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Preparation and characterization of new dielectric ceramics $Ba_5LnTi_2Nb_3O_{18}$ (Ln = La, Nd)

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Two new $A_6B_5O_{18}$ type cation-deficient perovskites $Ba_5LnTi_2Nb_3O_{18}$ (Ln = La, Nd) were prepared by the conventional solid-state reaction route. The phase and structure of the ceramics were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM). Both compounds crystallize in the trigonal system. $Ba_5LaTi_2Nb_3O_{18}$ has a dielectric constant of 56.6, a high quality factors ($Q_u \times f > 16{,}700$ at 4.3331 GHz), and a relatively large temperature coefficient of resonant frequency (τ_f) + 142 ppm°C^{-1} at room temperature; $Ba_5NdTi_2Nb_3O_{18}$ has a higher dielectric constant of 47.3 with high quality factors $Q_u \times f > 15{,}000$ at 4.6830 GHz, and τ_f + 128 ppm °C^{-1}.

1. Introduction

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 (>25) for miniaturization, high quality factor ($Q > 2000$) for selectivity and low temperature coefficient of resonant frequency ($\tau_f < \pm 20$ ppm°C^{-1}) 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 [3–6]. Recently, the microwave dielectric properties of several $A_5B_4O_{15}$ type cation-deficient hexagonal perovskites such as $Ba_5Nb_4O_{15}$, $Ba_{5-x}Sr_xNb_4O_{15}$, $Ba_5Ta_4O_{15}$, and $ALa_4Ti_4O_{15}$ (A = Ca, Sr and Ba) have been reported by Sebastian and Vineis *et al.* [7–13]. These ceramics are characterized by high dielectric constant up to 50.6, high quality factors with $Q \times f$ up to 50,215 GHz, and low τ_f in the range −25 to +78 ppm °C^{-1}. Compared with $A_5B_4O_{15}$ type perovskites, however, very little data are available on the dielectric properties of $A_6B_5O_{18}$ type cation-deficient perovskites except for $Ba_2La_4Ti_5O_{18}$ and $Ca_2La_4Ti_5O_{18}$ [9, 11]. $Ba_2La_4Ti_5O_{18}$ is characterized by a higher dielectric constant of 46, a smaller τ_f of −36.4 ppm°C^{-1} with a higher $Q \times f$ of 31839 than those of $Ca_2La_4Ti_5O_{18}$ where the values are 44.7, +6 ppm°C^{-1} and 20112, respectively [9, 11]. 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 preparation, characterization and dielectric properties of two new $A_6B_5O_{18}$ type cation-deficient phases $Ba_5LnTi_2Nb_3O_{18}$ (Ln = La and Nd) in the BaO-Ln_2O_3-TiO_2-Nb_2O_5 system, for the first time.

2. Experimental

The ceramics were prepared through the solid-state ceramics route. High purity raw powders of $BaCO_3$ (99.9%), Ln_2O_3 (99.99%), TiO_2 (>99.95%) and Nb_2O_5 (99.9%), all Aldrich Chemical were used. The powders were weighed according to the stoichiometry of $Ba_5LnTi_2Nb_3O_{18}$ (Ln = La and Nd) and ball milled in distilled water medium for 12 h in an plastic bottle using zirconia balls. The wet mixtures were dried and calcined at 1200 °C for 4 h, then ground and again

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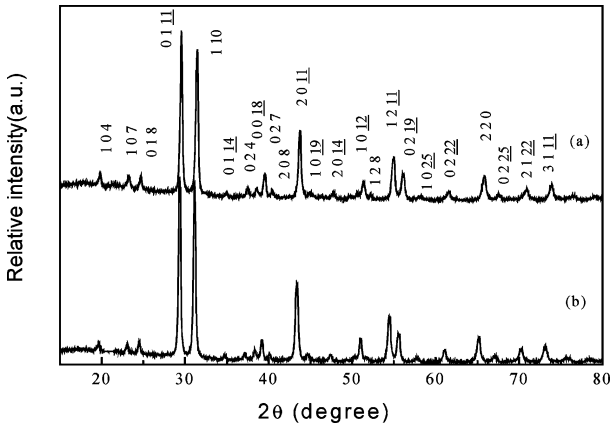


Figure 1 XRD pattern of (a) $Ba_5LaTi_2Nb_3O_{18}$ and (b) $Ba_5NdTi_2Nb_3O_{18}$.

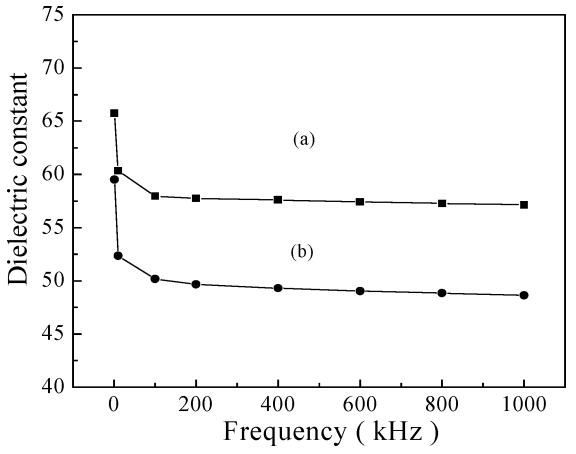


Figure 3 Variation of the dielectric constants with frequency for (a) $Ba_5LaTi_2Nb_3O_{18}$ and (b) $Ba_5NdTi_2Nb_3O_{18}$.

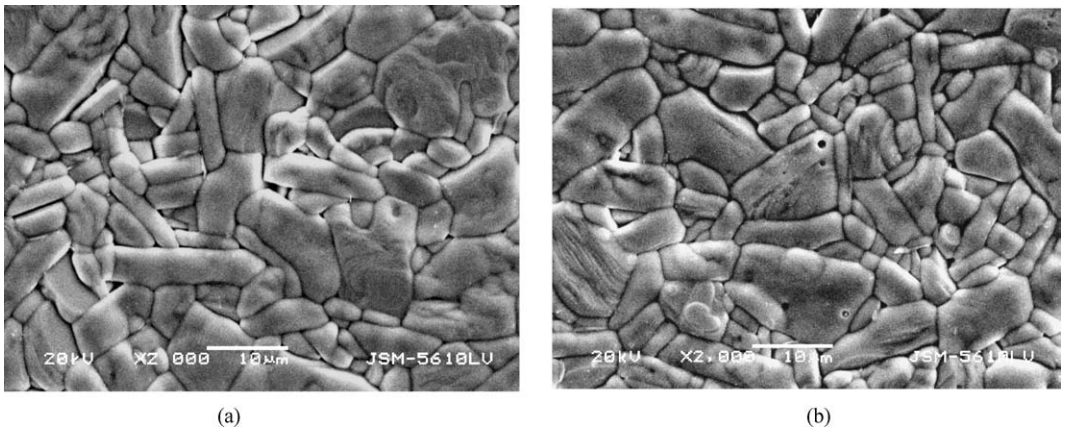
calcined at 1380–1400 °C for 4 h. The calcined powders were thoroughly reground and mixed with 5% solution of polyvinyl alcohol (PVA) as a binder. The slurries were then dried, ground and then pressed into cylindrical disks of different thickness in the range 5–7 mm and 11 mm in diameter under a pressure of 180 MPa. The sintering was carried out for a duration of 3 h in air. The green pellets were sintered at different temperatures in the range of 1440–1480 °C for 4 h. The optimized sintering temperatures were 1460 °C for $Ba_5LaTi_2Nb_3O_{18}$ and 1480 °C for $Ba_5NdTi_2Nb_3O_{18}$. The sintered samples were typically annealed at 1400 °C for 6 h to minimize the reduction of titanium ions.

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 XRD using a Rigaku D/MAX-RB X-ray diffractometer using Cu K_α radiation ($\lambda = 0.154\,06$ nm). The surface morphology of the ceramics was studied using a JSM-5610LV scanning electron microscope (SEM). The sintered samples were thermally etched at temperature 80 °C lower than their respective sintering temperature for 30 min and were used for recording 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 constants was calculated using TE_{011} mode under the end-shorted condition using the method suggested by Hakki and Coleman and modified by Courtney [14, 15]. 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 XRD patterns recorded for the ceramics using Cu K_α radiation are shown in Fig. 1. The patterns are identical and match with the one reported for $Ba_2La_4Ti_5O_{18}$ by Saltykova *et al.* (JCPDS file No.38-1039) [16]. All of the peaks were indexed and there was no evidence of any second phases(s) present, therefore, both ceramics are single-phase pure. Both compounds crystallize in the trigonal system with unit cell parameters $a = 5.7325(2)$ Å; $c = 42.139(2)$ Å, $V = 1199.20(3)$ Å^3 and $Z = 3$ for $Ba_5LaTi_2Nb_3O_{18}$; and $a = 5.7160(2)$ Å, $c = 42.102(2)$ Å, and $V = 1191.30(3)$ Å^3 for $Ba_5NdTi_2Nb_3O_{18}$, refined by the least square method. The unit cell parameters of $Ba_5LaTi_2Nb_3O_{18}$ are slightly larger than those



(a) (b)

Figure 2 SEM micrographs of (a) $Ba_5LaTi_2Nb_3O_{18}$ and (b) $Ba_5NdTi_2Nb_3O_{18}$ ceramics.

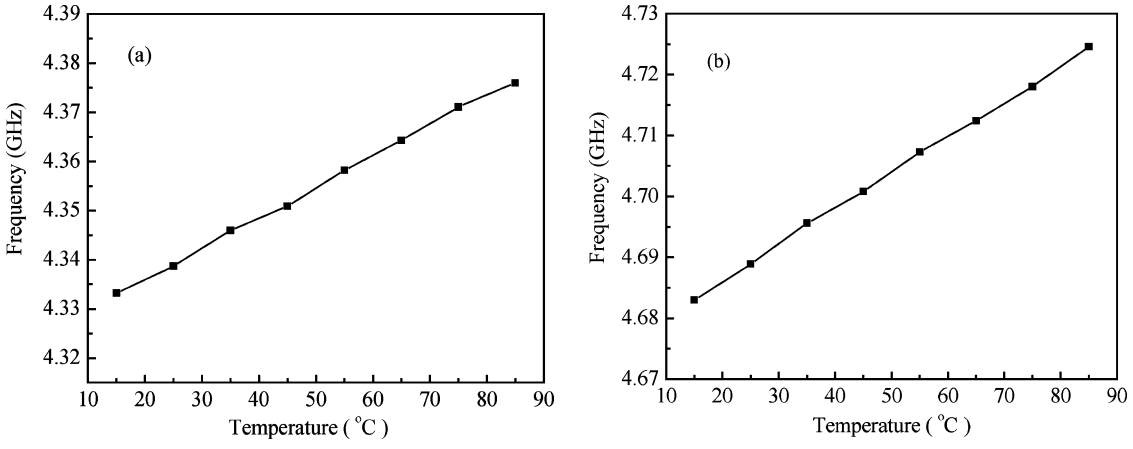


Figure 4 Variation of resonant frequency of (a) $Ba_5LaTi_2Nb_3O_{18}$ and (b) $Ba_5NdTi_2Nb_3O_{18}$ as a function of the temperature.

of $Ba_5NdTi_2Nb_3O_{18}$ as the radius of La^{3+} is larger than that of Nd^{3+}. The two compounds belong to $A_6B_5O_{18}$ perovskite-related structure where the Ba and Ln 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 layers of vacant octahedral [17, 18].

$Ba_5LaTi_2Nb_3O_{18}$ and $Ba_5NdTi_2Nb_3O_{18}$ ceramics were sintered into dense bodies, and their relative densities are 96.2 and 95.3% of their theoretical densities, respectively. Fig. 2 shows the SEM micrographs of the polished surfaces of the $Ba_5LaTi_2Nb_3O_{18}$ and $Ba_5NdLa_2Nb_3O_{18}$ ceramics. The two ceramics have a close microstructure with low porosity, and the packed grains are in the size range of 4–15 μm for both ceramics.

The dielectric constant ε_r of the $Ba_5LnTi_2Nb_3O_{18}$ ceramics in the 1 kHz–1 MHz region is shown in Fig. 3 as a function of the frequency. The ε_r of $Ba_5LaTi_2Nb_3O_{18}$ ceramic decreases from 65.75 to 57.44 with increasing frequency from 1 kHz to 1 MHz due to the reduction of active polarization mechanism, and the ε_r of $Ba_5NdTi_2Nb_3O_{18}$ ceramic decrease from 59.51 to 48.03. The microwave dielectric properties were measured using TE_{011} mode. The $Ba_5LaTi_2Nb_3O_{18}$ ceramic shows a high ε_r of 56.64 calculated from the TE_{011} resonance, and a Q_u factor of 3870 at 4.3331 GHz. Compared with $Ba_5LaTi_2Nb_3O_{18}$, the $Ba_5NdTi_2Nb_3O_{18}$ ceramics has a lower ε_r of 47.33 with a slightly smaller Q_u factor of 3210 at 4.6830 GHz. The dielectric constants are in good agreement with the values obtained at 1 MHz, and they are higher than those of $Ba_2La_4Ti_5O_{18}$ (46) and $Ca_2La_4Ti_5O_{18}$ (44.7) [9, 11].

Fig. 4 shows the variation of resonant frequencies in the TE_{011} mode of $Ba_5LaTi_2Nb_3O_{18}$ and $Ba_5NdTi_2Nb_3O_{18}$ ceramics as a function of the temperature. The temperature coefficient of the resonant frequency τ_f is calculated using the equation:

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

The τ_f of $Ba_5LaTi_2Nb_3O_{18}$ and $Ba_5NdTi_2Nb_3O_{18}$ ceramics are $+142$ ppm $^\circ C^{-1}$ and $+128$ ppm $^\circ C^{-1}$ respectively, which are much higher compared to those of $Ba_2La_4Ti_5O_{18}$ (-36.4 ppm $^\circ C^{-1}$) and $Ca_2La_4Ti_5O_{18}$ ($+6$ ppm $^\circ C^{-1}$). Although the ε_r and Q_u of these ceramics are encouraging, their 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.

4. Conclusion

Two new dielectric ceramics, $Ba_5LaTi_2Nb_3O_{18}$ and $Ba_5NdTi_2Nb_3O_{18}$, have been prepared through the solid-state ceramic route and characterized by XRD and SEM. The two compounds adopt a cation-deficient trigonal $A_6B_5O_{18}$ perovskite structure. The microwave dielectric properties of the ceramics have been studied. $Ba_5LaTi_2Nb_3O_{18}$ has a high dielectric constant of 56.6, a high quality factors with $Q \times f$ of 16,769 GHz, and a positive τ_f of $+142$ ppm $^\circ C^{-1}$; $Ba_5NdTi_2Nb_3O_{18}$ shows a ε_r of 47.3 with high $Q \times f$ of 15,302 GHz, and a positive τ_f of $+128$ ppm $^\circ C^{-1}$.

Acknowledgments

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