

Short communication

# Low temperature firing microwave dielectric ceramics ( $K_{0.5}Ln_{0.5}$ )MoO<sub>4</sub> (Ln = Nd and Sm) with low dielectric loss

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## Abstract

In the present work, novel low temperature firing microwave dielectric ceramics ( $K_{0.5}Ln_{0.5}$ )MoO<sub>4</sub> (Ln = Nd and Sm) were prepared via the traditional solid state reaction method. A pure monoclinic phase can be formed at a low sintering temperature around 680 °C for both ( $K_{0.5}Nd_{0.5}$ )MoO<sub>4</sub> and ( $K_{0.5}Sm_{0.5}$ )MoO<sub>4</sub> ceramics. The densification temperature for the ( $K_{0.5}Nd_{0.5}$ )MoO<sub>4</sub> and ( $K_{0.5}Sm_{0.5}$ )MoO<sub>4</sub> ceramics are 700 °C and 800 °C for 2 h, respectively. The best microwave dielectric properties for ( $K_{0.5}Nd_{0.5}$ )MoO<sub>4</sub> was obtained in ceramic sample sintered at 760 °C for 2 h, with a dielectric permittivity of 9.8, a Qf about 69,000 GHz and a temperature coefficient of frequency about –62 ppm/°C. The best microwave dielectric properties for ( $K_{0.5}Sm_{0.5}$ )MoO<sub>4</sub> was obtained in ceramic sample sintered at 800 °C for 2 h, with a dielectric permittivity of 9.7, a Qf about 20,000 GHz and a temperature coefficient of frequency about –65 ppm/°C.

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**Keywords:** Sintering; Dielectric properties

## 1. Introduction

With the development of wireless communication and satellite broadcasting industry, the multilayer co-fired ceramics (MLCC) and low-temperature co-fired ceramics technology (LTCC) have played an important role in the fabrication process to meet the requirement of miniaturization and integration. The LTCC technology requires the microwave dielectric ceramics to have lower sintering temperatures than that of the inner electrode materials. In addition to the common method of adding sintering aids, such as low melting point oxides and low softening glasses, the employment of materials with intrinsic low sintering temperatures (so called low firing ceramics) is also an efficient way and has attracted much attention in recent years.<sup>1–4</sup>

In the past more than ten years, most of the low firing ceramics are TeO<sub>2</sub>-rich compounds, such as BaO–TeO<sub>2</sub> system,<sup>5,6</sup> MgO–TeO<sub>2</sub> system,<sup>7</sup> ZnO–TeO<sub>2</sub> system,<sup>8</sup> CaO–TeO<sub>2</sub> system,<sup>9</sup> Bi<sub>2</sub>O<sub>3</sub>–TeO<sub>2</sub> system,<sup>10</sup> and (Zr,Ti,Sn)O<sub>2</sub>–TeO<sub>2</sub> system.<sup>11,12</sup> In the recent few years, the research on the low firing ceramics was not only limited in the TeO<sub>2</sub>-rich systems but expanded to the universal oxide systems with low melting points, such as Bi<sub>2</sub>O<sub>3</sub>-rich compounds, V<sub>2</sub>O<sub>5</sub>-rich compounds, MoO<sub>3</sub>-rich compounds, P<sub>2</sub>O<sub>5</sub>-rich compounds, B<sub>2</sub>O<sub>3</sub>-rich compounds.<sup>13–20</sup> Among them, many MoO<sub>3</sub>-rich low firing ceramics show high microwave dielectric performance and some of them can be co-fired with aluminum.<sup>4,15,20</sup> In this work, novel MoO<sub>3</sub>-rich ( $K_{0.5}Ln_{0.5}$ )MoO<sub>4</sub> (Ln = Nd and Sm) compounds were prepared via the solid state reaction method. The phase evolution, microstructure, and microwave dielectric properties were investigated.

## 2. Experimental

Proportionate amounts of reagent-grade starting materials of K<sub>2</sub>CO<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub> (>99%, Guo-Yao Co, Ltd, Shanghai,

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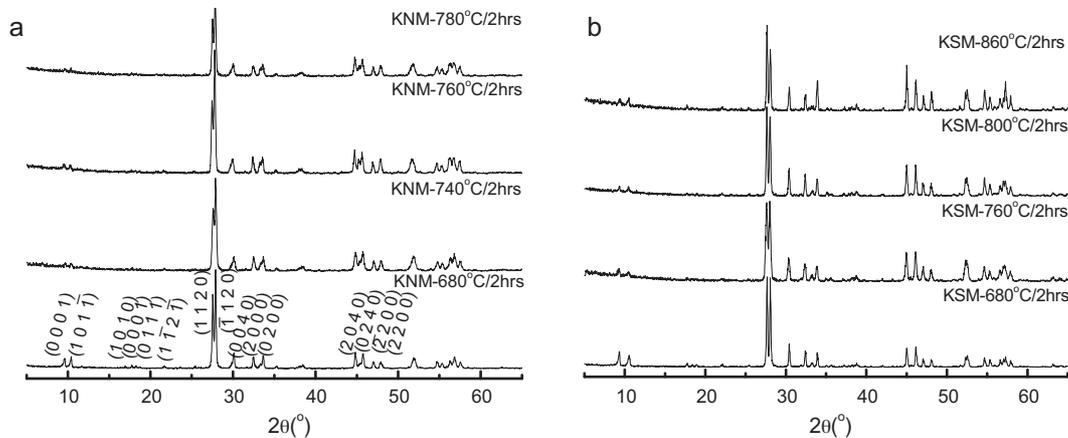


Fig. 1. X-ray diffraction patterns of the  $(K_{0.5}Ln_{0.5})MoO_4$  ( $Ln = Nd$  and  $Sm$ ) ceramics calcined and sintered at different temperatures.

China) and  $MoO_3$  (>99%, Fuchen Chemical Reagents, Tianjin, China) were weighed according to the stoichiometric formulation  $(K_{0.5}Ln_{0.5})MoO_4$  ( $Ln = Nd$  and  $Sm$ ) compositions. Powders were mixed and milled for 4 h using a planetary mill (Nanjing Machine Factory, Nanjing, China) by setting the running speed at 150 rpm with the Ytria Stabilized Zirconia (2 mm in diameter) milling media. The mixed oxides were then calcined at 600 °C for 4 h. After being crushed and re-milled for 5 h using the  $ZrO_2$  milling media and deionized water, powders were pressed into cylinders (10 mm in diameter and 5 mm in height) in a steel die with 5 wt.% PVA binder addition under a uniaxial pressure of 200 MPa. Samples were sintered in the temperature range from 640 °C to 860 °C for 2 h.

The crystalline structures of samples were investigated using X-ray diffraction with  $Cu K\alpha$  radiation (Rigaku D/MAX-2400 X-ray diffractometer, Tokyo, Japan). Microstructures of sintered ceramic were observed on the as-fired surface and fractured surfaces with scanning electron microscopy (SEM) (JSM-6460, JEOL, Tokyo, Japan). Dielectric behaviors at microwave frequency were measured with the  $TE_{01\delta}$  shielded cavity method with a network analyzer (8720ES, Agilent, Palo Alto, CA) and a temperature chamber (Delta 9023, Delta Design, Poway, CA). The temperature coefficient of resonant frequency  $\tau_f$  (TCF) was calculated with the following formula:

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

where  $f_{85}$  and  $f_{25}$  were the  $TE_{01\delta}$  resonant frequencies at 85 °C and 25 °C, respectively.

### 3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the  $(K_{0.5}Ln_{0.5})MoO_4$  ( $Ln = Nd$  and  $Sm$ ) ceramics calcined and sintered at different temperatures. It was reported that there exist many different modifications of the structure for  $(K_{0.5}Ln_{0.5})MoO_4$  compounds ( $Ln =$  rare earth element), depending on the size and nature of the rare earth element and the compound formation conditions.<sup>21–23</sup> In general, these compounds can be divided into two groups: (1) scheelite-type modifications including phases with an  $(K_{0.5}Eu_{0.5})MoO_4$ -type structure (space group  $P\bar{1}$ ) and (2) non-scheelite modifications with the  $(K_{0.5}Y_{0.5})MoO_4$ -type structure (space group  $Pbcn$ ).<sup>24</sup> Comparing our experimental data with the literatures', it is found that both the  $(K_{0.5}Nd_{0.5})MoO_4$  and  $(K_{0.5}Sm_{0.5})MoO_4$  prepared via the solid state reaction method here have the same structure with  $(K_{0.5}Eu_{0.5})MoO_4$  (PDF: 31-1006).<sup>25</sup> Using a  $Ag_{1/8}Pr_{5/8}MoO_4$ <sup>26</sup> structure as the starting model, Morozov et al.<sup>24</sup> found that both the  $(K_{0.5}Nd_{0.5})MoO_4$  and  $(K_{0.5}Eu_{0.5})MoO_4$  could be well indexed in the same monoclinic superspace group,  $I2/b(\alpha\beta)00$ . The XRD patterns of  $(K_{0.5}Nd_{0.5})MoO_4$  as shown in Fig. 1(a) was also indexed as this superspace group. Similarly, the detailed crystal structure report on the  $(K_{0.5}Sm_{0.5})MoO_4$  has been done by Arakcheeva

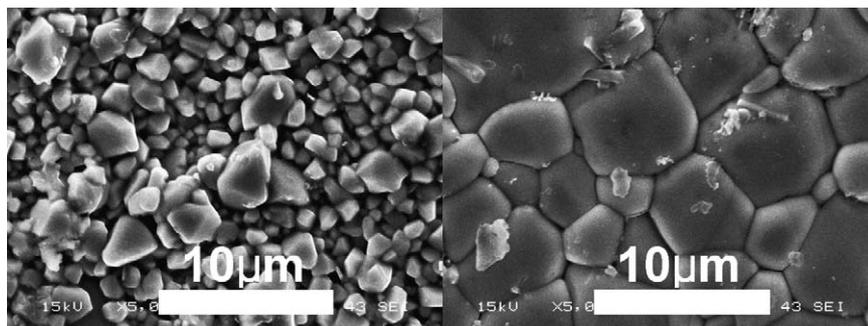


Fig. 2. SEM photos of the  $(K_{0.5}Nd_{0.5})MoO_4$  ceramic sintered at 760 °C for 2 h and  $(K_{0.5}Sm_{0.5})MoO_4$  ceramic sintered at 800 °C for 2 h.

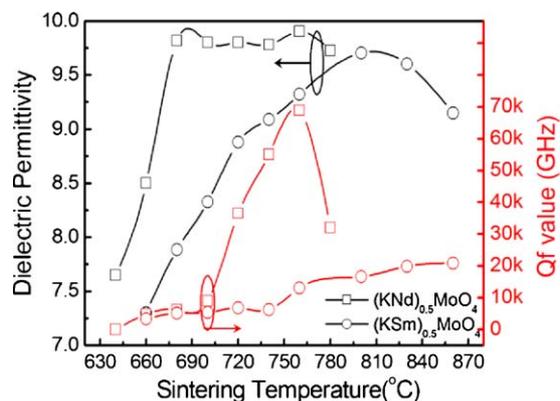


Fig. 3. Microwave dielectric permittivity and Qf values of the  $(K_{0.5}Ln_{0.5})MoO_4$  ( $Ln = Nd$  and  $Sm$ ) ceramics as a function of sintering temperature.

et al.<sup>27</sup> and it also can be indexed as the monoclinic superspace group,  $I2/b(\alpha\beta)00$ . From Fig. 1(b), our experimental results agree well with the literatures'. Furthermore, this monoclinic scheelite-related phase can be formed at a low temperature 680 °C for both  $(K_{0.5}Nd_{0.5})MoO_4$  and  $(K_{0.5}Sm_{0.5})MoO_4$  prepared via the simple solid state reaction method.

The SEM photos of the  $(K_{0.5}Nd_{0.5})MoO_4$  ceramic sintered at 760 °C for 2 hrs and  $(K_{0.5}Sm_{0.5})MoO_4$  ceramic sintered at 800 °C for 2 h are shown in Fig. 2. Both homogenous and dense microstructure can be observed. It is seen that the grain size of  $(K_{0.5}Nd_{0.5})MoO_4$  ceramic sintered at 760 °C for 2 h lies between 1 and 3  $\mu m$ , which is much smaller than 3–7  $\mu m$  for  $(K_{0.5}Sm_{0.5})MoO_4$  ceramic sintered at 800 °C/2 h. In fact, from the density results (the figure is not presented here), the  $(K_{0.5}Nd_{0.5})MoO_4$  ceramic can be well densified when the sintering temperature is above 700 °C while the densification temperature of  $(K_{0.5}Sm_{0.5})MoO_4$  ceramic is 800 °C. The SEM photos also confirm this result.

Microwave dielectric permittivity and Qf value of the  $(K_{0.5}Ln_{0.5})MoO_4$  ( $Ln = Nd$  and  $Sm$ ) ceramics as a function of sintering temperature are shown in Fig. 3. The microwave dielectric permittivity of  $(K_{0.5}Nd_{0.5})MoO_4$  ceramic first increased sharply from 7.6 at a sintering temperature of 640 °C to about 9.8 for the ceramic sample sintered at 680 °C along with the elimination of pores during the sintering process. It kept stable in the sintering temperature range 680–760 °C and then decreased slightly, which might be caused by the secondary grain growth, potassium volatilization, etc. The microwave dielectric permittivity of  $(K_{0.5}Sm_{0.5})MoO_4$  ceramic has the similar trend but its densification temperature is around 800 °C. The Qf value of microwave dielectric ceramics is influenced by many factors during the sintering process, such as the grain size, grain size distribution, pores, etc. Although the intrinsic part can be extrapolated from the infrared spectra data, the real Qf value including both intrinsic and extrinsic parts can only be analyzed qualitatively. The largest Qf value about 69,000 GHz of  $(K_{0.5}Nd_{0.5})MoO_4$  ceramic was obtained in ceramic sample sintered at 760 °C for 2 h. It is very sensitive to the sintering temperature, and large Qf values can only be obtained in a very narrow sintering temperature range. The Qf value of  $(K_{0.5}Sm_{0.5})MoO_4$  ceramic was about 20,000 GHz when

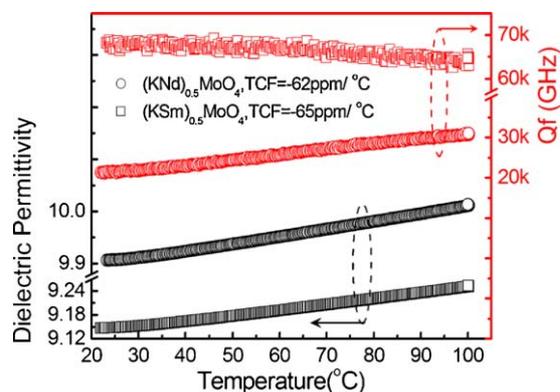


Fig. 4. Microwave dielectric permittivity and Qf values of the  $(K_{0.5}Ln_{0.5})MoO_4$  ( $Ln = Nd$  and  $Sm$ ) ceramics as a function of temperature.

above 800 °C, which was smaller than that of  $(K_{0.5}Nd_{0.5})MoO_4$  ceramic, but it seems much more stable against the sintering temperature.

To further understand the temperature dependence of the microwave dielectric properties of  $(K_{0.5}Ln_{0.5})MoO_4$  ( $Ln = Nd$  and  $Sm$ ) ceramics, the microwave dielectric permittivity and Qf value measured in the temperature range 25–120 °C are demonstrated in Fig. 4. It can be seen that the microwave dielectric permittivity of both  $(K_{0.5}Nd_{0.5})MoO_4$  and  $(K_{0.5}Sm_{0.5})MoO_4$  ceramics linearly increased with the temperature slightly without any abnormality. The Qf value of  $(K_{0.5}Nd_{0.5})MoO_4$  ceramic decreased slightly from 69,000 GHz at 20 °C to 64,000 GHz at 120 °C. The Qf value of  $(K_{0.5}Sm_{0.5})MoO_4$  ceramic increased slightly from 20,000 GHz at 20 °C to 31,000 GHz at 120 °C. The temperature coefficient for  $(K_{0.5}Nd_{0.5})MoO_4$  and  $(K_{0.5}Sm_{0.5})MoO_4$  ceramics are  $-62$  ppm/°C and  $-65$  ppm/°C, respectively.

#### 4. Conclusion

The monoclinic  $(K_{0.5}Nd_{0.5})MoO_4$  and  $(K_{0.5}Sm_{0.5})MoO_4$  ceramics were prepared via the solid state reaction method. The best microwave dielectric properties for  $(K_{0.5}Nd_{0.5})MoO_4$  was obtained in ceramic sample sintered at 760 °C for 2 h, with a dielectric permittivity of 9.8, a Qf about 69,000 GHz and a temperature coefficient of frequency about  $-62$  ppm/°C. The best microwave dielectric properties for  $(K_{0.5}Sm_{0.5})MoO_4$  was obtained in ceramic sample sintered at 800 °C for 2 h, with a dielectric permittivity of 9.7, a Qf about 20,000 GHz and a temperature coefficient of frequency about  $-65$  ppm/°C.

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