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Preparation and dielectric characterization of $BaLaAlO_4$ ceramics

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Abstract In the present work, $BaLaAlO_4$ ceramics with orthorhombic structure similar to K_2SO_4 in space group $P2_12_12_1$ were prepared by a solid state sintering process. The dense $BaLaAlO_4$ ceramics with minor amount of secondary phase have a low dielectric loss and a temperature stable dielectric constant with obvious frequency dependence. A dielectric constant around 15 was obtained at 12 GHz in the present ceramics together with a Qf value over 5,000 GHz.

Keywords $BaLaAlO_4$ · Microwave dielectric properties · Ceramics · Sintering · Microstructures

1 Introduction

Recently, a group of compounds with general chemical formula $ABCO_4$ (A=Ca or Sr; B=Y, La, Nd or Sm; C=Al or Ga) and tetragonal K_2NiF_4-type structure within space group I4/mmm have attracted much scientific attention because of their potential applications as substrates for high-T_c superconductor thin films [1–10]. In the author's group, $SrRAlO_4$ (R = La, Nd, Sm) and $CaRAlO_4$ (R = Nd, Sm, Y) ceramics have been systematically investigated for microwave resonator application, and the best microwave dielectric characteristics were obtained in $SrSmAlO_4$ and $CaSmAlO_4$ among these ceramics [11–13].

On the other hand, compounds with the similar compositions of $BaRAlO_4$ and $BaRGaO_4$ (R = rare earth elements) are not tetragonal with K_2NiF_4 structure, but orthorhombic structure similar to K_2SO_4 in space group $P2_12_12_1$ [8,14]. It is an interesting issue to investigate the dielectric properties of $BaRAlO_4$ and $BaRGaO_4$.

In the present work, $SrLnAlO_4$ (Ln = Nd and Sm) ceramics are prepared by the solid state reaction method, and the microwave dielectric properties are characterized together with the microstructures.

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2 Experimental procedure

$BaLaAlO_4$ ceramics were prepared by a solid-state reaction process using reagent-grade $BaCO_3$ (99.93%), La_2O_3 (99.99%), and Al_2O_3 (>99.98%) powders as the raw materials. The weighed raw materials were mixed by ball milling with zirconia media in distilled water for 24 h, and the mixtures were heated at 1350 °C in air for 6 h after drying. The calcined powders, with 6 wt% of PVA added, were pressed into disks measuring 12 mm in diameter and 2–6 mm high and then sintered at 1350 °C–1550 °C in air for 3 h. After cooling from the sintering temperature to 1100 °C at a rate of 2 °C/min, the ceramics were cooled inside the furnace.

Ground and thermal-etched surfaces of the sintered samples were observed by scanning electron microscopy (SEM), and the crystal phases were determined by powder x-ray diffraction (XRD) using Cu-Kα radiation after crushing and grinding. Dielectric properties were first measured at 10, 100 kHz and 1 MHz by an LCR meter (HP4284A) in the temperatures range of −50~100 °C, and then the microwave dielectric constant ε and quality factor Q (the inverse of dielectric loss, tanδ) were evaluated around 10 GHz using the resonator method [15]. Because Q factor generally varies inversely with the frequency, in the

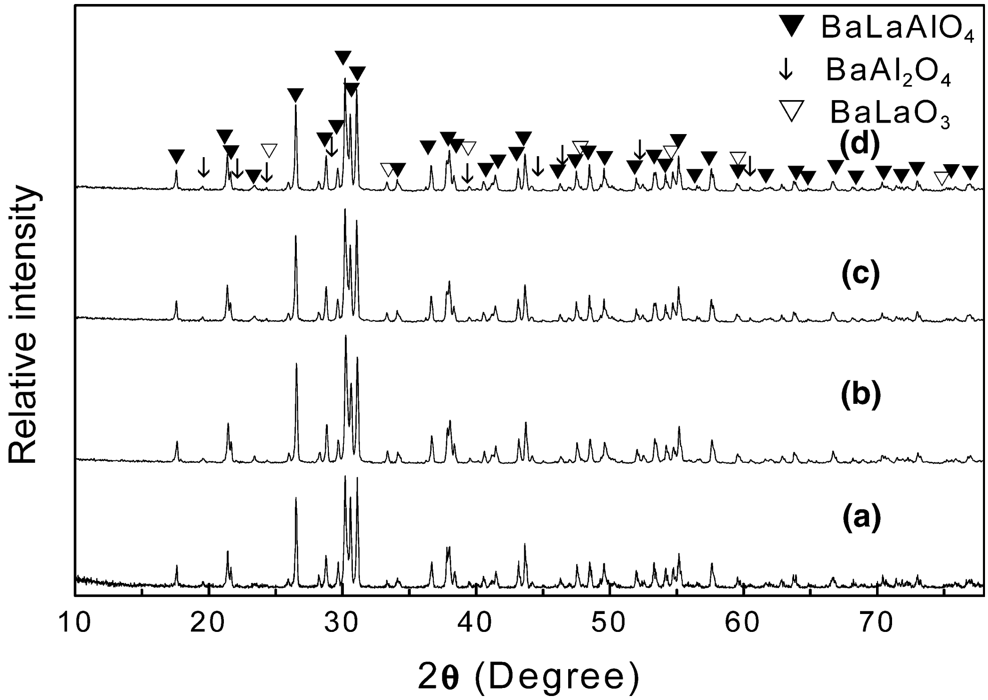

Fig. 1 XRD patterns of $BaLaAlO_4$ ceramics: (**a**) powders calcined at 1350°C in air for 6 h,(**b**) sintered at 1475 °C in air for 3 h, (**c**) sintered at 1500 °C in air for 3 h and (**d**) sintered at 1525 °C in air for 3 h

microwave region, the product of Qf was used to evaluate the dielectric loss instead of Q.

3 Results and discussion

XRD patterns of $BaLaAlO_4$ ceramics are shown in Fig. 1. $BaLaAlO_4$ major phase is observed together with minor amount of $BaAl_2O_4$ and $LaAlO_3$ secondary phases. With varying sintering temperature, no significant difference can be distinguished in XRD patterns. The highest bulk density of 5.4718 g/cm3 was obtained in the samples sintered at 1500 °C in air for 3 h.

SEM micrographs on fractured surfaces of $BaLaAlO_4$ ceramics are shown in Fig. 2, which display the microstructure varying with sintering temperature. The grain growth can be obviously observed. When sintered at 1475 °C, some grains are still cuboids distinct from the ground grains. The grains grow more integrated and bigger as the sintering temperature increases.

Figure 3 gives the frequency dependence of dielectric characteristics of $BaLaAlO_4$ ceramics sintered at various temperatures. Both dielectric constant and dielectric loss show the frequency dependence, and they tend to be stable as the frequency is above 10 kHz. Sintering temperature has a significant influence on dielectric characteristics. Dense $BaLaAlO_4$ ceramics show a higher dielectric constant around 18. Sintering temperature shows significant effects on the frequency dependence of dielectric characteristics in $BaLaAlO_4$ ceramics, the strongest frequency dependence is determined in the $BaLaAlO_4$ ceramics sintered at 1525 °C, which may be resulted from the over sintering. Moreover, the dielectric constant is temperature stable between −40 and 100 °C, and the temperature dependence of dielectric constant increases with decreasing frequency (see Fig. 4).

The microwave dielectric properties of $BaLaAlO_4$ ceramics sintered at different temperatures are listed in Table 1. At microwaves, a dielectric constant around 15 is observed, which is much lower than that at 1 MHz and lower frequencies, while the dielectric loss is much higher. The Qf value is 5,000 GHz at 10.5 to 12.5 GHz, and the best one is 5,259 GHz for $BaLaAlO_4$ ceramics sintered at 1500 °C.

Compared with $SrLaAlO_4$ (ε=17.1, tanδ=0.00035, Qf=30770 GHz),$SrSmAlO_4$ (ε=18.8, tanδ=0.00016, Qf=54880 GHz), $SrNdAlO_4$(ε=17.8, tanδ=0.00040, Qf=25700 GHz) and $CaNdAlO_4$(ε=18.1, tanδ=0.00064, Qf=16855GHz) [11, 13], the Qf and ε values of $BaLaAlO_4$ ceramics are much lower than that for $SrRAlO_4$ (R = La, Sm) and $CaNdAlO_4$ ceramics [5, 8, 13, 16], while the tanδ is much higher. The great distinctness should result from the apparently different structure.

$BaLaAlO_4$ has a different structure from most Sr- and Ca-based $ABCO_4$ compounds. According to literatures [5, 8, 13, 15], Sr- and Ca-based $ABCO_4$ compounds generally have the tetragonal structure with space group I4/mmm. However, $BaLaAlO_4$ and $BaNdGaO_4$ crystal are not tetragonal with $CaTiO_3$ or K_2NiF_4 structure, but orthorhombic similar to K_2SO_4 in space group $P2_12_12_1$ [8, 14]. The coordination polyhedrons of both are octahedron and tetrahedron, respectively.

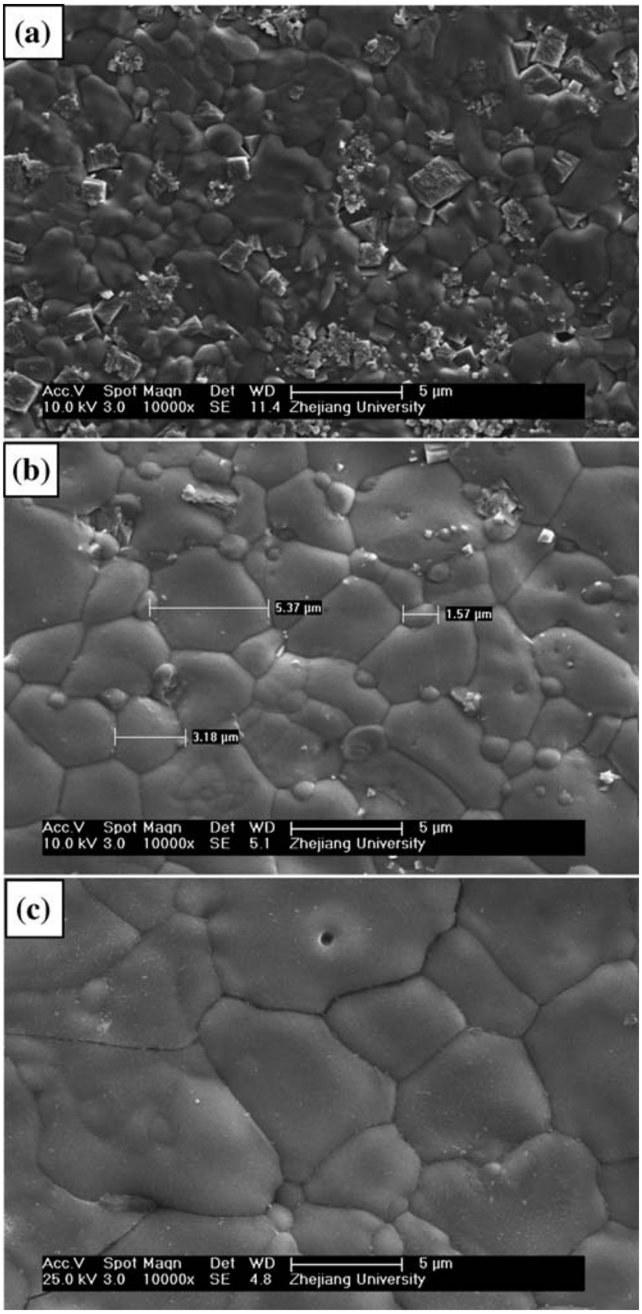

Fig. 2 SEM micrographs of $BaLaAlO_4$ ceramics sintered at (**a**) 1475 °C, (**b**) 1500 °C and (**c**) 1525 °C in air for 3 h

So in a K_2NiF_4-type $ABCO_4$ crystal cell, all the CO_6 octahedrons have the same orientation, in which C-atoms tend to shift in the same direction when affected by external electric field, making greater polarization and lower dielectric loss. In contrast, CO_4 tetrahedrons in a K_2SO_4-type $ABCO_4$ cell have different orientations and small space, thus it is hard for the C-atoms to behave the same in external electric field. So the displacement of C-atoms in K_2SO_4-type is resisted stronger than that in K_2NiF_4 type. As a result, it is hard for K_2SO_4-type $ABCO_4$ to polarize and therefore the dielectric loss is larger.

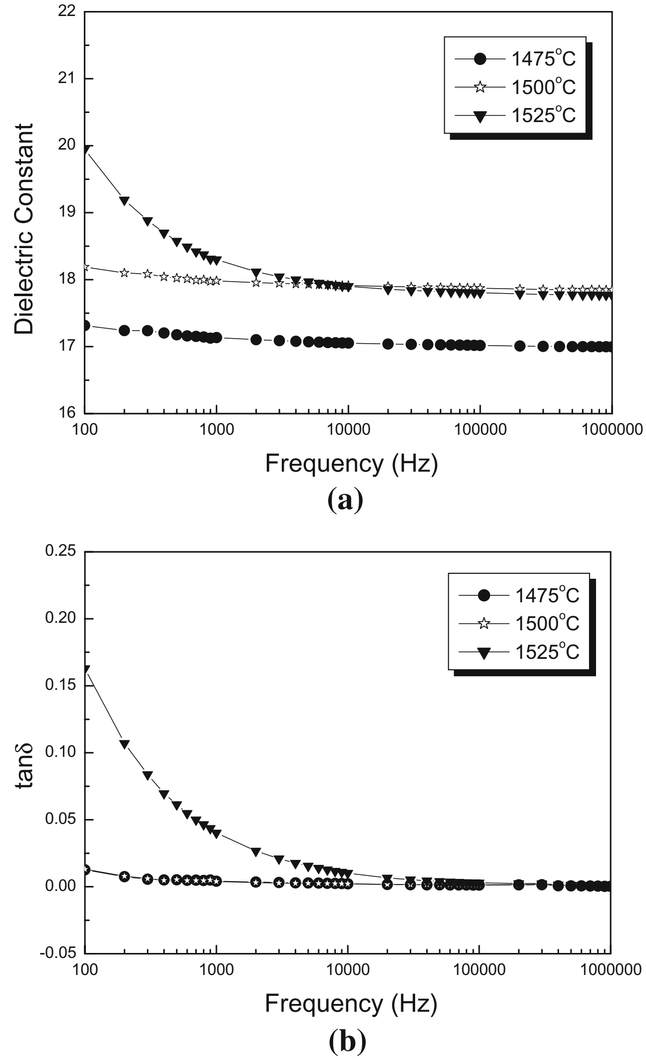

Fig. 3 Frequency dependence of dielectric characteristics of $BaLaAlO_4$ ceramics sintered at various temperatures: (**a**) dielectric constant, (**b**) dielectric loss

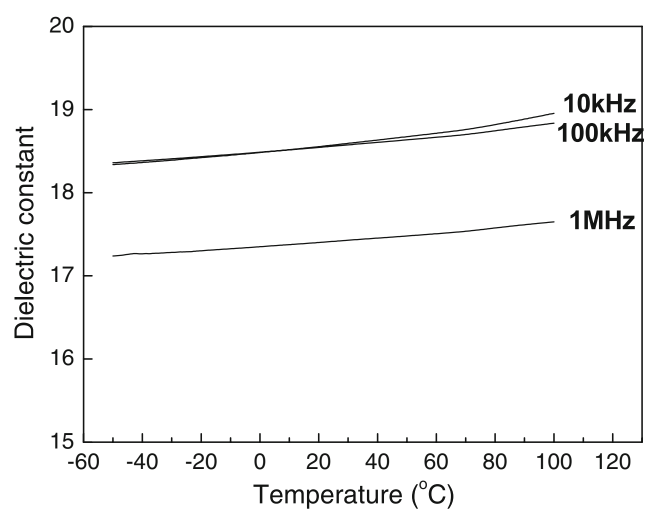

Fig. 4 Temperature dependence of dielectric constant of $BaLaAlO_4$ ceramics sintered at 1500 °C in air for 3 h

Table 1 Microwave dielectric characteristics of $BaLaAlO_4$ ceramics sintered on various conditions.

Sintering condition	f_0 (GHz)	E	tanδ	Qf (GHz)
1475°C/3 h	12.57	14.2	0.0024	5,238
1500°C/3 h	11.57	15.4	0.0022	5,259
1525°C/3 h	10.54	16.5	0.0022	4,977

4 Conclusion

$BaLaAlO_4$ ceramics were prepared by a solid state sintering process, and the major phase with orthorhombic structure similar to K_2SO_4 in space group $P2_12_12_1$ was observed together with minor amount of $BaLaO_3$ and $BaAl_2O_4$. A low dielectric loss was determined combined with a temperature stable dielectric constant with slight frequency dependence in the present ceramics, and dielectric constant around 15 was obtained at 12 GHz together with a Qf value over 5,000 GHz. The improved Qf value is expected through the microstructure optimizing especially eliminating the secondary phases.

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