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Novel Method to Achieve Temperature Stable Microwave Dielectric Ceramics: A Case in Fergusonite Structured NdNbO₄ System

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ABSTRACT

Microwave dielectric ceramics with permittivity (ϵ_r) ~ 20 play an important role in massive multiple-input multiple-output (MIMO) technology in 5G. Although fergusonite-structured materials with low dielectric loss are good candidates for 5G application, tuning the temperature coefficient of resonant frequency (TCF) remains a problem. In the present work, smaller V^{5+} ions ($r_V = 0.355 \text{ \AA}$, with coordination number (C.N.) = 4) were substituted for Nb^{5+} ($r_{Nb} = 0.48 \text{ \AA}$ with C.N. = 4) in the $Nd(Nb_{1-x}V_x)O_4$ ceramics which, according to *in-situ* X-ray diffraction data, lowered the fergusonite to scheelite phase transition (T_{F-S}) to $400 \text{ }^\circ\text{C}$ for $x = 0.2$. The thermal expansion coefficient (α_L) of the high temperature scheelite phase was $+11 \text{ ppm}/^\circ\text{C}$, whereas for the low temperature fergusonite phase $+14 < \alpha_L < +15 \text{ ppm}/^\circ\text{C}$. The abrupt change in α_L , the associated negative temperature coefficient of permittivity (τ_ϵ) and the minimum value of ϵ_r at T_{F-S} resulted in a near-zero TCF $\sim (+7.8 \text{ ppm}/^\circ\text{C})$ for the $Nd(Nb_{0.8}V_{0.2})O_4$ ($\epsilon_r \sim 18.6$ and $Qf \sim 70,100 \text{ GHz}$). A method to design near-zero TCF compositions based on modulation of τ_ϵ and α_L at T_{F-S} is thus demonstrated that may also be extended to other fergusonite systems.

Keywords: Microwave dielectric ceramics; Fergusonite; Scheelite; Dielectric Resonator; Temperature coefficient of resonant frequency

1. Introduction

Dielectric ceramics play a key role in modern microwave devices as dielectric resonators and filters, antenna substrates, class I multilayer capacitors and low temperature co-fired ceramics (LTCC).¹⁻⁵ With the development of 5th generation technology (5G), demand of dielectric filters with ultra-high quality factors ($Q=1/\text{dielectric loss}$) is increasing for massive MIMO (multiple-input multiple-output) technology, which is widely used in the current generation of 5G base stations (sub-6 GHz).⁶⁻⁹ The resonant frequency (f) is well-known to be proportional to the inverse square root of dielectric constant / permittivity (ϵ_r) ($f \propto \frac{1}{\sqrt{\epsilon_r}}$) and ceramics with $\epsilon_r \sim 20$ (commercially referred to as K20) are suitable for dielectric filters working at sub-6 GHz with dimensions of the order of a few centimeters.

Now, the market for K20 ceramics is mainly met by $\text{MgTiO}_3\text{-(Ca, Sr, Ln)TiO}_3$ or $\text{Mg}_2\text{TiO}_4\text{-(Ca, Sr, Ln)TiO}_3$ ($\text{Ln} = \text{Lanthanides}$) due to the low-cost, acceptable Qf ($> 60,000 \text{ GHz}$) and low bulk density (3.6 g/cm^3).¹⁰⁻¹⁶ The main phase of this system is ilmenite-structured MgTiO_3 which has a high Qf but negative temperature coefficient of frequency (TCF) which is compensated by CaTiO_3 which has a large positive TCF. However, microwave dielectric properties of this system are unstable over the whole of the anticipated working temperature ($- 55 \text{ }^\circ\text{C}$ to $+ 125 \text{ }^\circ\text{C}$). Compared with $\text{MgTiO}_3\text{-CaTiO}_3$ system, the Ruddlesden-Popper structured $\text{CaLnAlO}_4\text{-Ca}_2\text{TiO}_4$ ($\text{Ln} = \text{lanthanide}$) system usually has a higher Qf ($90,000 \text{ GHz}$) and a wider range of temperature stability¹⁷⁻²² but its bulk density is 4.9 g/cm^3 , adding unnecessary weight to 5G base stations. Moreover, Li_2TiO_3 solid solutions have also caught massive attention due to their high Qf ($>90,000 \text{ GHz}$) and relative low sintering temperature $< 1150 \text{ }^\circ\text{C}$ ²³⁻²⁶ but the weak solubility of Li_2CO_3 in water adds complexity and cost to

ceramic fabrication. Microwave dielectric properties of the above systems are summarized in Table 1.

In addition to the above three ceramic systems, fergusonite-structured $LnNbO_4$ (Ln = lanthanide) is also a potential K20 microwave dielectric with high Q_f (>30,000 GHz). $LnNbO_4$ series materials undergo ferroelastic phase transition from monoclinic fergusonite to tetragonal scheelite structure whose temperature (T_{F-S}) varies with the Ln ion radius from ~ 480°C of $LaNbO_4$ to 860°C of $SmNbO_4$.^{3,27-33} In the previous work,³³ we have demonstrated anomalous dielectric behavior in $La(Nb_{0.9}V_{0.1})O_4$ such that a minimum (not a usual maximum value at phase transition temperature) of ϵ_r is observed at T_{F-S} (~350 °C). This phenomenon was explained by a combination of the Shannon's additive rule and Clausius–Mosotti relation based on the assumption of linear increases in ionic polarizabilities. Here, an unique ϵ_r minimum is explored to design a temperature-independent K20 microwave dielectric ceramic with high Q_f in the solid solution, $Nd(Nb_{1-x}V_x)O_4$.

2. Materials and methods

a) Sample preparation.

Traditional solid state reaction method was employed to prepare the $Nd(Nb_{1-x}V_x)O_4$ ($0 \leq x \leq 0.2$) ($x = 0, 0.1$ and 0.2) ceramics, using Nd_2O_3 (> 99.9%), V_2O_5 , (> 99.2%) and Nb_2O_5 (> 99.5%) as initial materials, with a calcination temperature ~ 1150 °C and sintering temperatures between 1250 °C to 1350 °C in air.

b) Characterization and Electrical measurements.

Room temperature powder X-ray diffraction (PXRD) was performed using with $CuK\alpha$ radiation (Bruker D2 Phaser) in the range of 10-75 ° with a step size of 0.02 °. PXRD patterns at high temperatures were collected using a Siemens D5000 diffractometer upon Pt foil holder from 25 to 700 °C. FULLPROF program was

selected to perform the refinements. Thermally etched surfaces were observed by using scanning electron microscopy (SEM, FEI, Inspect F). Thermal expansion data were monitored in temperature range from 25 to 750 °C. Dielectric properties were obtained over gold coated ceramics from 25 to 700 °C with a heating/cooling rate of 1 °C/min using a LCR meter (Agilent E4980A) in a temperature chamber at frequencies 100 kHz ~ 1 MHz. Room temperature infrared spectra were collected using a Bruker IFS 66v FT-IR spectrometer at the National Synchrotron Radiation Lab (NSRL), China (Infrared beamline station, U4). Dielectric properties at microwave frequencies (about 7 GHz) were measured using the TE_{01δ} method³⁴ with a network vector analyzer equipped with a home-made heating system. Temperature coefficients of resonant frequency TCF/τ_f were calculated according to the following equation:

$$TCF(\tau_f) = \frac{f_{85} - f_{25}}{f_{25} \times (85 - 25)} \times 10^6, \quad (1)$$

where f_{85} and f_{25} are the TE_{01δ} resonant frequencies at 85 °C and 25 °C, respectively.

3. Results and Discussions

As shown in Fig. 1, all the Nd(Nb_{1-x}V_x)O₄ ceramics crystallize in the fergusonite structure with no secondary phase, indicating that V feasibly substitutes Nb in the system. The crystal structure and PXRD data refinement profiles of Nd(Nb_{0.9}V_{0.1})O₄ and Nd(Nb_{0.8}V_{0.2})O₄ ceramics are shown in Fig. 1(e) and (f), giving the refined unit cell parameters of the Nd(Nb_{0.9}V_{0.1})O₄ ceramic at 25 °C of $a = 5.4367(5)$ Å, $b = 11.3356(6)$ Å, $c = 5.1590(7)$ Å, $\beta = 93.699(3)^\circ$, with the space group *I12/c1* (No. 15) and $a = 5.3982(9)$ Å, $b = 11.3828(7)$ Å, $c = 5.1751(9)$ Å, $\beta = 92.865(1)^\circ$, with space group *I12/c1* (No. 15) of Nd(Nb_{0.8}V_{0.2})O₄. All the details of refinements are presented in Table 2 and Table 3. From the XRD patterns, as x increases, the (1 $\bar{2}$ 1) and the (031)

peaks gradually converge, suggesting that the β angle in the unit cell continuously decreases to ~ 90 degrees. Fig. 1(b) and (c) present the *in-situ* PXRD patterns from 25 to 700 °C and 25 to 500 °C for Nd(Nb_{0.9}V_{0.1})O₄ and Nd(Nb_{0.8}V_{0.2})O₄, respectively. The characteristic peaks (011)/(110), ($\bar{1}\bar{2}1$)/(031), (002)/(200) move closer to each other as temperature increases and eventually merge into respective single-peaks at 600 °C and 400 °C of Nd(Nb_{0.9}V_{0.1})O₄ and Nd(Nb_{0.8}V_{0.2})O₄, respectively, again demonstrating that the crystal structure changes continuously from the monoclinic fergusonite structure to the tetragonal scheelite one. Compared with Nb⁵⁺ (0.48 Å in tetrahedron), V⁵⁺ has a smaller ionic radius (0.355 Å with CN = 4)³⁵ and the substitution over Nb in the fergusonite structure diminishes the distortion of the tetrahedra, as shown in the schematic of Fig. 1(d). Nb⁵⁺ ions prefer 6 coordinated environment in most circumstances, for instance, BiNbO₄, Ba(Zn_{1/3}Nb_{2/3})O₃ etc.^{36,37} However, in the monoclinic fergusonite structure, Nb⁵⁺ ions are effectively 4-coordinated due to two of the Nb-O bonds are significantly longer than the other four (2.47 Å >> 1.92 Å > 1.84 Å). In most compounds, V⁵⁺ ions are 4 coordinated³⁸ and the subsequent substitution over Nb⁵⁺ results in a reduction of the degree of distortion at the BO₄ tetrahedra. Correspondingly, a decrease of the ferroelastic phase transition temperature from 720 °C (NdNbO₄) to 400 °C (Nd(Nb_{0.8}V_{0.2})O₄) was observed.

The unit cell parameters of Nd(Nb_{0.9}V_{0.1})O₄ and Nd(Nb_{0.8}V_{0.2})O₄ as a function of temperature are plotted in Fig. 2(a), derived from the high temperatures PXRD refinement results. As temperature increases, the unit cell parameter a decreases while c increases accompanied by a decrease in β . At the temperature point T_{F-S}, a and c become equal and the β angle resolves to 90°, indicating the occurrence of the phase transition to the tetragonal scheelite structure. b continuously increases in the whole

temperature range and is much larger than a and c . The cell volumes of $\text{Nd}(\text{Nb}_{0.9}\text{V}_{0.1})\text{O}_4$ and $\text{Nd}(\text{Nb}_{0.8}\text{V}_{0.2})\text{O}_4$ present similar change trends to those of b . This may be the reason of the abrupt change in thermal expansion coefficient at $T_{\text{F-S}}$, see Fig. 2b, from +14 ~ +15 ppm/°C to +11 ppm/°C of the fergusonite and the scheelite phases, respectively. This anomaly in thermal expansion was first observed in $\text{La}(\text{Nb}_{0.9}\text{V}_{0.1})\text{O}_4$ at the $T_{\text{F-S}}$ transition point and also in BiVO_4 at the monoclinic to tetragonal scheelite structure transition temperature point.^{33,38}

Further HRTEM images were captured to illustrate the relationship among V substitution, microstructure and dielectric properties, as seen from Fig. 3. Clear domain regions and lattice fringes could be observed in both $\text{Nd}(\text{Nb}_{0.9}\text{V}_{0.1})\text{O}_4$ and $\text{Nd}(\text{Nb}_{0.8}\text{V}_{0.2})\text{O}_4$ ceramics. Meanwhile, the differences between the two sets of HRTEM images are apparent. With a larger amount of V substitution, the size of the domains reduces from 28(2) nm, $x = 0.1$, to 9.6(6) nm, $x = 0.2$, along with the (2 0 0) plane average interplanar spacing reduction from 2.62(3) Å, $x = 0.1$, to 2.53(3) Å, $x = 0.2$. The result is not surprising because of the ionic radii difference. This may also be the reason for the present of the anomaly in the temperature-dependent dielectric permittivity spectra. Moreover, the domain alternation could be indicated as $\sim 94^\circ$ rotation, equivalent to the β angle.

SEM images of the $\text{Nd}(\text{Nb}_{1-x}\text{V}_x)\text{O}_4$ ($0 \leq x \leq 0.2$) solid solution ceramics are shown in Fig. 4. The microstructures present homogeneous and dense (> 98.5% relative) in all the ceramics sintered at optimal temperatures. However, the substitution of Nb by V did not lower the sintering temperature remarkably as expected but could decrease the grain size from 4 ~ 8 μm to 1 ~ 3 μm .

The dielectric permittivity ϵ_r and the dielectric loss of the $\text{Nd}(\text{Nb}_{1-x}\text{V}_x)\text{O}_4$ ($x = 0.1$ and 0.2) ceramics as a function of temperature at 100 kHz, 250 kHz, 1 MHz and 7.2

GHz are plotted in Fig. 5. ϵ_r of $\text{Nd}(\text{Nb}_{0.9}\text{V}_{0.1})\text{O}_4$ and $\text{Nd}(\text{Nb}_{0.8}\text{V}_{0.2})\text{O}_4$ ceramics reach their minimum value at $T_{\text{F-S}}$, concomitant with the change trend of the thermal expansion coefficient and also seen in the $\text{La}(\text{Nb}_{0.9}\text{V}_{0.1})\text{O}_4$.³³ The correlation of the change in thermal expansion coefficient and ϵ_r relates to the change in cell volume and its influence on ionic polarizability at $T_{\text{F-S}}$.³³ Notably, the dielectric anomaly is frequency-dependent in $\text{Nd}(\text{Nb}_{0.9}\text{V}_{0.1})\text{O}_4$ but not in $\text{Nd}(\text{Nb}_{0.8}\text{V}_{0.2})\text{O}_4$. Moreover, there is a secondary broad anomaly in $\text{Nd}(\text{Nb}_{0.9}\text{V}_{0.1})\text{O}_4$ in the range of 25 ~ 200 °C but is absent in $\text{Nd}(\text{Nb}_{0.8}\text{V}_{0.2})\text{O}_4$, both of which require further investigation. Limited by the equipment, microwave dielectric properties at 7.2 GHz were obtained from room temperature to 120 °C. The ϵ_r at 7.2 GHz data is smaller than that measured at lower frequencies but shows a similar trend, supporting the calculated TCF value.

The microwave dielectric properties (ϵ_r , Qf and TCF) of the $\text{Nd}(\text{Nb}_{1-x}\text{V}_x)\text{O}_4$ ($0 \leq x \leq 0.2$) ceramics as a function of x are presented in Fig. 6. ϵ_r decreased linearly from 19.6 of NdNbO_4 to 18.6 of $\text{Nd}(\text{Nb}_{0.8}\text{V}_{0.2})\text{O}_4$, which could be attributed to the smaller ionic polarizability of V^{5+} than that of Nb^{5+} ($2.92 \text{ \AA}^3 < 3.97 \text{ \AA}^3$).^{33,38-41} The Qf value increases from ~ 33,000 GHz to ~ 70,100 GHz as x increases from 0 to 0.2, along with the TCF shifts from - 39 ppm/°C to + 7.8 ppm/°C. The latter may be understood by ϵ_r -temperature dependence and thermal expansion associated with $T_{\text{F-S}}$ transition. The relation function between TCF and temperature-dependence of permittivity could be written as

$$\text{TCF} = -(\alpha_L + 1/2\tau_\epsilon) \quad (2)$$

in which τ_ϵ is the temperature coefficient of ϵ_r and α_L is the linear thermal expansion. As x increases to 0.2, the decrease in ϵ_r at 400 °C leads to a negative τ_ϵ value, which is opposite to the positive thermal expansion coefficient and correspondingly resulting in near zero TCF. Phase transition temperatures obtained from the *in-situ* XRD were

also plotted in Fig. 6(b). It is clearly that at room temperature all the $\text{Nd}(\text{Nb}_{1-x}\text{V}_x)\text{O}_4$ ceramics belong to single fergusonite structure and the modifications of TCF can be attributed totally to the complex influence of negative τ_e and positive α_L values. To avoid other extrinsic influence, such as space charge polarizations and dipole polarizations, we further studied intrinsic dielectric properties of the $\text{Nd}(\text{Nb}_{1-x}\text{V}_x)\text{O}_4$ ($x = 0.1$ and 0.2) ceramics, far-infrared reflectivity spectra were fitted to calculate the complex permittivity (ϵ_r) as shown in Fig. 7. Good agreements of measured and fitted infrared spectra were obtained and the extrapolated ϵ_r to the microwave region agrees well with the measured values by $\text{TE}_{01\delta}$ method, which further confirms that only the lattice vibrations at infrared region of the $\text{Nd}(\text{Nb}_{1-x}\text{V}_x)\text{O}_4$ ($x = 0.1$ and 0.2) ceramics give contributions to the ϵ_r and phonon absorptions determine the intrinsic dielectric loss in the microwave region. Combined with the crystal structure, thermal expansion, and microwave dielectric properties above, this novel mechanism to tune TCF is feasible in other LnNbO_4 ($\text{Ln} = \text{lanthanide}$) microwave dielectric ceramics, proved by far-infrared reflectivity analysis where the ionic polarization mainly dominates the microwave ϵ_r and dielectric loss. The comparisons of microwave dielectric properties of K20 materials discussed here are listed in Table 1 for comparison with other K20s. Taking advantage of the permittivity “valley” of LnNbO_4 ($\text{Ln} = \text{lanthanide}$) materials at ferroelastic phase transition, near-zero TCF values could be achieved by rational design.

4. Conclusions

The substitution V over Nb in the NdNbO_4 ceramic lowered the ferroelastic phase transition ($T_{\text{F-S}}$) from $720\text{ }^\circ\text{C}$ of NdNbO_4 to $400\text{ }^\circ\text{C}$ of $\text{Nd}(\text{Nb}_{0.8}\text{V}_{0.2})\text{O}_4$, resulting in not only a minimum occurrence in permittivity at $T_{\text{F-S}}$ in $\text{Nd}(\text{Nb}_{0.9}\text{V}_{0.1})\text{O}_4$ and $\text{Nd}(\text{Nb}_{0.8}\text{V}_{0.2})\text{O}_4$ ceramics at $600\text{ }^\circ\text{C}$ and $400\text{ }^\circ\text{C}$, respectively, but also an abrupt

change in thermal expansion coefficient. The negative temperature coefficient of permittivity and positive thermal expansion coefficient of the $\text{Nd}(\text{Nb}_{0.8}\text{V}_{0.2})\text{O}_4$ ceramic leads to a near-zero temperature coefficient of resonant frequency. Excellent microwave dielectric properties performance could be achieved in the $\text{Nd}(\text{Nb}_{0.8}\text{V}_{0.2})\text{O}_4$ ceramic with the permittivity ~ 18.6 , the $Q_f \sim 70,100$ GHz and the TCF $\sim +7.8$ ppm/ $^{\circ}\text{C}$. Eventually, a novel method of tuning temperature stability in microwave dielectric ceramics with high Q_f value in the $\text{Nd}(\text{Nb}_{1-x}\text{V}_x)\text{O}_4$ ($0 \leq x \leq 0.2$) ceramics is demonstrated through adjusting T_{F-S} with an associated modification of α_L and τ_{ϵ} . Further study on modifications of the wide temperature stability will benefit various applications of microwave dielectric devices.

Declaration of Competing Interest

The authors declare no competing interests.

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References

- (1) Sebastian, M. T.; Jantunen, H. Low Loss Dielectric Materials for LTCC Applications: A Review. *Int. Mater. Rev.* **2008**, *53*, 57–90.
- (2) Reaney, I. M.; Iddles, D. M. Microwave Dielectric Ceramics for Resonators and Filters in Mobile Phone Networks. *J. Am. Ceram. Soc.* **2006**, *89*, 2063–2072.
- (3) Wu, F. F.; Zhou, D.; Du, C.; Jin, B. B.; Li, C.; Qi, Z. M.; Sun, S. K.; Zhou, T.; Li, Q.; Zhang, X. Design of a Sub-6 GHz Dielectric Resonator Antenna with Novel Temperature Stabilized $(\text{Sm}_{1-x}\text{Bi}_x)\text{NbO}_4$ ($x=0-0.15$) Microwave Dielectric Ceramics. *ACS Appl. Mater. Interfaces* **2022**, *14*[5], 7030–7038.
- (4) Du, C.; Fu, M. S.; Zhou, D.; Guo, H. H.; Chen, H. T.; Zhang J.; Wang, J. P.; Wang, S. F.; Liu, H. W.; Liu, W. F.; Li, L.; Xu, Z. Dielectric Resonator Antenna with $\text{Y}_3\text{Al}_5\text{O}_{12}$ Transparent Dielectric Ceramics for 5G Millimeter-Wave Applications. *J. Am. Ceram. Soc.* **2021**, *104*[9], 4659-4668.
- (5) Qin J. C.; Liu Z. F.; Ma, M. S.; Liu, F.; Qi, Z. M.; Li, Y. X. Structure and Microwave Dielectric Properties of Gillespite-Type $\text{ACuSi}_4\text{O}_{10}$ ($A = \text{Ca}, \text{Sr}, \text{Ba}$) Ceramics and Quantitative Prediction of the $Q \times f$ Value via Machine Learning. *ACS Appl. Mater. Interfaces* **2021**, *13*[15], 17817-17826.
- (6) Elijah, O.; Leow, C. Y.; Rahman, T. A.; Nunoo, S.; Iliya, S. Z. Comprehensive Survey of Pilot Contamination in Massive MIMO 5G System. *IEEE Commun. Surv. Tutorials* **2016**, *18*, 905–923.
- (7) Xiao, K.; Gong, L.; Kadoch, M. Opportunistic Multicast NOMA with Security Concerns in a 5G Massive MIMO System. *IEEE Commun. Mag.* **2018**, *56*, 91–95.
- (8) Khan, I.; Zafar, M.; Jan, M.; Lloret, J.; Basher, M.; Singh, D. Spectral and Energy Efficient Low-Overhead Uplink and Downlink Channel Estimation for 5G Massive

MIMO Systems. *Entropy* **2018**, *20*, 92.

(9) Liu, F.; Guo, J.; Zhao, L.; Shen, X.; Yin, Y. A Meta-Surface Decoupling Method for Two Linear Polarized Antenna Array in Sub-6 GHz Base Station Applications. *IEEE Access* **2019**, *7*, 2759–2768.

(10) Li, H.; Tang, B.; Li, X.; Qing, Z.; Li, Y.; Yang, H.; Wang, Q.; Zhang, S. The Structure and Properties of 0.95MgTiO₃–0.05CaTiO₃ Ceramics Doped with Co₂O₃. *J. Mater. Sci.* **2014**, *49*, 5850–5855.

(11) H. Jantunen, R. Rautioaho, A. Uusimäki, S. Leppävuori, Compositions of MgTiO₃-CaTiO₃ Ceramic with Two Borosilicate Glasses for LTCC Technology. *J. Eur. Ceram. Soc.* **2000**, *20*, 2331-2336.

(12) Huang, C. L.; Chen, J. Y.; Li, B. J. A New Dielectric Material System Using (1 – x)(Mg_{0.95}Co_{0.05})₂TiO₄–xCa_{0.8}Sm_{0.4/3}TiO₃ at Microwave Frequencies. *Mater. Chem. Phys.* **2010**, *120*, 217–220.

(13) Huang, C. L.; Chen, J. Y.; Huang G. S. A New Low-loss Dielectric using CaTiO₃-Modified (Mg_{0.95}Mn_{0.05})TiO₃ Ceramics for Microwave Applications. *J. Alloys Comp.* **2010**, *499*, 48–52.

(14) Huang, C. L.; Chen, J. Y.; Li B. J. A New Dielectric Material System using (1-x)(Mg_{0.95}Co_{0.05})₂TiO₄–xCa_{0.8}Sm_{0.4/3}TiO₃ at Microwave Frequencies. *Mater. Chem. Phys.* **2010**, *120*, 217–220.

(15) Huang, C. L.; Liu S.S. Dielectric Characteristics of the (1-x)Mg₂TiO₄–xSrTiO₃ Ceramic System at Microwave Frequencies. *J. Alloys Comp.* **2009**, *471*, L9–L12.

(16) Huang, C. L.; Liu S.S. High-Q Microwave Dielectric in the (1-x)MgTiO₃–xCa_{0.6}La_{0.8/3}TiO₃ Ceramic System with A Near-zero Temperature

- Coefficient of the Resonant Frequency. *Mater. Lett.* **2008**, 62, 3205–3208.
- (17) Fan, X. C.; Chen, X. M. Effects of Ca/Ti Co-Substitution upon Microwave Dielectric Characteristics of CaSmAlO₄ Ceramics. *J. Am. Ceram. Soc.* **2009**, 92, 433–438.
- (18) Ren, G. R.; Zhu, J. Y.; Li, L.; Liu, B.; Chen, X. M. SrLa(R_{0.5}Ti_{0.5})O₄ (R=Mg, Zn) Microwave Dielectric Ceramics with Complex K₂NiF₄-Type Layered Perovskite Structure. *J. Am. Ceram. Soc.* **2017**, 100[6], 2582-2589.
- (19) Mao, M. M.; Chen, X. M.; Liu, X. Q. Structure and Microwave Dielectric Properties of Solid Solution in SrLaAlO₄-Sr₂TiO₄ System. *J. Am. Ceram. Soc.* **2011**, 94[11], 3948-3952.
- (20) Liu, B.; Yi, L.; Li L.; Chen, X. M. Densification and Microwave Dielectric Properties of Ca_{1.15}Sm_{0.85}Al_{0.85}Ti_{0.15}O₄ Ceramics with B₂O₃ Addition. *J. Alloys Comp.* **2015**, 653, 351-357.
- (21) Mao, M. M.; Fan, X. C.; Chen, X. M. Effect of A-Site Ionic Radius on the Structure and Microwave Dielectric Characteristics of Sr_{1+x}Sm_{1-x}Al_{1-x}Ti_xO₄ Ceramics, *Int. J. Appl. Ceram. Technol.* **2010**, 7, E156-E162.
- (22) Xiao, Y.; Chen, X. M.; Liu, X. Q. Microstructures and Microwave Dielectric Characteristics of CaRAlO₄ (R = Nd, Sm, Y) Ceramics with Tetragonal K₂NiF₄ Structure. *J. Am. Ceram. Soc.* **2004**, 87, 2143-2146.
- (23) Pang, L. X.; Zhou, D. Microwave Dielectric Properties of Low-Firing Li₂MO₃ (M = Ti, Zr, Sn) Ceramics with B₂O₃-CuO Addition. *J. Am. Ceram. Soc.* **2010**, 93[11], 3614-3617.
- (24) Bian, J. J.; Dong, Y. F. New High Q Microwave Dielectric Ceramics with Rock Salt Structures: (1-x)Li₂TiO₃+xMgO System (0 ≤ x ≤ 0.5). *J. Eur. Ceram. Soc.* **2010**, 30, 325–330.

- (25) Guo, H. H.; Fu, M. S.; Zhou, D.; Du, C.; Wang, P. J.; Pang, L. X.; Liu, W. F.; Sombra, A. S. B.; Su, J. Z. Design of High Efficiency and Gain Antenna Using Novel Low Loss, Temperature Stable $\text{Li}_2\text{Ti}_{1-x}(\text{Cu}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$ Microwave Dielectric Ceramics. *ACS Appl. Mater. Interfaces*, **2021**, *13*[1], 912–923.
- (26) Guo, H. H.; Zhou, D.; Du, C.; Wang, P. J.; Liu, W. F.; Pang, L. X.; Wang, Q. P.; Su, J. Z.; Singh, C.; Trukhanov, S. Temperature Stable $\text{Li}_2\text{Ti}_{0.75}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.25}\text{O}_3$ Based Microwave Dielectric Ceramics with Low Sintering Temperature and Ultra-Low Dielectric Loss for Dielectric Resonator Antenna Applications. *J. Mater. Chem. C* **2020**, *8*, 4690–4700.
- (27) Kim, D. W.; Kwon, D. K.; Yoon, S. H.; Hong, K. S. Microwave Dielectric Properties of Rare-Earth Ortho-Niobates with Ferroelasticity. *J. Am. Ceram. Soc.* **2006**, *89*, 3861–3864.
- (28) McCarthy, G. J. X-Ray Studies of RENbO_4 Compounds. *Acta Cryst.* **1971**, *B27*, 2285–2286.
- (29) Zhang, P.; Song, Z.; Wang, Y.; Li, L. Effect of Ion Substitution for Nd^{3+} Based on Structural Characteristic on the Microwave Dielectric Properties of NdNbO_4 Ceramic System. *J. Am. Ceram. Soc.* **2014**, *97*, 976–981.
- (30) Pang, L. X.; Zhou, D. Modification of NdNbO_4 Microwave Dielectric Ceramic by Bi Substitutions. *J. Am. Ceram. Soc.* **2019**, *102*, 2278–2282.
- (31) Ramarao, S. D.; Murthy, V. R. K. Structural Phase Transformation and Microwave Dielectric Studies of $\text{SmNb}_{1-x}(\text{Si}_{1/2}\text{Mo}_{1/2})_x\text{O}_4$ Compounds with Fergusonite Structure. *Phys. Chem. Chem. Phys.* **2015**, *17*, 12623–12633.
- (32) Lim, H.; Oh, Y. J. Low-Temperature Sintered $\text{Bi}_{1-x}\text{Sm}_x\text{NbO}_4$ Microwave Dielectrics. *J. Eur. Ceram. Soc.* **2020**, *40*, 1191–1197.
- (33) Zhou, D.; Guo, H. H.; Fu, M. S.; Yao, X. G.; Lin, H. X.; Liu, W. F.; Pang, L. X.;

- Singh, C.; Trukhanov, S.; Trukhanov, A.; Reaney, I. M. Anomalous Dielectric Behaviour During the Monoclinic to Tetragonal Phase Transition in $\text{La}(\text{Nb}_{0.9}\text{V}_{0.1})\text{O}_4$. *Inorganic Chemistry Frontiers*, **2021**, 8, 156–163.
- (34) Krupka, J.; Derzakowski, K.; Riddle, B.; Baker-Jarvis, J. A Dielectric Resonator for Measurements of Complex Permittivity of Low Loss Dielectric Materials as A Function of Temperature. *Meas. Sci. Technol.* **1998**, 9, 1751–1756.
- (35) Shannon, R. D. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Cryst.* **1976**, A32, 751-767.
- (36) Roth, R.S.; Waring, J. L. Phase Equilibrium Relations in the Binary System Bismuth Sesquioxide-Niobium Pentoxide. *J. Res. National Bureau Standards Sec. A-Phys. Chem.* **1962**, 66[6], 451-463.
- (37) Mani, R.; Bhuvanesh, N. S. P.; Ramanujachary, K. V.; Green, W.; Lofland, S. E.; Gopalakrishnan, J. A Novel One-Pot Metathesis Route for The Synthesis of Double Perovskites, $\text{Ba}_3\text{MM}'_2\text{O}_9$ (M = Mg, Ni, Zn; M' = Nb, Ta) with 1 : 2 Ordering of M and M' Atoms. *J. Mater. Chem.* **2007**, 17, 1589-1592.
- (38) Zhou, D.; Pang, L. X.; Wang, D. W.; Reaney, I. M. BiVO_4 Based High k Microwave Dielectric Materials: A Review. *J. Mater. Chem. C* **2018**, 6, 9290-9313.
- (39) Yamauchi, H.; Tsunekawa, S.; Tomiyoshi, S.; Fukuda, T.; Kamiyama, T.; Asano, H. Anomalous Paramagnetic Property of NdNbO_4 Single Crystals. *J. Phys. Soc. Japan*, **1990**, 59[7], 2602-2603.
- (40) Tsunekawa, S.; Kamiyama, T.; Sasaki, K.; Asano, H.; Fukuda, T. Precise Structure Analysis by Neutron Diffraction for RNbO_4 and Distortion of NbO_4 Tetrahedra. *Acta Crystallographica A* **1993**, 49, 595-600.
- (41) Shannon, R. D. Dielectric Polarizabilities of Ions in Oxides and Fluorides. *J. Appl. Phys.* **1993**, 73, 348–366.

Table 1 Microwave dielectric properties of K20 materials

System	S.	T.	ϵ_r	Qf	TCF	Ref.
	(°C)			(GHz)	(ppm/°C)	
MgTiO ₃ / Mg ₂ TiO ₄ - (Ca, Ln)TiO ₃ ,	1250	19~23		60,000	~ -5 ~ +5	10-16
Ln = lanthanide	~1350			10,000		
(Ca, Sr)LnAlO ₄ , Ln= lanthanide	1400	18~20		30,000	~ -10 ~ +10	22
	~1550			50,000		
(Ca, Sr)Ln(Al, Ti)O ₄ , Ln= lanthanide	1450	19~22		80,000	~ -5 ~ +5	17-21
	~1550			10,000		
Li ₂ (Ti, (M ²⁺ _{1/3} M ⁵⁺ _{2/3}))O ₃ , M ²⁺ =Zn,	1000	18~20		60,000	~ -5 ~ +5	23-26
Mg, Cu; M ⁵⁺ =Nb, Ta	~1200			10,000		
LnNbO ₄ , Ln= lanthanide	1250	18~20		30,000	~ -40 ~ +10	27
	~1500			60,000		
Ln(Nb, V)O ₄ , Ln= lanthanide	1250	17~20		40,000	~ -5 ~ +5	28-33
	~1400			80,000		

Table 2 Refined atomic fractional coordinates from XRD data for Nd(Nb_{0.9}V_{0.1})O₄ sample at room temperature and the lattice parameters are $a = 5.4367(5) \text{ \AA}$, $b = 11.3356(6) \text{ \AA}$, $c = 5.1590(7) \text{ \AA}$, $\beta = 93.699(3)^\circ$. The space group is I12/c1 (No. 15).

Atom	Site	Occ.	x	y	z	B (\AA^2)
Nd	4e	0.5	0.2500	0.1203(1)	0.0000	0.65(6)
Nb	4e	0.45	0.2500	0.6433(1)	0.0000	0.39(3)
V	4e	0.05	0.2500	0.6433(1)	0.0000	0.39(3)
O1	8f	1.00	0.0068(7)	0.7097(2)	0.1913(9)	1.10(5)
O2	8f	1.00	0.9241(7)	0.4482(3)	0.2414(3)	2.17(1)

Table 3 Refined atomic fractional coordinates from XRD data for Nd(Nb_{0.8}V_{0.2})O₄ sample at room temperature and the lattice parameters are a = 5.3982(9) Å, b = 11.3828(7) Å, c = 5.1751(9) Å, $\beta = 92.865(1)^\circ$. The space group is I12/c1 (No. 15).

Atom	Site	Occ.	x	y	z	B (Å ²)
Nd	4e	0.5	0.2500	0.1215(3)	0.0000	0.26(2)
Nb	4e	0.4	0.2500	0.6398(5)	0.0000	0.38(7)
V	4e	0.1	0.2500	0.6398(5)	0.0000	0.38(7)
O1	8f	1.00	0.0146(5)	0.7121(8)	0.1849(4)	2.31(1)
O2	8f	1.00	0.9218(1)	0.4549(8)	0.2377(2)	1.41(3)

Figures Captions

Fig. 1. (a) Room temperature PXRD patterns of the $\text{Nd}(\text{Nb}_{1-x}\text{V}_x)\text{O}_4$ ($0 \leq x \leq 0.2$) ceramics, (b) *in-situ* high temperature PXRD patterns of the $\text{Nd}(\text{Nb}_{0.9}\text{V}_{0.1})\text{O}_4$, (c) $\text{Nd}(\text{Nb}_{0.8}\text{V}_{0.2})\text{O}_4$, (d) schematics of the crystal structures of fergusonite and scheelite crystal structures and associated refinements of $\text{Nd}(\text{Nb}_{1-x}\text{V}_x)\text{O}_4$ for $0 \leq x \leq 0.2$, experimental (circles) and calculated (line) XRD profiles for the $\text{Nd}(\text{Nb}_{0.9}\text{V}_{0.1})\text{O}_4$ (e) with $R_p = 8.39\%$, $R_{wp} = 11.4\%$, $R_{exp} = 9.31\%$, (a) and $\text{Nd}(\text{Nb}_{0.8}\text{V}_{0.2})\text{O}_4$ (f) sample at room temperature with $R_p = 6.31\%$, $R_{wp} = 8.44\%$, $R_{exp} = 6.59\%$, (The short vertical lines below the patterns mark the positions of Bragg reflections. The bottom continuous line is the difference between the observed and the calculated intensity.)

Fig. 2. The unit cell parameters (a) and the thermal expansion data (b) of $\text{Nd}(\text{Nb}_{0.9}\text{V}_{0.1})\text{O}_4$ and $\text{Nd}(\text{Nb}_{0.8}\text{V}_{0.2})\text{O}_4$ as a function to temperature.

Fig. 3. HRTEM images of the $\text{Nd}(\text{Nb}_{0.9}\text{V}_{0.1})\text{O}_4$ ceramic (a) and (c) in left, and the $\text{Nd}(\text{Nb}_{0.8}\text{V}_{0.2})\text{O}_4$ ceramic (b) and (d) in right.

Fig. 4. SEM images of the thermal etched surfaces of the $\text{Nd}(\text{Nb}_{1-x}\text{V}_x)\text{O}_4$ ($0 \leq x \leq 0.2$) ceramics sintered at optimal temperatures (a) $x = 0$ sintered at $1300\text{ }^\circ\text{C}$, (b) $x = 0.1$ sintered at $1280\text{ }^\circ\text{C}$ and (c) $x = 0.2$ sintered at $1280\text{ }^\circ\text{C}$.

Fig. 5. Relative permittivity (a) and dielectric loss (b) of the $\text{Nd}(\text{Nb}_{1-x}\text{V}_x)\text{O}_4$ ($x = 0.1$ and 0.2) (not clear in the figure) ceramics as a function of temperature at different frequencies (100 kHz , 250 kHz , 1 MHz and 7.2 GHz).

Fig. 6. Microwave permittivity, Qf values (a), TCF values and phase transition temperatures (b) of the $\text{Nd}(\text{Nb}_{1-x}\text{V}_x)\text{O}_4$ ($0 \leq x \leq 0.2$) ceramics as a function of x .

Fig. 7. Measured and calculated infrared reflectivity spectra and complex permittivity of the $\text{Nd}(\text{Nb}_{1-x}\text{V}_x)\text{O}_4$ ($x=0.1$ and 0.2) ceramics (solid line for fitting values and circle for measured values)

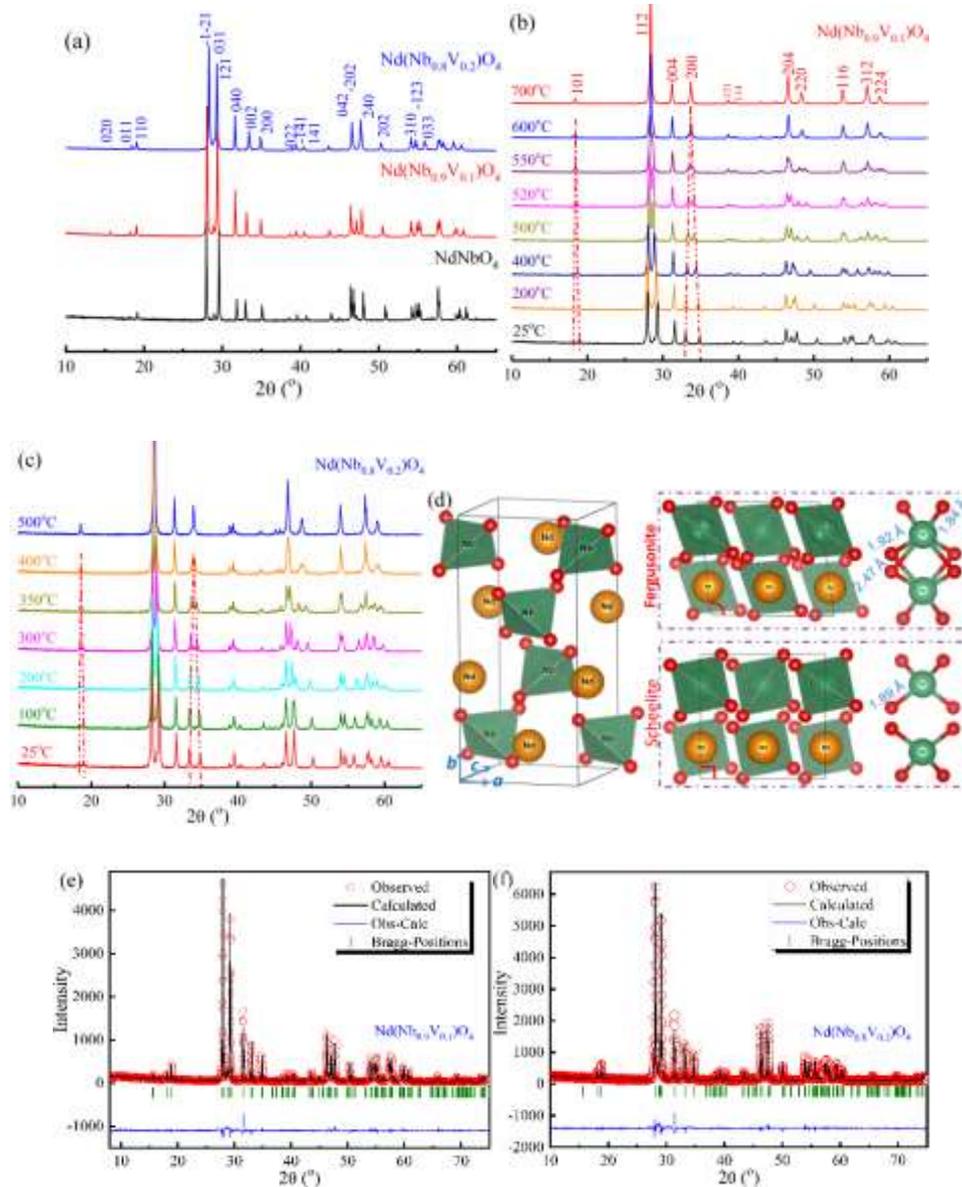


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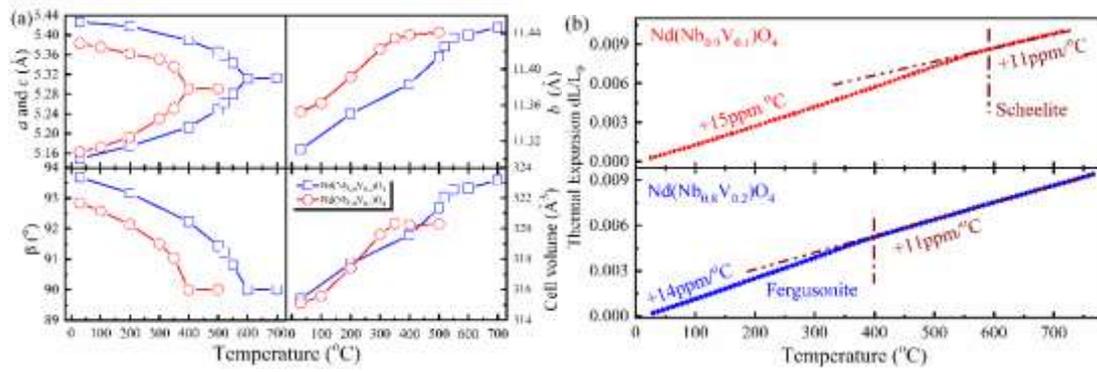


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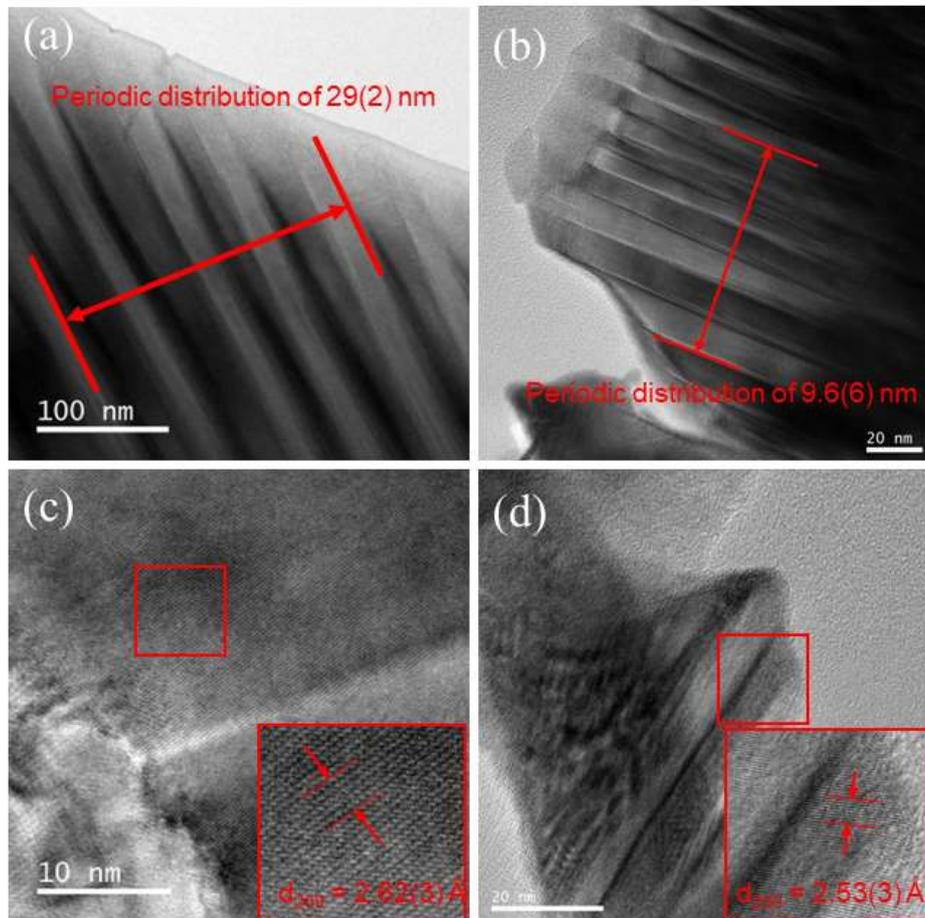


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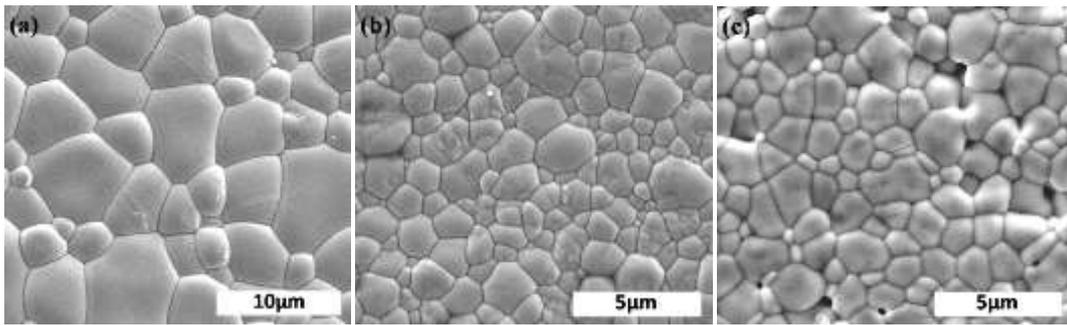


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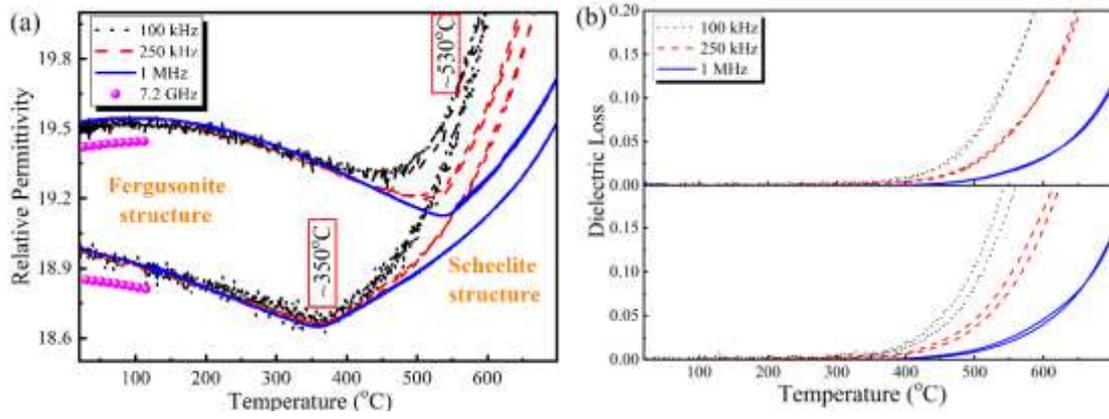


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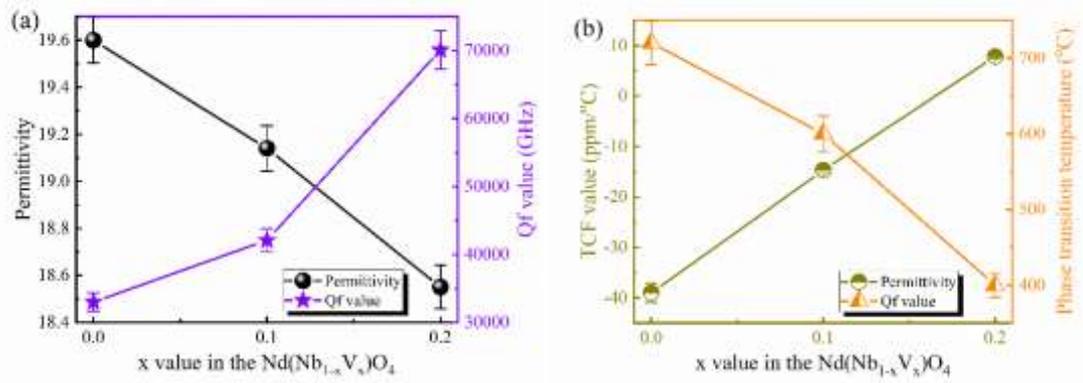


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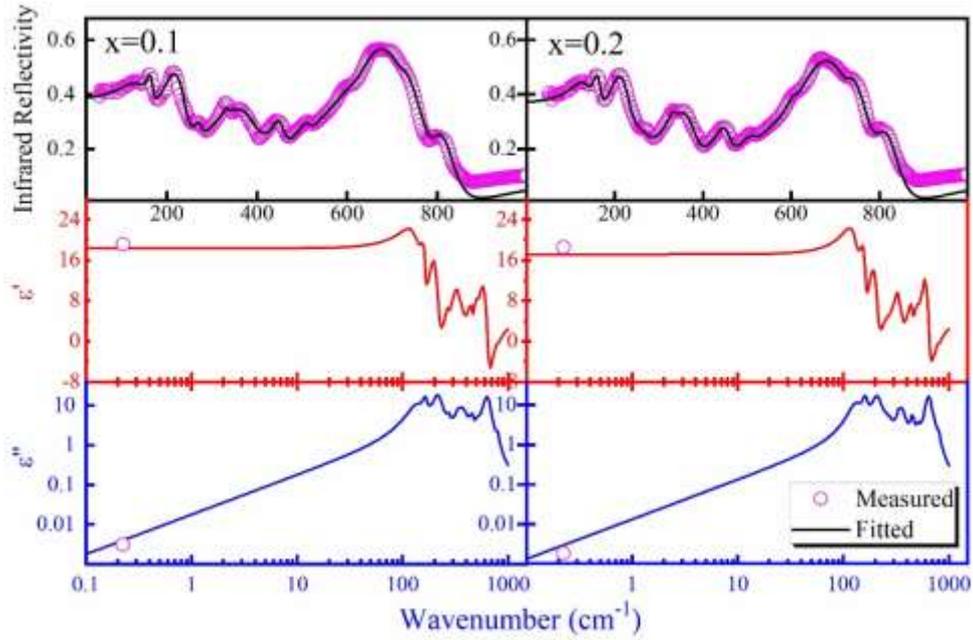


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