Preparation and microwave dielectric properties of a new A$_4$B$_3$O$_{12}$-type cation-deficient perovskite BaLa$_3$Ti$_2$NbO$_{12}$

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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 ($\varepsilon_r > 25$) 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$_4$O$_9$, Ba$_2$Ti$_9$O$_{20}$, (Zr, Sn)TiO$_4$, and Ba$_6$–$\delta$RE$_{8+2}$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$_n$B$_{n-1}$O$_n$ ($n=5, 6, 7$ and $8$) cation-deficient hexagonal perovskites such as A$_5$B$_4$O$_{15}$ (A = Ba, Sr; B = Nb, Ta), MLa$_4$Ti$_4$O$_{15}$ (M = Ba, Sr, and Ca), M$_2$La$_4$Ti$_{18}$O$_{54}$, Ba$_7$Ti$_5$Nd$_9$O$_{24}$ and Ba$_8$Ti$_3$Nb$_4$O$_{24}$ 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$_4$B$_3$O$_{12}$-type cation-deficient hexagonal perovskites, then it is worth-while to investigate whether A$_4$B$_3$O$_{12}$ perovskites might have equivalent or superior properties. In the present paper, we report the synthesis, characterization and dielectric properties of a new A$_4$B$_3$O$_{12}$-type cation-deficient perovskite, BaLa$_3$Ti$_2$NbO$_{12}$, for the first time.

Polycrystalline sample of BaLa$_3$Ti$_2$NbO$_{12}$ was prepared using high temperature solid-state reaction techniques. The stoichiometric mixtures of the high purity powders of BaCO$_3$ (99.9%), La$_2$O$_3$ (99.99%), TiO$_2$ (>99.95%) and Nb$_2$O$_5$ (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$_3$Ti$_2$NbO$_{12}$. 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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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 CuKα radiation ($\lambda = 0.154\, 06\, \text{nm}$) 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 $\varepsilon_r$ 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 TE011 mode was selected for the measurements. The $\tau_f$ was measured by noting the temperature variation of the TE011 resonance in the temperature range 15–85 °C.

The room temperature XRD pattern recorded for the ceramics using CuKα radiation is shown in Fig. 1. The pattern is similar and matches with those reported for Ba3LaNb3O12 by Rother and Kemmler [22, 23] (JCPDS file No. 44-929 and 73-914). 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, $V = 736.86(5)\, \text{Å}^3$ and $Z=3$, refined by the least-squares method. The unit cell parameters and unit-cell volume of BaLa3Ti2NbO12 are smaller than those of Ba3LaNb3O12 [22] since the Shannon’s effective ionic radius [29] of La³⁺ (1.36 Å) is smaller than that of Ba²⁺ (1.61 Å) and the radius of Ti⁴⁺ (0.605 Å) is smaller than that of Nb⁵⁺ (0.64 Å). This compound is isostructural with Ba3LaNb3O12 and adopts an A2B3O12-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 consisting of identical perovskite-like blocks, three corner-sharing BO₆ octahedral thick, separated by layers of vacant octahedral [22, 23].

The BaLa3Ti2NbO12 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 ($\varepsilon_r$) of the BaLa3Ti2NbO12 ceramic in the 1 kHz–1 MHz region is shown in Fig. 3 as a function of the frequency. The $\varepsilon_r$ of BaLa3Ti2NbO12 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 Ba₄La₂Ti₃Nb₂O₁₈, Ba₄LaMNb₃O₁₅ (M = Ti and Sn) and Pb₃LaTi₃Nb₇O₃₀ [16, 24]. The microwave dielectric properties were measured under TE011 mode. The BaLa3Ti2NbO12 ceramic shows an $\varepsilon_r$ of 42.42 calculated from the TE011 resonance, and a high quality factors with $Q_u$ of 4775 GHz at 7.0495 GHz. The microwave dielectric constant at microwave frequency is in good agreement with the value obtained at 1 MHz, which is similar to those of Ba₂La₃Ti₃NbO₁₅ (42.83), and the value of $Qf$ (33,661) is much higher than that of Ba₂La₃Ti₃NbO₁₅ (21,726) [19].