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Improved sintering characteristics and microwave dielectric properties of NdNbO₄ ceramic system

P. Zhang^{*1}, Z. K. Song¹, B. L. Gao², Y. Wang¹, T. Wang¹, Y. M. Han¹, W. S. Xia¹ and L. X. Li¹

NdNbO_{4-x}CuO ($x=0, 0.15, 0.2, 0.3, 0.4, 0.5, 1$ wt-%) ceramics with improved sintering characteristic and microwave dielectric properties were prepared by conventional mixed oxide route. The effects of CuO addition on the microstructures and microwave dielectric properties of NdNbO₄ ceramics were investigated systematically. Microscopic analysis showed that CuO doped NdNbO₄ ceramics possess second phases of CuNb₂O₆ and Nd₂Cu₂O₅. With a further increase in the amount of CuO, Cu₃Nb₂O₈ phase appeared in the system. The addition of CuO effectively reduced the sintering temperature of NdNbO₄ ceramics by $\sim 275^\circ\text{C}$. The microwave dielectric properties were strongly dependent on the CuO addition. Optimal microwave dielectric properties of $\epsilon_r=19.76$, $\tau_f=-24$ ppm $^\circ\text{C}^{-1}$ and $Q \times f=39\,000$ GHz were observed for 0.2 wt-%CuO doped NdNbO₄ ceramics sintered at 975°C for 4 h.

Keywords: NdNbO₄ ceramics, CuO addition, Microwave dielectric properties, Microstructure

Introduction

With the rapid development of science and technology, multifunctional materials and structures, at the levels of micro- and nanoscale, have grown rapidly due to the requirement of an increasing safety margin of all engineering elements, infrastructure and biomedical. Multifunctional material systems are capable of performing multiple 'primary' functions simultaneously or sequentially in time and are specially developed to improve system performance through a reduction of redundancy between subsystem materials and functions. Multifunctional materials and structures are not only the basic tendency for the development of ocean materials but also the inevitable result of the mankind's eagerness to explore new materials and structures. Namely, materials themselves can intrinsically possess multi-function related with their mechanical, thermal, electrical and other properties, and mankind always takes the initiative to optimise or combine the advantages of all kinds of materials.

The family of orthoniobate materials has similar structure and property with RENbO₄, where RE=lanthanoid atoms, being La to Lu as well as Y. There are two characteristics that exist in these materials: one is that many niobate based materials having [NbO₆] octahedral structures proved to have excellent microwave dielectric properties, and the other is that rare

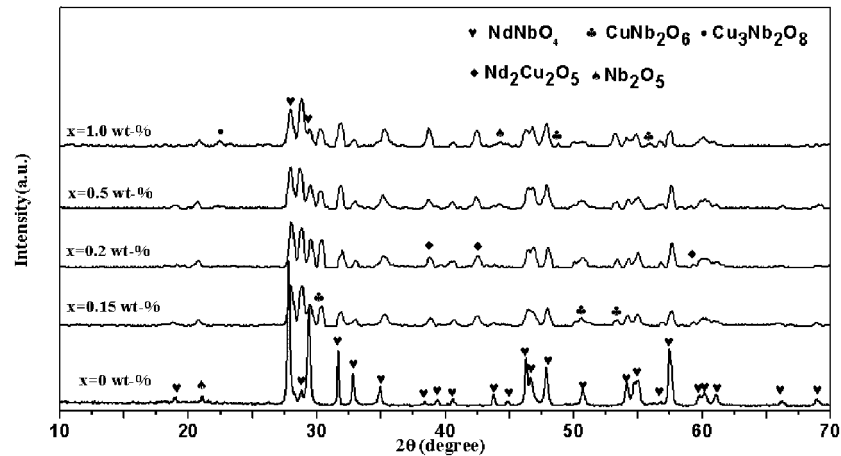
earth cations play an important role in novel materials. Both of these factors present in the family of RENbO₄ with a fergusonite type structure (monoclinic, C_{2/c}).¹ In addition, these materials have many exceptional characteristics, making them promising in applications as multifunction materials, such as luminescence characteristic, phase transformation characteristic, unique domain structures and high thermal stability.²⁻⁵ In the past several years, considerable attention has been paid to satellite broadcasting and microwave telecommunication, and many researches have focused on developing dielectric materials with high dielectric constant, low dielectric loss and a near zero temperature coefficient of resonant frequency. Many microwave devices using dielectric resonators have been well developed, which have also become indispensable components in microwave communication systems.⁶⁻⁸ However, the microwave dielectric properties of RENbO₄ ceramics system had been unnoticed. Recently, scientists are paying more attention to the microwave dielectric properties of the RENbO₄ ceramics system. With attracting more attention to these materials, novel application scenarios can be envisaged in the field of microelectronics and optoelectronics.

From the practical application point, researches have recently focused on decreasing the sintering temperatures and improving the dielectric properties of microwave dielectric materials. Generally, four methods have been employed to reduce the sintering temperature of dielectrics, that is, adding low melting point glasses, using chemical processing method and starting materials with smaller particle sizes, and searching for new material systems with low sintering temperature.⁹ For

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1 X-ray diffraction patterns of NdNbO₄-xCuO ($x=0, 0.15, 0.2, 0.5, 1$ wt-%) ceramics sintered at 975°C

example, significantly lowering the sintering temperature of LaNbO₄ from 1250 to 950°C using CuO additions has been studied by Lee *et al.*¹⁰ In addition, the modified system possessed excellent microwave dielectric properties. Decreasing the sintering temperature of the Mg(Zr_{0.05}Ti_{0.95})O₃ ceramics by 120°C with the inclusion of 1.5 wt-%CuO has been studied by Tseng.¹¹ BiNbO₄ ceramics can be sintered at 920°C with 0.5 wt-%CuO addition, and the CuO doped BiNbO₄ system exhibits excellent microwave dielectric properties and improves the densification of BiNbO₄ ceramics that were found by Cheng *et al.*⁹

The NdNbO₄ ceramic was widely investigated as a ferroelastic material with domain structures and spontaneous strains.^{1,12,13} Pure NdNbO₄ phase possesses a $Q \times f$ of 33 000 GHz, ϵ_r of 19.6 and τ_f of -24 ppm °C⁻¹.¹⁴ However, the sintering temperature at 1250°C is too high for the application of low melting point electrode materials. During our previous studies, the microwave dielectric properties of NdNbO₄ have been improved by the addition of CaF₂.¹ However, decreased sintering temperature of NdNbO₄ has been elusive.

In this paper, CuO was chosen as the modifier to decrease the sintering temperature of NdNbO₄ ceramics, and the microstructure and microwave dielectric properties of NdNbO₄-xCuO systems were also investigated.

Experimental

In the present research, NdNbO₄ based microwave dielectric ceramics were prepared by a conventional mixed oxide method. High pure (>99%) oxide powders of Nd₂O₃, Nb₂O₅ and CuO were used as raw materials. The NdNbO₄ ceramics were mixed according to stoichiometry of Nd/Nb=1.15:1 based on the results of our previous study. The mixed powders were milled for 6 h with distilled water in a nylon container with ZrO₂ balls. All the slurries were dried and presintered at 900°C for 4 h. The presintered powders with different amounts of CuO ($x=0, 0.15, 0.2, 0.3, 0.4, 0.5, 1$ wt-%) additions were remilled for 6 h. After drying and sieving, the powders were pressed into 10 mm diameter and 5 mm thickness pellets. Then, these pellets were sintered at 900–1100°C for 4 h.

The crystalline phases of the sintered samples were identified by X-ray diffraction (XRD, Rigaku D/max

2550 PC, Tokyo, Japan) with Cu K_α radiation generated at 40 kV and 40 mA. The microstructure of the ceramic surfaces was performed and analysed by a scanning electron microscopy (SEM, Philips XL30 ESEM, The Netherlands). The microwave dielectric properties were measured by an HP8720ES network analyser using Hakki-Coleman's dielectric resonator method.^{15,16} The temperature coefficient of resonant frequency τ_f was measured in the temperature range from 25 to 85°C. τ_f (ppm °C⁻¹) can be calculated by noting the change in resonant frequency Δf

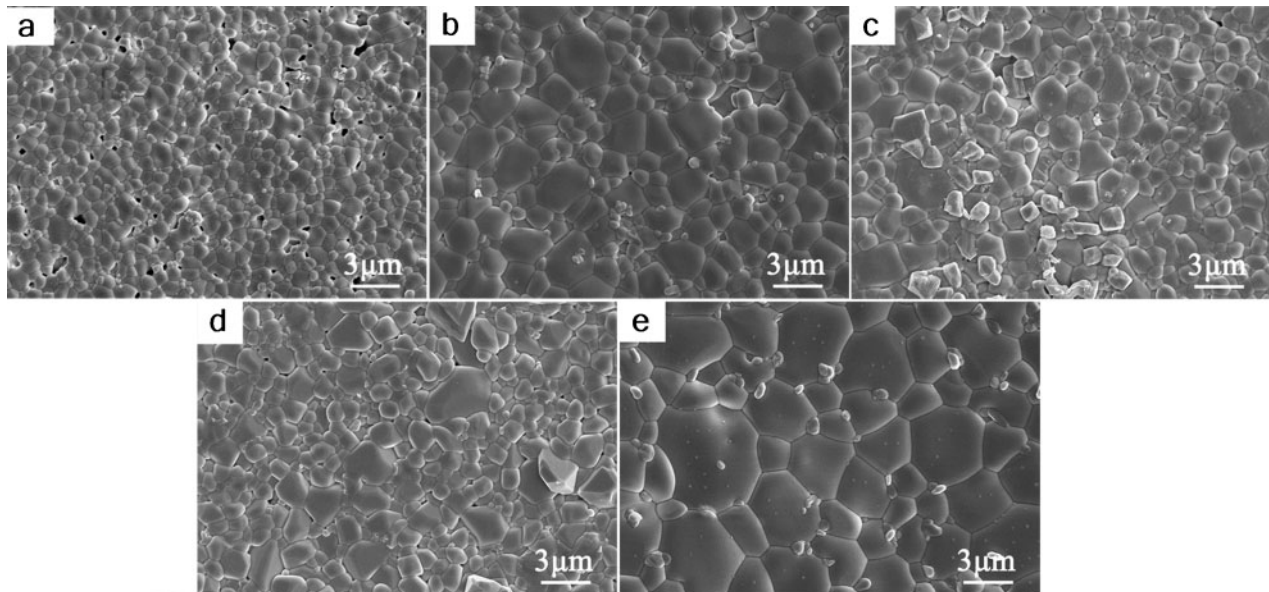
$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \quad (1)$$

where f_1 is the resonant frequency at T_1 , and f_2 is the resonant frequency at T_2 .

Results and discussion

The XRD patterns of NdNbO₄-xCuO ($x=0, 0.15, 0.2, 0.5, 1$ wt-%) ceramics were sintered at 975°C (Fig. 1). It did not change much with increasing the amount of CuO. From the XRD patterns, the NdNbO₄ diffraction peaks at $\sim 2\theta=43^\circ$ and 44° disappeared with the increase in CuO adding, and it should be the reaction of NdNbO₄ with CuO. However, the second phases of CuNb₂O₆ (ϵ_r , ~ 17.1 ; $Q \times f$, ~ 17 000 GHz; τ_f , ~ -45 ppm °C⁻¹)⁷ and Nd₂Cu₂O₅ (Ref. 17) appeared with certain amounts of CuO ($x=0.15, 0.2, 0.5$) addition. When the addition of CuO reached 1 wt-%, it was found that the Cu₃Nb₂O₈ (ϵ_r , ~ 18.2 ; $Q \times f$, ~ 56 545 GHz; τ_f , ~ -75 ppm °C⁻¹)¹⁸ diffraction peak (at $\sim 2\theta=22.5^\circ$) appeared according to the XRD patterns. It matched well with the Powder Diffraction File (PDF) file no. 33-0476.

The surface microstructures of CuO doped NdNbO₄ sintered at 975°C are demonstrated by SEM (Fig. 2a–d). The CuO doped NdNbO₄ specimens have a smaller grain size compared with the pure NdNbO₄ specimen sintered at 1250°C for 4 h (Fig. 2e). The size distribution of the NdNbO₄ grain is mainly determined by the amount of CuO addition. The grain size decreased with the increase in CuO additions. The 0.15 wt-% CuO doped NdNbO₄ ceramics, isolated particles and pores are observed (Fig. 2a). The 0.2 wt-%CuO doped specimen showed no discontinuous grain growth and homogeneously fine microstructures with almost no pores observed (Fig. 2b). It should be related to the addition of low melting point



2 Images (SEM) of NdNbO₄-*x*CuO ceramics sintered at 975°C with different additions of a *x*=0.15 wt-%, b *x*=0.2 wt-%, c *x*=0.5 wt-%, d *x*=1 wt-% and e *x*=0 wt-% sintered at 1250°C

CuO.⁹ For 0.5 and 1 wt-%CuO doped NdNbO₄ ceramics, relative rough surface can be observed (Fig. 2c and d).

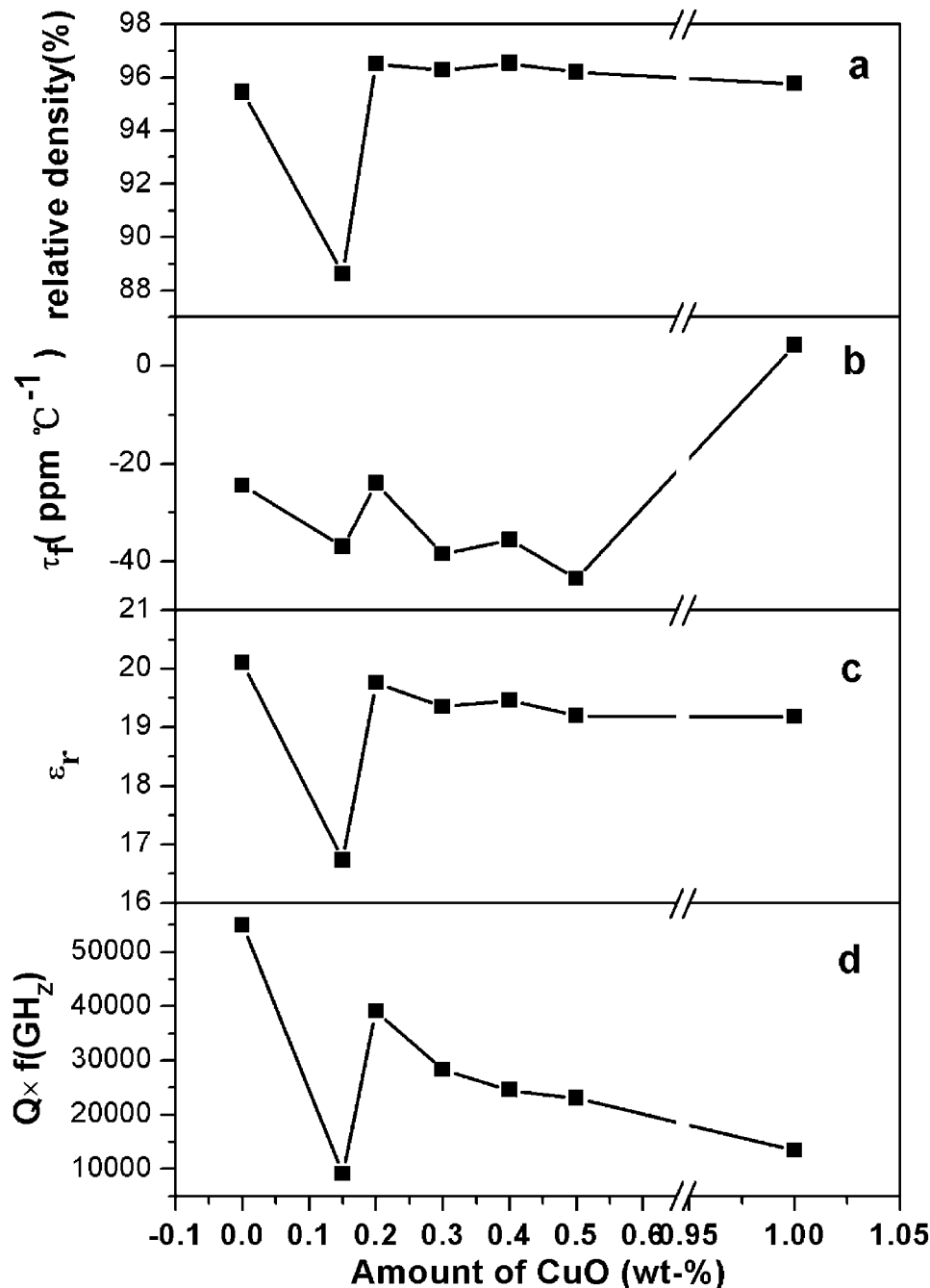
The undoped NdNbO₄ ceramics in our present work displays the dielectric constant ϵ_r of 20.1, quality factor $Q \times f$ of 55 000 GHz and temperature coefficients of the resonant frequency τ_f of $-24.5 \text{ ppm } ^\circ\text{C}^{-1}$, which are different from those of pure NdNbO₄ ceramic (ϵ_r , ~ 19.6 ; $Q \times f$, $\sim 33\,000 \text{ GHz}$; τ_f , $\sim -24 \text{ ppm } ^\circ\text{C}^{-1}$), as reported by Kim *et al.*¹⁴ Variations of the density, dielectric constant ϵ_r , resonant frequency temperature coefficients τ_f and quality factor $Q \times f$ of the NdNbO₄-*x*CuO (*x*=0, 0.15, 0.2, 0.3, 0.4, 0.5, 1 wt-%) ceramics sintered at 975°C are illustrated (Fig. 3). The relative density of 0.15 wt-%CuO doped NdNbO₄ is 88.62% (density, $\sim 5.59 \text{ g cm}^{-3}$) (Fig. 3a), which is much lower than the others, 95.51–95.53% (density, ~ 6.02 – 6.04 g cm^{-3}). It should relate to the appearance of pores on the surface of the NdNbO₄ ceramic, as we can see from the SEM images (Fig. 2a). With a further increase in the CuO additions (0.2–1 wt-%), the relative density increased first and then was kept stable, owing to the presence of the CuO liquid phase and enlarged grain size as observed in Fig. 2b–d. It indicates that increasing the addition of CuO ($0.2 \leq x \leq 1 \text{ wt-%}$) has no significant influence on the relative density.

The dielectric constants of NdNbO₄ ceramics with different amounts of CuO additions sintered at 975°C are shown in Fig. 3b. The relationships between ϵ_r values and the amount of CuO show the same trend with the relative densities. The increase in ϵ_r value could be explained with the higher relative densities. The ϵ_r values of the NdNbO₄ ceramics with appropriate CuO doped in the range of 0.2–1 wt-% ranged from 19.18 to 19.78.

The variation of τ_f with $0.15 \leq x \leq 1 \text{ wt-%}$ CuO additions is illustrated in Fig. 3c. The τ_f value of 0.15 wt-%CuO doped specimen decreased compared with the undoped NdNbO₄. τ_f is known to be governed by the composition, the additives and the second phase of the materials. At the point of *x*=0.15 wt-%, the decrease in τ_f values should be caused by the presence of CuNb₂O₆ (τ_f , $\sim -45 \text{ ppm } ^\circ\text{C}^{-1}$) phase. It increased with the CuO

additions, and the relative large τ_f was obtained at *x*=0.2 wt-%. However, as the value of *x* exceeded 0.2 wt-%, τ_f has a trend of decrease entirely. However, when *x*=1 wt-%, τ_f becomes positive. According to the XRD patterns (Fig. 1), Cu₃Nb₂O₈ phases formed when a relative large amount of CuO was added to the system. Lee *et al.*^{19–21} reported that τ_f , which may depend on the lattice energy of the compounds, is correlated to the unit cell volume of them. They suggested that the unit cell volume is inversely proportional to the lattice energy if the compounds are of the same structure. It was reported that the structure of Cu₃Nb₂O₈ is monoclinic and belongs to the space group C_{2/c},¹⁸ and NdNbO₄ also belongs to it. The unit cell volumes of Cu₃Nb₂O₈ and NdNbO₄ are 148.1 (PDF file no. 33-0476) and 317.3 (PDF file no. 33-0680) respectively. Cu₃Nb₂O₈ has much larger lattice energy compared with NdNbO₄. The τ_f values of NdNbO₄ increase to positive values with the formation of Cu₃Nb₂O₈. It should attribute to the corresponding decrease in unit cell volume, which came from the solid solution of Cu₃Nb₂O₈ and NdNbO₄. It was also found that Cu₃Nb₂O₈ ceramics had a very low sintering temperature.¹⁹ Therefore, the positive of τ_f with 1 wt-% CuO doped could be due to the presence of the Cu₃Nb₂O₈ phases.

As shown in Fig. 3d, the variation of $Q \times f$ values with CuO additions also presents a different trend with relative density and dielectric constant. Kucheiko *et al.*²² reported that $Q \times f$ increases with the average grain size. When the grain size increases and grain boundary area and the pores decrease, the lattice imperfections are reduced and the $Q \times f$ values are increased.²³ At the point of *x*=0.15 wt-%, the $Q \times f$ values decreased sharply. It should be caused by the decrease in grain size that increases the area of the grain boundary and the appearance of much pores (Fig. 2a). When *x*=0.2 wt-%, the specimens showed homogeneously fine microstructures, relative big grains and small grain boundaries with almost no pores (Fig. 2b); therefore, the lattice imperfections caused by pores and grain boundaries could be reduced and $Q \times f$ values are increased. A maximum



3 Relative density, dielectric constant ϵ_r , quality factor $Q \times f$ and temperature coefficient of resonant frequency τ_f of NdNbO₄ ceramics as function of CuO content sintered at 975°C

$Q \times f$ of 39 000 GHz was obtained for NdNbO₄ specimens with 0.2 wt-% CuO addition sintered at 975°C for 4 h. With increasing the CuO additions, the $Q \times f$ values decline. It should be that the formation of second phase CuNb₂O₆ with a smaller $Q \times f$ value (~ 17 000 GHz) decreased the $Q \times f$ values of the specimens. Moreover, as CuO content exceeded 0.2 wt-%, the grain boundary area increased with the decrease in the grain size, which resulted in the increase in dielectric loss, and the appearance of pores (Fig. 2c and d) also caused the $Q \times f$ value to significantly decrease.

Conclusions

The microstructure and microwave dielectric properties of NdNbO₄ ceramics with different CuO additions were

investigated systematically in this study. The phase composition, grain shape and dielectric properties found strongly correlate to the amount of CuO. The addition of 0.15 wt-% CuO worsens the dielectric properties of the system. With increasing the CuO content from 0.2 to 1 wt-%, the relative density and dielectric constant ϵ_r were kept at a stable value, while the quality factor $Q \times f$ decreased. Moreover, the temperature coefficients of the resonant frequency τ_f shifted towards negative sides at first and then become a positive value as the CuO contents increase. The positive of τ_f with the increase in CuO could relate to the existence of the Cu₃Nb₂O₈ and NdNbO₄ phases. Sintered at 975°C, 0.2 wt-% CuO doped NdNbO₄ ceramics possesses optimal microwave dielectric properties of $\epsilon_r = 19.76$, $Q \times f = 39$ 000 GHz and $\tau_f = -24$ ppm °C⁻¹, which is comparable to those of

pure NdNbO₄ ceramics sintered at 1250°C ($\epsilon_r=20.1$, $Q \times f=55\,000$ GHz and $\tau_f=-24.5$ ppm °C⁻¹). Of particular interest, the sintering temperature of the NdNbO₄ ceramic system was largely reduced without the degradation of the microwave dielectric properties.

Acknowledgements

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References

1. P. Zhang, T. Wang, W. S. Xia and L. X. Li: 'Microwave dielectric properties of a new ceramic system NdNbO₄ with CaF₂ addition', *J. Alloys Compd.*, 2012, **535**, 1–4.
2. L. H. Brixner, J. F. Whitney, F. C. Zumsteg and G. A. Jones: 'Ferro-elasticity in LnNbO₄-type rare-earth niobates', *Mater. Res. Bull.*, 1997, **12**, 17.
3. J. Li and C. M. Wayman: 'Monoclinic-to-tetragonal phase transformation in a ceramic rare-earth orthoniobate, LaNbO₄', *J. Am. Ceram. Soc.*, 1997, **80**, (3), 803–806.
4. S. K. Lee, H. Chang, C. H. Han, H. J. Kim, H. J. Jang and H. D. Park: 'Electronic structures and luminescence properties of YNbO₄ and YNbO₄: Bi', *J. Solid State Chem.*, 2001, **156**, 267–273.
5. Y. H. Chen, H. Wang, L. X. Pang, H. F. Zhou and X. Yao: 'Effect of Zn²⁺ substitution on sintering behavior and dielectric properties of NdNbO₄ ceramics', *Ferroelectrics*, 2010, **407**, (1), 61–68.
6. M. Makimoto and S. Yamashita: 'Microwave resonators and filters for wireless communication: theory, design and application'; 2001, Berlin, Springer.
7. M. T. Sebastian: 'Dielectric materials for wireless communications'; 2008, Oxford, Elsevier Publishers.
8. W. Wersing: 'Microwave ceramics for resonators and filters', *Curr. Opin. Solid State Mater. Sci.*, 1996, **1**, 715–731.
9. C. M. Cheng, S. H. Lo and C. F. Yang: 'The effect of CuO on the sintering and properties of BiNbO₄ microwave ceramics', *Ceram. Int.*, 2000, **26**, 113–117.
10. H. W. Lee, J. H. Park, S. Nahm, D. W. Kim and J. G. Park: 'Low-temperature sintering of temperature-stable LaNbO₄ microwave dielectric ceramics', *Mater. Res. Bull.*, 2010, **45**, 21–24.
11. C. F. Tseng: 'The effect CuO additive on the microwave dielectric properties of Mg(Zr_{0.05}Ti_{0.95})O₃ ceramics', *J. Alloys Compd.*, 2010, **494**, 252–255.
12. M. Omori, Y. Kobayashi and T. Hirai: 'Dilatometric behavior of martensitic transformation of NdNbO₄ polycrystals', *J. Mater. Sci.*, 2000, **35**, (3), 719–721.
13. V. S. Stubican: 'High temperature transitions in rare earth niobates and tantalates', *J. Am. Ceram. Soc.*, 1964, **47**, (2), 55–58.
14. D. W. Kim, D. K. Kwon, S. H. Yoon and K. S. Hong: 'Dielectric properties of rare-earth ortho-niobates with ferro-elasticity', *J. Am. Ceram. Soc.*, 2006, **89**, (12), 3861–3864.
15. B. W. Hakki and P. D. Coleman: 'A dielectric resonator method of measuring inductive capacities in the millimeter range', *IEEE Trans. Microwave Theory Tech.*, 1960, **8**, 402.
16. W. E. Courtney: 'Analysis and evaluation of a method of measuring the complex permittivity and permeability of microwave insulators', *IEEE Trans. Microwave Theory Tech.*, 1970, **18**, (8), 476–485.
17. J. M. S. Skakle and A. R. West: 'The preparation, structure and stability of Nd₂Cu₂O₅', *J. Mater. Chem.*, 1995, **5**, (5), 765–768.
18. D. W. Kim, I. T. Kim, B. Park and K. S. Hong: 'Microwave dielectric properties of (1-x)Cu₃Nb₂O₈-xZn₃Nb₂O₈ ceramics', *J. Mater. Res.*, 2001, **16**, (5), 1465–1470.
19. H. Langbein and G. Wolki: 'Preparation of copper niobates by thermal decomposition of freeze-dried complex oxalate solutions', *Thermochim. Acta.*, 1995, **264**, 67–73.
20. H. J. Lee, K. S. Hong, S. J. Kim and I. T. Kim: 'Dielectric properties of MNb₂O₆ compounds (where M=Ca, Mn, Co, Ni, or Zn)', *Mater. Res. Bull.*, 1997, **32**, 847.
21. H. J. Lee, I. T. Kim and K. S. Hong: 'Dielectric properties of AB₂O₆ compounds (A=Ca, Mg, Co, Ni, Zn, and B=Nb, Ta)', *J. Appl. Phys.*, 1997, **36**, (2), 1318–1320.
22. S. Kucheiko, J. W. Choi, H. J. Kim and H. J. Jung: 'Microwave dielectric properties of CaTiO₃-Ca(Al_{1/2}Ta_{1/2})O₃ ceramics', *J. Am. Ceram. Soc.*, 1996, **79**, 2739–2743.
23. H. Tamura: 'Microwave loss quality of (Zr_{0.8}Sn_{0.2})TiO₄', *J. Am. Ceram. Soc. Bull.*, 1994, **73**, 92–95.