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$A_5B_4O_{15}$ (A=Ba, Sr, Mg, Ca, Zn; B=Nb, Ta) microwave dielectric ceramics

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Abstract

The microwave dielectric properties of $A_5B_4O_{15}$ (A=Ba, Sr, Mg, Ca, Zn; B=Nb, Ta) ceramics are investigated. The ceramics are prepared through the solid-state ceramic route. The dielectric properties are studied at microwave frequencies and structure and microstructure by XRD and scanning electron micrograph (SEM) methods. The ceramics show ϵ_r in the range 11–51, $Q \times f$ is in the range 2400–88,000 GHz and τ_f in the range -73 – 232 ppm/ $^{\circ}$ C.

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1. Introduction

Dielectric materials with dielectric constant greater than 20 and high quality factors ($Q \times f > 2000$) are needed for microwave applications. Cation-deficient hexagonal perovskites are attractive in this regard. Galasso and Katz [1] reported the existence of $Ba_5Ta_4O_{15}$, $Ba_5Nb_4O_{15}$ and $Sr_5Ta_4O_{15}$ ceramics. This type of materials is called cation-deficient perovskites in the sense that, if written in the perovskite form (ABO_3), $A_5B_4O_{15}$ reduces to $AB_{0.8}O_3$. Hence, there is a vacancy of 0.2 B cation per 1 A cation, i.e., overall 1 B cation vacancy per 5 A cations. The structures of $Ba_5Ta_4O_{15}$, $Ba_5Nb_4O_{15}$ and $Sr_5Ta_4O_{15}$ are well studied [1–5]. These compounds have hexagonal structure and crystallize in the $P\bar{3}m1$ space group with one formula

unit per cell ($Z=1$). The compounds have five-layer closest packing of oxygen and barium ions [1–5]. The tantalum or niobium ions are located in the octahedral holes between layers with one layer of octahedral holes are missing tantalum or niobium ions to accommodate the charge neutrality. The $Ba_5Nb_4O_{15}$ is a hexagonal polytype i.e., the (5H) member of a series of polytypes characterized by Hutchison and co-workers [3,4] containing 4, 5, 6, 8, 10 and 12 layered (4H, 5H, 6H, 8H, 10H, and 12H) species. Whiston and Smith [6] have reported the existence of $Sr_5Nb_4O_{15}$ iso-structural with the tantalum analogue. Though Weiden et al. [7] reported monoclinic structure (C_{2h}^1-P2/m with $Z=2$) for the compound; its structure was later confirmed to be hexagonal based on Raman, IR and single crystal X-ray diffraction [8–11] studies. The c -parameter is doubled due to an anti-tilting of TiO_6 octahedra ($\sim 15^{\circ}$) around the c -axis [11]. The structure of all four above-mentioned compounds consists of five AO_3 close-packed layers with B ions located in corner-

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sharing octahedral holes between the layers. No B atom lies between the third and the fourth layer.

Brook et al. [12] synthesised single crystal fibres of $\text{Mg}_5\text{Nb}_4\text{O}_{15}$. Kasper [13] reported tri-pseudo-brookite super structure for $\text{Mg}_5\text{Nb}_4\text{O}_{15}$ and $\text{Mg}_5\text{Ta}_4\text{O}_{15}$ with three-fold unit cell. They reported that the compound $\text{Mg}_5\text{Nb}_4\text{O}_{15}$ is stable above 1400 °C and $\text{Mg}_5\text{Ta}_4\text{O}_{15}$ above 1475 °C. Abbatista et al. [14] reported the existence of $\text{Mg}_5\text{Nb}_4\text{O}_{15}$ in the $\text{MgO-Nb}_2\text{O}_5$ system and is stable between 1200 °C and its incongruent melting point at 1580 °C. Pagola et al. [15] studied the structure of both compounds with the help of neutron diffraction and found that the compounds are isostructural with pseudo-brookite Fe_2TiO_5 , and the presence of any superstructure could not be noticed. The compounds crystallize with the orthorhombic structure within the space group $D_{2h}^{17}-Cmcm$ with $Z=4$. The structure consists of double chains of $(\text{Mg}, \text{B})\text{O}_6$ units, sharing edges of the bc plane, interconnected through common oxygen along the a -axis to give a three-dimensional array [15]. The microwave dielectric properties of one of the compounds ($\text{Ba}_5\text{Nb}_4\text{O}_{15}$) in the $\text{A}_5\text{B}_4\text{O}_{15}$ are reported earlier [16,17]. In the present report, we make a detailed study of the preparation, characterization and microwave dielectric properties of title compounds $\text{A}_5\text{B}_4\text{O}_{15}$ ($\text{A}=\text{Ba}, \text{Sr}, \text{Mg}, \text{Ca}, \text{Zn}; \text{B}=\text{Nb}, \text{Ta}$).

2. Preparation and characterization

The ceramics were prepared through the conventional solid-state ceramic route. The high purity carbonates or oxides i.e., BaCO_3 (99.5% Aldrich Chemicals), SrCO_3 (99.9% Aldrich), CaCO_3 (>99.5% Aldrich Chemicals), MgO (99+%, CDH India), ZnO (99.99%, Aldrich Chemicals), Nb_2O_5 (99.9%, NFC, Hyderabad, India) and Ta_2O_5 (99.9%, NFC) were used. The MgO is calcined at 1000 °C for 3 h to remove hydroxides or carbonates [26]. $\text{Mg}_5\text{Nb}_4\text{O}_{15}$ and $\text{Mg}_5\text{Ta}_4\text{O}_{15}$ were prepared using both calcined MgO and un-calcined MgO . The oxide or carbonate powders were weighed as per the molar ratios to get a gross amount of about 20 g, mixed thoroughly in agate mortar using distilled water or acetone as the wetting medium for a duration of 1 h, dried and again mixed for 1 h. The reaction mixtures of the niobates were calcined at 1050–1275 °C and tanta-

lates at 1200–1400 °C for a duration ranging from 4 to 8 h. The calcined mixture is ground well for 1 h, 3 wt.% PVA is added, dried and again ground. The fine powder is uni-axially pressed at a pressure of 150 MPa using a tungsten carbide die of 11-mm diameter. The dimensions of the ceramic compacts are controlled such that the sintered body has aspect ratio (D/L) of 1 to 1.3 or 2 to 2.3 to obtain maximum mode separation during measurements. Stearic acid dissolved in isopropyl alcohol is used as lubricant while pressing. This can reduce the friction between powder and die wall. The samples are heated at the rate 270 °C/h up to 800 °C for burning out PVA and then fast heating rate of 600 °C/h is applied up to the sintering temperature. The pellets were sintered in the temperature range 1175–1625 °C for 2 to 4 h.

The sintering temperatures are optimised to get maximum density for constant duration. The sintered densities of the samples were measured using Archimedes method. The pellets were polished well and shaped to avoid any surface irregularities.

The X-ray diffraction spectra of the sintered samples were recorded after grinding them into fine powder. The spectra were recorded using a Philips X-ray diffractometer with Cu K_α radiation with Ni filter. The surface of the sintered specimens were analysed through scanning electron micrograph (SEM) using a JEOL Scanning Electron Microscope. For the SEM studies, the finely polished samples were thermally etched at 25–50 °C less than their respective sintering temperature for 30 min. The surface is gold coated before recording SEM.

The microwave dielectric properties of the compounds are measured using an HP 8510 C Network Analyser. The dielectric constant and temperature coefficient of resonant frequency are measured using the Hakki–Coleman method [18]. The quality factor is measured using a transmission mode cavity [19].

3. Results and discussion

3.1. Density and X-ray diffraction

Table 1 gives the calcination temperature, sintering temperature, density and percentage density of all the ceramics. The ceramics could be sintered into

Table 1

The list of calcination temperatures, sintering temperatures, densities and percentage densities of the $A_5B_4O_{15}$ ceramics

Material	Calcination temp (°C)	Sintering temp (°C)	Density (g/cm)	% Density
$Mg_5Ta_4O_{15}$	1400	1550	6.47	–
$Mg_5Ta_4O_{15}^a$	1400	1560	5.56	91
$Sr_5Ta_4O_{15}$	1400	1610	7.00	96
$Ba_5Ta_4O_{15}$	1325	1550	7.63	95
$Mg_5Nb_4O_{15}$	1300	1475	4.20	–
$Mg_5Nb_4O_{15}^a$	1300	1450	3.90	94
$Ba_5Nb_4O_{15}$	1250	1380	6.07	96
$Ba_4SrNb_4O_{15}$	1250	1400	5.64	92
$Ba_3Sr_2Nb_4O_{15}$	1250	1400	5.44	93
$Ba_2Sr_3Nb_4O_{15}$	1250	1400	5.41	95
$BaSr_4Nb_4O_{15}$	1250	1400	5.46	95
$Sr_5Nb_4O_{15}$	1250	1400	5.20	93
$5ZnO-2Nb_2O_5$	1050	1220	5.61	–
$5CaO-2Ta_2O_5$	1400	1550	6.25	–
$5CaO-2Nb_2O_5$	1300	1500	4.20	–

–, % Density could not be evaluated due to multiphase.

^a Prepared from MgO powder heat treated at 1000 °C for 3 h.

dense bodies. Most of the compounds have sintered densities more than 93% of their theoretical densities. The pure $Mg_5Nb_4O_{15}$ and $Mg_5Ta_4O_{15}$ phase are obtained by calcining at 1300 °C for 8 h and at 1400 °C for 8 h, respectively, using calcined MgO. The $Ba_5Ta_4O_{15}$, $Ba_5Nb_4O_{15}$, $Sr_5Nb_4O_{15}$ and $Sr_5Ta_4O_{15}$ are hexagonal structured in agreement with the earlier reports. When uncalcined MgO was used, the sintered product contained $MgNb_2O_6$ and $MgTa_2O_6$ as the secondary phases. Single phase $Mg_5Ta_4O_{15}$ could not densify more than 91% without additives. CeO_2 , Nd_2O_3 , Sm_2O_3 , MnO_2 and Bi_2O_3 (1 wt.%) are tried as sintering aids to $Mg_5Nb_4O_{15}$ and $Mg_5Ta_4O_{15}$, both prepared from MgO heat treated to 1000 °C for 3 h. Table 2 shows the densities of the compounds with 1 wt.% of the sintering aids. The addition of sintering aids did not increase the sintered density in the case of $Mg_5Nb_4O_{15}$. However, 1 wt.% Bi_2O_3 added as sintering aid has improved the density to 96% in the case of $Mg_5Ta_4O_{15}$.

All the ceramics gave single phase except the compounds of calcium and zinc. Attempts to prepare $Zn_5Nb_4O_{15}$ were not successful, but resulted in multiphase. The multiphase ceramics were a mixture of $ZnNb_2O_6$ and $Zn_3Nb_2O_8$. The calcium-based ceramics $Ca_5Nb_4O_{15}$ and $Ca_5Ta_4O_{15}$ also did not form. The

Table 2

The densities, ϵ_r and $Q \times f$ with 1 wt.% of dopant to $Mg_5Nb_4O_{15}$ and $Mg_5Ta_4O_{15}$

Ceramics	Dopant	% Density	ϵ_r	$Q \times f$ (GHz)
$Mg_5Nb_4O_{15}^a$	Pure	94	11.0	37,400
	CeO_2	93	11.8	24,700
	Nd_2O_3	92	11.6	27,000
	Sm_2O_3	92	11.6	21,600
	MnO_2	91	11.4	25,700
$Mg_5Ta_4O_{15}^a$	Bi_2O_3	92	11.5	14,000
	Pure	91	11.0	18,100
	CeO_2	90	11.2	18,600
	Nd_2O_3	92	14.0	14,000
	Sm_2O_3	89	12.0	14,500
	MnO_2	93	14.7	6500
	Bi_2O_3	96	15.2	10,100

^a MgO is heat treated at 1000 °C for 3 h.

different phases present in the resultant ceramics could not be identified. Fig. 1 shows the XRD patterns of $Mg_5Nb_4O_{15}$, $Mg_5Ta_4O_{15}$, $5CaO-2Nb_2O_5$, $5CaO-2Ta_2O_5$ and $5ZnO-2Nb_2O_5$ ($ZnNb_2O_6+Zn_3Nb_2O_8$). Fig. 2 shows the XRD patterns of $Ba_5Ta_4O_{15}$, $Sr_5Nb_4O_{15}$, $Ba_5Nb_4O_{15}$ and $Sr_5Ta_4O_{15}$.

Fig. 3 shows the SEM pictures of $Mg_5Nb_4O_{15}$, $Mg_5Ta_4O_{15}$ and $5CaO-2Nb_2O_5$. The presence of

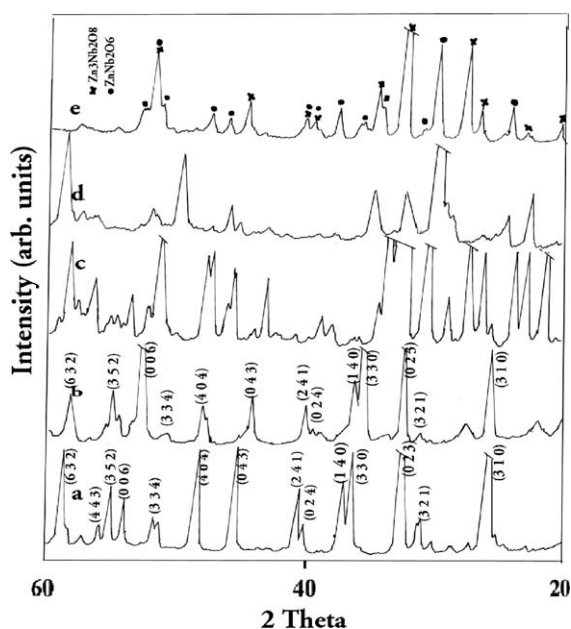


Fig. 1. The XRD patterns of (a) $Mg_5Nb_4O_{15}$, (b) $Mg_5Ta_4O_{15}$, (c) $5CaO-2Nb_2O_5$, (d) $5CaO-2Ta_2O_5$ and (e) $5ZnO-2Nb_2O_5$.

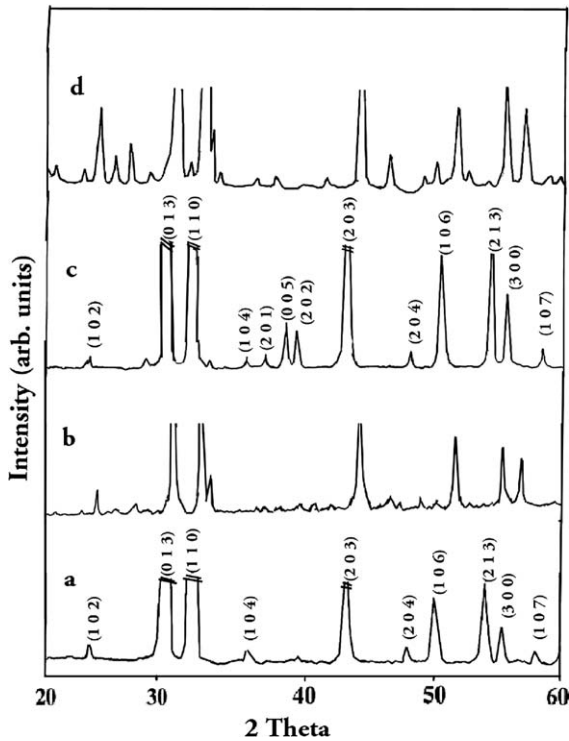


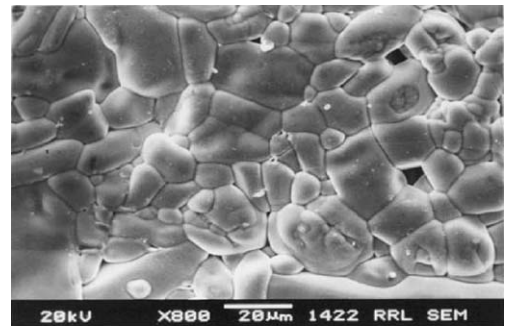
Fig. 2. XRD patterns of (a) $\text{Ba}_5\text{Ta}_4\text{O}_{15}$, (b) $\text{Sr}_5\text{Nb}_4\text{O}_{15}$, (c) $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ and (d) $\text{Sr}_5\text{Ta}_4\text{O}_{15}$.

porosity of $\text{Mg}_5\text{Nb}_4\text{O}_{15}$ and $\text{Mg}_5\text{Ta}_4\text{O}_{15}$ is evident from the SEM. The grains are relatively large in size of about $20\ \mu\text{m}$. Fig. 4 shows the SEM picture of $5\text{ZnO}-2\text{Nb}_2\text{O}_5$ ($\text{ZnNb}_2\text{O}_6+\text{Zn}_3\text{Nb}_2\text{O}_8$). The grains are very large up to $40\ \mu\text{m}$ in size. The $5\text{ZnO}-2\text{Nb}_2\text{O}_5$ ceramics is dense. A possible liquid phase sintering might have taken place, which is the cause for bigger grains and lower porosity. The presence of two types of grains is evident in Fig. 4.

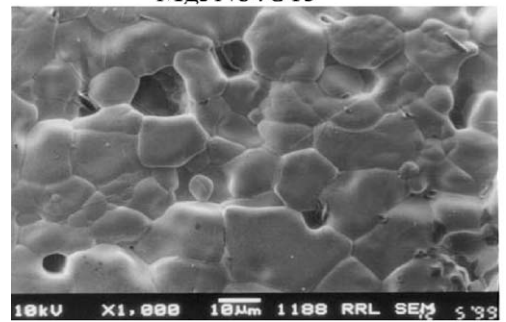
3.2. Microwave dielectric properties

The ceramics showed good resonance at microwave frequencies. The microwave dielectric properties of the ceramics were summarised in Table 3. The ceramics have ϵ_r in the range 11–51, $Q \times f$ in the range 2400–88,000 GHz and τ_f in the range -73 – $+232$ ppm/ $^\circ\text{C}$. The $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ has a lower $\epsilon_r=28$ than that of analogous $\text{Ba}_5\text{Nb}_4\text{O}_{15}$, which has $\epsilon_r=39$. However, this is in contrary to the expectation that the tantalum analogue should have higher dielectric

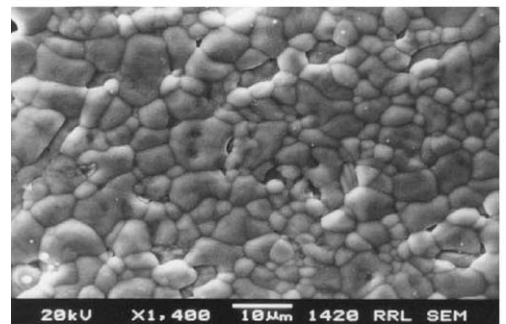
constant than the niobium compound due to the larger ionic polarisability [20,21] of tantalum compared to niobium which provided both the ceramics crystallise in the same symmetry group. Spectroscopic studies by Massa et al. [22,23] shows that the lattice of $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ is stable whereas that of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ is going to collapse to a lower symmetry state and hence there may be increased lattice anharmonicity in the compound. This may be reason for



$\text{Mg}_5\text{Nb}_4\text{O}_{15}$

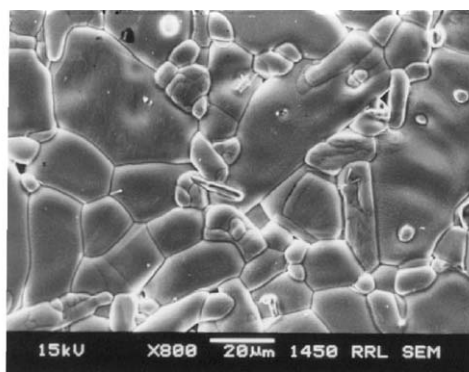


$\text{Mg}_5\text{Ta}_4\text{O}_{15}$



$5\text{CaO}-2\text{Nb}_2\text{O}_5$

Fig. 3. The SEM pictures of $\text{Mg}_5\text{Nb}_4\text{O}_{15}$, $\text{Mg}_5\text{Ta}_4\text{O}_{15}$ and $5\text{CaO}-2\text{Nb}_2\text{O}_5$.



5ZnO-2Nb2O5

Fig. 4. The SEM picture of 5ZnO–2Nb₂O₅ (ZnNb₂O₆+Zn₃Nb₂O₈).

the higher dielectric constant of Ba₅Nb₄O₁₅. It is interesting to note that the τ_f of the Ba₅Ta₄O₁₅ (+12 ppm/°C) is considerably lower than that of Ba₅Nb₄O₁₅ (+78 ppm/°C). Orthorhombic structured Mg₅Nb₄O₁₅ and Mg₅Ta₄O₁₅ showed a comparatively lower dielectric constant of 11 than the hexagonal phases that we have discussed and having the general formula A₅B₄O₁₅. The lower dielectric constant may be due to the lower ionic polarisability of Mg ions and their different structures. The phase pure Mg₅Nb₄O₁₅ and Mg₅Ta₄O₁₅ ceramics have $Q \times f$ up to 37,400 GHz and τ_f of –54 ppm/°C each. In the case where uncalcined MgO is used, the Mg deficiency in the above ceramics leads to MgNb₂O₆ and MgTa₂O₆ as the secondary phases. Presence of MgTa₂O₆ whose $\epsilon_r = 30.3$, $Q \times f = 59,600$ GHz and $\tau_f = +30$ ppm/°C [24] increases dielectric constant of Mg₅Ta₄O₁₅ (prepared using uncalcined MgO) into 17 where as its τ_f decreases to –15 ppm/°C. In a similar way, deficiency of Mg in Mg₅Nb₄O₁₅ (non-stoichiometry) leads to the formation of MgNb₂O₆ as the secondary phase which has $\epsilon_r = 21.4$, $Q \times f = 93,800$ GHz and $\tau_f = -70$ ppm/°C [24]. The presence of the MgNb₂O₆ secondary phase increases the dielectric constant for 11 to 14 and τ_f from –54 to –58 ppm/°C, but decreases the quality factor than the pure compound. The phase pure Mg₅Ta₄O₁₅ could not densify more than 91%. Hence, we have added 1 wt.% Nd₂O₃, Sm₂O₃, Bi₂O₃, CeO₂, and MnO₂ into powders of Mg₅Nb₄O₁₅ and Mg₅Ta₄O₁₅ and then studied the densification and microwave dielectric properties. The results are summarised in Table 2. In the case of

Mg₅Nb₄O₁₅, the addition of Nd₂O₃, Sm₂O₃, Bi₂O₃, CeO₂, and MnO₂ all decreased the density but slightly increased the dielectric constant whereas the $Q \times f$ deteriorated. In the case of Mg₅Ta₄O₁₅, 1 wt.% of Nd₂O₃, Bi₂O₃ and MnO₂ increased the density but CeO₂ and Sm₂O₃ decreased the density. The presence of additives increased the dielectric constant. Addition of 1 wt.% CeO₂ has increased the $Q \times f$ of 18,600 GHz, but other additives decreased the quality factor. Though the addition of 1 wt.% of Bi₂O₃ has increased the density and dielectric constant, it reduced the Q factor.

The 5ZnO–2Nb₂O₅ composition does not give single-phase compounds analogous to A₅B₄O₁₅ (Zn₅Nb₄O₁₅). Instead they give a mixture of ZnNb₂O₆ and Zn₃Nb₂O₈. The ZnNb₂O₆ is reported to have $\epsilon_r = 25$, $Q \times f = 83,700$ GHz and $\tau_f = -56$ ppm/°C [24]. The Zn₃Nb₂O₈ has ϵ_r about 22, $Q \times f = 83,300$ GHz and $\tau_f = -71$ ppm/°C [25]. The 5ZnO–2Nb₂O₅ showed $\epsilon_r = 21$, $Q \times f = 88,000$ GHz and $\tau_f = -73$ ppm/°C. Similarly, single phases analogous to A₅B₄O₁₅ (i.e., Ca₅Nb₄O₁₅) could not be obtained for 5CaO–2Nb₂O₅ and 5CaO–2Ta₂O₅. However, the ceramics show good microwave dielectric properties and are given in Table 3. The 5CaO–2Nb₂O₅ has $\epsilon_r = 32$, $Q \times f = 6500$ GHz and $\tau_f = -37$ ppm/°C, whereas 5CaO–2Ta₂O₅ has $\epsilon_r = 41$, $Q \times f = 5900$ GHz and $\tau_f = +140$ ppm/°C.

Table 3

The list of dielectric constants, quality factors, frequencies, and temperature coefficient of resonant frequencies of A₅B₄O₁₅ ceramics

Material	ϵ_r	f (GHz)	$Q \times f$ (GHz)	τ_f (ppm/°C)	Structure
Mg ₅ Ta ₄ O ₁₅	17	7.19	14,400	–15	Orthorhombic
Mg ₅ Ta ₄ O ₁₅ *	11	9.06	18,100	–54	Orthorhombic
Mg ₅ Nb ₄ O ₁₅	14	7.28	14,600	–58	Orthorhombic
Mg ₅ Nb ₄ O ₁₅ *	11	8.30	37,400	–54	Orthorhombic
Sr ₅ Ta ₄ O ₁₅	41	5.99	2400	–**	Hexagonal
Ba ₅ Ta ₄ O ₁₅	28	5.55	31,600	12	Hexagonal
Ba ₅ Nb ₄ O ₁₅	39	4.73	23,700	78	Hexagonal
Ba ₄ SrNb ₄ O ₁₅	48	4.70	14,600	140	Hexagonal
Ba ₃ Sr ₂ Nb ₄ O ₁₅	50	4.71	16,500	232	Hexagonal
Ba ₂ Sr ₃ Nb ₄ O ₁₅	51	4.61	21,200	117	Hexagonal
BaSr ₄ Nb ₄ O ₁₅	45	4.57	23,300	82	Hexagonal
Sr ₅ Nb ₄ O ₁₅	40	4.84	19,400	55	Hexagonal
5ZnO–2Nb ₂ O ₅	21	6.98	88,000	–73	Multiphase
5CaO–2Ta ₂ O ₅	41	5.90	5900	140	Multiphase
5CaO–2Nb ₂ O ₅	32	6.48	6500	–37	Multiphase

4. Conclusion

The $A_5B_4O_{15}$ ($A = \text{Ba, Sr, Mg, Ca, Zn}$; $B = \text{Nb, Ta}$) ceramics are prepared through the solid-state ceramic route. The structure and phases are studied using XRD and SEM. The dielectric properties are studied at microwave frequencies. Among the reported materials, the compositions $5\text{CaO}-2\text{Nb}_2\text{O}_5$, $5\text{CaO}-2\text{Ta}_2\text{O}_5$, $5\text{ZnO}-2\text{Nb}_2\text{O}_5$ do not result in single phase compounds analogous to $A_5B_4O_{15}$. The ceramics show ϵ_r in the range 11–51, $Q \times f$ in the range 2400–88 000 GHz and τ_f in the range -73 – $+232$ ppm/ $^\circ\text{C}$.

Acknowledgements

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References

- [1] F. Galasso, L. Katz, *Acta Cryst.* 14 (1961) 647.
- [2] J. Shannon, L. Katz, *Acta Cryst.* B26 (1970) 102.
- [3] J.L. Hutchison, A.J. Jacobson, *Acta Cryst.* B31 (1975) 1442.
- [4] J.L. Hutchison, *Chem. Scr.* 14 (1978–79) 181.
- [5] L.M. Kovba, L.N. Lykova, M.V. Paromova, L.M. Lopato, A.V. Shevchenko, *Russ. J. Inorg. Chem.* 22 (10) (1997) 1544.
- [6] C.D. Whiston, A.J. Smith, *Acta Cryst.* 23 (1967) 82.
- [7] M. Weiden, A. Grauel, J. Norwig, S. Horn, F. Staglich, *J. Alloys Compd.* 218 (1995) 13.
- [8] H. Sreemoolanadhan, M.T. Sebastian, P. Mohanan, *Mater. Res. Bull.* 30 (1995) 653.
- [9] R. Ratheesh, H. Sreemoolanadhan, M.T. Sebastian, *J. Solid State Chem.* 131 (1997) 2.
- [10] S. Kamba, J. Petzelt, D. Haubrich, P. Vanek, P. Kuzel, I.N. Jawahar, M.T. Sebastian, P. Mohanan, *J. Appl. Phys.* 89 (2001) 3900.
- [11] N. Tenaze, D. Mercurio, G. Trolliard, J.C. Champarnaud-Mesjard, *Z. Kristallogr. NICS* 215 (2000) 11.
- [12] E. Brook, R.K. Route, R.J. Raymakers, R.S. Feigelson, *J. Cryst. Growth* 128 (1993) 842.
- [13] H. Kasper, *Z. Anorg. Allg. Chem.* 354 (1967) 208 (Ger).
- [14] F. Abbattista, P. Rolondo, G. Boroni Grassi, *Ann. Chim.* 60 (1970) 426.
- [15] S. Pagola, R.E. Carbonio, M.T. Fernandez-Diaz, J.A. Alonso, *J. Solid State Chem.* 137 (1998) 359.
- [16] W.H. Jung, J.H. Sohn, Y. Inaguma, M. Itoh, *Korean J. Ceram.* 2 (1996) 111.
- [17] C. Veneis, P.K. Davies, T. Negas, S. Bell, *Mater. Res. Bull.* 31 (1996) 431.
- [18] B.W. Hakki, P.D. Coleman, *IRE Trans. Microwave Theory Tech.* MTT-8 (1960) 402.
- [19] J. Krupka, K. Derzakowsky, B. Riddle, J.B. Jarvis, *Meas. Sci. Technol.* 9 (1998) 1751.
- [20] R.D. Shannon, *J. Appl. Phys.* 73 (1993) 348.
- [21] R.D. Shannon, *Acta Cryst.* A32 (1976) 751.
- [22] N.E. Massa, S. Pagola, R. Carbonio, *Phys. Rev.* B53 (1996) 8148.
- [23] N.E. Massa, S. Pagola, R.E. Carbonio, J.A. Alonso, I. Rasines, G. Polla, G. Leyva, *SPIE International Symposium*, San Jose, CA, USA.
- [24] S.H. Ra, P.P. Phule, *J. Mater. Res.* 14 (1999) 4259.
- [25] D.W. Kim, I.T. Kim, B. Park, K.S. Hong, *J. Mater. Res.* 16 (2001) 1465.
- [26] H.J. Lee, I.T. Kim, K.S. Hong, *Jpn. J. Appl. Phys.* 36 (1997) L1318.