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Structure evolution and improved microwave dielectric characteristics in CaTi_1- $_{\rm X}({\rm Al}_{0.5}{\rm Nb}_{0.5})_{\rm X}{\rm O}_3$ ceramics

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Author contributions

I.H. performed most of the experiments. X.Q.L. contributed to XRD analysis. L.L. contributed the microwave characterization. M.Y.L. conducted TEM observation. X.M.C. directed the research work. All authors contributed to the discussion of the results and preparation of the manuscript.



Structure evolution and improved microwave dielectric characteristics in CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO₃ ceramics

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5 Abstract

Enhanced characteristics of microwave dielectrics in (Al_{0.5}Nb_{0.5})-co-substituted CaTiO₃ ceramics 6 7 was examined by means of structure evolution. $CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO_3$ solid solutions with orthorhombic structure in space group Pbnm were attained throughout the entire composition 8 range x ≤ 0.75 . The near-zero temperature coefficient of resonant frequency τ_f and significantly 9 improved quality factor Qf value were achieved, while a tunable medium dielectric constant ε_r 10 was achieved in the present ceramics. τ_f was tuned from 750 ppm/°C to 5 ppm/°C and became -11 80 ppm/°C finally (at x=0.75), the Qf was first increased from 11,500 GHz up to 49,700 GHz 12 due to the stable perovskite structure with increased bond strength and degree of covalency (%) 13 and then slightly decreased to 43,100 GHz at x=0.75. The best combination of significantly 14 improved microwave dielectric characteristics was achieved at x=0.45 (ε_r =55.1, Qf=49,700 15 GHz, $\tau_{f=5ppm/^{\circ}C}$). The present ceramics showed the great application potential in future 16 wireless communication systems. 17

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2 **1. Introduction:**

The continuous progresses in microwave communication systems such as satellite 3 communications and cellular devices had driven the great development in microwave 4 dielectric ceramics^{1, 2, 3}. Three parameters are important to be satisfied by the dielectric 5 materials for microwave application: a high ε_r (for miniaturized devices), a high quality 6 7 factor Q (adequate frequency tunability to discover more channels within a selective band; the Qf is usually used to evaluate Q at different frequency f) and a near-zero temperature 8 coefficient of resonance frequency τ_f (for better temperature stability)³. In addition, cheap 9 raw materials are always more preferred for the industrial application⁴. It is extremely 10 challenging to emerge all these four characteristics into some particular material^{5, 6}. To 11 solve these problems, many researchers have investigated numerous materials and further 12 findings are on the track. 13

Over past few decades, complex perovskite structure composed of alkaline earth titanates 14 and their solid solutions have received huge interest in the electronics industry because of 15 their high dielectric constants and considered to be more reliable for practical applications⁷, 16 ⁸. In the early 1970's, Kell et al⁹ firstly reported the dielectric characteristics of CaTiO₃ 17 which exhibited the following properties: $\varepsilon_r = 170$, Of=3500 GHz and $\tau_f \approx +800$ ppm/°C. 18 Subsequently, a number of research work has been performed relating CaTiO₃-based 19 materials and their microwave dielectric characteristics has been published by many 20 researchers^{10, 11, 12, 13, 14}. CaTiO₃-based materials have captivated extensive importance due 21 22 to high dielectric constant, though, they possess a large τ_f . Numerous attempts have been made to adjust τ_f of CaTiO₃-based materials to near-zero by mixing materials with negative 23 $\tau_f^{15,16}$ Recently, A or B-site substitution has played much significant role in enhancing the 24

microwave dielectric characteristics of many materials¹⁴ ^{17, 18}. As reported by some researchers, the substitution at Ti-site, with combined acceptor and donor ions could considerably improve the microwave dielectric properties, also it can hinder the Ti⁴⁺ reduction into Ti³⁺ which is very common in Ti-based materials because of high temperature sintering ¹⁹. In the previous work of the authors, Sr₂TiO₄ ceramics with R-P structure exhibited significant improvements due to B-site substitution of Ti⁴⁺ with $(Al_{0.5}Nb_{0.5})^{20}$.

Lately, Chen et al. ²¹ reported thermally stable CaTiO₃ co-substituted by Al/Nb and 8 investigated its microwave dielectric characteristics as ε_r ~52.6, Qf ~22,900GHz and τ_f 9 ~6.4ppm/°C. However, the mechanism for this improved τ_f was remained unclear, and the 10 *Of* value was not high enough for future application. There might be two primary reasons 11 involved for the low *Qf* value: the low purity of raw materials, and longer holding time 12 13 used in the calcination and sintering processes i.e. 6 hours and 4 hours respectively. This longer holding time at higher temperatures formed more oxygen vacancies and resulted in 14 Ti^{4+} reduction into Ti^{3+} which attributes to inhibit the Qf value²². And so, it would be 15 invoking concern to reconsider the effects of (Al_{0.5}Nb_{0.5}) co-substitution for Ti in CaTiO₃ 16 ceramics by using high purity raw powders and optimized processing conditions. 17 Conversely, the ultimate aim of the existing work is to achieve the deep physical 18 understanding on the effects of (Al_{0.5}Nb_{0.5}) co-substitution on the microwave dielectric 19 characteristics. On the other hand, because of the rapid development of cellular base 20 stations and satellite communications, there is still an increasing need to develop the 21 microwave dielectric ceramics with medium ε_r around 50 together with an ultra-high *Qf* 22 value and near-zero τ_{f}^{23} 23

state reaction method with the controlled processing conditions, and the effects of
(Al_{0.5}Nb_{0.5}) co-substitution for Ti upon microwave characteristics were determined and
discussed with deep physical understanding by linking them with the structure evolution.

5 II. Experimental procedures

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 $CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO_3$ (x=0, 0.10, 0.30, 0.45, 0.60 and 0.75) ceramics were prepared through a 6 standard solid state reaction route, by using high-purity powders such as CaCO₃ (99.99%), 7 8 Al₂O₃ (99.99%), Nb₂O₅ (99.95%) and TiO₂ (99.99%) as the starting materials. The raw powders were weighed (keeping stoichiometric ratios) and mixed via ball-milling in absolute 9 alcohol with ZrO₂ media for 24 hours. The mixtures were dried and calcinated at 1200°C in air 10 for 3 hours and ball-milled again with similar conditions performed before calcination. After 11 drying, all calcined powders were sieved and then granulated with an amount of 4% polyvinyl 12 13 alcohol (PVA), and then were pressed into pellets under a pressure of 120MPa, with 12mm in diameter and 2-6 mm in thickness. All the samples were sintered at 1500-1575°C in air for 3 14 hours, followed by the cooling to 1000 °C at a rate of 1°C/min, and further cooling was done 15 inside the furnace. 16

The density of all sintered ceramics was measured by Archimedes method. The crystal structure of the sintered pellets was determined using X-Ray diffractrometer (XRD) (BRUKER D8 Advance, Germany) using CuKα radiations. The valuable Rietveld refinement was carried out for the structural analyses with FULLPROOF software. The microstructures of the thermally etched surfaces were observed by scanning electron microscopy (SEM) (S-3400; Hitachi, Tokyo, Japan), wherein the related ceramics were finely polished and thermally etched at 50°C temperature lower than their actual sintering temperatures for 30 minutes. The selected area electron diffraction (SAED) reflections and high-resolution transmission electron
microscopy images (HRTEM) were obtained by TEM (transmission electron microscopy)
(Tecnai G2-F20, FEI Co., Hillsboro, OR) operated at 200 kV. Sample preparation for TEM
analysis was done by disaggregating the ceramics into fine powders through grinding in an
agate mortar and sieving through 300 mesh, and then suspended in alcohol for 10-15 minutes,
and then dispersed on the top of a carbon-coated-mirco-grid.

7 The dielectric properties of CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO₃ ceramics were evaluated at microwave 8 frequencies using a vector network analyzer (E8363B, Agilent Technologies Inc., Santa Clara, 9 CA). The dielectric constant ε_r and temperature coefficient of resonant frequency τ_f were 10 measured by Hakki-Coleman method ²⁴ and τ_f was calculated as the following formula:

11
$$\tau_f = \frac{f_{80} - f_{20}}{(80 - 20)(f_{20})} \times 10^6$$
(1)

where, f_{80} and f_{20} signified as resonant frequencies at 80°C and 20°C, respectively. The quality factor Q was evaluated by resonant-cavity method²⁵, by a silver-coated cavity coupled with network analyzer. As the Q-factor keeps inverse relationship with frequency (f) in microwave range, the product of Qf was used despite only Q, to estimate the dielectric loss.

16 III. Results and discussions

Fig. 1 demonstrates XRD patterns for $CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO_3 x \le 0.75$ ceramics sintered at 1550 °C for 3 hours, and Fig.2 displays the Rietveld refinement curves of the present ceramics for x=0.30 & x=0.45. The orthorhombic perovskite structure in space group *Pbnm* is identified in the entire compositions range, and the relevant peaks have been marked with their corresponding crystallographic planes of CaTiO₃ which are consistent with indices of JCPD card (78-1013). There is no secondary phase in entire XRD patterns which

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indicates the solid solution limit is at least out of x=0.75. A very slight shift towards a
 higher 2θ angle has been observed for the diffraction peaks of CaTiO₃ phase attributed to
 the smaller ionic radius of (Al_{0.5}Nb_{0.5})⁴⁺ (0.586Å) than Ti⁴⁺ (0.605 Å)²⁶.

Fig. 3(a) and Fig. 3(b) shows the lattice parameters (a,b,c) and the tolerance factor *t* for CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO₃ ceramics as functions of *x*, respectively. The cell parameters '*a*' and '*c*' increase almost linearly from 5.3795 to 5.3855 and 7.6408 to 7.6433 respectively, as *x* increases from x=0 to x=0.75. While cell parameter '*b*' decreases non-linearly from 5.4430 at x=0 to 5.4323 at x=0.75. Therefore, the resulting cell volume also increases from 223.72 at x=0 to 223.88 at x=0.60 and then decreases slightly to 223.61. The tolerance factor *t* of CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO₃ ceramics was calculated by the following formula ²⁷:

11
$$t = \frac{r_{Ca^{2+}r_{O^{2-}}}}{\sqrt{2}(r_{B}+r_{O^{2-}})}$$
(2)

12

13
$$r_{\rm B} = (1-x) r_{\rm Ti^{4+}} + x^* 0.5 (r_{\rm Al^{3+}} + r_{\rm Nb^{5+}})$$

where, r_{Ca²⁺}, r_{Ti⁴⁺}, r_{Al³⁺}, r_{Nb⁵⁺} and r_{O²⁻} are the effective ionic radii of Ca²⁺, Ti⁴⁺, Al³⁺
Nb⁵⁺ and O²⁻ respectively. As the (Al_{0.5}Nb_{0.5})⁴⁺ substitution increases from x=0 to x=0.75,
the tolerance factor increases linearly from 0.9663 to 0.9732 respectively (see Fig.3 (ii)
Table.1).

and

(3)

Table.1 illustrates the related lattice parameters, reliability parameters and tolerance factor for all the compositions. Smaller values of reliability parameters refer to the accuracy of XRD data. Fig.4 displays the relative density of $CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO_3$ ceramics as a function of sintering temperature. All the ceramics are well densified at 1525-1550°C. At

 $x \le 0.30$, there is no significant variation in the relative density (see Table 3). However, 1 with further increasing x (x>0.3), the relative density reaches to the highest value of 99.3%2 at x=0.45. That is, the densification characteristics are improved significantly by the co-3 substitution of $(Al_{0.5}Nb_{0.5})$ in the present ceramics. It is a general case in ceramics, that the 4 densification characteristics could be improved by forming solid solutions due to the 5 6 possible effects of precipitation and the subsequent liquid phase sintering. The slight decrease of relative density at x=0.60 and x=0.75 could be ascribed by the slightly 7 increased porosity because of the inhomogeneous microstructure. 8

Fig.5 exhibits the surface morphology of the present ceramics sintered at 1550°C. Higher 9 relative density can also be confirmed by the SEM images of the ceramics where the uniform 10 and well-densified microstructure with fine grains is observed (see Fig.5). The grain size is 11 12 reduced slightly when x=0.025, but with further increase in x, the grain size increases significantly until x=0.45 and then reduces again with increasing x. The average grain size as 13 function of composition is presented in Table 3. There is an obvious variation in the average 14 grain size with increasing x, which could be associated with the growth process of grains. For 15 16 the pure CaTiO₃ ceramics, the average grain size is $\sim 16.53 \mu m$, and with small amount of x, the average grain size is decreased considerably to $\sim 9.33 \mu m$ at x=0.025 due to the 17 18 segregation of some ions residing at the grain boundaries (see Fig. 5(b)). However, the grains exhibit a significant growth at the expense of x, and reaches the maximum value of 19 ~35.20 μ m at x=0.45. This could be ascribed to the cation motion of Al³⁺ and Nb⁵⁺ coherently 20 promoted with each other²⁸. The grain growth is inhibited again at x=0.60 and x=0.75 due to 21 the appearance of some pores and inhomogeneous grains (see Fig.5). 22

For x=0.45, the SAED pattern and its high resolution TEM (HRTEM) image at zone axis 1 $[01\overline{1}]_c$ is presented in Fig. 6. For the present ceramics, array of super-lattice reflections at 2 $\pm 1/2$ (hkl) integral i.e. $[1\overline{1}\overline{1}]_c$, $[3\overline{1}\overline{1}]_c$ can be observed from the SAED image. As shown in 3 Fig.6, the superlattice modulation 0.36nm and 0.29 nm corresponds to $[1\overline{1}\overline{1}]_c$ and $[200]_c$. 4 Although there is no occurrence of phase transition in the current ceramics, the magnitude of 5 tilting or cation ordering must have affected the τ_f . The presence of $\frac{1}{2}[hkl]$ superlattice 6 reflections are in accordance with the existence of anti-phase tilting of the oxygen octahedra²⁹⁻ 7 30 . The superlattice reflections in the SAED patterns, are supposed to be kinematically 8 forbidden, and those reflections could possibly be present by 1:1 cation ordering or by anti-9 phase tilting of oxygen octahedral³¹⁻³². The basic approach to examine the structural variations 10 is to see types of the superlattice reflections which occur through cell doubling affected by 11 octahedral tilt transitions³³⁻³⁴. As suggested by Levin et al.³³ the odd-odd-odd (000) super-12 lattice reflection in the $[01\overline{1}]_c$ zone axis is supposed to be dominated by octahedral tilting 13 whereas the (000) super-lattice reflection in the $[\bar{1}10]_c$ zone axis was entirely associated to 14 cation-ordering in Ca(Al_{1/2}Nb_{1/2})O₃-based ceramics. Similarly, from XRD refined structure for 15 all the ceramic compositions, there is no superstructure peaks detected as shown in Fig.1. 16 17 Conversely, the super-lattice reflections in the current ceramics cannot be attributed to 1:1 18 cation ordering. Rather it could be attributed to the anti-phase tilting.

The microwave dielectric characteristics of $CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO_3$ ceramics sintered at their optimal sintering temperatures are presented in Fig. 7 and Table.2. The ε_r reduces linearly from 170 to 30 with increasing *x* from *x*=0 to *x*=0.75. The temperature coefficient of resonance frequency τ_f is suppressed substantially from a large value of +760ppm/°C to 5ppm/°C as *x* increases and is further reduced to a negative value of -80 ppm/°C at x=0.75.

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1 While, the *Qf* value increases almost linearly as a function of *x* throughout all the 2 composition, since it sharply arouse from 11,500 GHz (at *x*=0) to 49,700 GHz (at *x*=0.45) and 3 finally it indicates a slight decrease to 43,100 GHz at *x*=0.75. Consequently, the *Qf* is 4 increased tremendously by the $(Al_{0.5}Nb_{0.5})^{4+}$ substitution, while a medium ε_r between 30-55 is

5 obtained together with the near-zero τ_{f} .

Fig.8 displays the synchronous tendency between ε_r and theoretical polarizabilities 6 $\alpha_{\text{Theo.}}(\text{\AA}^3)$ of $\text{CaTi}_{1-x}(\text{Al}_{0.5}\text{Nb}_{0.5})_x\text{O}_3$ ceramics as a function of x. The ε_r is continuously 7 decreases by increasing $(Al_{0.5}Nb_{0.5})$. In general, the dielectric constant is influenced by 8 various factors such as structural characteristics of the oxygen octahedron such as tilting, 9 distortion, rattling effect etc, and also affected by the relative density³⁵. In the present work, 10 dielectric constant ε_r is primarily ascribed by the reduced polarizability. The theoretical 11 polarizabilities $\alpha_{\text{Theo}}(\text{\AA}^3)$ could be calculated by Shannon's ³⁶ additive rule that can be 12 presented as follows: 13

14

where, α(Ca²⁺,Ti⁴⁺,Al³⁺,Nb⁵⁺,O²⁻) are the ionic polarizabilities of corresponding ions indicated in
Eq. (3). As shown in Fig 8, α_{Theo}(Å³) declines linearly with the increase in x value which is
attributed to the smaller ionic polarizabilities of (Al_{0.5}Nb_{0.5})⁴⁺ (2.38 Å³)³⁷ than Ti⁴⁺ (2.94 Å³)³⁷.
So the decreasing tendency of dielectric constant is well-consistent with the decreased ionic
polarizabilities.

 $\alpha_{theo}(CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO_3)$

 $=\alpha(Ca^{2+})+(1-x)\alpha(Ti^{4+})+0.5x\alpha(Al^{3+})+0.5x\alpha(Nb^{5+})+3\alpha(O^{2-})$ (4)

 τ_f can be strongly affected by structural characteristics of oxygen octahedra, rattling effect and secondary phase etc ^{30, 38, 39}. Therefore, the variation of τ_f can be determined by the degree of octahedral tilting for the present perovskite structure. The value of tolerance factor *t* is closely

related with the tilting degree of oxygen octahedra, therefore it is predictable to infer the tilting 1 type with the findings of Reaney *et al.* 30,40 Anti-phase tilting can be predictable in our CaTi₁. 2 $_{x}(Al_{0.5}Nb_{0.5})_{x}O_{3}$ ceramic systems, since the value of tolerance factor t lies between 0.9632 and 3 0.9732 (see Fig.3). However, the appearance of superlattice reflections at 1/2(hlk) can also be 4 observed in SAED pattern (Fig.6), which confirms the onset of anti-phase tilting of the oxygen 5 octahedra⁴¹. According to Glazers ³², CaTiO₃ perovskite holds $b^{-}b^{-}c^{+}$ tilt system for orthorhombic 6 Pbnm space group. This refers to two similar out-of-phase and one in-phase tilt systems. Fig.9 7 8 shows the variation between the magnitude of anti-phase tilting and τ_f . The magnitude of the anti-phase tilting has been calculated with VESTA program.⁴² It can be clearly seen that as x9 increases, tilting angle weakens (accompanied by the increase in t with x). At certain axis, the 10 unit cell with doubled lengths are formed due to octahedral tilting³². Therefore the tilting features 11 can be accurately specified through the various classes of distinctive super-lattice reflections for 12 the certain zone axis in the SAED patterns⁴³. Significantly, a or b tilting are accountable for the 13 odd-odd (000) type reflections, while, c⁺ tilting generates odd-odd-even (000) type 14 reflections³¹. It is proposed by Glazers³², that tilting of the octahedra produces doubling of the 15 unit cell axes, i.e. additional reflections are formed which are positioned at the 1/2-integral 16 reciprocal lattice planes. These reflections can be indexed with some odd indices; however, the 17 major reflections comprise all [hkl] even. 18

19 Temperature coefficient of resonant frequency τ_f is also linked to the temperature coefficient of 20 ε_r i.e. τ_{ε_r} and α_L (linear thermal expansion coeff.) as following⁴⁴:

21
$$\tau_f = -\left(\frac{\tau_\varepsilon}{2} + \alpha_L\right) \tag{5}$$

22 where, α_L doesn't vary much for the perovskite structure, and it is about 10-20ppm/°C⁴⁰.

One key factor adjusting τ_f value is the onset of oxygen octahedral tilting which could deeply 1 affect the temperature coefficient of permittivity (τ_{ε}) and temperature coefficient of resonant 2 frequency $(\tau_f)^{40}$ Since τ_{ε} and τ_f are correlated with each other as given in Eq(5). If τ_f is much 3 larger than $\alpha_{\rm L}$, the correlation between dielectric constant ε_r and temperature coefficient of 4 resonant frequency τ_f becomes almost linear, which is predictable in high range of ε_r^{45} . For the 5 present system, τ_f was primarily adjusted by τ_{ε} which ultimately depends on the dielectric 6 constant because the τ_f and ε_r exhibited similar decreasing trend as Al/Nb content increases in 7 $CaTi_{1-x}(Al_{0.5}Nb_{0.5})_{x}O_{3}$ ceramics as shown in Fig. 6. Also, in another aspect, τ_{f} indicates 8 symmetrical variation with ε_r as the co-substitution increases (Fig.7), and similarly, τ_{ε} becomes 9 more negative as octahedral tilting reduces with increasing tolerance factor t^{30} . As a result, the 10 temperature coefficient is predominantly reduced from 750ppm/°C to near-zero (5ppm/°C at 11 x=0.45) which is acceptable for the microwave devices and at higher value of x it varies towards 12 13 negative.

The formation of stable perovskite structure could be confirmed by the some standard range of 14 values for tolerance factor t and electronegativity difference Δe , which is $t \ge 0.80$ and Δe 15 \geq 1.465[46]. Tolerance factor (*t*) approximates the structure stability while the electro-negativity 16 difference (Δe) predicts the extent at which the excess binding energy exists between 'A' and 17 'B'-site atoms. Larger the electronegative difference (Δe), greater the structure stability[47]. 18 The value of t increases linearly as a function of x (see Table.1) representing the stable 19 perovskite structure which ultimately leads to the improved dielectric properties. The 20 electronegativity difference Δe is calculated by Pauling⁴⁸. For the present ceramics, both 21 conditions are fulfilled as t>0.96 and $\Delta e>2$. The bond characteristics of the present ceramics 22

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have been evaluated by degree of covalency of B-site calculated through the correlation 1 between bond strength (s) and covalency (f_c) given in. the following equations ⁴⁹⁻⁵⁰: 2 $s = \left(\frac{R}{R_1}\right)^{-N}$ (6)3 $f_c = as^M$ 4 (7)Degree of covalency (%) = $\frac{f_c}{s} \times 100$ 5 (8) where, R, R1 and N represents the refined average bond length, empirical constants and these 6 are different for each octahedral cation $-O^{-2}$ ion pair. Moreover, a and M in Eq. (7) are also the 7 empirical constants dependent upon the number of electrons ⁴⁹. Table 4. enlists the bond 8 strength (s) and average covalency (%) of $CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO_3$ ceramics. The bond strength 9 (s) and the relevant covalency (%) of the B-site atoms increases from (s=0.657 to 0.672) and 10 (covalency%=38.56 to 39.06%) with increase in x. 11

The Of increases with increasing the Al/Nb substitution in the present system as shown in Fig.7 12 13 (ii). It reaches to a maximum low loss value of 49,700 GHz at x=0.45 sintered at optimal temperature. The quality factor of any material depends on several extrinsic and intrinsic 14 factors such as defects, microstructural imperfections (pores, grain boundaries, and 15 dislocations), bond characteristics, secondary phases, density, structure stability etc⁵¹. As the 16 bond strength and the degree of covalency (%) increases by increasing the substitution of 17 Al/Nb at B-site, the stability of crystal structure enhances by the influence of lower vibration 18 restoring force 52-54. Therefore, for the composition x ≤ 0.45 it is considerable to relate 19 increasing trend of Qf with the increase in bond strength, degree of covalency (%) and reduced 20 rattling effect between B-site cation and oxygen octahedra. The rattling effect strongly relies on 21 the bond strength between the cation and oxygen ion in oxygen octahedron as it creates more 22

rigid octahedra which could decrease the rattling effect and consequently decreases the 1 dielectric constant⁵⁵. Moreover, as described above, the extrinsic dielectric losses also play 2 significant role affecting the Qf value for some compositions which includes grain size, 3 inhomogeneity, presence of secondary phases, impurities and grain boundary defects etc 56-57 4 Since there is no secondary phase detected in the entire composition range, its effect can be 5 neglected. The average grain size increases nonlinearly from ~16.53 to ~35.20 μ m between x=0 6 to x=0.45, boosting the Qf in the meanwhile. At x=0.45, the largest average grain size exhibited 7 the maximum value of Qf (see Table 3). The increase in average grain size enhances the Qf as 8 there are least grain boundaries which consecutively yields less grain boundary defects. For 9 compositions x \geq 0.60, a slight decline in *Of* value is dominated by the decrease in average grain 10 size which subsequently increases the grain boundary defects and inhomogeneities ⁵⁷. As a 11 result, for composition $x \le 0.45$ both intrinsic and extrinsic factors were promising for the 12 enhancement of *Qf*. However, for x \geq 0.60, the small deterioration of *Qf* was primarily effected 13 by the extrinsic dielectric loss. Fig. 7 shows the Qf value as a function of tolerance factor t. As t 14 is approaching to 1, the Qf value is increasing continuously. Since t ascribes the stability of 15 perovskite structure, so it should show favorable role in the improvement of Qf value. 16

17 Compared with the previous work on Sr_2TiO_4 -based solid solutions with Ruddlesdon Popper 18 structure,²⁰ the similar effects of (Al_{0.5}Nb_{0.5})-substitution are confirmed in the present system. 19 However, there are also some obvious differences between the previous and present systems, 20 and the biggest difference is the tuning mechanism on τ_f . The suppressed τ_f is mainly attributed 21 to the increased covalency (%) in the previous one, and the improved τ_f is primarily due to the 22 decreased tilting angle of oxygen octahedra.

1 IV. Conclusions

Single phase $CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO_3$ solid solutions with orthorhombic structure in space 2 group *Pbnm* were obtained throughout all composition range $x \le 0.75$. Both the temperature 3 coefficient of resonant frequency τ_f and and Qf value were significantly improved in the 4 present ceramics together with a medium dielectric constant of 30-50. The temperature 5 coefficient was tuned from 750 ppm/°C to near-zero (5ppm/°C, at x=0.45), and the Qf 6 value was increased from 11,500 GHz to 49,700 GHz. The best combination of microwave 7 dielectric characteristics were achieved at x=0.45 (ε_r =55.1, Qf=49,700 GHz, τ_f =5ppm/°C). 8 The present modified ceramics showed the great application potential in future wireless 9 communication systems. 10

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	<i>x</i> =0	<i>x</i> =0.025	<i>x</i> =0.10	<i>x</i> =0.30	<i>x</i> =0.45	<i>x</i> =0.60	<i>x</i> =0.75
a(Å)	5.3795	5.3805	5.3830	5.3846	5.3847	5.3863	5.3855
$b(\text{\AA})$	5.4430	5.4418	5.4443	5.4410	5.4385	5.43629	5.43232
$c(\text{\AA})$	7.6408	7.6415	7.6452	7.6455	7.6448	7.64572	7.6433
V[Å ³]	223.72	223.74	224.06	223.98	223.88	223.88	223.61
R _p	9.33	8.72	8.34	9.11	8.09	10.2	9.48
\mathbf{R}_{wp}	12.8	12.1	11.7	11.5	10.7	13.7	13.6
χ^2	1.96	1.75	1.77	1.98	1.84	1.86	1.95
t	0.9632	0.9665	0.9673	0.9691	0.9705	0.9719	0.9732

Table 1 Lattice parameters, Reliability factors and tolerance factor t of CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO₃ ceramics.

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Table 2 Dielectric properties of CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO₃ ceramics

Composition	Qf (GHz)	E _r	τ _f (ppm/°C)
<i>x</i> =0	11,500	170	760
<i>x</i> =0.025	15,400	148	682
<i>x</i> =0.10	21,500	115	487
<i>x</i> =0.30	34,300	70.3	120
<i>x</i> =0.45	49,700	55.1	5
<i>x</i> =0.60	45,550	33	-47
<i>x</i> =0.75	43,100	30	-80

CaTi ₁ . x(Al _{0.5} Nb _{0.5})xO ₃	Sintering condition (°C/3h)	Relative Density (%)	Average grain size (µm)
<i>x</i> =0	1525	98.5	16.53
<i>x</i> =0.025	1550	98.6	9.33
<i>x</i> =0.10	1550	98.3	26.60
<i>x</i> =0.30	1550	98.0	20.14
<i>x</i> =0.45	1550	99.3	35.20
<i>x</i> =0.60	1550	98.8	12.50
<i>x</i> =0.75	1550	98.9	18.95

Table 3 Relative density (%) and average grain size (μm) of CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO₃ ceramics

Table 4 Bond strength (s) and Covalency (%) of the B-site atoms for $CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO_3$ mics

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		R(Å)	R ₁	Ν	S	$f_{ m c}$	Covalency (%)	
<i>x</i> =0	Ti-O	1.958	1.806	5.2	0.656	0.2533	38.56	
<i>x</i> =0.025	Ti-O	1.9557	1.806	5.2	0.661	0.2557	38.69	
<i>x</i> =0.10	Ti-O	1.9578	1.806	5.2	0.657	0.2535	38.58	
<i>x</i> =0.30	Ti-O	1.9545	1.806	5.2	0.663	0.2571	38.76	
<i>x</i> =0.45	Ti-O	1.9534	1.806	5.2	0.665	0.2582	38.83	
<i>x</i> =0.60	Ti-O	1.9511	1.806	5.2	0.669	0.2607	38.97	
<i>x</i> =0.75	Ti-O	1.9580	1.806	5.2	0.672	0.2624	39.06	

List of Figure Captions

- 2 **Fig. 1** XRD patterns for $CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO_3$ ceramics: (a) x = 0, (b) x = 0.025, (c) x = 0.10 (d)
- 3 x = 0.30, (e) x = 0.45, (f) x = 0.60, (g) x=0.75.
- 4 **Fig. 2** Rietveld refinement patterns for $CaTi_{1-x}(Al_{0.5}Nb_{0.5})xO_3$ ceramics for x=0.30 and x=0.45.
- 5 **Fig. 3** (a) Variation of unit cell volume of $CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO_3$ ceramics and (b) tolerance 6 factor *t* as a function of x.
- **Fig. 4** Bulk density of $CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO_3$ ceramics as function of sintering temperature.
- Fig. 5 SEM micrographs of polished and thermally etched surfaces of CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO₃
 ceramics: (a) x = 0, (b) x = 0. 025, (c) x = 0. 10 (d) x = 0.30, (e) x = 0.45, (f) x = 0.60, (g) x=0.75.
- Fig. 6 (I) SAED pattern and (II) its corresponding high resolution TEM (HRTEM) image at zone
 axis [011]_c for x=0.45.
- Fig. 7 (a) Variation of ε_r and τ_f as a function of x ,(b) variation tendency of Qf as a function of x for CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO₃ ceramics.
- 15 **Fig. 8** Relationship between dielectric constant ε_r and dielectric polarizabilities $\alpha_{\text{Theo.}}(\text{Å}^3)$ for 16 CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO₃ ceramics.
- 17 **Fig. 9** Relationship between τ_f and tilting degree angle as a function of x.
- Fig. 10 (a) Variation tendency between Qf and degree of covelancy of B-site and (b) tolerance factor *t* for CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO₃ ceramics.
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Fig. 1 XRD patterns for CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO₃ ceramics: (a) x = 0, (b) x = 0.025, (c) x = 0.10 (d) 4 x = 0.30, (e) x = 0.45, (f) x = 0.60, (g) x=0.75.



Fig. 2 Rietveld refinement patterns for $CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO_3$ ceramics for x=0.30 and x=0.45.

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4 factor *t* as a function of x.

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Fig. 4 Bulk density of $CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO_3$ ceramics as function of sintering temperature.







2 Fig. 6 (I) SAED pattern and (II) its corresponding high resolution TEM (HRTEM) image at zone

3 axis $[01\overline{1}]_c$ for x=0.45.



Fig. 7 (a) Variation of ε_r and τ_f as a function of x ,(b) variation tendency of Qf as a function of x

4 for $CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO_3$ ceramics.

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Fig. 8 Relationship between dielectric constant ε_r and dielectric polarizabilities $\alpha_{\text{Theo.}}(\text{Å}^3)$ for 5 $\text{CaTi}_{1-x}(\text{Al}_{0.5}\text{Nb}_{0.5})_x\text{O}_3$ ceramics.



Fig. 9 Relationship between τ_f and tilting degree angle as a function of x.



Fig. 10 (a) Variation tendency between Qf and degree of covalency of B-site and (b) tolerance factor *t* for CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO₃ ceramics.

Highlights

- CaTi_{1-x}(Al_{0.5}Nb_{0.5})_xO₃ solid solutions with orthorhombic structure in space group Pbnm were attained.
- The near-zero temperature coefficient of resonant frequency τ_f and significantly • improved Qf value were achieved.
- The best combination of microwave dielectric characteristics was achieved at x=0.45: ε_r=55.1, *Qf*=49,700 GHz, τ_f=5ppm/°C.

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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