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Characterization and microwave dielectric properties of a new $A_6B_5O_{18}$-type cation-deficient perovskite $Ba_4Nd_2Ti_3Nb_2O_{18}$

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Recent progress in wireless communications has demanded the need for good quality ceramics 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 [1, 2]. Relatively few ceramics systems, such as $Ba(Zn_{1/3}Ta_{2/3})O_3$, $Ba_2Ti_9O_{20}$, (Zr, Sn)TiO_4, and $Ba_{6-3x}Re_{8+2x}Ti_{18}O_{54}$ (Re = Nd, Sm), are currently available with the properties needed for practical application at various operating frequencies [1, 2]. Therefore, the search for new materials having high ε_r, high Q and low τ_f is in rapid progress owing to the drive for further system miniaturization and improved filtering capabilities [3–11]. Recently, the microwave dielectric properties of some $A_6B_5O_{18}$ type cation-deficient hexagonal perovskites such as $A_2La_4Ti_5O_{18}$(A = Ca, Ba), $Ba_5LaTi_2Nb_3O_{18}$, $Ba_4La_2Ti_3Nb_2O_{18}$ and $Ba_3La_3Ti_4NbO_{18}$ have been characterized by high dielectric constant up to 57, high quality factors with Q × f up to 31 839 GHz, and low τ_f in the range −36.4 to +138 ppm°C^{-1} [12–17]. Among them $Ba_4La_2Ti_3Nb_2O_{18}$ ceramics have great potential in microwave application if its relatively large τ_f (+65 ppm °C^{-1}) can be suppressed to an acceptable level (-20 ppm °C$^{-1} < \tau_f < +20$ ppm °C^{-1}) [16]. Considering the replacement of La with Nd in $Ba_{6-3x}Re_{8+2x}Ti_{18}O_{54}$ system can significantly decrease the value of τ_f [18], then in the present paper we report the synthesis, characterization and dielectric properties of a new $A_6B_5O_{18}$ type cation-deficient perovskite $Ba_4Nd_2Ti_3Nb_2O_{18}$, for the first time.

Polycrystalline sample of $Ba_4Nd_2Ti_3Nb_2O_{18}$ was prepared using high temperature solid-state reaction techniques. The stoichiometric mixtures of the high purity powders of $BaCO_3$ (99.9%), Nd_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 at 1200 °C for 4 hr, then ground and again calcined at 1350 °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 discs of different thickness in the range 5–7 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 5 °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 1450 °C for $Ba_4Nd_2Ti_3Nb_2O_{18}$. The sintering was carried out for a duration of 8 hr. The sintered sample was typically annealed at 1400 °C for 6 hr to minimize the reduction of titanium ions.

The density of the ceramic was measured by the Archimedes method. The phase identification was done using a Rigaku D/MAX-RB powder X-ray diffractometer (XRD) using Cu-K$_\alpha$ radiation ($\lambda = 0.154\,06$ 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 1350 °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 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 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

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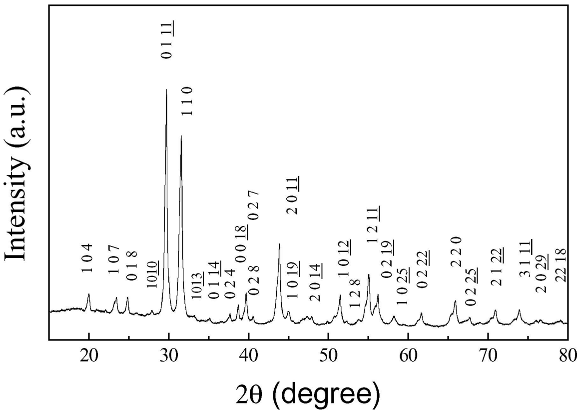

Figure 1 XRD pattern of $Ba_4Nd_2Ti_3Nb_2O_{18}$.

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 Cu-K_α radiation is shown in Fig. 1. The pattern is similar and matches with the one reported for $Ba_4La_2Ti_3Nb_2O_{18}$ by Fang *et al.* [16]. All peaks found were indexed and there was no evidence of any second phase(s) present, therefore, the ceramic is single-phase pure. The compound crystallizes in the trigonal system with unit cell parameters $a = 5.6607(1)$ Å, $c = 41.855(1)$ Å, $V = 1161.5$ Å^3 and Z = 3, refined by the least-squares method. The unit cell parameters and unit-cell volume of $Ba_4NdTi_2Nb_3O_{18}$ is smaller compared to those of $Ba_4La_2Ti_3Nb_2O_{18}$ [16] since the Shannon's effective ionic radius [21] of Nd^{3+} (1.27 Å) is smaller than that of La^{2+} (1.36 Å). This compound is isostructural with $Ba_4La_2Ti_3Nb_2O_{18}$ and adopts $A_6B_5O_{18}$ type perovskite-related structure where the Ba and Nd 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 [15].

The $Ba_4Nd_2Ti_3Nb_2O_{18}$ ceramic was sintered into a dense body with bulk density of 6.058 g/cm^3, and the relative density is 97.2% of its theoretical density (6.234 g/cm^3). Fig. 2 shows the SEM micrograph of polished surface of the ceramic. The ceramic has a close microstructure with low porosity, and the packed grains are in the size range of 2–12 μm.

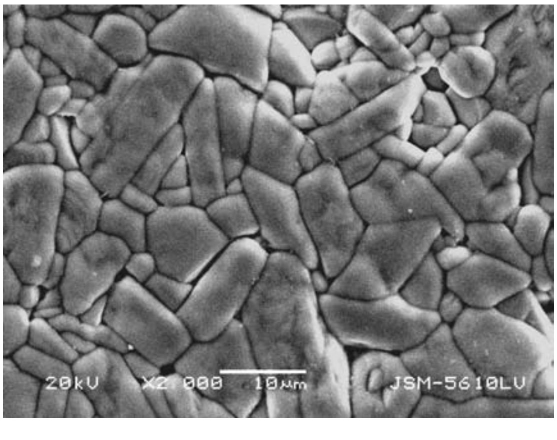

Figure 2 SEM micrograph of $Ba_4Nd_2Ti_3Nb_2O_{18}$.

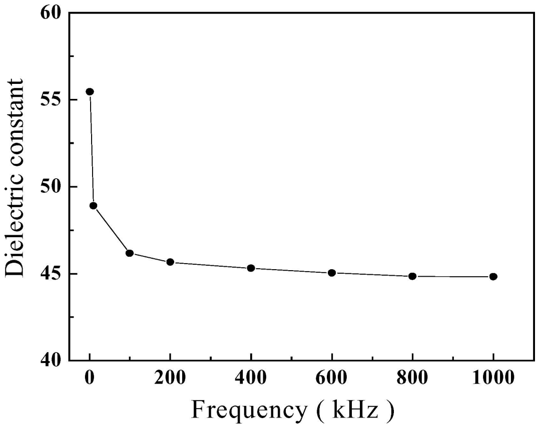

Figure 3 Variation of the dielectric constant with frequency for $Ba_4Nd_2Ti_3Nb_2O_{18}$.

The dielectric constant (ε_r) of the $Ba_4Nd_2Ti_3Nb_2O_{18}$ ceramic in the 1 kHz–1 MHz region is shown in Fig. 3 as a function of the frequency. The ε_r of $Ba_4Nd_2Ti_3Nb_2O_{18}$ ceramic significantly decreases from 55.45 to 46.17 with increasing frequency from 1 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 interfacials/surface polarization is minimized [22], then the dielectric constant slightly decreases to 44.83 at 1 MHz. This feature is similar to those observed in some dielectric oxides such as $Ba_4La_2Ti_3Nb_2O_{18}$, $Ba_3M_3Ti_5Nb_5O_{30}$ (M = Sm,Y) and $Pb_5LaTi_3Nb_7O_{30}$ [16, 22, 23]. The microwave dielectric properties were measured under TE_{011} mode. The $Ba_4Nd_2Ti_3Nb_2O_{18}$ ceramic shows an ε_r of 44.61 calculated from the TE_{011} resonance, and a high quality factors with Q_u of 2380 GHz at 5.5210 GHz. The dielectric constant at microwave frequency is in good agreement with the value obtained at 1 MHz.

Fig. 4 shows the variation of resonant frequencies in the TE_{011} mode of $Ba_4Nd_2Ti_3Nb_2O_{18}$ ceramics as

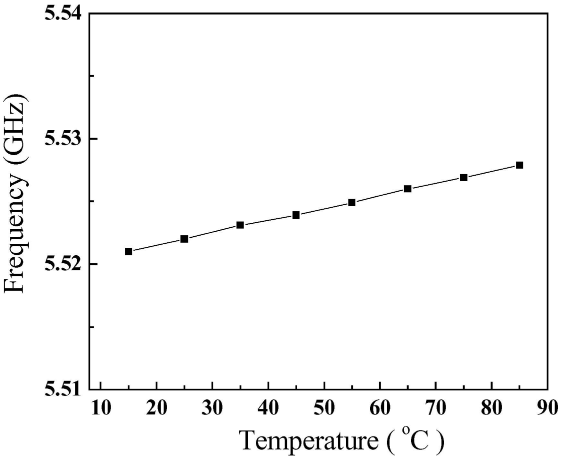

Figure 4 Variation of resonant frequency of $Ba_4Nd_2Ti_3Nb_2O_{18}$ as a function of the temperature.

a function of the temperature. The temperature coefficient of the resonant frequency τ_f is calculated using the equation:

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

The τ_f of $Ba_4Nd_2Ti_3Nb_2O_{18}$ ceramic is $+18$ ppm °C^{-1} as compared to $Ba_4La_2Ti_3Nb_2O_{18}$ which is reported to have a τ_f of $+65$ ppm °C^{-1} and a ε_r of 54.7 [16], the substitution of Nd for La at A site can obviously reduce the value of τ_f, while the ε_r also decreases. This result is similar to those reported for Nd replacing La in $Ba_{6-3x}Re_{8+2x}Ti_{18}O_{54}$ system [18]. According to the correlation between τ_f and unit-cell volume discussed by Lee *et al.* [24] in the compounds with same structure, and the reduction in $\tau_f$as Nd replacing La in $Ba_4La_2Ti_4Nb_2O_{18}$ may be resulted from the decrease of unit-cell volume. Further, the dielectric constant of the single-phase ceramics with high relative density is known to be largely depended on ionic polarizability (α) at microwave frequency [24], and the values of the ionic polarizabilities of Nd^{3+} (5.01 Å^3) is smaller than that of La^{3+} (6.07 Å^3) reported by Shannon [25], then the substitution of Nd for La leads to the decrease of ε_r in these ceramics.

A new dielectric ceramic $Ba_4Nd_2Ti_3Nb_2O_{18}$ has been prepared and characterized. The compound adopts a cation-deficient trigonal $A_6B_5O_{18}$-type perovskite structure. It has a high dielectric constant of 44.6, a high quality factors with $Q \times f$ of 13 139 GHz, and a small positive τ_f of $+18$ ppm °C^{-1}. Considering practical microwave application, the key issue of this ceramic was to lower the dielectric loss further and to obtain near zero τ_f through appropriated substitution or the use of additives.

Acknowledgments

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