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Microwave dielectric ceramic with intrinsic low firing temperature: $BaLa_2(MoO_4)_4$

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ABSTRACT

A low firing microwave dielectric ceramic $BaLa_2(MoO_4)_4$ with monoclinic structure was prepared via a solid state reaction method. The $BaMoO_4$ and $La_2(MoO_4)_3$ phases were first formed at 600 °C and then the monoclinic $BaLa_2(MoO_4)_4$ phase was formed gradually above 700 °C. Dense and homogeneous microstructure can be obtained in ceramic sample sintered at 800–860 °C for 2 h with grain size lying between 3–7 μm. Optimal microwave dielectric properties can be obtained in ceramic sintered at 860 °C for 2 h with a permittivity of ~10.3, a Qf value of ~29,800 GHz and a temperature coefficient of resonant frequency of ~−76 ppm/°C at about 9.9 GHz.

1. Introduction

With the fast development of miniaturization and integration of electronic devices, the low temperature co-fired ceramic (LTCC) technology has become an important fabrication method due to its simplicity and high efficiency. Commercially available LTCC systems not only provide the platform and components for fabrication of complex electronic circuitry within a three-dimensional (3-D) matrix, but LTCC tapes can also be shaped to form integrated micro system elements such as micro fluidic channels. LTCC requires the microwave dielectric ceramics with high performance and low sintering temperature (usually lower than 900 °C). The introduction of low melting point aids to the matrix ceramic by addition or substitution is a common method to lower the sintering temperature besides the use of nano-size starting materials[1–7]. Recently, considerable attention has been paid to developing new microwave dielectrics with intrinsic low firing temperature, such as Bi_2O_3-rich compounds, Li_2O-rich compounds, TeO_2-rich compounds, MoO_3-rich compounds, etc. [8–11]. In this work, a MoO_3-rich composition $BaLa_2(MoO_4)_4$ was prepared via the solid state reaction method. The phase evolution, microstructure and microwave dielectric properties were studied.

2. Experimental procedure

Proportionate amounts of reagent-grade starting materials of $BaCO_3$ (>99%, Shu-Du Powders Co. Ltd., Chengdu, China), La_2O_3 (>99%, Guo-Yao Co, Ltd, Shanghai, China) and MoO_3 (>99%, Fuchen Chemical Reagents, Tianjin, China) were prepared according to the stoichiometric formulation $BaLa_2(MoO_4)_4$ (La_2O_3 was pre-fired at 850 °C for 4 h). Powders were mixed and milled for 4 h, and then calcined at 600 and 700 °C for 4 h. After being crushed and re-milled for 5 h, powders were pressed into cylinders (10 mm in diameter and 5 mm in height). Samples were sintered in the temperature range from 700 to 890 °C for 2 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). Microstructures of sintered ceramic were observed on the as-fired surface with scanning electron microscopy (SEM) (JSM-6460, JEOL, Tokyo, Japan). Microwave dielectric behaviors 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 (TCF or τ_f value) was calculated with the following formula:

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

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

3. Results and discussion

Fig. 1 shows the XRD patterns of the $BaLa_2(MoO_4)_4$ powders calcined at 600 and 700 °C for 4 h, and ceramic samples sintered at 770–890 °C. It can be seen that the scheelite $BaMoO_4$ phase and $La_2(MoO_4)_3$ phase were first formed at 600 °C. With the increase of temperature to 700 °C, the $BaLa_2(MoO_4)_4$ phase started to appear. Till the sintering temperature up to above 800 °C, the $BaMoO_4$ and $La_2(MoO_4)_3$ phases cannot be observed from the XRD patterns. All the

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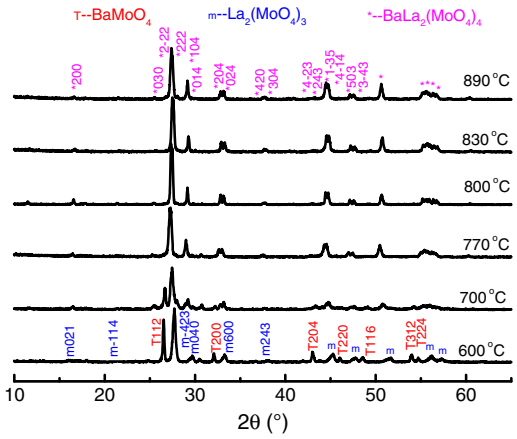

Fig. 1. XRD patterns of the $BaLa_2(MoO_4)_4$ ceramics calcined and sintered at different temperatures.

peaks can be indexed as a pure monoclinic $BaLa_2(MoO_4)_4$, which agrees well with Egorovo's report [12]. The phase evolutions during the calcining and sintering processes can be described as the following chemical reactions:

$$BaCO_3 + MoO_3 \xrightarrow{\approx 600\,^{\circ}C} BaMoO_4 + CO_2\uparrow \quad (2)$$

$$La_2O_3 + 3MoO_3 \xrightarrow{\approx 600\,^{\circ}C} La_2(MoO_4)_3 \quad (3)$$

$$BaMoO_4 + La_2(MoO_4)_3 \xrightarrow{700\text{–}800\,^{\circ}C} BaLa_2(MoO_4)_4 \quad (4)$$

SEM micrographs of $BaLa_2(MoO_4)_4$ ceramics sintered at 800–890 °C for 2 h are shown in Fig. 2. Dense and homogeneous microstructures with almost no pores were revealed in $BaLa_2(MoO_4)_4$ ceramics sintered at 800–860 °C. The grain size of $BaLa_2(MoO_4)_4$ ceramics sintered at 800 °C lies between 3 and 7 μm. When sintering temperature increased to 830 and 860 °C, the grain size increased little, which indicates that there was no secondary grain growth in the sintering temperature range of 800~860 °C. When sintering temperature increased to 890 °C, the pores caused by the melt volatilization appeared. This result indicates that the $BaLa_2(MoO_4)_4$ ceramic can be well densified at 800–860 °C.

Table 1
Microwave dielectric permittivity and Qf value of $BaLa_2(MoO_4)_4$ ceramic.

S. T. (°C)	Permittivity	Frequency (GHz)	Q	Qf (GHz)
700	8.0	10.0	770	7700
740	10.3	9.8	770	7500
770	10.6	9.6	1020	9800
800	10.6	9.7	2190	21,400
830	10.4	9.9	2480	24,700
860	10.3	9.9	3010	29,800
890	10.2	9.9	2480	24,600

S. T. — sintering temperature.

Microwave dielectric permittivity and Qf value of $BaLa_2(MoO_4)_4$ ceramic are shown in Table 1. As the sintering temperature increases, the dielectric permittivity increases firstly and reaches a saturated value about 10.4 as there is an elimination of the pores[13,14]. With the further increase of sintering temperature, the microwave dielectric permittivity decreased slightly and this phenomenon can be observed in many other systems[15]. This phenomenon might be caused by the volatilization of the low melting point oxides. Although the $BaMoO_4$ and $La_2(MoO_4)_3$ phases were reported to possess high Qf values [16,17], the Qf values of samples sintered at 700–770 °C for 2 h are very low due to the pores in ceramics and complex phase composition. With the increase of sintering temperature, the $BaLa_2(MoO_4)_4$ phase dominated and the pores were eliminated from the ceramics gradually, and the Qf value reached a maximum about 29,800 GHz (at about 9.9 GHz) at sintering temperature 860 °C, which is due to a complex influence of grain size, grain size distribution etc. The Qf value decreased to 24,600 GHz when sintering temperature increased to 960 °C because of the melt volatilization when over-sintered.

The microwave dielectric permittivity and Qf value of $BaLa_2(MoO_4)_4$ ceramic measured in the temperature range from 30 to 115 °C are shown in Fig. 3. It is seen that as temperature increases from 30 to 115 °C, the microwave dielectric permittivity linearly increases from 10.21 to 10.35 and the Qf value decreases from 26,800 to 22,500 GHz. The temperature coefficient of microwave dielectric

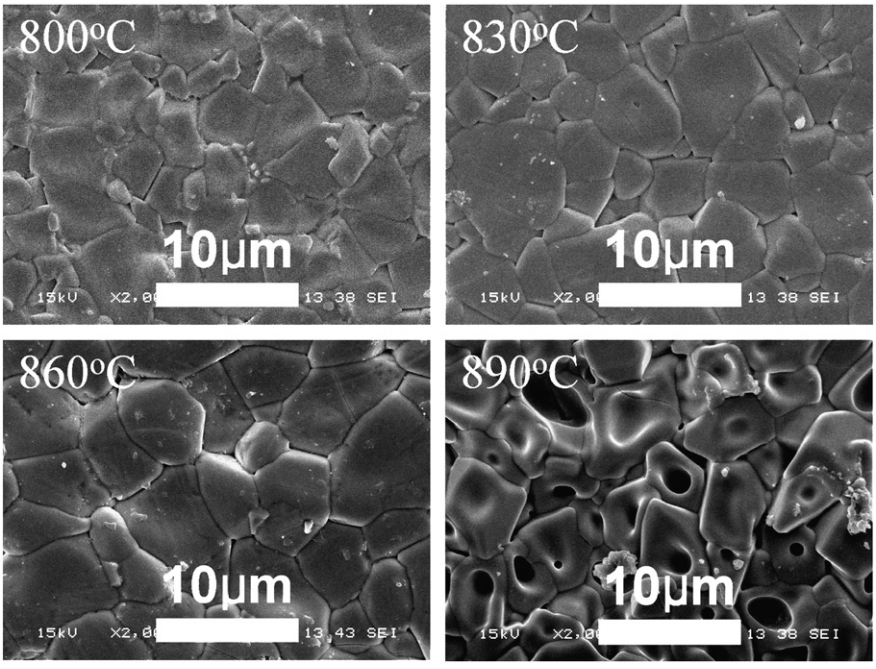

Fig. 2. SEM photos of $BaLa_2(MoO_4)_4$ ceramics sintered at 800–890 °C for 2 h.

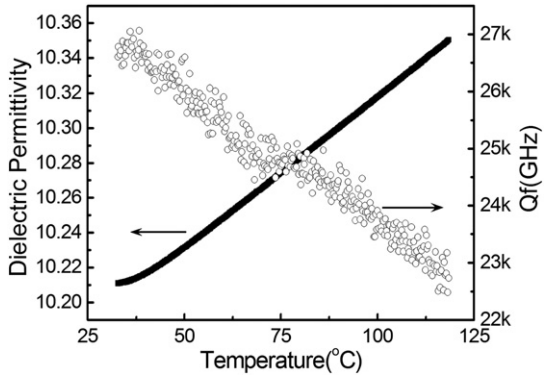

Fig. 3. Microwave dielectric permittivity and Qf values of $BaLa_2(MoO_4)_4$ ceramic vs temperature.

permittivity (TCP) calculated from a similar equation to formula (1) is about +160 ppm/°C. Meanwhile, the TCF value of $BaLa_2(MoO_4)_4$ ceramic calculated from formula (1) is about −76 ppm/°C. The relation between TCF and TCP can be expressed in the following equation [18]:

$$TCF = -\alpha_L - \frac{1}{2}TCP \quad (5)$$

where α_L is the linear thermal expansion coefficient of the dielectric ceramic material which is usually a small positive value and can be ignored.

4. Conclusions

The $BaLa_2(MoO_4)_4$ ceramic with monoclinic structure was prepared via a solid state reaction method. The $BaMoO_4$ and $La_2(MoO_4)_3$ phases were first formed at 600 °C and then the monoclinic $BaLa_2(MoO_4)_4$ phase was formed gradually above 700 °C. Dense and homogeneous microstructure can be obtained in ceramic sample sintered at 800–860 °C for 2 h. Optimal microwave dielectric properties can be obtained in ceramic sintered at 860 °C for 2 h with a permittivity of ~10.3, a Qf value of ~29,800 GHz and a temperature coefficient of resonant frequency of ~−76 ppm/°C.

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