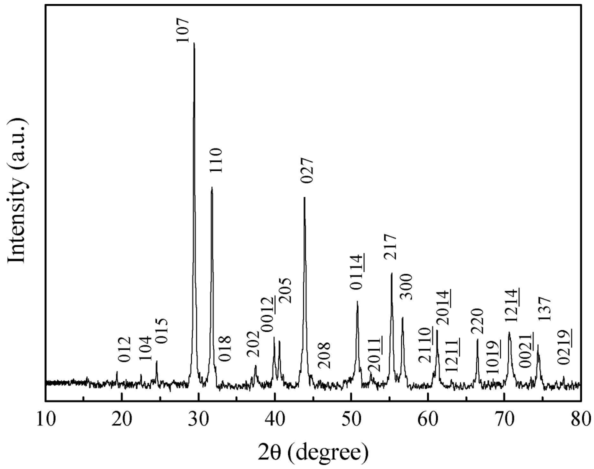

Figure 1 XRD pattern of $BaLa_2Ti_2NbO_2$.

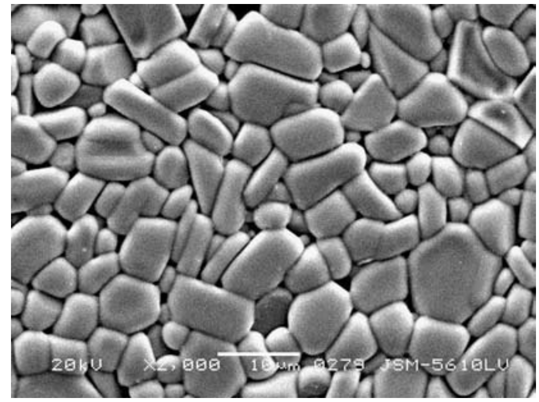

Figure 2 SEM micrograph of $BaLa_3Ti_2NbO_{12}$.

The density of the ceramic was measured by the Archimedes method. The phase identification were done using a Rigaku D/MAX-RB powder X-ray diffractometer (XRD) using CuK_α radiation (λ=0.154 06 nm) in a 2θ range from 10 to 80° at a scan rate of 1°/min. The sintered sample was polished and thermally etched at 1380 °C for 30 min. The surface microstructure was characterized using a JEOL JSM-5610LV scanning electron microscope (SEM).

Thin discs of about 2 mm thickness were used as a capacitor to determine the dielectric constant ε_r at low frequency (1 kHz–1 MHz) using an HP4284A LCR meter at room temperature. Silver paste was applied to the surfaces of these discs, then dried at 600 °C for 30 min and cooled naturally to room temperature. 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 [19, 20]. 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.

The room temperature XRD pattern recorded for the ceramics using CuK_α radiation is shown in Fig. 1. The pattern is similar and matches with those reported for $Ba_3LaNb_3O_{12}$ by Rother and Kemmler *et al.* (JCPDS file No. 44-929 and 73-914) [22, 23]. All peaks found were indexed and there was no evidence of any second phases(s) present, therefore, the ceramic is single-phase pure. The compound crystallizes in the trigonal system with unit cell parameters a=5.6128(2) Å, c=27.008(2) Å, V=736.86 (5) Å^3 and Z=3, refined by the least-squares method. The unit cell parameters and unit-cell volume of $BaLa_3Ti_2NbO_{12}$ are smaller than those of $Ba_3LaNb_3O_{12}$ [22] since the Shannon's effective ionic radius [29] of La^{3+} (1.36 Å) is smaller than that of Ba^{2+} (1.61 Å) and the radius of Ti^{4+} (0.605 Å) is smaller than that of Nb^{5+} (0.64 Å).This compound is isostructural with $Ba_3LaNb_3O_{12}$ and adopts an $A_4B_3O_{12}$-type cation-deficient hexagonal perovskite structure where the Ba and La ions occupy the A sites with coordination numbers of 12, and Nb and Ti ions occupy the B sites with coordination numbers of 6. The crystal structure can be described as consisting of identical perovskite-like blocks, three corner-sharing BO_6 octahedra thick, separated by layers of vacant octahedral [22, 23].

The $BaLa_3Ti_2NbO_{12}$ ceramic was sintered into a dense body without the use of any additive. It showed a bulk density of 6.143 g cm^3, and the relative density is 97.2% of its theoretical density. Fig. 2 shows the SEM micrograph of the fracture surface of the ceramic. The ceramic has a close microstructure with low porosity, and the packed grains are in the size range of 3∼12 μm.

The dielectric constant (ε_r) of the $BaLa_3Ti_2NbO_{12}$ ceramic in the 1 kHz∼1 MHz region is shown in Fig. 3 as a function of the frequency. The ε_r of $BaLa_3Ti_2NbO_{12}$ ceramic significantly decreases from 49.47 to 45.46 with increasing frequency from 1 kHz to 100 kHz, which suggests that at low frequencies the electronic, ionic, dipolar, and interfacial/surface polarizations contribute to the dielectric constant. However, above 100 kHz the contribution from the interfacial/surface polarization is minimized [24], then the dielectric constant slightly decreased to 44.21 at 1 MHz. This feature is similar to those observed in some dielectric oxides such as $Ba_4La_2Ti_3Nb_2O_{18}$, $Ba_4LaMNb_3O_{15}$ (M = Ti and Sn) and $Pb_5LaTi_3Nb_7O_{30}$ [16, 24]. The microwave dielectric properties were measured under TE_{011} mode. The $BaLa_3Ti_2NbO_{12}$ ceramic shows an ε_r of 42.42 calculated from the TE_{011} resonance, and a high quality factors with Q_u of 4775 GHz at 7.0495 GHz. The dielectric constant at microwave frequency is in good agreement with the value obtained at 1 MHz, which is similar to those of $Ba_2La_3Ti_3NbO_{15}$ (42.83), and the value of *Qf* (33,661) is much higher than that of $Ba_2La_3Ti_3NbO_{15}$ (21,726) [19].

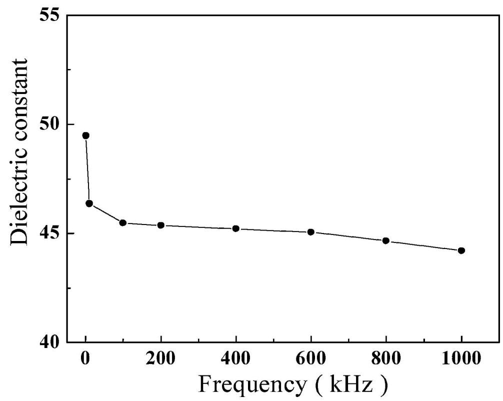

Figure 3 Variation of the dielectric constant with frequency for $BaLa_3Ti_2NbO_{12}$.

The dielectric constant can be calculated from the Clausius–Mossotti equation:

$$\varepsilon_r = \frac{3V_\mathrm{m} + 8\pi\alpha_D^T}{3V_\mathrm{m} - 4\pi\alpha_D^T} \tag{1}$$

where V_m is the molar volume and α_D^T is the sum of ionic polarizabilities of individual ions given by Shannon [25]. The calculated dielectric constants usually agree well with the experimental values for well-behaved ceramics [25]. However, an inconsistency is found when the equation is applied to the La containing $A_nB_{n-1}O_{3n}$ compounds such as $BaLa_4Ti_4O_{15}$ and $Ba_2La_4Ti_5O_{18}$ [10, 12]. It has been suggested by Veneis *et al*. that if the ionic polarizability of the La ion (α_La) is changed to 4.82 instead of 6.07 given by Shannon, the inconsistency can be avoided [10]. Using α_La=4.82, the dielectric constant of $BaLa_3Ti_2NbO_{12}$ is calculated as 43.96, which is in good agreement with the experimental values of 44.25 corrected for porosity using Rushman and Strivens equation [26]

$$\varepsilon_\mathrm{corr} = \varepsilon_\mathrm{obs}(2 + V_2)/(2 - V_2),$$

where V_2 is the volume fraction of porosity in the sintered compact. The small difference is due to deviations from the cubic symmetry and also the fact that the sample is a ceramic and not a single crystal [12].

Fig. 4 shows the variation of resonant frequencies in the TE_{011} mode of $BaLa_3Ti_2NbO_{12}$ ceramics as a function of the temperature. The temperature coefficient of the resonant frequency τ_f is calculated using the equation:

$$\tau_f = \frac{1}{f}\cdot\frac{\Delta f}{\Delta T} \tag{2}$$

The τ_f of $BaLa_3Ti_2NbO_{12}$ ceramic is 6 ppm $^\circ C^{-1}$, which is close to zero compared to those of $Ba_2La_3Ti_3NbO_{15}$ (-8 ppm $^\circ C^{-1}$) and $Ba_3La_3Ti_4NbO_{18}$ (35.2 ppm $^\circ C^{-1}$) [15, 17, 19], and it suggests that this material may be suitable for practical application as dielectric resonators.

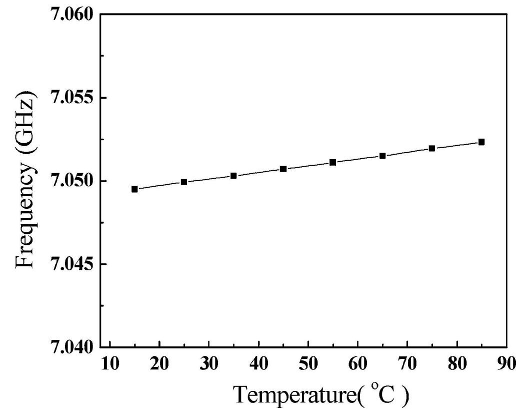

Figure 4 Variation of resonant frequency of $BaLa_3Ti_2NbO_{12}$ as a function of the temperature.

A new dielectric ceramic $BaLa_3Ti_2NbO_{12}$ has been prepared and characterized. The compound adopts a cation-deficient hexagonal $A_4B_3O_{12}$ perovskite structure. It has a high dielectric constant of 42.42, a high quality factors with *Qf* of 33,661 GHz, and a small positive τ_f of 6 ppm $^\circ C^{-1}$, and it is a potential candidate for practical applications as dielectric resonators at microwave frequency.

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