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Novel series of MLa$_2$WO$_7$(M = Sr, Ba) microwave dielectric ceramic systems with monoclinic structures

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Abstract
Novel series of MLa$_2$WO$_7$(M = Sr, Ba) ceramics were prepared via a traditional solid-state reaction method. The sintering characteristic, crystal structures, micromorphology and microwave dielectric performances of systems were systematically investigated. X-ray diffraction (XRD) and Rietveld refinement display that both SrLa$_2$WO$_7$(SLW) and BaLa$_2$WO$_7$(BLW) ceramics are monoclinic structure with *Fdd* (No. 14) space group. SLW and BLW ceramics have high relative density (more than 94%). The SLW ceramics sintered at 1400 °C exhibited good microwave dielectric performances with $\mathcal{E}_r$ = 23.2, $Q\times f$ = 29,720 GHz, τ_f = − 127 ppm/°C and the BLW ceramics sintered at 1300 °C had excellent properties of $\mathcal{E}_r$ = 25.3, $Q\times f$ = 36,473 GHz, τ_f = − 108 ppm/°C. These results show that MLa$_2$WO$_7$(M = Sr, Ba) ceramics could be candidates for microwave devices.

1 Introduction

With the rapid development of mobile communication, the microwave dielectric materials should be miniaturization, low cost, high efficiency, nontoxicity, etc [1–5]. Moreover, the application of microwave materials should require three basic performances: an appropriate relative permittivity ($\mathcal{E}_r$) to satisfy the applications for different frequency ranges, a high quality factor ($Q\times f$) to decrease the power loss, and a near-zero temperature coefficient of resonant frequency (τ_f) to ensure the temperature stability of devices [6–10]. Currently, the application of microwave dielectric materials is becoming more and more extensive in military and commercial terms; the materials have been commonly applied in communication systems, especially for the fifth generation (5G) telecommunication which the characteristics are fast transmission speed [11, 12]. Therefore, to better adapt to the 5G new era technology tide, researchers need to study the improvement of material properties such as using different preparation methods (sol–gel method, hot-press sintering method, plasma sputtering method), adding vary sintering aids (B_2O_3,MnO_2,V_2O_5) and discover new materials to replace the original materials to meet the needs of products.

Researchers have been paying attention to the titanium-based, molybdenum-based, vanadium-based, silicon-based, germanium-based and tungsten-based ceramics for better microwave dielectric properties. Especially, the tungsten-based ceramics exhibited good microwave dielectric properties because the W^{6+} has good ionic polarization of [W–O] polyhedron. For example, Sebastian et al. [13] reported that the $Sr_2La_2MgW_2O_{12}$ ceramics sintered at 1525 °C had microwave dielectric performances of $\mathcal{E}_r$ = 24.7, $Q\times f$ = 35,000 GHz, and τ_f = − 83 ppm/°C, but high sintering temperature limited its further commercial applications. $La_6Mg_4A_2W_2O_{24}$ (A = Ta and Nb) ceramics possessed microwave dielectric properties of $\mathcal{E}_r$ = 25.2, $Q\times f$ = 13,600 GHz, and τ_f = − 45 ppm/°C for $La_6Mg_4Ta_2W_2O_{24}$ ceramic sintered at 1350 °C, and $\mathcal{E}_r$ = 25.8, $Q\times f$ = 16,400 GHz, and τ_f = − 56 ppm/°C for $La_6Mg_4Nb_2W_2O_{24}$ ceramics sintered at 1400 °C; however, the expensive of the raw materials (Nb_2O_5 and Ta_2O_5) hindered their further applications [14]. Therefore, to find a better tungsten-based microwave dielectric performance material, MLa$_2$WO$_7$(M = Sr, Ba) ceramics were designed. Furthermore, the sintering characteristic,

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phase structure, microstructure and microwave dielectric performances of ceramics were also investigated.

2 Experimental procedure

The MLa$_2$WO$_7$(M = Sr, Ba) ceramics were prepared via the traditional solid-state reaction method using $SrCO_3$ (≥ 99%), $BaCO_3$ (≥ 99%), La_2O_3(≥ 99%), and WO_3(≥ 99%) as the raw materials. The rare-earth oxide of La_2O_3 was hygroscopic, so La_2O_3 was preheated at 900 °C for 2 h to remove the moisture before weighing. The raw powders were weighted according to the stoichiometric of MLa$_2$WO$_7$(M = Sr, Ba) and ball-milled in the ethanol media for 6 h with ZrO_2 balls. After drying, the mixtures were calcined at 1150 °C for 4 h, and the calcined powders were milled with ZrO_2 balls for 6 h in ethanol again. After drying and sieving, the powders were added 7wt% polyvinyl alcohol solution and pressed into pellets with ~ 12 mm in diameter and ~ 6.0 mm in height under a pressure of 150 MPa. Finally, the pellets were sintered at 1250–1450 °C for 4 h.

The phase purity of product ceramic powders was analyzed by an X-ray diffraction (XRD; Model X Pert PRO, Almelo, the Netherlands). The microstructure on surface of the samples was observed by a scanning electron microscopy (JSM6380-LVSEM, Japan). Microwave dielectric performances of specimens were measured by a network analyzer (Model E5071 CENA, USA) at a room temperature environment. The temperature coefficient of resonant frequency was calculated by $\tau_f = \Delta f/(f_0 \Delta T)$ in the temperature range from 25 to 85 °C.

3 Results and discussion

Figure 1 shows the XRD patterns of MLa$_2$WO$_7$(M = Sr, Ba) ceramics sintered at different temperatures. The diffraction peaks of all samples are matched well with the JCPDS 01-077-2426, 049-0353, respectively, indicating that the MLa$_2$WO$_7$(Sr, Ba) ceramics belong to a monoclinic structure with *Fdd* (No. 14) space group. With rising the sintering temperature, BLW ceramics exhibited a single pure phase, but SLW ceramics had a second phase peak. With increasing the sintering temperature, diffraction peak position of samples kept stable, showing that the cell volume of ceramics did not changed. In addition, to further explore the cations occupancy in ceramics, the Rietveld refinement in view of XRD profile for BLW ceramics sintered at 1300 °C/4 h was done and the result is demonstrated in Fig. 2. The Bragg strength was very close to experimental data and gained as $R_p = 7.07\%$, $R_{wp} = 10.36\%$, and $\chi^2 = 5.21$, which indicated that the data are credible. Meanwhile, the refinement parameters are listed in the Table 1. It can be seen that [WO_6] octahedron, [BaO_6] octahedron and [LaO_8] dodecahedron share an oxygen atom, and [WO_6] octahedron was used as an intermediate bridge to form the structural framework of BLW ceramics.

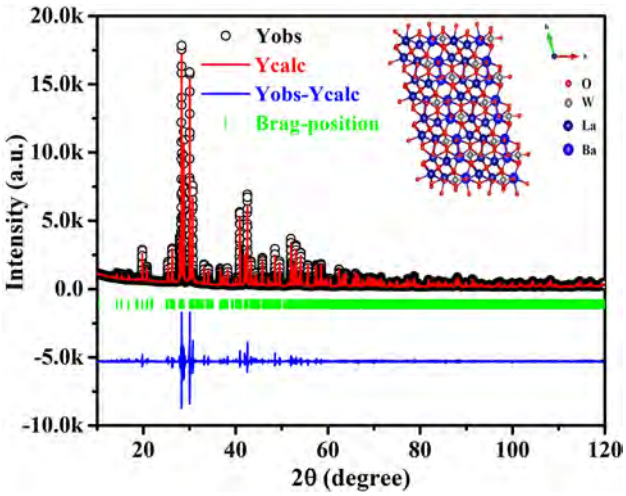

Fig. 2 Rietveld refinement and crystal structure of BLW ceramics sintered at 1300 °C

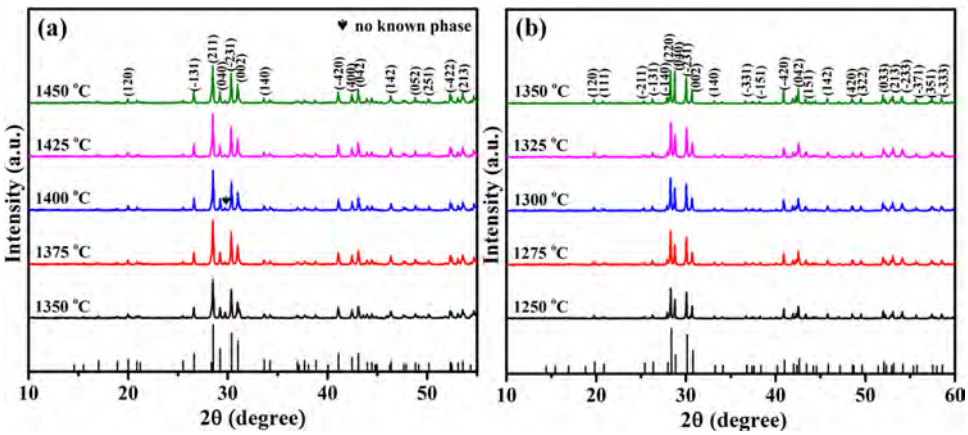

Fig. 1 XRD patterns of MLa$_2$WO$_7$ ceramics: (a) M = Sr, (b) M = Ba

Table 1 Refinement parameters of BLW ceramics sintered at 1300 °C

$BaLa_2WO_7$	Lattice parameters (Å)			Lattice parameters (Å)			Vol (Å^3)
	a	*b*	*c*	*α*	*β*	*γ*	641.773
	8.8579	12.8725	5.8303	90.0000	90.0000	105.1233	
	x		*y*	*z*			Occupancy
W1	0.4791		0.5071	0.2226			0.9818
W2	0.9130		0.8277	0.2752			1.0141
Ba1	0.6764		0.2997	0.2370			1.0444
Ba2	0.7141		0.0318	0.2719			0.9920
La1	0.0018		0.5824	0.2421			0.9770
La2	0.3945		0.7505	0.2640			1.0033
La3	0.1322		0.3006	0.2658			0.9865
La4	0.2639		0.0345	0.2340			1.0031
O1	0.6471		0.8067	0.2013			1.2082
O2	0.4459		0.5423	− 0.0301			0.8738
O3	0.9416		0.2384	0.4602			1.0298
O4	0.4663		0.5705	0.5065			1.2791
O5	0.1492		0.8272	0.2225			1.0540
O6	0.2622		0.5014	0.1642			1.0838
O7	0.7053		0.5328	0.1805			1.1497
O8	0.9250		0.7320	0.0160			1.2960
O9	0.4660		0.9230	0.0520			1.2370
O10	0.4420		0.3830	0.4120			1.1904
O11	0.9900		0.5068	0.9026			1.2247
O12	0.9390		0.4399	0.5474			0.8778
O13	0.2016		0.6422	0.4953			1.0550
O14	0.2016		0.1924	− 0.0012			1.1031

Figure 3 illustrates the SEM photographs of $M La_2WO_7$(M = Sr, Ba) ceramics sintered at different temperatures. The grains were tightly connected and had a clear grain boundary, no liquid phase appeared in all samples. As the sintering temperature increases, the grain size of ceramics gradually increases and further tends to inhomogeneous. In particular, too high sintering temperature will result in the pores between the grains or the crack, as shown in Fig. 3c, f. The EDS analysis consequence reveals that all elements ratios are approximate to the chemical composition of the $M La_2WO_7$(M = Sr,Ba) ceramics, as listed in Table. 2.

Figure 4 shows the bulk density and relative density as a function of the sintering temperature for $M La_2WO_7$(M = Sr, Ba) ceramics. The theoretical densities of SLW ceramics and BLW ceramics were obtained by the XRD analysis software and the values are 7.05 g/cm^3 and 7.36 g/cm^3, respectively. All samples have high density (more than 94% of relative density). The densities of SLW ceramics and BLW ceramics were increased firstly and then decreased with the change of sintering temperature. The highest density of SLW ceramics and BLW ceramics were 6.87 g/cm^3 and 7.21 g/cm^3 as the sintering temperatures were 1300 °C and 1400 °C, respectively. However, the densities of the $M La_2WO_7$(M = Sr, Ba) ceramics were reduced continuously with increasing the sintering temperature, which could be the over-sintering, as shown in Fig. 3c, f.

It was well known that the relative permittivity is affected by the internal factors (crystal structure, packing fraction, lattice energy, material composition) and the external factors (defects such as grain boundaries, pores, liquid phase) [15–19]. Initially, the relative permittivity of ceramics increased significantly with increasing the sintering temperature, and decreased with further increasing the sintering temperature, as shown in Fig. 4. Obviously, the changing trend of $M La_2WO_7$(M = Sr, Ba) ceramics in $\mathcal{E}_r$ was in accordance with the density. To minimize the effect of the pore on $\mathcal{E}_r$, the corrected relative permittivity ($\mathcal{E}_{corr}$) was obtained by the Bosman and Having's formula [20]:

$$\varepsilon_{\mathrm{corr}} = \varepsilon_{\mathrm{r}}(1 + 1.5p) \quad (1)$$

where P is the fraction porosity, $\mathcal{E}_{\mathrm{corr}}$ and $\mathcal{E}_r$ are the corrected and measured values of the permittivity, respectively.

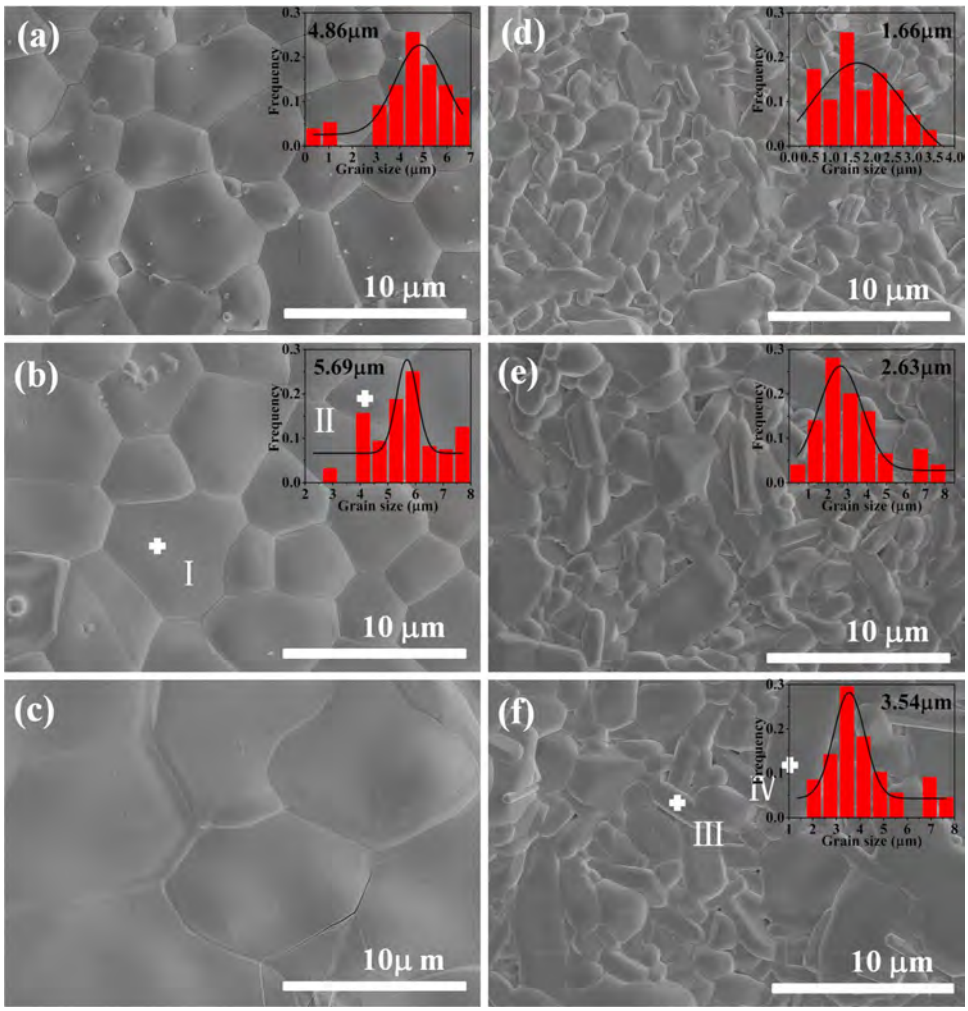

Fig. 3 SEM images of MLa$_2$WO$_7$(M = Sr,Ba) ceramics sintered at **a** 1275 °C, **b** 1300 °C, **c** 1325 °C for SLW ceramics, **d** 1375 °C, **e** 1400 °C, **f** 1425 °C for BLW ceramics

Table 2 EDS results of MLa$_2$WO$_7$(M = Sr,Ba) ceramics

Spot	Element (%)				
	Sr	Ba	La	W	O
I	14.15		20.78	9.96	55.11
II	13.03		17.84	8.93	60.20
III		9.68	18.85	10.72	60.72
IV		9.01	17.11	10.06	63.81

The corrected value ($\mathcal{E}_{corr}$) was always higher than that of the measured value ($\mathcal{E}_r$), as shown in Fig. 4.

The quality factor and temperature coefficient of resonant frequency for MLa$_2$WO$_7$(M = Sr, Ba) ceramics are shown in Fig. 5. Initially, it can be discovered that the quality factor of ceramics was increased to a maximum of 29,720 GHz for SLW ceramics, and 36,473 GHz for BLW ceramics, respectively, which was the similar with the density, demonstrating that the density was a key indicator in microwave dielectric performance. The quality factor value of SLW and BLW ceramics decreased as

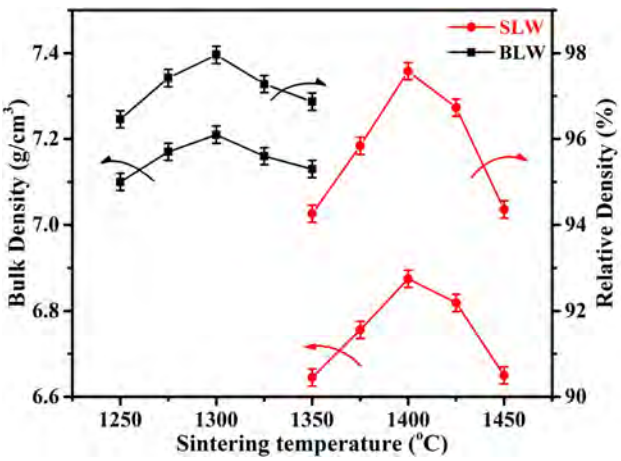

Fig. 4 Bulk density and relative density of MLa$_2$WO$_7$(M = Sr,Ba) ceramics as a function of sintering temperatures

the sintering temperature exceeds 1300 °C and 1400 °C, respectively, which may be due to the abnormal grain growth or grain cracks, as shown in Fig. 3c. The τ_f

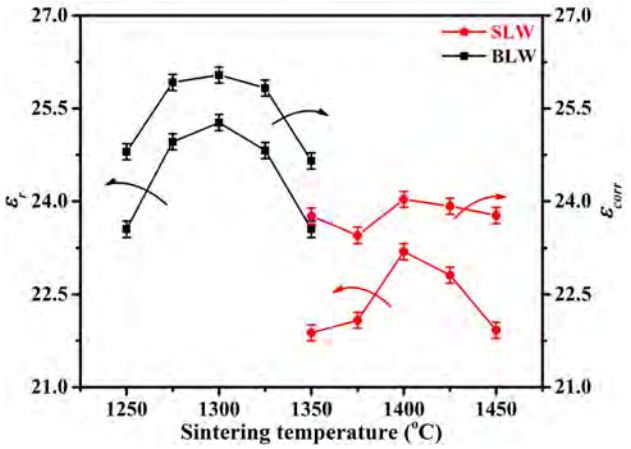

Fig. 5 $\mathcal{E}_r$ and $\mathcal{E}_{corr}$ of MLa$_2$WO$_7$(M = Sr,Ba) ceramics as a function of sintering temperatures

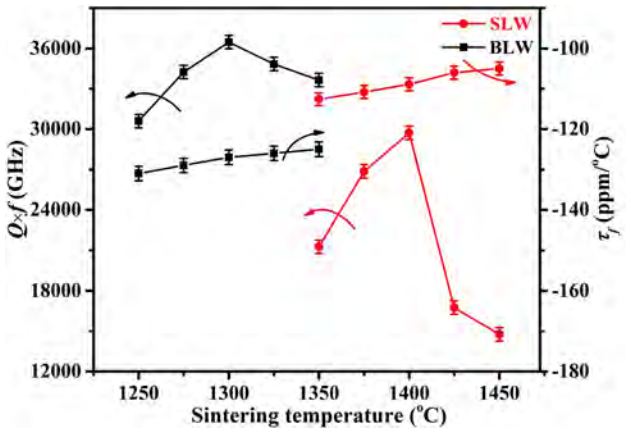

Fig. 6 $Q\times f$ and τ_f value of MLa$_2$WO$_7$(M = Sr, Ba) ceramics as a function of sintering temperatures

of MLa$_2$WO$_7$(M = Sr,Ba) ceramics has a large negative value. The MLa$_2$WO$_7$(M = Sr, Ba) ceramics could adjust the τ_f value to near zero by adding an appropriate amount of CaTiO$_3$. Table 3 lists the comparison of the microwave dielectric properties for some compounds with similar relative permittivity. The SrNdGaO$_4$ [21], Ba$_5$Nb$_3$TaO$_{15}$ [24] and Ca(Gd$_{1/2}$Ta$_{1/2}$)O$_3$ [26] ceramics have the near-zero τ_f values, but high raw materials of GaO$_2$ and Ta$_2$O$_5$ restricted their further applications. LaYbO$_3$ [25], SmZrTaO$_6$ [22] and BaHfO$_3$ [23] ceramics exhibited poor dielectric performance and high sintering temperatures. Although SrLaGaO$_4$ [21] has a low sintering temperature, the quality value is inferior. By contrast, the MLa$_2$WO$_7$(M = Sr, Ba) ceramics have cheaper raw materials and low sintering temperature, indicting that these materials could be the candidates for microwave devices (Fig. 6).

4 Conclusions

In this work, MLa$_2$WO$_7$(M = Sr, Ba) ceramics have been prepared via the traditional solid-state reaction method. The MLa$_2$WO$_7$(M = Sr, Ba) ceramics belong to the monoclinic structure. The density of samples had a close relationship with the relative permittivity and quality factor value. The SLW ceramics exhibited good microwave dielectric performances with $\mathcal{E}_r$ = 23.2, $Q\times f$ = 29,720 GHz, τ_f = − 127 ppm/°C. The BLW ceramics had excellent microwave dielectric properties with $\mathcal{E}_r$ = 25.3, $Q\times f$ = 36,473 GHz, τ_f = − 108 ppm/°C. In next work, an appropriate amount of CaTiO$_3$ was added to adjust the temperature coefficient of resonance frequency of MLa$_2$WO$_7$(M = Sr, Ba) ceramics to near zero.

Table 3 Comparison of the microwave dielectric properties for some compounds with similar relative permittivity

Material systems	Sintering temperature (°C)	$\mathcal{E}_r$	$Q\times f$ (GHz)	τ_f (ppm/°C)	Refs.
SrLaGaO$_4$	1275	20.3	16,200	− 34	[21]
SmZrTaO$_6$	1650	21.2	24,190	− 58	[22]
SrNdGaO$_4$	1300	21.4	16,600	7	[21]
BaHfO$_3$	1750	24.2	14,250	111	[23]
Ba$_5$Nb$_3$TaO$_{15}$	1500	25.7	21,600	16	[24]
LaYbO$_3$	1600	26.0	20,600	− 22	[25]
Ca(Gd$_{1/2}$Ta$_{1/2}$)O$_3$	1600	27.2	26,000	− 16	[26]
SrLa$_2$WO$_7$	1400	23.3	29,720	− 127	This work
BaLa$_2$WO$_7$	1300	25.3	36,473	− 108	This work

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