Synthesis characterization and dielectric properties of a new cation-deficient perovskite $Ba_4La_2Ti_3Nb_2O_{18}$

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Recent progress in microwave telecommunication and satellite broadcasting has demanded the need for good quality ceramic dielectric resonators (DR). The important characteristics required for a DR are high dielectric constant (ε_r) for miniaturization, high quality factor (Q) for selectivity and low temperature coefficient of resonant frequency (τ_f) for stability. Several DR materials such as $Ba(Zn_{1/3}Ta_{2/3})O_3$, $Ba_2Ti_9O_{20}$, $BaTi_4O_9$, $(Zr,Sn)TiO_4$, and $Ba_{6-3x}Re_{8+2x}Ti_{18}O_{54}$ (Re = Nd, Sm) system have been investigated for practical application [1, 2]. Still, the search for new materials having those properties is in rapid progress [3–8]. Recently, the microwave dielectric properties of some $A_5B_4O_{15}$ type cation-deficient hexagonal perovskites such as $Ba_5Nb_4O_{15}$, $Ba_{5-x}Sr_xNb_4O_{15}$, $Ba_5Ta_4O_{15}$, $ALa_4Ti_4O_{15}$(A = Ca, Sr and Ba) have attracted much attention [9–15], while only two $A_6B_5O_{18}$ type perovskites $A_2La_4Ti_5O_{18}$ (A = Ca, Ba) so far have been reported [11–13]. Both ceramics are characterized by high dielectric constant up to 50.6, high quality factors with $Q \times f$ up to 31 839 GHz, and low τ_f in the range -36.4 to $+6$ ppm $°C^{-1}$ [11, 13]. It is worthwhile to investigate whether other $A_6B_5O_{18}$ perovskites might have equivalent or superior properties. In the present paper, we report the synthesis, characterization and dielectric properties of a new $A_6B_5O_{18}$ type cation-deficient perovskite $Ba_4La_2Ti_3Nb_2O_{18}$, for the first time.

Polycrystalline sample of $Ba_4La_2Ti_3Nb_2O_{18}$ 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 hrs in a plastic bottle using zirconia balls. The wet mixture was dried and calcined in the range 1200 °C for 4 hrs, then ground and again calcined at 1400 °C for 4 hrs. 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 5–7 and 11 mm in diameter under a pressure of 180 MPa. The green compacts were initially fired at a rate of 3 °C/min up to 600 °C and then at a rate of 12 °C/min to the sintering temperature. An intermediate soaking at 600 °C for 2 hrs was given to expel the binder. The optimized sintering temperature was 1465 °C for $Ba_4La_2Ti_3Nb_2O_{18}$. The sintering was carried out for a duration of 4 hrs. The sintered sample was typically annealed at 1400 °C for 6 hrs to minimize the reduction of titanium ions.

The density of the ceramic was measured by the Archimedes method. The phase identification and microstructure characterization were done using a Rigaku D/MAX-RB powder X-ray diffractometer (XRD) using Cu K_α radiation ($\lambda = 0.154$–0.6 nm) in a 2θ range from 10 to 80 ° and 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 to 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 such as dielectric constant and unloaded Q (Q_u) factor were measured using an Agilent 8722ET network analyzer; the dielectric constant was calculated using TE_{011} mode under the end-shorted condition using the method suggested by Hakki and Coleman and modified by Courtney [16, 17]. 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 Cu K_α radiation is shown in Fig. 1. The pattern is similar and matches with the one reported for $Ba_2La_4Ti_5O_{18}$ by Saltykova *et al.* (JCPDS file No. 38-1039) [18]. All peaks found were indexed and there was no evidence of any second phases(s) present, therefore, the ceramic is single-phase pure. The

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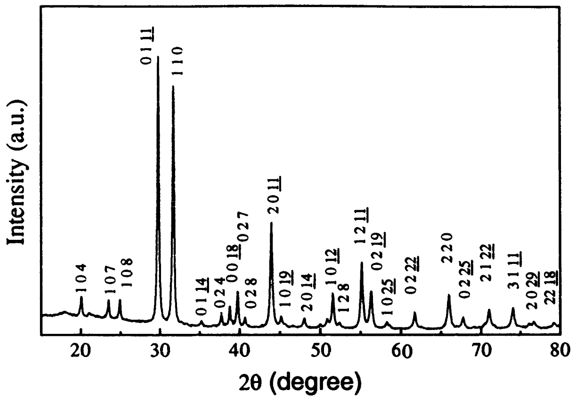

Figure 1 XRD pattern of $Ba_4La_2Ti_3Nb_2O_{18}$.

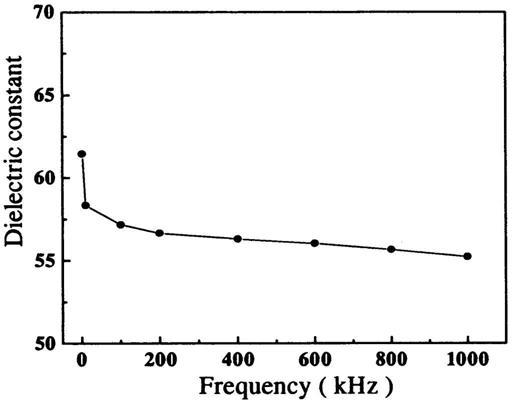

Figure 3 Variation of the dielectric constant with frequency for $Ba_4La_2Ti_3Nb_2O_{18}$.

compound crystallizes in the trigonal system with unit cell parameters $a = 5.6647(1)$ Å; $c = 41.8629(7)$ Å, $V = 1163.36(3)$ Å^3 and $Z = 3$, refined by the least-squares method. The compound belongs to $A_6B_5O_{18}$ perovskite-related 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, five corner-sharing BO_6 octahedra thick, separated by vacant octahedral layers [19, 20].

The $Ba_5LaTi_2Nb_3O_{18}$ ceramic was sintered into a dense body, and the relative density is 94.2% of its theoretical density. Fig. 2 shows the SEM micrograph of the fracture surface of the ceramic. The microstructure indicates a monophase constitution with packed hexagonal grains in the size range 4–10 μm.

The dielectric constant (ε_r) of the $Ba_4La_2Ti_3Nb_2O_{18}$ ceramic in the 1 kHz–1 MHz region is shown in Fig. 3 as a function of the frequency. The ε_r of $Ba_4La_2Ti_3Nb_2O_{18}$ ceramic decreases from 61.45 to 55.23 with increasing frequency from 1 kHz to 1 MHz due to the reduction of active polarization mechanism. The microwave dielectric properties were measured under TE_{011} mode. The $Ba_4La_2Ti_3Nb_2O_{18}$ ceramic shows an ε_r of 54.73 calculated from the TE_{011} resonance, and a high quality factor with Q_u of 3775 GHz at 4.7210 GHz. The dielectric constant at microwave frequency is in good agreement with the value obtained at 1 MHz, which is higher than those of $Ba_2La_4Ti_5O_{18}$ (46) and $Ca_2La_4Ti_5O_{18}$ (44.7) [11, 13].

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

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

where V_m is the molar volume and α_D^T is the sum of ionic polarizabilities of individual ions given by Shannon [21]. The calculated dielectric constants usually agree well with the experimental values for well-behaved ceramics [21]. 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 $Ba_2La_4Ti_5O_{18}$ [11, 13]. 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 [11]. Using $\alpha_{La} = 4.82$, the dielectric constant of $Ba_4La_2Ti_3Nb_2O_{18}$ is calculated as 60.73, which is in good agreement with the experimental values of 59.78 corrected for porosity using Rushman and Strivens equation [22] $\varepsilon_{corr} = \varepsilon_{obs}(2 + V_2)/(2 - 2V_2)$, 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 [13].

Fig. 4 shows the variation of resonant frequencies in the TE_{011} mode of $Ba_4La_2Ti_3Nb_2O_{18}$ ceramics as

Figure 2 SEM micrograph of $Ba_4La_2Ti_3Nb_2O_{18}$.

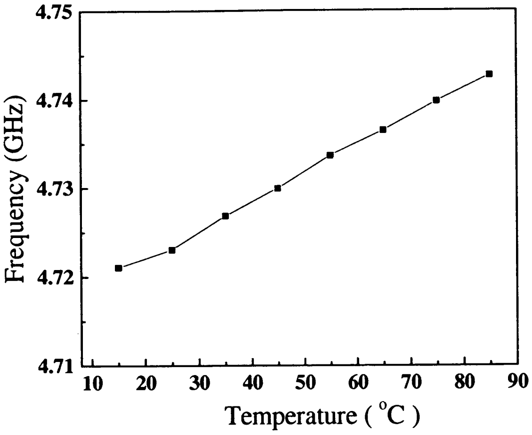

Figure 4 Variation of resonant frequency of $Ba_4La_2Ti_3Nb_2O_{18}$ as a function of the temperature.

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 $Ba_4La_2Ti_3Nb_2O_{18}$ ceramic is $+65$ ppm °C^{-1}, which is relatively higher compared to those of $Ba_2La_4Ti_5O_{18}$ (-36.4 ppm °C^{-1}) and $Ca_2La_4Ti_5O_{18}$ ($+6$ ppm °C^{-1}) [11, 13].

A new dielectric ceramic $Ba_4La_2Ti_3Nb_2O_{18}$ has been prepared and characterized. The compound adopts a cation-deficient trigonal $A_6B_5O_{18}$ perovskite structure. It has a high dielectric constant of 54.7, a high quality factor with $Q \times f$ of 17,821 GHz, and a positive τ_f of $+65$ ppm °C^{-1}. Although the ε_r and Q_u of the ceramic are encouraging, its relatively high τ_f precludes their use as dielectric resonators for practical applications. However, through appropriated substitution or the use of additives, it may be possible to obtain a nearly temperature compensated dielectric.

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