



Ln₂Mo₃O₁₂ (Ln = La, Nd): A novel group of low loss microwave dielectric ceramics with low sintering temperature

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ABSTRACT

Ln₂Mo₃O₁₂ (Ln = La, Nd) ceramics with a defect scheelite related structure were prepared via a solid state reaction method. The La₂Mo₃O₁₂ ceramics sintered at 930 °C for 2 h exhibited a low dielectric permittivity of 10.1, a high quality factor (Qf value) of 60,000 GHz and a temperature coefficient of -80 ppm/°C at 12.7 GHz. The Nd₂Mo₃O₁₂ ceramics sintered at 945 °C for 2 h possessed a dielectric permittivity of 8.2, a Qf value of 80,000 GHz, and a temperature coefficient of -60 ppm/°C at 15.8 GHz. This group of ceramics could be good candidates for microwave substrate applications.

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1. Introduction

Recently, a lot of efforts have been made to search for new dielectric materials with very high quality factors, Qf ($Q = 1/\text{dielectric loss}$, and $f = \text{resonant frequency at GHz}$). These microwave dielectric ceramics can be used as dielectric resonators, filters, integrated passive components, substrates, etc. To be used as substrate materials for high speed devices, dielectric ceramics should have a low permittivity of about 10 to reduce the signal delay time, a high quality factor (Qf value) for frequency selectivity and a near zero temperature coefficient of resonant frequency (TCF) for temperature stability [1–6].

Mo and W based scheelite (Ca,Sr,Ba)(Mo,W)O₄ and wolframite (Mg,Mn,Zn)(Mo,W)O₄ compounds have been reported to possess low permittivity ($\epsilon_r = 7\text{--}15$) and high quality factor ($Qf = 37,000\text{--}90,000$ GHz) by Choi et al. and Yoon et al. [7,8]. It is easy to bring high defect concentrations at the A site of scheelite structure. The defect phase can be expressed as $A_{1-x}\phi_x\text{MoO}_4$, where ϕ stands for vacancies [9]. In some lanthanite molybdate systems, the defect value ϕ can be as high as 1/3, such as $\text{La}_{0.67}\phi_{0.33}\text{MoO}_4$, which could be obtained by quenching [10]. However, the cation vacancies have an ordered arrangement if the samples are cooled down at a sufficiently low rate [11–13]. In this case, the structure has a vacancy ordering of 1/3 of the A sites. It is composed of 9 scheelite subcells, which means that there are 12 formula units per unit cell. Nearest-neighbor

environments of the cations resemble those of scheelite. However, there has been no report on sintering behaviors and microwave dielectric properties of the ordered scheelite phases. In the present work, we investigated the microwave dielectric behaviors of Ln₂Mo₃O₁₂ (Ln = La, Nd) ceramics synthesized via a solid state reaction process. The relationships between microstructure, cell parameters and microwave dielectric properties were discussed.

2. Experimental procedure

Reagent-grade starting materials of La₂O₃, Nd₂O₃ (>99%, Guo-Yao Co, Ltd, Shanghai, China) and MoO₃ (>99%, Fuchen Chemical Reagents, Tianjin, China) were mixed thoroughly according to Ln₂Mo₃O₁₂ (Ln = La, Nd) compositions. The mixed powders were calcined at temperatures between 800 and 850 °C for 5 h. After being crushed, the calcined powders were re-milled for 5 h using ZrO₂ balls in deionized water. Then the powders were dried and mixed with a PVA binder. They were pressed into cylinders (10 mm in diameter and 5 mm in thickness) in a steel die at a uniaxial pressure of 200 MPa. The green samples were sintered at temperatures ranging from 915 to 1005 °C for 2 h.

Crystalline structures of the sintered samples were investigated by using X-ray diffraction with Cu K α radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). The microstructures of the sintered ceramics were examined by observing both the as-fired surface and fractured surface with scanning electron microscopy (SEM) (JSM-6460, JEOL, Tokyo, Japan). Their apparent densities were measured by using Archimedes' method. Dielectric behaviors at a microwave frequency were measured by the TE₀₁₈ shielded cavity method with a network analyzer (8720ES, Agilent, Palo Alto, CA) and a temperature

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chamber (Delta 9023, Delta Design, Poway, CA). The temperature coefficient of resonant frequency TCF (τ_f) was calculated by the following formula:

$$\text{TCF} = \frac{f_{85} - f_{25}}{f_{25}(85 - 25)} \times 10^6 \text{ (ppm/}^\circ\text{C)}, \quad (1)$$

where f_{85} and f_{25} were the TE₀₁₆ resonant frequencies at 85 and 25 °C respectively.

3. Results and discussion

Room temperature XRD patterns and SEM micrographs of both the natural and fractured surfaces of the Ln₂Mo₃O₁₂ (Ln = La, Nd) ceramics sintered at 930 °C/2 h are shown in Fig. 1. For both La₂Mo₃O₁₂ and Nd₂Mo₃O₁₂ ceramics, all peaks can be indexed as a monoclinic single-phase with a defect scheelite type structure (C2/c). The lattice parameters were calculated to be $a = 16.998 \text{ \AA}$, $b = 11.948 \text{ \AA}$, $c = 16.089 \text{ \AA}$ and $\beta = 108.44$ for La₂Mo₃O₁₂ and $a = 16.704 \text{ \AA}$, $b = 11.698 \text{ \AA}$, $c = 15.812 \text{ \AA}$ and $\beta = 108.54$ for Nd₂Mo₃O₁₂, which agreed well with the results reported by Jeitschko [13], Evdokimov et al. [14] and Brixner et al. [10]. For La₂Mo₃O₁₂, a dense and fine microstructure can be observed in the sample sintered at 930 °C. Its average grain size was 4 μm. For Nd₂Mo₃O₁₂ ceramic sintered at 930 °C for 2 h, a small amount of pores can be observed. Its apparent density was 4.82 g/cm³, which was about 93% of its theoretical density (5.179 g/cm³). When the sintering temperature was increased to 945 °C, the apparent density and relative density of the Nd₂Mo₃O₁₂ ceramics were 5.03 g/cm³ (as shown in Table 1) and 97%, respectively. Meanwhile, the relative density can reach as high as 97% (apparent density = 4.72 g/cm³, theoretical density = 4.865 g/cm³) for the La₂Mo₃O₁₂ ceramics sintered at 930 °C.

The microwave dielectric properties of the La₂Mo₃O₁₂ and Nd₂Mo₃O₁₂ ceramics as a function of the sintering temperature are shown in Fig. 2. As the sintering temperature was increased from 915 to 930 °C, the dielectric permittivity of the La₂Mo₃O₁₂ ceramics increased from 7.5 to 10.1 and then decreased slightly as the temperature was increased further. The dielectric permittivity of the Nd₂Mo₃O₁₂ ceramics got a saturated value of about 8.2 at 945 °C. Well sintered La₂Mo₃O₁₂ ceramics had a Qf value of 60,000 GHz and a temperature coefficient of −80 ppm/°C at 12.7 GHz. The well densified Nd₂Mo₃O₁₂ ceramics had a

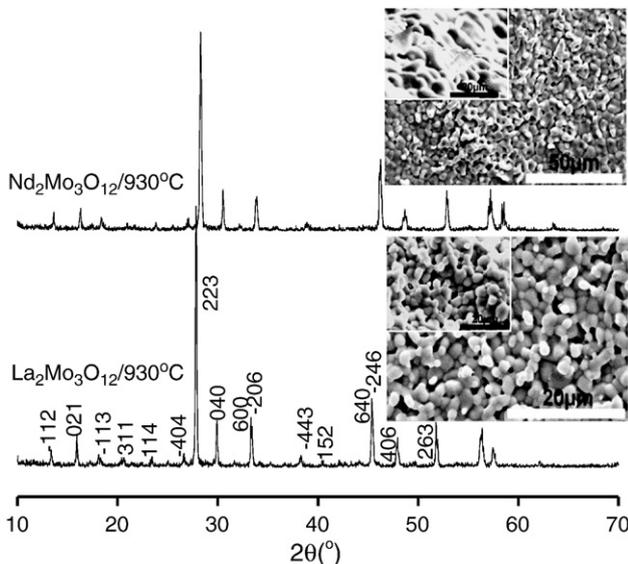


Fig. 1. XRD patterns and SEM photos (natural and fractured surfaces) of the Ln₂Mo₃O₁₂ (Ln = La, Nd) ceramics sintered at 930 °C for 2 h.

Table 1

Densities and microwave dielectric properties of the Ln₂Mo₃O₁₂ (Ln = La, Nd) ceramics.

Composition	S.T. (°C)	Density (g/cm ³)	α (Å ³)	V (Å ³)	ϵ_{cal}	ϵ_{mea}	f (GHz)	Qf (GHz)	TCF (ppm/°C)
La ₂ Mo ₃ O ₁₂	930	4.72	46.1	258.53	9.85	10.1	12.55	60,000	−80
Nd ₂ Mo ₃ O ₁₂	945	5.03	44.0	245.63	9.99	8.2	15.89	80,000	−60

S.T. – sintering temperature.

Qf value of 80,000 GHz and its TCF stabilized at −60 ppm/°C at 15.8 GHz.

Molecular dielectric polarizability α_x , which contains both ionic and electronic components, can be calculated from dielectric constant and molar volume, V_x in Å³, using the Clausius–Mossotti relation:

$$\alpha_x = \frac{V_x \times (\epsilon_x - 1)}{b \times (\epsilon_x + 2)}, \quad (2)$$

where b is assumed to be $4\pi/3$ for a cubic material and ϵ_x is the calculated dielectric constant of Ln₂Mo₃O₁₂ (Ln = La, Nd). Shannon [15] and Subramanian [16] pointed out that although this equation is strictly valid for compounds with cubic symmetry, it can also be used as a good approximation for many non-cubic materials. The dielectric polarizability for Ln₂Mo₃O₁₂ (Ln = La, Nd) follows the oxide additivity rule [17]:

$$\alpha_{\text{Ln}_2\text{Mo}_3\text{O}_{12}} = 2 \times \alpha_{\text{Ln}^{3+}} + 3 \times \alpha_{\text{Mo}^{6+}} + 12\alpha_{\text{O}^{2-}}, \quad (3)$$

where $\alpha_{\text{Ln}_2\text{Mo}_3\text{O}_{12}}$ is the total dielectric polarizability for Ln₂Mo₃O₁₂ (Ln = La, Nd), while $\alpha_{\text{Ln}^{3+}}$, $\alpha_{\text{Mo}^{6+}}$ and $\alpha_{\text{O}^{2-}}$ are the polarizabilities of Ln³⁺,

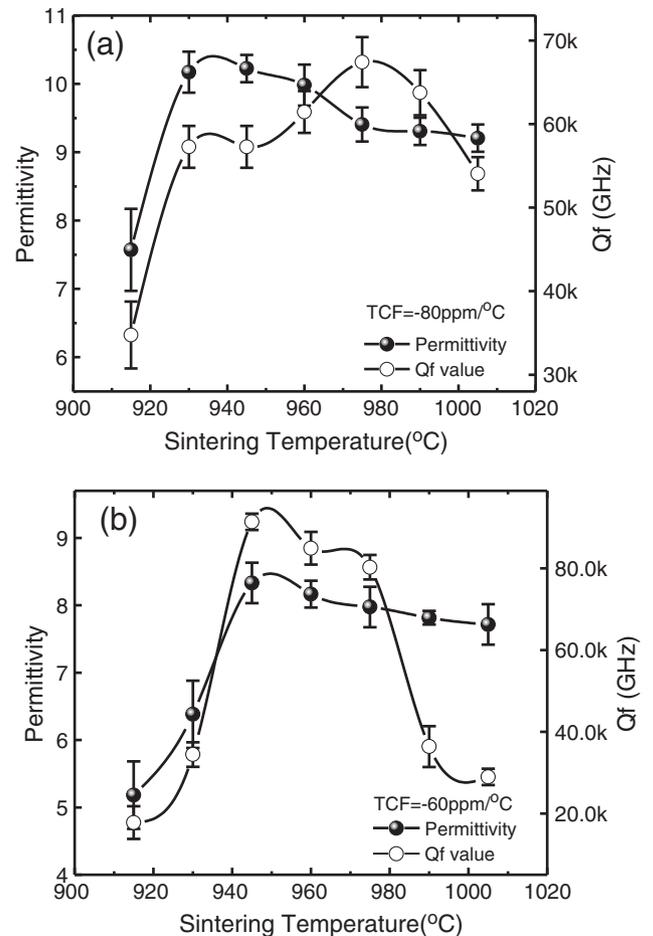


Fig. 2. Microwave dielectric constant and Qf values of the Ln₂Mo₃O₁₂ ceramics as a function of the sintering temperature: (a) Ln = La and (b) Ln = Nd.

Mo^{6+} and O^{2-} respectively [7,15]. The dielectric permittivity ϵ_{cal} of the $\text{Ln}_2\text{Mo}_3\text{O}_{12}$ ($\text{Ln} = \text{La}, \text{Nd}$) ceramics were calculated and listed in Table 1 along with their measured counterparts. The relative errors of the calculated values are smaller than 20%. In general, valence, coordination environment and bonding can all determine the polarizability of an ion. The unit volume polarization determines dielectric permittivity. The permittivities of $\text{Ln}_2\text{Mo}_3\text{O}_{12}$ increase with decreasing cell volume and decrease with decreasing Ln ions' polarizabilities. This could be the reason why the ϵ_{cal} of $\text{La}_2\text{Mo}_3\text{O}_{12}$ is smaller than that of $\text{Nd}_2\text{Mo}_3\text{O}_{12}$ although the measured values are contrary.

4. Conclusions

$\text{Ln}_2\text{Mo}_3\text{O}_{12}$ ($\text{Ln} = \text{La}, \text{Nd}$) ceramics can be sintered well at 930–945 °C and have good microwave dielectric properties. Considering their easy preparation, simple phase composition, fine microstructure, low sintering temperature and good microwave dielectric properties, the $\text{Ln}_2\text{Mo}_3\text{O}_{12}$ ($\text{Ln} = \text{La}, \text{Nd}$) ceramics can be promising candidates for microwave substrate applications.

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References

- [1] Obryan HM, Gallagher PK, Berkstresser GW, Brandle CD. *J Mater Res* 1990;5:183.
- [2] Surendran KP, Sebastian MT, Manjusha MW, Philip J. *J Appl Phys* 2005;98:044101.
- [3] Sebastian MT, Jantunen H. *Int Mater Rev* 2008;53:57.
- [4] Choi YJ, Park JH, Park JH, Park JG. *Mater Lett* 2004;58:3102.
- [5] Cho IS, Choi GK, An JS, Kim JR, Hong KS. *Mater Res Bull* 2009;44:173.
- [6] Fang CF, Chen YC, Tzou WC, Chang SL. *Mater Lett* 2003;57:2945.
- [7] Choi GK, Kim JR, Yoon SH, Hong KS. *J Eur Ceram Soc* 2007;27:3063.
- [8] Yoon SH, Kim DW, Cho SY, Hong KS. *J Eur Ceram Soc* 2006;26:2051.
- [9] Sleight AW, Linn WJ. *Ann NY Acad Sci* 1976;272:22.
- [10] Brixner LH, Sleight AW, Lics MS. *J Solid State Chem* 1972;5:247.
- [11] Templeton DH, Zalkin A. *Acta Crystallogr* 1963;16:762.
- [12] Cesari M, Perego G, Zazzetta A, Manara G, Notari B. *J Inorg Nucl Chem* 1971;33:3595.
- [13] Jeitschko W. *Acta Crystallogr B* 1973;29:2074.
- [14] Evdokimov AA, Sirotinkin VP. *Zh Neorg Khim* 1982;27:2388.
- [15] Shannon RD. *J Appl Phys* 1993;73:348.
- [16] Subramanian MA. *Mater Res Bull* 1989;24:1477.
- [17] Heydweiller A. *Z Phys* 1920;3:308.