

Crystal structure and microwave dielectric properties of a new $A_4B_3O_{12}$ -type cation-deficient perovskite $Ba_3LaTa_3O_{12}$

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Abstract

A new microwave dielectric ceramic $Ba_3LaTa_3O_{12}$ has been prepared by conventional solid-state ceramic route. Through Rietveld refinement of X-ray powder diffraction data, the compound is identified as an $A_4B_3O_{12}$ -type B-site cation-deficient perovskite with space group $R\bar{3}m$ and lattice constants $a = 5.7573(2) \text{ \AA}$, $c = 28.2386(2) \text{ \AA}$, $V = 810.62(4) \text{ \AA}^3$ and $Z = 3$. The microwave dielectric properties of $Ba_3LaTa_3O_{12}$ were investigated. The compound exhibits a relative dielectric constant (ϵ_r) of 36.8, a quality factor $Q_u \times f$ of 21,965 at 6.4040 GHz and a small negative temperature coefficient of resonant frequency (τ_f) of $-49.6 \text{ ppm/}^\circ\text{C}$.

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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 ($\epsilon_r > 25$) for miniaturization, high quality factor ($Q > 2000$) for selectivity and low temperature coefficient of resonant frequency ($\tau_f < \pm 20 \text{ ppm}$) 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 $Ba_{6-3x}RE_{8+2x}Ti_{18}O_{54}$ ($Re = Nd, Sm, La$) 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 [3–5].

Recently, the microwave dielectric properties of some $A_nB_{n-1}O_{3n}$ ($n = 5, 6, 7$ and 8) cation-deficient hexagonal

perovskites have been reported [6–13]. These ceramics are characterized by high dielectric constant up to 56, high quality factors with $Q \times f$ up to 88,000 GHz. More recently, we have reported the synthesis and microwave properties of two new $A_4B_3O_{12}$ -type hexagonal perovskites $Ba_2La_2TiNb_2O_{12}$ and $BaLa_3Ti_2NbO_{12}$ [14,15], and Sinclair et al. reported the microwave dielectric properties of $Ba_3LaNb_3O_{12}$ [16]. Since the Shannon's effective ionic radii (0.64 \AA) [17] and charge are the same for Nb^{5+} and Ta^{5+} ions, then it is worthwhile to investigate whether Ta-based $A_4B_3O_{12}$ hexagonal perovskites might have equivalent or superior properties. However, there is few report so far on the microwave dielectric properties of any Ta-based $A_4B_3O_{12}$ -type cation-deficient hexagonal perovskites. In the present paper, we report the synthesis, crystal structure and dielectric properties of a new $A_4B_3O_{12}$ -type cation-deficient perovskite, $Ba_3LaTa_3O_{12}$.

2. Experimental

Polycrystalline sample of $Ba_3LaTa_3O_{12}$ 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%) and Ta_2O_5 (99.9%) were weighed and ground in ethanol medium for 12 h in a plastic bottle using SiO_2 balls. The wet mixture was dried and calcined at 1200°C for 4 h, then ground and again calcined at 1300°C for 4 h. The calcined powders were thoroughly reground and mixed with 5% solution of polyvinyl alcohol (PVA) as a binder.

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The slurry was then dried, ground and then pressed into cylindrical pellets of different thickness in the range of 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 after holding this temperature for 2 h to expel the binder, then fired again at a rate of 6 °C/min to the sintering temperature. The optimized sintering temperature was 1520 °C for Ba₃LaTa₃O₁₂ for 4 h.

Microstructure of as-fired surface was examined using a JEOL JSM6380-LV scanning electron microscopy (SEM). Backscattered electron images were obtained. X-ray diffraction data were collected on a D/MAX-RB powder X-ray diffractometer (XRD) using Cu K_{α1} radiation ($\lambda = 0.15406$ nm) in a 2θ range from 8° to 90°. The step size was 0.02° with a counting time of 2 s per data point. For Rietveld refinement calculations the program Fullprof-Suite was used [18].

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 by the dielectric post resonator method suggested by Hakki and Coleman and modified by Courtney [19,20] using an Agilent 8722ET network analyzer. The τ_f was obtained from the temperature variation of the TE₀₁₁ resonance in the temperature range of 15–85 °C.

3. Results and discussion

3.1. Rietveld structure refinement of Ba₃LaTa₃O₁₂

The room temperature XRD pattern recorded for the calcined powder of Ba₃LaTa₃O₁₂ using Cu K_{α1} radiation is shown in Fig. 1. The pattern is similar and matches with those for Ba₃LaNb₃O₁₂ (JCPDS file no. 44–929 and 73–914) reported by Rother et al. [21]. All peaks found were indexed with the space group $R\bar{3}m$, the lattice parameters from which were $a = 5.7573(2)$ Å, $c = 28.2386(2)$ Å, $V = 810.62(4)$ Å³ and $Z = 3$.

These parameters were used as the starting lattice parameter for the Rietveld refinement, and the atomic coordinates of the unit cell were taken from Ba₃LaNb₃O₁₂ reported by Rother et al. [21]. A pseudo-Voigt function was selected as the profile fitting function. A total of 18 parameters including scale factor, lattice parameters, full width at half maximum (FWHM),

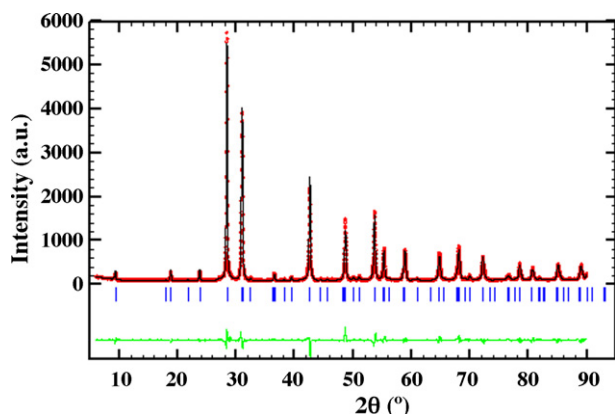


Fig. 1. Observed, calculated data and difference plots from Rietveld refinement of X-ray diffraction data for Ba₃LaTa₃O₁₂. Observed data are shown as open circles, the fit calculated from the model as a solid line, and the difference divided by the estimated standard deviation of each point is given below. Tick marks indicate the calculated position of the Bragg reflections.

Table 1

Structural parameters for Ba₃LaTa₃O₁₂ derived from XRD-Rietveld refinements

Formula	Ba ₃ LaTa ₃ O ₁₂
Space group	$R\bar{3}m$ (166)
Lattice parameters (hexagonal system)	$a = 5.75733(17)$ Å, $c = 28.2386(10)$ Å
Unit cell volume	810.62(4) Å ³
Formula units per unit cell	$Z = 3$
Calculated density	7.901 g/cm ³
Formula weight	3857.36
Profile function	Pseudo-Voigt
Reliable parameter	$R_p = 0.0596$, $R_{wp} = 0.0785$, $R_E = 0.0716$
χ^2	0.0120

Table 2

Fractional atomic coordinates and thermal parameters of Ba₃LaTa₃O₁₂

Atom	Position	x	y	z	Occupancy	Biso (Å ²)
Ta1	6c	0	0	0.42139(10)	1	0.0042(1)
Ta2	3a	0	0	0	1	0.0042(1)
Ba1/La1	6c	0	0	0.13813(13)	0.75, 0.25	0.0032(1)
Ba2/La2	6c	0	0	0.28566(16)	0.75, 0.25	0.0032(1)
O1	18h	1/6	5/6	0.6247(6)	1	0.0127(2)
O2	18h	1/6	5/6	0.4567(4)	1	0.0127(2)

preferred orientation, atomic coordinates, site occupancy and isotropic thermal parameters were refined. The refinement terminated with $R_p = 0.0596$, $R_{wp} = 0.0785$ when the La and Ba atoms are randomly distributed in the Ba₃LaTa₃O₁₂ structure. If one lets the B1 positions by Ba atoms and B2 positions by Ba and La, the refinement terminated with $R_p = 0.0598$, $R_{wp} = 0.0787$. Therefore, it seems more reasonable that the La and Ba atoms randomly distributed on two 6c positions in Ba₃LaTa₃O₁₂. Details of the refinement are summarized in Table 1. The final results for the atomic coordinates, site occupancy and isotropic thermal parameters are given in Table 2. Selected interatomic distances are listed in Table 3. Fig. 1 shows X-ray powder diffraction profile, along with the calculated and difference profiles after Rietveld refinement of the structure of Ba₃LaTa₃O₁₂. Fig. 2 shows the crystal structure. Ba₃LaTa₃O₁₂ are isostructural with Ba₃LaNb₃O₁₂ [21] adopting A₄B₃O₁₂-type cation-deficient hexagonal perovskite structure which can be described as consisting of identical perovskite-like blocks with three corner-sharing BO₆ octahedra thick separated by layers of vacant octahedral.

Table 3

Selected interatomic distances for Ba₃LaTa₃O₁₂ (Å)

Bond	Distance (Å)
Ba1/La1–O2	2.623(10) × 3
Ba1/La1–O2	2.909(2) × 6
Ba1/La1–O2	3.184(15) × 3
Ba2/La2–O2	2.712(10) × 3
Ba2/La2–O1	2.883(1) × 6
Ba2/La2–O1	3.022(15) × 3
Ta1–O2	1.938(7) × 3
Ta1–O1	2.112(11) × 3
Ta2–O1	2.041(10) × 6

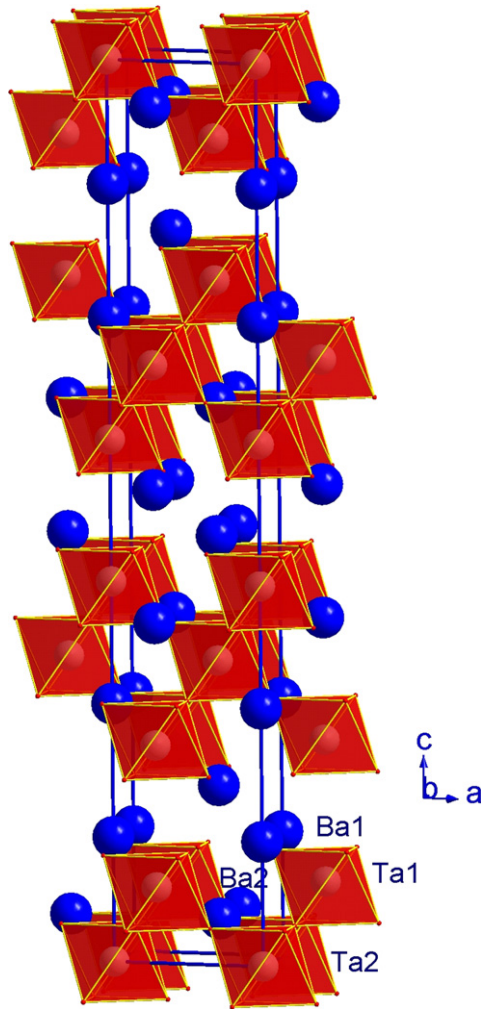


Fig. 2. Crystal structure of $\text{Ba}_3\text{LaTa}_3\text{O}_{12}$.

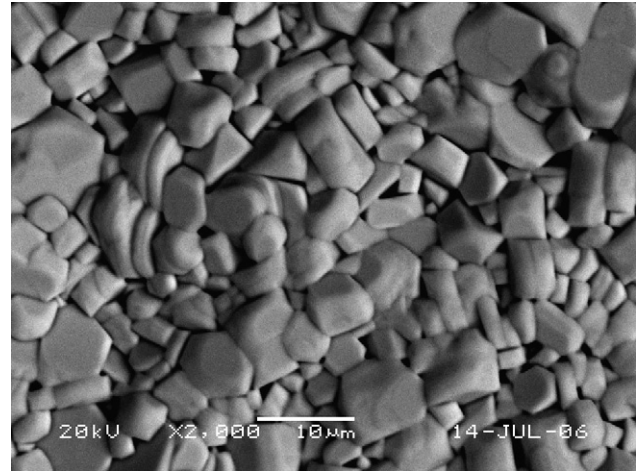


Fig. 3. Backscattered electron image of the as-fired surface of $\text{Ba}_3\text{LaTa}_3\text{O}_{12}$ ceramic.

dielectric oxides such as $\text{Ba}_4\text{LaMNb}_3\text{O}_{15}$ ($M = \text{Ti}$ and Sn) [10].

The microwave dielectric properties of $\text{Ba}_3\text{LaTa}_3\text{O}_{12}$ ceramic were measured under TE_{011} mode. The ceramic shows a ϵ_r of 36.8 with an unloaded Q_u factor of 3430 at 6.4040 GHz microwave. The ϵ_r measured at microwave frequencies is in good agreement with the value obtained at 1 MHz, which is smaller than those of $\text{Ba}_3\text{LaNb}_3\text{O}_{12}$ (44) [16] and $\text{Ba}_2\text{La}_2\text{TiNb}_2\text{O}_{12}$ (42.83) [14]. The value of $Q_u \times f_r$ (21,965 GHz) is higher than that of $\text{Ba}_3\text{LaNb}_3\text{O}_{12}$ (9000) [16]. This result is similar to those of $\text{Ba}_5\text{Nb}_{4-x}\text{Ta}_x\text{O}_{15}$ and $\text{Sr}_5\text{Nb}_{4-x}\text{Ta}_x\text{O}_{15}$ ($x = 0$ and 4) [8]. Ratheesh et al. [22] has suggested larger short-range interaction parameter in O–Ta–O bond as the cause of lower dielectric constant and lower dielectric loss for tantalum compounds than the niobium compounds. τ_f was measured over the temperature range of 15–85 °C and was established to be ~ -49.6 ppm/°C, which is much close to zero compared to that of $\text{Ba}_3\text{LaNb}_3\text{O}_{12}$ (-100 ppm/°C) [16].

3.2. Microwave dielectric properties of $\text{Ba}_3\text{LaTa}_3\text{O}_{12}$

The $\text{Ba}_3\text{LaTa}_3\text{O}_{12}$ ceramic was sintered into a dense body without the use of any additives. It showed a bulk density of 7.445 g/cm³, which is 94.2% of its theoretical X-ray density. Fig. 3 shows the typical backscattered electron image recorded for $\text{Ba}_3\text{LaTa}_3\text{O}_{12}$ sintered at 1520 °C. It seemed not any apparent contrast caused by the phase separation or segregation in the image of the microstructure. The ceramic has a close microstructure with low porosity, and the packed grains are in the size range of 3–10 µm.

The dielectric constant (ϵ_r) measured (for $\text{Ba}_3\text{LaTa}_3\text{O}_{12}$ ceramic sintered at 1520 °C) in the 1 kHz–1 MHz region is shown in Fig. 4 as a function of the frequency. The ϵ_r of $\text{Ba}_3\text{LaTa}_3\text{O}_{12}$ ceramic significantly decreases from 44.15 to 38.64 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, then the dielectric constant slightly decreased to 37.48 at 1 MHz. This feature is similar to those observed in some

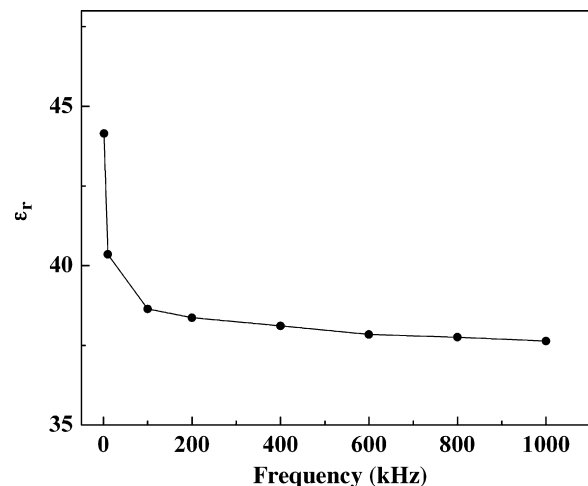


Fig. 4. Variation of ϵ_r with frequency for $\text{Ba}_3\text{LaTa}_3\text{O}_{12}$ ceramic.

4. Conclusions

A new microwave dielectric ceramic $\text{Ba}_3\text{LaTa}_3\text{O}_{12}$ has been synthesized and characterized in the $\text{BaO-L}_2\text{O}_3\text{-Ta}_2\text{O}_5$ system. $\text{Ba}_3\text{LaTa}_3\text{O}_{12}$ is identified as the $\text{A}_n\text{B}_{n-1}\text{O}_{3n}$ ($n=4$) type cation-deficient perovskites with space group $R\bar{3}m$ and lattice constants $a=5.7573(2)\text{ \AA}$, $c=28.2386(2)\text{ \AA}$, $V=810.62(4)\text{ \AA}^3$ and $Z=3$. The ceramics exhibits a dielectric constant of 36.8, a high quality factors ($Q \times f$) of 21,965 GHz at 6.4040 GHz, and a negative temperature coefficient of resonant frequency τ_f of $-49.6\text{ ppm/}^\circ\text{C}$.

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