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Microwave dielectric properties of the $(1-x)La(Nb_{0.9}V_{0.1})O_4$ -xCaMoO₄ $(0.05 \le x \le 0.50)$ scheelite solid solution ceramics

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Abstract

The CaMoO₄ was added into La(Nb_{0.9}V_{0.1})O₄ ceramics by solid state reaction method to adjust the temperature coefficient of frequency (TCF) values. The series of (1-x)La(Nb_{0.9}V_{0.1})O₄-xCaMoO₄ (0.05 $\leq x \leq 0.5$) ceramics were sintered at 1060 ~ 1180°C and found to possess permittivity (ε_r) = 10.38 ~ 17.73, Q×f = 31,820 ~ 76,570 GHz (Q = 1 / dielectric loss, f = resonant frequency lying between 8.5 ~ 9 GHz), and TCF = -26.3 ~ +160.7 ppm/°C. The structures of ceramic samples changed from monoclinic fergusonite to tetragonal scheelite continuously at x = 0.20 along with the shift of TCF values from positive to negative. The best microwave dielectric properties with ε_r = 15.71, Q×f = 76,310 GHz (at 8.825 GHz), and TCF = - 26.3 ppm/°C were obtained in 0.8La(Nb_{0.9}V_{0.1})O₄-0.2CaMoO₄ ceramics sintered at 1160°C and these ceramics might be good candidates for microwave devices.

Keywords: Microwave dielectric; LaNbO₄; low temperature co-fired ceramic (LTCC)

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1. Introduction

Today, microwave dielectric ceramics are being studied by more and more people because of their universal application as dielectric resonators, filters, RF substrates and waveguides [1-3]. Generally, ceramics are prepared by conventional solid state reaction methods. The key point of this approach is mainly the presence of ceramic processing, which makes the ceramic compact enough. Microwave dielectric ceramics have been studied for decades to pursue good microwave dielectric properties, namely high Q×f (Q=1/dielectric and f=resonant frequency), high relative dielectric constant (ε_r) and near-zero resonant frequency temperature coefficient (TCF) [4-6]. Compared with the traditional perovskite (ABO₃) materials, recently the universal ABO₄ systems, including wolframite (MgWO₄), scheelite (CaWO₄), fergusonite (LaNbO₄), rutile (TiO₂) and zircon (NdVO₄) materials, have attracted more and more attention due to the structure adaptability [7-9].

It has been reported that the LaNbO₄ material transitions from fergusonite structure to scheeelite structure at about 600°C [10] and at the same time there is remarkable thermal expansion transition. Besides, there is a wide temperature gap 450-750°C, which can be revealed from Neutron and X-ray diffraction due to the existence of multicrystals [11,12]. Stubican et al. [13] noticed that the related phase transition temperature increased with decrease of rare earth ionic radius, and the niobates have lower phase transition temperatures than the corresponding tantalates. Based on the literatures' results, some researchers have provided solutions that use Ta instead of Nb or reduce the ionic radius of rare earth ions [14,15]. In 1980s, Bastide et al. [16] concluded that phase transition of ABX₄ ceramics according to the radius ratio of cation and anion. Subsequently, this work was supplemented by Manjon et al., [17] which mainly aimed at current research focusing on materials including orthorhombic,

wolframite, fergusonite scheelite and zircon structures. It is well known that the phase evolution from high-temperature scheelite to low-temperature multicrystal is attributed to decrease of B-site cation.[16-18] Brik et al. [18] noticed that the phase transition temperature of LaNbO₄ ceramics could be adjusted to near room temperature in the manner of replacing by vanadium with smaller radius than niobium. Therefore, Brandão et al. [19] studied the influence of electrons and protons by scheelite retention.

Brower and Choi et al. reported microwave dielectric properties of the CaMoO₄ ceramics sintered at 1100°C with $\varepsilon_r = 10.8 \sim 11.7$, Q×f = 55,000 ~ 89,700 GHz and $\tau_r = -50 \sim -60$ ppm/°C [20-24]. Vidya et al. [23] found that the CaMoO₄ nano-ceramics could be densified at a quite low sintering temperature ~ 775°C. However, the large negative TCF of CaMoO₄ ceramic still limited the practical applications. Recently, a temperature stable LTCC (low temperature co-fired ceramics technology) materials have been achieved by using TiO₂ to adjust performance of the CaMoO₄ ceramics [23]. Meanwhile, Ca²⁺ in CaMoO₄ ceramics could be substituted for by (Li_{0.5}Bi_{0.5})²⁺ ions and this resulted in near-zero TCF values [24]. Meanwhile, the low sintering temperatures of the (Li_{0.5}Bi_{0.5})MoO₄-CaMoO₄ solid solution ceramics make them good candidates for LTCC technology [24,25]. We recently reported that the La(Nb_{0.9}V_{0.1})O₄ ceramics have good microwave dielectric properties including a large positive TCF value [26]. In the present study, we primarily researched the relation of microwave dielectric properties and structure of the (1–x)La(Nb_{0.9}V_{0.1})O₄-xCaMoO₄ ceramics.

2. Experimental Procedure

Reagent-grade raw materials of Nb_2O_5 (> 99.5%, Guo-Yao Co. Ltd.), La_2O_3 (> 99.95%, Guo-Yao Co. Ltd.), V_2O_5 (> 99%, Fuchen Chemical Reagent, Tianjin, China),

CaCO₃ (> 99%, Guo-Yao Co. Ltd.) and MoO₃ (>99%, Guo-Yao Co. Ltd.) were measured stoichiometric according to the compositions of the $(1-x)La(Nb_{0.9}V_{0.1})O_4-xCaMoO_4$ (0.05 $\leq x \leq 0.50$). La₂O₃ powders were treated at 1000°C for 5 h before weighting to remove carbonates. Powder mixtures were milled for 5 h using a planetary mill (QM-1F; Nanjing Machine Factory, Nanjing, China) at 200 rpm with the milling media (zirconia balls). After drying the mixtures were calcined at 800°C for 5 h and then re-milled at 250 rpm for 5 h to obtain fine powders. The fine powders were pressed into pellets (11 mm in diameter and $4 \sim 5$ mm in height) with 5 wt. % polyvinyl alcohol (PVA). All the samples were sintered in the air at 1000° C ~ 1200° C for 2 h.

Phase compositions and crystal structures of the $(1-x)La(Nb_{0.9}V_{0.1})O_4$ -xCaMoO₄ ($0.05 \le x \le 0.50$) ceramics were investigated using X-ray diffraction (XRD) with Cu K α radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan) and Rietveld refinement method was used to analyze the details of crystal structures. Microstructures were studied using a scanning electron microscopy (SEM; Quanta 250 F, FEI). Microwave dielectric properties were measured using the shielded resonant cavity method using the TE_{01δ} mode to calculate the permittivity and Q values, a network analyzer (8720ES, Agilent, Palo Alto, CA), and a temperature chamber (Delta 9023, Delta Design, Poway, CA). The TCF / τ_f values were obtained from the following formula:

$$TCF = \frac{f_T - f_{T_0}}{f_{T_0} \times (T - T_0)} \times 10^6 (ppm/{}^{\circ}C)$$
(1)

where $f_{\rm T}$ and $f_{\rm T0}$ are the resonant frequencies at 85°C and 25°C, respectively.

3. Results and Discussions

Figure 1 shows XRD patterns of the $(1-x)La(Nb_{0.9}V_{0.1})O_4-xCaMoO_4$ ($0 \le x \le 1$)

ceramics sintered at their optimal temperatures for 2 h, which can help us understand the mechanism of two kinds of phase transition. The lattice parameters of pure La(Nb_{0.9}V_{0.1})O₄ ceramic were calculated to be a = 5.508(9) Å, b = 11.603(8) Å, c =5.236(0) Å, $\beta = 94.920^{\circ}$, and cell volume = 334.274(4) Å³. As the substitution content increased, the phase transition from fergusonite to tetragonal sheelite structure can be clearly observed from XRD patterns. In the range $0 \le x \le 0.1$, the $(1-x)La(Nb_{0.9}V_{0.1})O_4$ -xCaMoO₄ ceramics belong to a fergusonite solid solution with a space group I2/a. It was clearly seen from Figure 1, XRD reflection peaks (-121)and (121) of $(1-x)La(Nb_{0.9}V_{0.1})O_4$ -xCaMoO₄ ($0 \le x \le 0.1$) ceramics moved to each other continuously with increase in CaMoO₄ contents. Finally at x = 0.2, (-121) and (121) merged into one peak (112), which indicates that crystal structure of the (1-x)La(Nb_{0.9}V_{0.1})O₄-xCaMoO₄ ceramics changed from fergusonite to scheelite. variations in Figure 2 shows the lattice parameters of the (1-x)La(Nb_{0.9}V_{0.1})O₄-xCaMoO₄ ceramics. As CaMoO₄ content increased, lattice parameters a, b and β ($\beta > 90^{\circ}$) in the solid solution region (x ≤ 0.1) decreased slowly. Lattice parameters c increased slightly. With further increase of x value, the a and c values became equal to each other. Meanwhile, the b increased to 11.430(3) Å at x = 0.2 in tetragonal structure. The variation of lattice parameters clearly suggested phase transition from fergusonite to scheelite structure the in the $(1-x)La(Nb_0 V_0 V_0)O_4$ -xCaMoO₄ ceramics. These changes are in accordance with XRD results analysis. In order to research the details of crystal structure, Rietveld refinements performed were to study the crystal structure of the $0.9La(Nb_{0.9}V_{0.1})O_4-0.1CaMoO_4$ and $0.8La(Nb_{0.9}V_{0.1})O_4-0.2CaMoO_4$ ceramics. The Rietveld refinement results are presented in Figure 3. The space group, occupancies and atomic positions are given in the Table 1 ($R_p = 9.94$ %, $R_{wp} = 12.9$ %, and $R_{exp} =$

7.06 %) and all the refinement results are acceptable. The $0.9La(Nb_{0.9}V_{0.1})O_4$ - $0.1CaMoO_4$ ceramic belongs to single fergusonite phase with a space group I2/a. The $0.8La(Nb_{0.9}V_{0.1})O_4$ - $0.2CaMoO_4$ ceramic belongs to standard sheelite structure with a space group I4₁/a accordingly.

SEM results of the (1-x)La(Nb_{0.9}V_{0.1})O₄-xCaMoO₄ ceramics sintered at 1160°C are shown in Figure 4. The dense micro-structure of the $(1-x)La(Nb_{0.9}V_{0.1})O_4-xCaMoO_4$ ceramics can be observed with almost no pores. With the increase of $CaMoO_4$ contents, grains of the ceramics become more homogeneous and very uniform grain distribution can be observed in the 0.8La(Nb_{0.9}V_{0.1})O₄-0.2CaMoO₄ ceramic. Figure 5 shows the variation of densities of the $(1-x)La(Nb_{0.9}V_{0.1})O_4$ -xCaMoO₄ $(0.05 \le x \le 0.5)$ ceramics function sintering temperature. of All the as a $(1-x)La(Nb_{0.9}V_{0.1})O_4$ -xCaMoO₄ ceramics can be well densified in wide sintering temperatures. Due to the atomic weight differences, the increase of CaMoO₄ content apparently resulted in decrease of the bulk densities.

Variation of permittivity and Q×f values of the $(1-x)La(Nb_0 V_{0,1})O_4-xCaMoO_4$ $(0.05 \le x \le 0.50)$ ceramics as a function of sintering temperature are shown in Figure 6. All the permittivity values keep stable in a quite wide sintering temperature range as shown in Figure 6(a) and this is in accordance with the change trend of bulk density. The largest permittivity about 17.63 obtained in the 0.95 was $La(Nb_{0.9}V_{0.1})O_4-05CaMoO_4$ ceramic. Variation of 0×f values of the $(1-x)La(Nb_{0.9}V_{0.1})O_4$ -xCaMoO₄ (0.05 $\leq x \leq 0.50$) ceramics s a function of sintering temperature are shown in Figure 6(b) (resonant frequency lying between $8.5 \sim 9$ GHz). Q×f values increase with sintering temperature first, and then decrease due to secondary grain growth at high temperatures. The 0.8 La(Nb_{0.9}V_{0.1})O₄-0.2CaMoO₄ ceramics sintered at 1160°C posses the highest Q×f values ~ 76,310 GHz at 8.825

GHz.

Figure 7 shows microwave dielectric permittivity and $Q \times f$ values of the $(1-x)La(Nb_{0.9}V_{0.1})O_4$ -xCaMoO₄ ($0 \le x \le 1$) ceramics as a function of CaMoO₄ content. Generally, permittivity is determined by dielectric polarization. In range of microwave frequency, dielectric polarization is the sum of both ionic and electronic components [27]. Shannon et al. [27] suggested that molecular polarizability could be estimated as the sum of individual ionic polarizabilities. Hence, polarizabilities (α_x) of the (1–x)La(Nb_{0.9}V_{0.1})O₄-xCaMoO₄ ceramics could be obtained as follows:

$$\alpha_{x} = (1 - x)\alpha_{La^{3+}} + 0.9(1 - x)\alpha_{Nb^{5+}} + 0.1(1 - x)\alpha_{V^{5+}} + x\alpha_{Ca^{2+}} + x\alpha_{Mo^{6+}} + 4\alpha_{O^{2+}}$$
(2)

where $\alpha_{La^{3+}}, \alpha_{Nb^{5+}}, \alpha_{V^{5+}}, \alpha_{Ca^{2+}}, \alpha_{Mo^{6+}}$ and $\alpha_{O^{2+}}$ are polarizabilities of La³⁺, Nb⁵⁺, V⁵⁺, Ca²⁺, Mo⁶⁺ and O²⁺ ions [27]. Using the Clausius-Mosotti relation, the dielectric permittivity can be calculated as follows:

$$\varepsilon_x = \frac{3V_x + 8\pi\alpha_x}{3V_x - 4\pi\alpha_x} \tag{3}$$

in which V_x is the cell volume (= 336.695 / 4= 84.17 Å³). Figure 7(a) shows that ε_{cal} and ε_r of the (1–x)La(Nb_{0.9}V_{0.1})O₄-xCaMoO₄ ceramics gradually decrease as the increase of CaMoO₄ content due to the smaller ionic polarizability of Ca²⁺ and Mo⁶⁺ than that of La³⁺ and Nb⁵⁺. Q×f values of the CaMoO₄ and La(Nb_{0.9}V_{0.1})O₄ ceramics are about 90,000 GHz and 60,000 GHz, respectively, as reported in literatures [21,26]. As shown in Figure 7(b), Q×f values increase with the content of CaMoO₄ as expected. Quite high Q×f values were obtained in the solid solution ceramics due to the good sinterability that resulted in homogeneous microstructures. The 0.8La(Nb_{0.9}V_{0.1})O₄-0.2CaMoO₄ ceramic possesses the highest Q×f value about 76,310 GHz at 8.825 GHz. The TCF values as a function of x value are presented in Figure 7(c). It can be seen that the TCF values are large positive within monoclinic fergusonite solid solution region (x < 0.2) and this is in accordance with results in the La(Nb,V)O₄ system.[26] Introduction of CaMoO4 into the La(Nb_{0.9}V_{0.1})O₄ lowered the ferroelastic phase transition temperature to near room temperature, resulting in composition-sensitive and unstable TCF values. When $x \ge 0.2$, the TCF values keep negative and increase with the CaMoO₄ content in scheelite region, which is quite normal in solid solution ceramics. The smallest TCF value about – 26.3 ppm/°C was obtained in the 0.8La(Nb_{0.9}V_{0.1})O₄-0.2CaMoO₄ ceramics. The intrinsic microwave dielectric properties were studied by far-infrared spectra as shown in Fig. S1 and Table S1. All the fitted and measured values were found to be in good agreements.

4. Conclusions

The 0.65La(Nb_{0.9}V_{0.1})O₄-0.35CaMoO₄ ceramic sintered at 1160°C was found to possesse a $\varepsilon_r = 15.00$, a Q×f = 69,720 GHz at 9 GHz, and a TCF/ $\tau_f = -30.6$ ppm/°C. obtained The best microwave dielectric properties were in the $0.8La(Nb_{0.9}V_{0.1})O_4$ - $0.2CaMoO_4$ ceramics sintered at 1160°C with a $\varepsilon_r = 15.71$, a Q×f = 76,310 GHz at 8.825 GHz, and $\tau_f = -26.3$ ppm/°C. The XRD analysis reveals that the ceramics changed from monoclinic fergusonite to tetragonal sheelite phase at x =0.2. Far-infrared reflectivity fitting of the 0.65La(Nb_{0.9}V_{0.1})O₄-0.35CaMoO₄ ceramic shows that the main polarization comes from ionic polarization rather than electronic ones. These materials are very promising candidates for high quality microwave devices.

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Table 1 Crystallographic parameters of the $0.9La(Nb_{0.9}V_{0.1})O_4$ - $0.1CaMoO_4$ and the $0.8La(Nb_{0.9}V_{0.1})O_4$ - $0.2CaMoO_4$ ceramics ($R_p = 9.94$ %, $R_{wp} = 12.9$ %, and $R_{exp} =$

/.06 %).	7.0	5%)	•
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x	Atom	Х	у	Z	Occupancy	Mult			
		Sp	ace group: I	2/a	R				
0.1	Ca	0.25000	0.12327	0.00000	0.050	4			
	La1	0.25000	0.12327	0.00000	0.450	4			
	Nb1	0.25000	0.63214	0.00000	0.405	4			
	V 1	0.25000	0.63214	0.00000	0.045	4			
	Mo1	0.25000	0.63214	0.00000	0.050	4			
	01	0.01472	0.71352	0.16672	1.000	8			
	O2	0.91465	0.45835	0.24286	1.000	8			
Space group: <i>I</i> 4 ₁ /a									
	Ca	0.00000	0.25000	0.62500	0.050	4			
	La1	0.00000	0.25000	0.62500	0.200	4			
	Nb1	0.00000	0.25000	0.12500	0.180	4			
0.2	V1	0.00000	0.25000	0.12500	0.020	4			
	Mo1	0.00000	0.25000	0.12500	0.050	4			
	01	0.15684	0.00500	0.20917	1.000	16			

Figure Captions

Fig. 1. XRD patterns of the $(1-x)La(Nb_{0.9}V_{0.1})O_4$ -xCaMoO₄ ($0 \le x \le 1$) ceramics sintered at their optimal temperatures.

Fig. 2. Lattice parameters variation in the $(1-x)La(Nb_{0.9}V_{0.1})O_4$ -xCaMoO₄ ($0 \le x \le 1$) ceramics.

Fig. 3. Observed XRD (red points) and calculated pattern (black solid line) along with difference plot (at the bottom) of (a) the $0.9La(Nb_{0.9}V_{0.1})O_4$ - $0.1CaMoO_4$ ceramics and (b) the $0.8La(Nb_{0.9}V_{0.1})O_4$ - $0.2CaMoO_4$ ceramics. Allowed Bragg reflections are indicated by vertical bars and goodness-of-fit shown in inset.

Fig. 4. SEM images of the $(1-x)La(Nb_{0.9}V_{0.1})O_4-xCaMoO_4$ (a) x = 0.05, (b) x = 0.10, (c) x = 0.20, (d) x = 0.35, (e) x = 0.50 ceramics sintered at 1160 o C for 2h.

Fig. 5 Variation of density of the $(1-x)La(Nb_{0.9}V_{0.1})O_4$ -xCaMoO₄ $(0.05 \le x \le 0.5)$ ceramics as a function of sintering temperature.

Fig. 6 Variation of permittivity (a) and Q×f values (b) of the $(1-x)La(Nb_{0.9}V_{0.1})O_4$ -xCaMoO₄ (0.05 $\le x \le 0.50$) ceramics as a function of sintering temperature.

Fig. 7 ϵ_{cal} and ϵ_r (a), Q×f value (b), and TCF (c) of the $(1-x)La(Nb_{0.9}V_{0.1})O_4$ -xCaMoO₄ ($0 \le x \le 1$) ceramics as a function of x value.





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Temperature (°C)







1, Fergusonite solid solutions were formed in (1-x)La(Nb_{0.9}V_{0.1})O₄-xCaMoO₄;

2, A pseudo phase diagram is given in $(1-x)La(Nb_{0.9}V_{0.1})O_4$ -xCaMoO₄;

3, High Q×f ~ 76,310 GHz was obtained in $0.8La(Nb_{0.9}V_{0.1})O_4\text{-}0.2CaMoO_4$ ceramic.