

# Phase evolution and microwave dielectric properties of $A_5M_5O_{17}$ -type ceramics

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A number of  $A_5M_5O_{17}$  ( $A = \text{Na, Ca, Sr, La, Nd, Sm, Gd, Dy, Yb}$ ;  $B = \text{Ti, Nb, Ta}$ ) type compounds were prepared by a solid-state sintering route and characterized in terms of structure, microstructure and microwave dielectric properties. The compatibility of rare earths with mixed niobate/tantalate and titanate phases was investigated. The larger ionic radii mismatch resulted in the formation of pyrochlore and/or mixed phases while in other cases, pure  $A_5M_5O_{17}$  phase was formed. The samples exhibited relative permittivity in the range of 35 to 82, quality factor ( $Q \times f_0$ ) = 897 GHz to 11946 GHz and temperature coefficient of resonance frequency ( $\tau_f$ ) =  $-120$  ppm/ $^{\circ}\text{C}$  to 318 ppm/ $^{\circ}\text{C}$ .

Keywords:  $A_5M_5O_{17}$ ; dielectrics; microwave properties

## 1. Introduction

Wireless telecommunication industry has seen enormous growth during the last few decades. This has prompted an increased demand for relatively cheaper materials with improved performance to meet the requirements of future systems [1–3]. The industrial benchmarks for such materials include: relative permittivity ( $\epsilon_r$ ) in the range of 4 to 120, high quality factor ( $Q \times f_0 > 5,000$  GHz), and near zero temperature coefficient of resonance frequency ( $\tau_f \sim 0$ ), depending on relevant application. Despite decades long continuous research, a limited number of temperature stable materials have been commercialized [4]. The development of dielectrically loaded antennas enabled extensive miniaturization of satellite-based handsets; however, further miniaturization is needed to meet the demands of high-end market [5].

Recently, ceramics with a general formula  $A_nB_nO_{3n+2}$  ( $n = 4.5$  and  $5$ ) have been reported to exhibit interesting microwave dielectric properties [6, 7]. The crystal structure of these compounds consists of layers of  $\text{BO}_6$  octahedra

separated by additional oxygen layers that are shifted with respect to each other by half the body diagonal. The symmetry of members of this structural series is either orthorhombic or monoclinic in which  $\text{BO}_6$  octahedra are tilted and strongly distorted [8]. Perovskites and perovskite-related structures have the flexibility to accommodate a variety of substitutions either at the A and/or B-site of the perovskite unit cell which enables tailoring of their properties for a wide range of applications. Among these,  $\text{SrLa}_4\text{Ti}_5\text{O}_{17}$  has been reported to crystallize into an orthorhombic (Pnnm) structure with lattice parameters  $a = 5.549(5)$  Å,  $b = 31.299(9)$  Å,  $c = 3.9104(3)$  Å and  $\epsilon_r = 60.8$ ,  $\tau_f = 117$  ppm/ $^{\circ}\text{C}$  and  $Q \times f_0 = 9969$  GHz [9]. Consequently, the effect of partial substitution of Ca for Sr on the dielectric properties of  $\text{Sr}_{1-x}\text{Ca}_x\text{La}_4\text{Ti}_5\text{O}_{17}$  series has been investigated in an attempt to tune its  $\tau_f$  through zero and improve the quality factor [9]. This study revealed substantial improvement in  $\tau_f$  from 117 ppm/ $^{\circ}\text{C}$  to  $-1.4$  ppm/ $^{\circ}\text{C}$  and  $Q \times f_0$  from 9969 GHz to 11,432 GHz along with a small decrease in  $\epsilon_r$  from 60.8 to 53.7. Similarly,  $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$  has been reported to exhibit  $\epsilon_r = 44$ ,  $Q \times f_0 = 13553$  GHz but its high negative  $\tau_f$  ( $= -120$  ppm/ $^{\circ}\text{C}$ ) rendered its use unsuitable for practical applications [10].

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The present study was carried out in an attempt to tune the large positive  $\tau_f$  of  $SrLa_4Ti_5O_{17}$  through zero using various dopants such as Nd, Sm, Gd, Dy, Yb, Nb and Ta at the A- and B-site of  $SrLa_4Ti_5O_{17}$ . Similarly, efforts were made to decrease the negative  $\tau_f$  of  $NaCa_4Nb_5O_{17}$  towards zero via La, Nd and Ti cationic substitutions. Furthermore, the substitution compatibility of various rare earth ions in  $A_5M_5O_{17}$ -type layered perovskites and their effect on the crystal structure and microwave dielectric properties was also investigated.

## 2. Experimental

A number of  $A_5M_5O_{17}$  type compounds (with A = Na, Ca, Sr, La, Nd, Sm, Gd, Dy, Yb and B = Ti, Nb, Ta) were prepared by a solid-state mixed oxide route. High purity  $Na_2CO_3$  (Alfa Aesar, 99 %),  $CaCO_3$  (Sigma Aldrich, 99.9 %),  $SrCO_3$  (Sigma Aldrich, 99.9 %),  $Nd_2O_3$  (Sigma Aldrich 99+ %),  $Sm_2O_3$  (Sigma Aldrich 99+ %),  $Gd_2O_3$  (Sigma Aldrich 99+ %),  $Dy_2O_3$  (Sigma Aldrich, 99+ %),  $Yb_2O_3$  (Sigma Aldrich, 99+ %),  $Nb_2O_5$  (Sigma Aldrich 99+ %) and  $TiO_2$  (Sigma Aldrich 99+ %) were used as initial ingredients. To ensure correct stoichiometry of the final products, carbonates and oxides were pre-heated overnight at 180 °C and 800 °C, respectively to remove the moisture prior to batch preparation. The powders were weighed in stoichiometric ratios and mixed-milled for 1 h in an Attritor mill using Y-toughened zirconia balls as milling media and isopropanol as lubricant. The resulting slurries were dried overnight at 95 °C and sieved to dissociate agglomerates (if any). The powders were calcined in the temperature range of 950 °C to 1450 °C at a heating/cooling rate of 5 °C/min for 6 h. The powders were milled again, dried, sieved and pressed into 3 mm to 5 mm high pellets of 10 mm diameter via a manual uniaxial pellet press. The pellets were placed on platinum foils to avoid contamination and sintered at 1200 °C to 1600 °C at a heating/cooling rate of 5 °C/min. The phase constitution of the calcined and sintered powder was investigated using a Philips (PW1830) X-ray diffractometer with  $CuK\alpha$  radiation (1.5418 Å), step size 0.05° and step time 1 s. The microstructure

of sintered samples was examined using a JEOL 6400 scanning electron microscope operating at 20 kV. For SEM examinations, samples of fractured surfaces were gold coated to avoid charging. The dielectric properties of sintered pellets were measured at microwave frequencies with a network analyzer (Agilent Rch3767CH), using a resonant cavity method.  $\tau_f$  was calculated using equation 1:

$$\tau_f = \frac{f_2 - f_1}{f_1 \times \Delta T} \quad (1)$$

where  $f_1$  and  $f_2$  are the resonant frequencies at temperatures  $T_1$  and  $T_2$  respectively.

## 3. Results and discussion

An analysis of room temperature XRD patterns of  $Sr_{5-x}Nd_xNb_{4-x}Ti_{1+x}O_{17}$  ( $0 \leq x \leq 4$ ) samples sintered at 1500 °C to 1600 °C for 4 h (Fig. 1) revealed the formation of single phase ceramics, i.e.  $Sr_5TiNb_4O_{17}$  (PDF# 04-009-3392) for  $x = 0, 1$  and  $SrNd_4Ti_5O_{17}$  (PDF# 04-009-0752) for  $x = 4$ . The compositions with  $x = 2$  and 3 crystallized into a mixture of a major  $SrNd_4Ti_5O_{17}$  phase and a pyrochlore-type  $Nd_2Ti_2O_7$  phase (PDF# 04-009-3392). The formation of the observed phases may be due to exceeding of the solubility limit of Nd in the mixed Nb/Ti based compounds, as reported previously by Li et al. [11] in case of  $Ca_{1+x}La_{4-x}Nb_xTi_{5-x}O_{17}$  ceramics. In another relevant study, Nd substitution has been reported [12] to form a single phase solid solution but in a pure Ti-based compound ( $SrLa_{4-x}Nd_xTi_5O_{17}$ ) at the B-site. The lattice parameters were observed to decrease with an increase in  $x$  due to the replacement of larger ionic radii Sr (1.44 Å) ions [13] by smaller Nd (1.27 Å) ions [13], Table 1.

Room temperature XRD patterns of  $Sr_{1+x}La_{4-x}Ta_xTi_{5-x}O_{17}$  ( $0 \leq x \leq 4$ ) samples sintered at 1575 °C to 1600 °C for 4 h are shown in Fig. 2 which demonstrates the formation of single phase  $SrLa_4Ti_5O_{17}$  (PDF# 04-009-3392) ceramics at  $x = 0$  and 1. An appropriate shift in the position of XRD peaks towards relatively lower  $2\theta$  angles with increasing  $x$  (from 0 to 1) may be attributed to the substitution of the larger ionic

Table 1. Refined lattice parameter of  $\text{Sr}_{5-x}\text{Nd}_x\text{Nb}_{4-x}\text{Ti}_{1+x}\text{O}_{17}$  ( $0 \leq x \leq 4$ ) and  $\text{Sr}_{1+x}\text{La}_{4-x}\text{Ta}_x\text{Ti}_{5-x}\text{O}_{17}$  ( $0 \leq x \leq 4$ ) ceramics.

$\text{Sr}_{5-x}\text{Nd}_x\text{Nb}_{4-x}\text{Ti}_{1+x}\text{O}_{17}$						
x	a [Å]	b [Å]	c [Å]	Z	Structure	$V_{\text{unit}}$ [Å <sup>3</sup> ]
0	5.6589	32.5216	3.9483	2	orthorhombic	726.56
1	5.6210	32.12	3.9378	2	orthorhombic	710.99
2	—	—	—	—	—	—
3	—	—	—	—	—	—
4	5.4726	31.268	3.8568	2	orthorhombic	659.9
$\text{Sr}_{1+x}\text{La}_{4-x}\text{Ta}_x\text{Ti}_{5-x}\text{O}_{17}$						
0	5.5322	31.2970	3.9086	2	orthorhombic	676.75
1	5.5305	31.4019	3.9048	2	orthorhombic	678.15
2	5.5799	31.8740	3.9296	2	orthorhombic	698.90
3	5.6155	32.2714	3.9395	2	orthorhombic	713.28
4	5.6644	32.8154	3.9390	2	orthorhombic	732.19

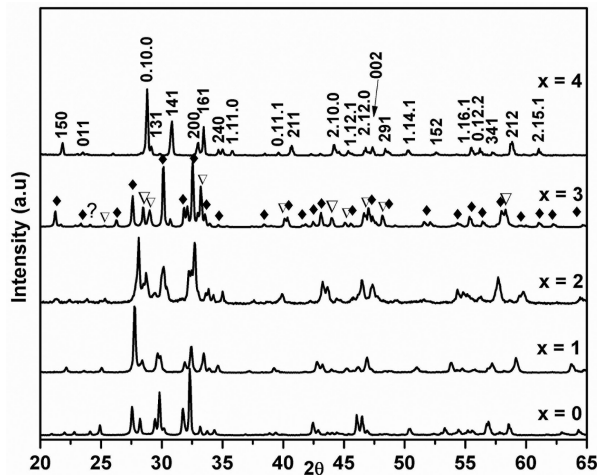


Fig. 1. XRD patterns of sintered  $\text{Sr}_{5-x}\text{Nd}_x\text{Nb}_{4-x}\text{Ti}_{1+x}\text{O}_{17}$  ( $0 \leq x \leq 4$ ) ceramics, showing the formation of single phase at  $x = 0, 1$  and  $4$ , and secondary phase(s) at  $x = 2$  and  $3$ , where ♦ and ∇ denote  $\text{SrNd}_4\text{Ti}_5\text{O}_{17}$  and  $\text{Nd}_2\text{Ti}_2\text{O}_{17}$  phases, respectively.

radii Sr (1.44 Å) ions for the smaller La (1.36 Å) ions [13]. Consequently, the lattice parameters and unit cell volume also increased (Table 1). The interplanar or d-spacings and relative intensities of the XRD peaks for the  $x = 2, 3$  and  $4$  samples matched PDF# 04-009-3392 for  $\text{Sr}_5\text{TiNb}_4\text{O}_{17}$ . A couple of additional low intensity peaks were also

observed on the same XRD, indicating secondary phase formation. These peaks could not be identified due to their small number and low intensities.

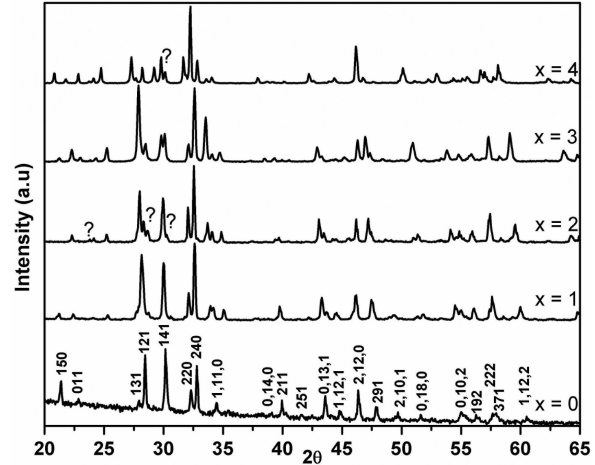


Fig. 2. XRD patterns of sintered  $\text{Sr}_{1+x}\text{La}_{4-x}\text{Ta}_x\text{Ti}_{5-x}\text{O}_{17}$  ( $0 \leq x \leq 4$ ) ceramics, showing unidentified additional peaks for samples with  $x \geq 2$ .

Fig. 3. shows the room temperature XRD patterns of  $\text{Na}_3\text{Re}_2\text{B}_5\text{O}_{17}$  (Re = La, Nd; B = Nb, Ta) samples sintered at 1500 °C for 4 h. It is interesting to note that in all the cases, the major phase is  $\text{NaBO}_3$  and the secondary phase is

$\text{ReBO}_4$ . The formation of single phase ceramics has been reported in this system but via the ion exchange method [14] which is an un-economical and complex route. The structural analysis of  $\text{Sr}_{5-x}\text{RE}_x\text{Nb}_{4-x}\text{Ti}_{1+x}\text{O}_{17}$  ( $\text{RE} = \text{Sm}, \text{Gd}, \text{Dy}, \text{Yb}$ ) revealed the formation of a mixture of pyrochlore and  $\text{SrTiO}_3$  phases, probably due to the large ionic radii difference between  $\text{Sr}^{2+}$  and RE ( $\text{Sm}, \text{Gd}, \text{Dy}, \text{Yb}$ ) ions [13]. Previously, Nd-doped  $\text{SrLa}_4\text{Ti}_5\text{O}_{17}$  composition has been reported to form a single phase solid solution [12] but the ionic radius of  $\text{Nd}^{+3}$  is relatively larger than that of  $\text{Sm}^{+3}$  which may favor the formation of a mixture of pyrochlore and cubic  $\text{SrTiO}_3$  phases, consistent with a previous study [15]. Similarly, La and Ti doped  $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$  with a general formula  $\text{NaCa}_{4-x}\text{La}_x\text{Nb}_{5-x}\text{Ti}_x\text{O}_{17}$  were also processed and XRD analysis of these compositions revealed the formation of a mixture of phases at  $x > 0$ . This result indicated the incompatibility of Na, La with the mix B-site Nb and Ti based layered perovskite compounds.

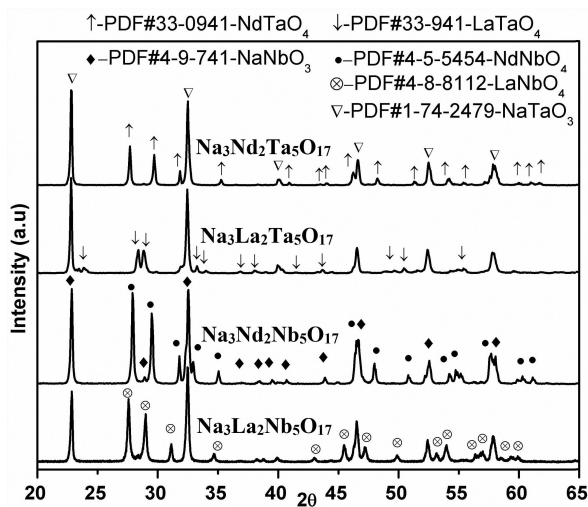


Fig. 3. XRD patterns of sintered  $\text{Na}_3\text{Re}_2\text{B}_5\text{O}_{17}$  ( $\text{Re} = \text{La}, \text{Nd}$ ;  $\text{B} = \text{Nb}, \text{Ta}$ ) ceramics, showing the formation of  $\text{Na}[\text{Nb}/\text{Ta}]\text{O}_3$  and  $\text{Re}[\text{Nb}/\text{Ta}]\text{O}_4$  phases.

Fig. 4 shows secondary electron SEM images of fractured surfaces of sintered  $\text{Sr}_{5-x}\text{Nd}_x\text{Nb}_{4-x}\text{Ti}_{1+x}\text{O}_{17}$  ( $0 \leq x \leq 4$ ) samples. The single-phase samples ( $x = 0, 1$  and  $4$ )

comprise plate-like grains, a typical grain morphology of  $A_5M_5O_{17}$  type ceramics. The compositions with  $x = 2$  and  $3$  are bi-phasic; however, the grains could not be resolved to ascertain their morphology (Fig. 4). Secondary electron SEM images of  $\text{Sr}_{1+x}\text{La}_{4-x}\text{Ta}_x\text{Ti}_{5-x}\text{O}_{17}$  ( $0 \leq x \leq 4$ ) samples shown in Fig. 5, comprise grains of similar morphology such as that of  $\text{Sr}_{5-x}\text{Nd}_x\text{Nb}_{4-x}\text{Ti}_{1+x}\text{O}_{17}$  ( $x = 0, 1$  and  $4$ ); however, some pores could be seen in the microstructure of  $x = 3$  and  $4$  compositions which may be attributed to the relatively higher Ta content which is known to promote refractoriness and hence, poor diffusion.

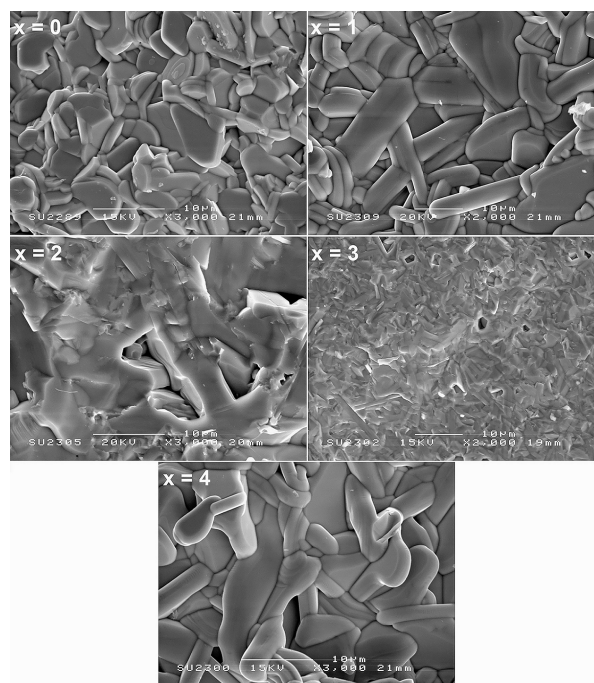


Fig. 4. Secondary electron SEM micrographs of sintered  $\text{Sr}_{5-x}\text{Nd}_x\text{Nb}_{4-x}\text{Ti}_{1+x}\text{O}_{17}$  ( $0 \leq x \leq 4$ ) ceramics.

The microwave dielectric properties of the samples sintered at their optimum sintering temperatures are given in Table 2. In case of  $\text{Sr}_{5-x}\text{Nd}_x\text{Nb}_{4-x}\text{Ti}_{1+x}\text{O}_{17}$  ( $0 \leq x \leq 4$ ), end members of this series have opposite sign  $\tau_f$ . Initially,  $\tau_f$  decreased from 286 ppm/°C to 7.8 ppm/°C with an increase in  $x$  from 0 to 1 and then suddenly increased with an increase in  $x$  from 2 to 3. This non-linear behavior may be due to the formation of the observed secondary phases (Fig. 1). At  $x = 4$ ,



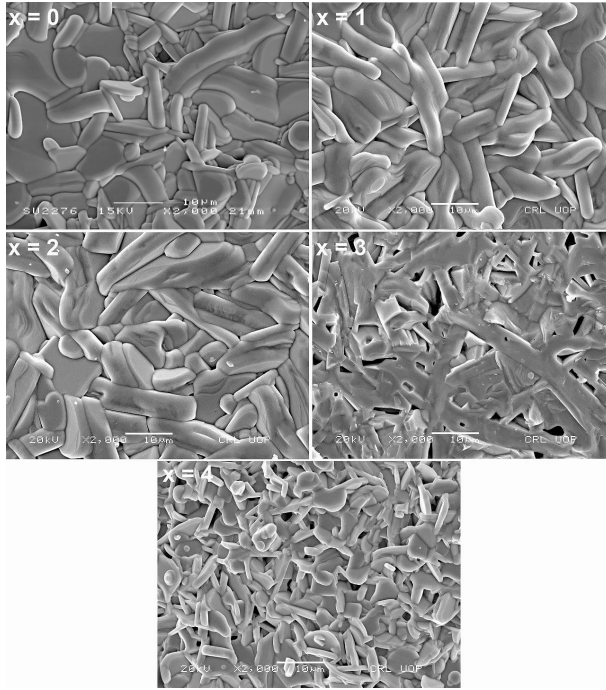


Fig. 5. Secondary electron SEM micrographs of sintered  $\text{Sr}_{1+x}\text{La}_{4-x}\text{Ta}_x\text{Ti}_{5-x}\text{O}_{17}$  ( $0 \leq x \leq 4$ ) ceramics, showing an increase in porosity with increasing Ta-content.

$\tau_f$  was  $-118 \text{ ppm}/^\circ\text{C}$  which is consistent with a previous study [12]. The observed decrease in  $\epsilon_r$  with increasing  $x$  is presumably due to dampening of the ionic mobility of Nd ions [16]. The more massive Nd ions (despite having higher ionic polarizability than Sr) interact weakly with the microwave field which decreases  $\epsilon_r$  [16]. Similarly, secondary phases may also affect the microwave dielectric properties [17]. A high  $\epsilon_r = 70$  and reasonable  $\tau_f = 7.85 \text{ ppm}/^\circ\text{C}$  were observed for the  $x = 1$  composition; however, its  $Q \times f_0 = 1226 \text{ GHz}$  was too low for any practical application.

In case of  $\text{Sr}_{5-x}\text{La}_x\text{Ta}_{4-x}\text{Ti}_{1+x}\text{O}_{17}$  ( $0 \leq x \leq 4$ ) ceramics,  $\text{SrLa}_4\text{Ti}_5\text{O}_{17}$  exhibited  $\tau_f = 73.6 \text{ ppm}/^\circ\text{C}$ ,  $\epsilon_r = 62$  and  $Q \times f_0 = 11596 \text{ GHz}$ , consistent with a previous study [18]. Partial substitution of Ta at the B-site and an increase in La content at the A-site decreased  $\epsilon_r$  which should, in principle, increase with Ta substitution for Nb on the basis of ionic polarizability [19]. The observed decrease may be due to a decrease in rattling effect

Table 2. Microwave dielectric properties of  $\text{A}_5\text{M}_5\text{O}_{17}$  (A = Na, Ca, Sr, La, Nd; B = Ti, Nb, Ta) ceramics.

$\text{Sr}_{5-x}\text{Nd}_x\text{Nb}_{4-x}\text{Ti}_{1+x}\text{O}_{17}$					
x	CT [°C]	ST [°C]	$\epsilon_r$	$Q \times f_0$ [GHz]	$\tau_f$ [ppm/°C]
0	1300/6 h	1550/4 h	82	2141	286
1	1400/6 h	1575/4 h	70	1226	7.8
2	1400/6 h	1575/4 h	62	1288	55.6
3	1400/6 h	1575/4 h	58	1456	102
4	1400/6 h	1600/4 h	46	9579	-118
$\text{Sr}_{1+x}\text{La}_{4-x}\text{Ta}_x\text{Ti}_{5-x}\text{O}_{17}$					
0	1400/6 h	1575/4 h	62	11596	73.6
1	1400/6 h	1625/4 h	61	4711	41.2
2	1400/6 h	1600/4 h	60	3235	98.5
3	1400/6 h	1625/4 h	58	2707	92.4
4	1400/6 h	1625/4 h	35	3245	-17.6
$\text{NaCa}_{4-x}\text{La}_x\text{Nb}_{5-x}\text{Ti}_x\text{O}_{17}$					
0	950/4 h	1200/4 h	44	13523	-120
1	1200/4 h	1400/6 h	57	1271	-1.1
2	1200/4 h	1450/6 h	70	897	170
3	1200/4 h	1450/6h	65	1220	93
4	1200/4 h	1450/6 h	66	1042	78
$\text{Na}_3\text{B}_2\text{Ta}_5\text{O}_{17}$ (B = La, Nd)					
La	1200/6 h	1500/4 h	78	1443	246
Nd	1200/6 h	1500/4 h	59	11946	318

with Ta substitution which may have decreased the effective ionic polarizability, hence,  $\epsilon_r$  [20]. Surprisingly, an unexpected non-linear change in  $\tau_f$  was observed which may be attributed to the formation of the secondary phase at  $x = 2, 3$  and 4. A similar trend in  $\tau_f$  was reported previously as well [21] for the  $\text{Sr}_{5-x}\text{La}_x\text{Nb}_{4-x}\text{Ti}_{1+x}\text{O}_{17}$  series; however, the crystal and defect chemistry of this system is not understood and needs further investigations. The  $Q \times f_0$  value should also, in principle, increase as a result of increasing Ta concentration which causes a decrease in the anharmonic lattice vibrations due to a decrease in rattling effect; however, the observed decrease in  $Q \times f_0$  may be attributed to the observed porosity, evident in the microstructure of these samples (Fig. 5).

$\text{Na}_3\text{Re}_2\text{Nb}_5\text{O}_{17}$  (Re = La, Nd) compounds did not resonate at microwave frequencies which may be due to the formation of non-centrosymmetric  $\text{NaNbO}_3$  phase, exhibiting high dielectric losses; however,  $\text{Na}_3\text{La}_2\text{Ta}_5\text{O}_{17}$  and  $\text{Na}_3\text{La}_2\text{Ta}_5\text{O}_{17}$  compositions exhibited  $\epsilon_r = 78$  and  $58.8$ ,  $Q \times f_0 = 1443$  and  $11946$  GHz but too high  $\tau_f = 246$  and  $318$  ppm/ $^\circ\text{C}$ , respectively. On the other hand, La doping at the A-site and Ti at the B-site of  $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$  resulted in the formation of multiphase ceramics with a high negative  $\tau_f$ , as discussed earlier. The  $x = 1$  composition exhibited promising temperature stability ( $\tau_f = -1.1$  ppm/ $^\circ\text{C}$ ) and a moderate  $\epsilon_r$  (57) but quality factor (1200 GHz) was too low for practical applications. Further increase in  $x$  increased  $\epsilon_r$  but deteriorated both the  $Q \times f_0$  and  $\tau_f$ .

#### 4. Conclusions

$A_5M_5O_{17}$  (A = Na, Ca, Sr, La, Nd, Sm, Gd, Dy, Yb; B = Ti, Nb, Ta) type compounds were processed via a mixed oxide solid state route and characterized for their application potential as microwave dielectrics. XRD analysis of  $\text{Sr}_{5-x}\text{Nd}_x\text{Nb}_{4-x}\text{Ti}_{1+x}\text{O}_{17}$  ( $0 \leq x \leq 4$ ) samples revealed the formation of single phase ceramics at  $x = 0, 1, 4$ , while secondary phases formed at  $x = 2, 3$ . Similarly, XRD analysis of  $\text{Sr}_{1+x}\text{La}_{4-x}\text{Ta}_x\text{Ti}_{5-x}\text{O}_{17}$  ( $0 \leq x \leq 4$ ) revealed single phase formation at  $x = 0$  to  $1$ , while the presence of secondary phases was observed for compositions with  $x \geq 2$ .  $\text{Na}_3\text{Re}_2\text{B}_5\text{O}_{17}$  (Re = La, Nd; B = Nb, Ta),  $\text{Sr}_{5-x}\text{RE}_x\text{Nb}_{4-x}\text{Ti}_{1+x}\text{O}_{17}$  (RE = Sm, Gd, Dy, Yb) and  $\text{NaCa}_{4-x}\text{La}_x\text{Nb}_{5-x}\text{Ti}_x\text{O}_{17}$  ( $x = 1$  to  $4$ ) also crystallized into a mixture of phases. The microstructural analysis revealed porosity in the Ta-based samples due to their refractory nature. Secondary phases significantly influenced the microwave dielectric properties.  $\text{Sr}_5\text{Ta}_5\text{TiO}_{17}$  exhibited a relatively good combination of microwave dielectric properties which may be enhanced using a sintering aid to improve the density.

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