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Microwave dielectric properties of low firing scheelite-related $(Na_{0.5}La_{0.5})MoO_4$ ceramic

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ABSTRACT

In this paper, the $(Na_{0.5}La_{0.5})MoO_4$ ceramic with a scheelite structure was prepared via a solid state reaction method and its microwave dielectric properties were reported for the first time. The $(Na_{0.5}La_{0.5})MoO_4$ ceramic sintered at 740 °C for 2 h possessed a low dielectric permittivity of 11.0, a quality factor (Qf value) of 25,050 GHz and a temperature coefficient of −59 ppm/°C at 8.83 GHz. The $(Na_{0.5}La_{0.5})MoO_4$ ceramic is chemically compatible with Ag electrode material at its sintering temperature. It can be a promising microwave dielectric material for low-temperature co-fired ceramics technology (LTCC).

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1. Introduction

In recent years, with the rapid development of commercial wireless technologies and satellite communication, the low temperature co-fired ceramics technology (LTCC) has played an important role due to its simplicity and advantage in minimizing and integrating electronic components [1–4]. In order to meet the miniaturization and integration demand for LTCC applications, dielectric ceramics need to fulfill the requirement of a low sintering temperature (below melting points of Ag, Al, Cu, Au, etc.), a range of dielectric permittivities (ε_r), a high quality factor (Qf) (f=resonant frequency, $Q=1/$(dielectric loss at f)), a near-zero temperature coefficient of resonant frequency ($\tau_f \approx 0$ ppm/°C), and chemical compatibility with inner metal electrodes [5–7]. In other words, the LTCC technology required the microwave dielectric ceramic matrix to be co-fired with metal electrode.

A traditional widely used method is to lower the sintering temperatures of ceramics with high performance of microwave dielectric properties by addition, such as low melting point oxides, low softening point glasses, etc. [5,6,8]. Recently, the search for microwave dielectric ceramics with intrinsic low sintering temperatures has become more and more popular; especially, in most cases MoO_3 and TeO_2 containing ceramics have interesting low sintering temperatures because of the low melting temperatures of TeO_2 (733 °C) and MoO_3 (795 °C) [9,10]. The scheelite structure with a general formula ABO_4 is a ubiquitous adaptive structure type, like the perovskite structure in ABO_3 system. Double molybdates $ALn(MoO_4)_2$ (A=Li, Na, K, Rb, Cs; Ln=trivalent rate earth ions) are interesting host materials for luminescent rare earth ions, and have been widely investigated for solid state laser media [11,12]. In such double molybdates structure, the alkaline ions and rare earth ions are randomly distributed at the cation sites. The different cations with different radii in the host compound induce some change in the sublattice structure around the luminescent center ions [13]. Unfortunately, up to now, microwave dielectric properties of double molybdates ($(Na_{0.5}La_{0.5})MoO_4$) have not been reported. In the present study, sintering behavior, microwave dielectric properties and chemical compatibility with Ag of the $(Na_{0.5}La_{0.5})MoO_4$ were studied in detail.

2. Experimental procedure

Proportionate amounts of reagent-grade starting materials, Na_2CO_3 (≥ 99% Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), La_2O_3 (> 99.99%, Sinopharm Chemical Reagen Co., Ltd., Shanghai, China) and MoO_3 (> 99%, Yutong Chemical Reagents, Tianjin, China) were used to prepare $(Na_{0.5}La_{0.5})MoO_4$ according to the stoichiometric formulation. Powders were mixed and milled for 4 h by using a planetary mill (Nanjing Machine Factory, Nanjing, China) operating at a running speed of 450 rpm with zirconia balls (2 mm in diameter) and anhydrous ethanol used as milling media and then calcined at 600 °C for 4 h. After being crushed the powders were re-milled for 5 h to increase reactivity and better homogeneity and then dried. The as-dried powders were mixed with 5 wt% polyvinyl alcohol (PVA) binder and

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granulated, and then these powders were pressed into cylinders (12 mm in diameter and 4–5 mm in height) in a steel die under a uniaxial pressure of 200 MPa. Samples were sintered in the temperature ranges from 700 °C to 780 °C for 2 h in ambient atmosphere. To investigate the chemical compatibility of $(Na_{0.5}La_{0.5})MoO_4$ ceramic with Ag powders, 20 wt% Ag was mixed with the compound and co-fired at the 740 °C for 4 h.

The crystalline structures of samples were investigated using X-ray diffraction (XRD) with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometer, Tokyo, Japan) at a scanning rate of 0.02°/s in a 2θ range of 10–70°. Microstructures of sintered ceramic were observed on the as-fired surface with scanning electron microscopy (SEM) (JSM-6460, JEOL, Tokyo, Japan). The apparent densities of ceramics were measured by Archimedes' methed. Microwave dielectric behaviors at microwave frequencies 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) in the temperature range of 25–85 °C. Temperature coefficient of resonant frequency (TCF or τ_f value) was calculated with the following formula:

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

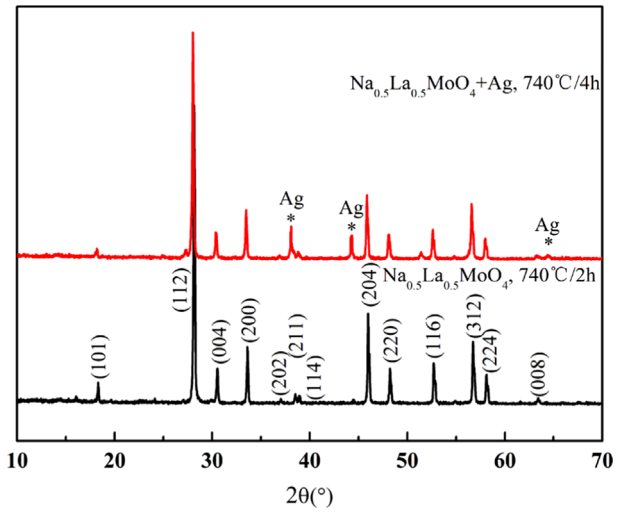


Fig. 1. XRD patterns of the $(Na_{0.5}La_{0.5})MoO_4$ ceramic and co-fired ceramic sample sintered at its optimal sintering temperature.

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

The calculation method of theoretical density is as follows:

$$\rho = \frac{zM}{NV},$$

where z is the number of atoms per unit cell; M is molar mass; N is Avogadro's number; and V is lattice volume.

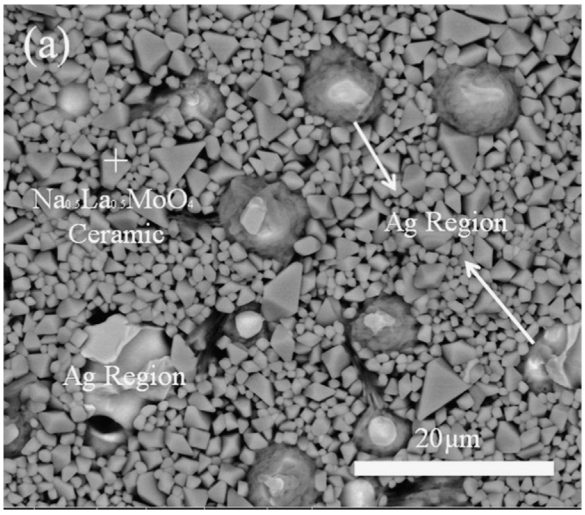
3. Results and discussions

Fig. 1 shows XRD patterns of the $(Na_{0.5}La_{0.5})MoO_4$ ceramic and its co-fired ceramic sample sintered at its optimal sintering temperature. All the diffraction peaks of the $(Na_{0.5}La_{0.5})MoO_4$ ceramic could be indexed as a tetragonal scheelite structure [space group $I4_1/a$ (88)] without secondary phases, and the lattice parameters were calculated as $a=5.341$ Å, $c=11.737$ Å, which agreed well with literature's reports ($a=5.343$ Å, $c=11.743$ Å from JCPDS Card no. 24-1103). For the co-fired ceramic sample with 20 wt% Ag powders, it is noted that only the peaks of $(Na_{0.5}La_{0.5})MoO_4$ phase and the respective metals phase are observed and there are no additional peaks in the XRD patterns to reflect a secondary phase formed, implying that $(Na_{0.5}La_{0.5})MoO_4$ ceramic does not react with silver at the sintering temperature 740 °C for 4 h.

The back-scattered electron image (BEI) and energy dispersive spectroscopy (EDS) analysis of the co-fired sample with 20 wt% silver powder are shown in Fig. 2. It is clearly seen that most grains with a gray color belong to the $(Na_{0.5}La_{0.5})MoO_4$ phase and the very few grains with a light white color are found to be pure silver. Form the XRD pattern together with the EDS analysis (Fig. 2b) of the nature surface of the co-fired ceramic, it was seen that there were only diffraction peaks of $(Na_{0.5}La_{0.5})MoO_4$ phase and silver phase in the co-fired ceramic. It indicates that the $(Na_{0.5}La_{0.5})MoO_4$ ceramic did not react with Ag powder and no secondary phases were formed when co-fired at 740 °C for 4 h.

SEM micrographs of natural surfaces of the $(Na_{0.5}La_{0.5})MoO_4$ ceramic sintered at different temperatures are shown in Fig. 3. Homogeneous microstructures with a few pores for the $(Na_{0.5}La_{0.5})MoO_4$ ceramic were revealed. From Fig. 3(a)–(d), with the increase of sintering temperature, the grain size increased from 1–5 μm at 720 °C to 3–8 μm at 780 °C.

Bulk density and the relative density of $(Na_{0.5}La_{0.5})MoO_4$ ceramic as a function of sintering temperature are shown in Fig. 4. When the $(Na_{0.5}La_{0.5})MoO_4$ ceramic was sintered at 740 °C,



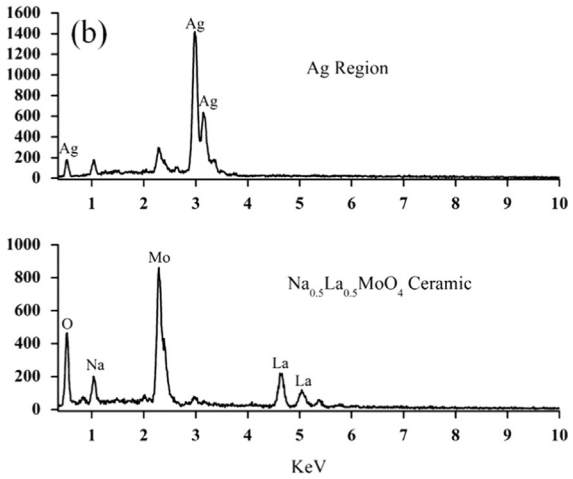


Fig. 2. Backscattered electron image (BEI) micrograph (a) and energy dispersive spectroscopy EDS analysis (b) of the co-fired sample with 20 wt% silver powder.

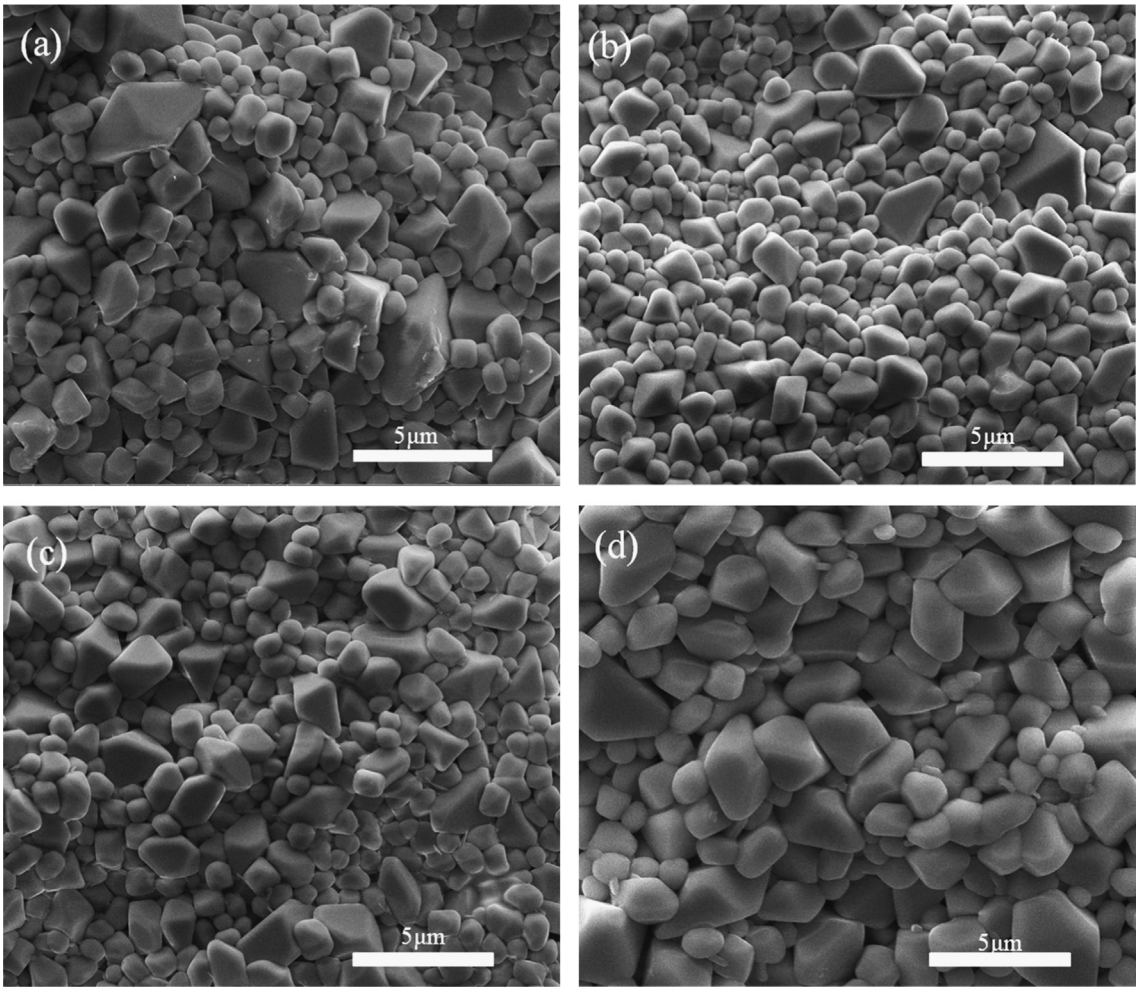


Fig. 3. SEM micrographs of the $(Na_{0.5}La_{0.5})MoO_4$ ceramic at (a) 700 °C/2 h; (b) 720 °C/2 h; (c) 740 °C/2 h; and (d) 760 °C/2 h.

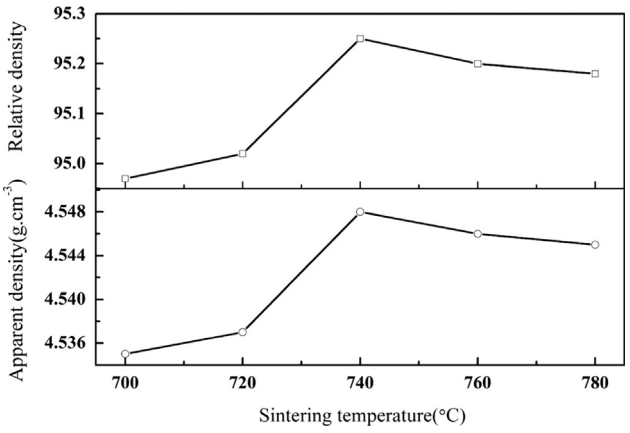


Fig. 4. Bulk densities and relative density of the $(Na_{0.5}La_{0.5})MoO_4$ ceramics as a function of sintering temperatures.

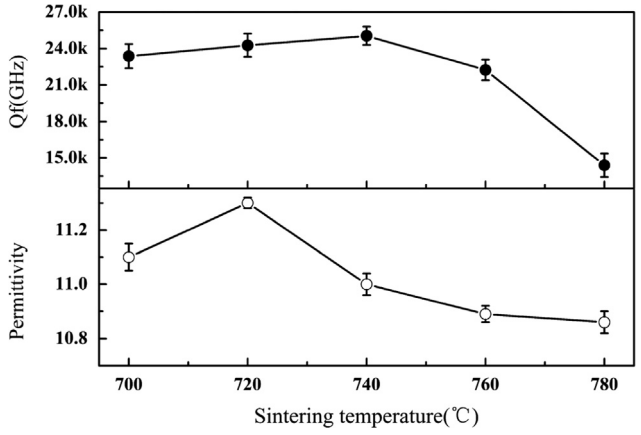


Fig. 5. Microwave dielectric properties (permittivity, *Qf* value) of the $(Na_{0.5}La_{0.5})MoO_4$ ceramics as a function of sintering temperatures.

the bulk density reached a maximum value of 4.548 g/cm^3 and the relative density is as high as 96%, which indicated that densification temperature of the $(Na_{0.5}La_{0.5})MoO_4$ ceramic was around 740 °C.

Microwave dielectric properties of the $(Na_{0.5}La_{0.5})MoO_4$ ceramic as a function of the sintering temperature are shown in Fig. 5. As the sintering temperature was increased from 700 to 780 °C, dielectric permittivity and *Qf* value of the $(Na_{0.5}La_{0.5})MoO_4$ ceramic increased from 11.1 to 11.3 and 23,375 GHz to 25,050 GHz, respectively. With the further increase of sintering temperature, the permittivity usually decreases slightly before melting due to the secondary grain growth, and grain deterioration of the dielectric constant. The *Qf* value of microwave dielectric ceramic is usually determined by the intrinsic and extrinsic dielectric losses. The extrinsic loss is influenced by many defects, such as grain boundaries, particle size, secondary grain, pores, etc. [14,15]. Excellent *Qf* value of 25,050 GHz (at 8.83 GHz) was

obtained in the $(Na_{0.5}La_{0.5})MoO_4$ ceramic sintered at 740 °C. TCF value did not change with the sintering temperature and remained stable at about −59 ppm/°C.

4. Conclusions

The $(Na_{0.5}La_{0.5})MoO_4$ microwave dielectric ceramic was prepared by the conventional solid state reaction method and well densified at about 740 °C. Excellent microwave dielectric properties were obtained by sintering at 740 °C for 2 h with a low permittivity of 11.0, a *Qf* value of 25,050 GHz, and a negative TCF value of −59 ppm/°C. The XRD, BEI, and EDS analysis show that the $(Na_{0.5}La_{0.5})MoO_4$ ceramic can co-fire with silver electrode at 740 °C. The $(Na_{0.5}La_{0.5})MoO_4$ ceramic can be a promising dielectric material for LTCC application.

Acknowledgments

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