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Journal of the European Ceramic Society 26 (2006) 1969–1971
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Microwave dielectric characteristics of $SrLaGaO_4$ and $SrNdGaO_4$ ceramics

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Available online 27 October 2005

Abstract

$SrLnGaO_4$ (Ln = La and Nd) ceramics with K_2NiF_4 structure were prepared by solid-state reaction approach, and the microwave dielectric properties and microstructures were characterized. The $SrLaGaO_4$ and $SrNdGaO_4$ ceramics with minor secondary phase, $Sr_3Ga_2O_6$, were obtained by sintering at 1250–1350 °C for 3 h, and good microwave dielectric characteristics were achieved: the ceramics had (1) $\varepsilon = 20.3$, $Q \times f = 16{,}219$ GHz, and $\tau_f = -33.5$ ppm/°C for $SrLaGaO_4$; and (2) $\varepsilon = 21.4$, $Q \times f = 16{,}650$ GHz, and $\tau_f = 7.1$ ppm/°C for $SrNdGaO_4$.
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Keywords: Dielectric properties; Sintering; X-ray methods; K_2NiF_4 structure

1. Introduction

The $ABCO_4$ oxide crystals (A = Sr, Ca, B = rare earth, C = Al, Ga) with tetragonal K_2NiF_4 structure have attracted much attention because of their potential applications as substrates for high-temperature superconductor thin films.[1,2] The dielectric constants of these compounds are around 20 combined with very low loss at microwave frequencies,[1] and their ceramics might be promising new candidates of low-loss microwave dielectric ceramics for resonator and filter applications. Compared with the typical low loss microwave dielectric ceramics such as $Ba(Mg_{1/3}Ta_{2/3})O_3$,[3] $Ba(Zn_{1/3}Ta_{2/3})O_3$,[4] and $LaAlO_3$,[5] $ABCO_4$ ceramics may have the merit of easy preparation because of their lower melt points. In the previous work, the $MLnAlO_4$ (M = Sr, Ca, Ln = La, Nd, Sm, Y) ceramics have been prepared and the microwave dielectric properties have been characterized.[6–8] The microwave dielectric properties of $SrLnAlO_4$ ceramics are $\varepsilon = 17$–19, $Q \times f = 25{,}000$–$55{,}000$ GHz, and $\tau_f \approx 4$ ppm/°C, and those of $CaLnAlO_4$ ceramics are $\varepsilon = 18$–19, $Q \times f = 18{,}000$–$51{,}000$ GHz, and $\tau_f = -52$–6 ppm/°C.

On the other hand, the dielectric loss of $SrLaGaO_4$ single crystal is lower than that of $SrLaAlO_4$ crystal at microwave frequencies,[1] so one could expect that the same case should be occurred at the corresponding ceramics. Till now, the dielectric properties of $SrLnGaO_4$ ceramics have not been characterized yet.

In the present work, $SrLnGaO_4$ (Ln = La and Nd) ceramics are prepared by the solid-state reaction method, and the microwave dielectric properties are characterized together with the microstructures.

2. Experimental procedure

Reagent-grade $SrCO_3$ (99.5% purity), La_2O_3 or Nd_2O_3 (99.99 or 99% purity) and Ga_2O_3 (99.9% purity) in 2:1:1 mole ratio were mixed by ball milling in deionized water using zirconia balls for 24 h. The slurry was dried and then calcined at 1100 °C for 3 h to prepare $SrLnAlO_4$ powders. The calcined powders, with 6 wt.% PVA (polyvinyl alcohol) added, were pressed into disc compacts of 12 mm in diameter and around 5 mm in height, and these compacts were sintered at temperatures from 1250 to 1350 °C in air for 3 h.

The microstructures were observed by scanning electron microscope (SEM, FMI Sirion FISEM), and the phase constitutions of the present ceramics were characterized by X-ray diffraction (XRD, RIGAKU D/max 2550 PC) analysis using Cu Kα radiation for crushed and ground powders, also the cell parameters of ceramics could be refined by the least square method using software MDI JADE accompanied with the instrument.

The microwave dielectric properties were evaluated at about 10 GHz by Hakki and Coleman's resonator method,[9] and the

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doi:10.1016/j.jeurceramsoc.2005.09.043

temperature coefficient of resonant frequency was estimated from the equation

$$\tau_f = -\frac{\tau_\varepsilon}{2} - \alpha \quad (1)$$

where α is the linear expansion coefficient ($\alpha \approx 10$ ppm/°C),[1] and τ_s the temperature coefficient of dielectric constant evaluated at 1 MHz by a LCR meter (HP 4284A) equipped with a thermostat range from 25 to 85 °C.

3. Results and discussion

The single-phase $SrLaGaO_4$ and $SrNdGaO_4$ powders could not be obtained by calcining at 1300 °C when the powder was shrunk to a bulk, and XRD results show that the phase constitution of powders calcined at 1100 °C is almost the same as that of 1300 °C, so the calcining temperature is selected as 1100 °C. Actually, the single-phase gallate is not easy to be obtained by conventional solid-state reaction.[10] In the perovskite system, the stability of perovskite structure could be characterized by the tolerance factor and electronegativity difference, and so does the $ABCO_4$ structure, for this structure is consisted by perovskite interleaved with rock-salt layer. The tolerant factors of $ABCO_4$ should be defined as:

$$t = \frac{d_{A/B-O}}{\sqrt{2}d_{C-O}} \quad (2)$$

where $d_{A/B-O}$ and d_{C-O} represent the mean equilibrium bond lengths between metal atoms and oxygen given by the sum of the room-temperature ionic radii.[11] According to Eq. (2), the tolerance factors of $SrLaGaO_4$ and $SrNdGaO_4$ are both smaller than those of $SrLaAlO_4$ and $SrNdAlO_4$ (0.93, 0.92 versus 0.97, 0.96), and the electronegativity differences of $SrLaGaO_4$ and $SrNdGaO_4$ are both smaller than those of $SrLaAlO_4$ and $SrNdAlO_4$ (2.07 versus 2.25). These results show that the crystal structures of gallate are less stable than those of aluminate in $ABCO_4$ series. The XRD patterns of $SrLaGaO_4$ and $SrNdGaO_4$ ceramics sintered at 1250–1350 °C for 3 h are shown in Fig. 1, and they indicate that the primary $SrLnGaO_4$ phase is co-existent with $Sr_3Ga_2O_6$ (JCPDF No. 24-1200) secondary phase in the present ceramics. The percentage densities of $SrLaGaO_4$ and $SrNdGaO_4$ ceramics are shown in Table 1, and the sintered densities are all relatively low.

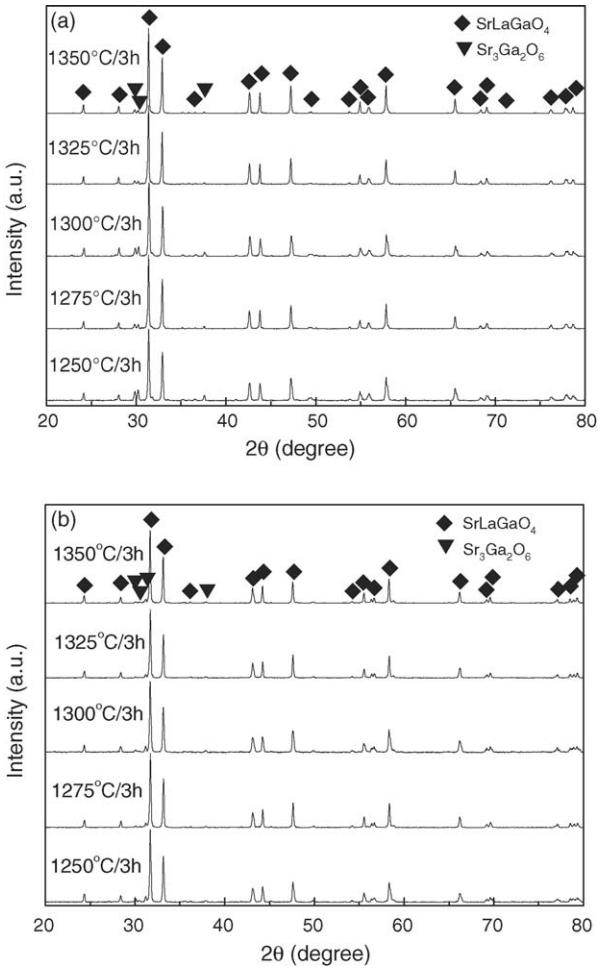

Fig. 1. XRD patterns of (a) $SrLaGaO_4$ and (b) $SrNdGaO_4$ ceramics sintered at different temperatures for 3 h.

The microwave dielectric properties of $SrLaGaO_4$ and $SrNdGaO_4$ ceramics are shown in Table 1. The dielectric constant varies slightly with the sintering temperature, and the dependence of dielectric constant on sintering temperature is consistent with that of bulk densities. The values of dielectric constant for $SrLaGaO_4$ and $SrNdGaO_4$ ceramics are around 20 and 21, respectively. The $Q \times f$ values of $SrLaGaO_4$ and $SrNdGaO_4$ ceramics increase with increasing sintering temperature initially and then decrease. The maximum $Q \times f$

Table 1
Microwave dielectric properties of $SrLaGaO_4$ and $SrNdGaO_4$ ceramics sintered at various temperatures

Composition	Sintering condition (°C/3 h)	Relative density (%)	Cell volume (Å^3)	ε	tan δ	$Q \times f$ (GHz)	τ_f (ppm/°C)
$SrLaGaO_4$	1250	93.6	187.61	20.4	0.00066	15,803	−40.1
$SrLaGaO_4$	1275	94.0	187.70	20.3	0.00064	16,219	−33.5
$SrLaGaO_4$	1300	93.3	187.38	20.1	0.00071	14,676	−40.5
$SrLaGaO_4$	1325	93.5	187.72	20.1	0.00072	14,458	−30.8
$SrLaGaO_4$	1350	93.4	187.71	19.9	0.00073	14,274	−33.2
$SrNdGaO_4$	1250	91.2	182.80	21.6	0.00063	15,714	6.6
$SrNdGaO_4$	1275	91.2	182.68	21.7	0.00063	15,778	10.3
$SrNdGaO_4$	1300	90.9	182.88	21.4	0.0006	16,650	7.1
$SrNdGaO_4$	1325	90.7	182.80	21.3	0.0006	16,667	11.5
$SrNdGaO_4$	1350	90.5	182.93	21.3	0.00063	15,937	6.9

values for $SrLaGaO_4$ and $SrNdGaO_4$ ceramics are 16,219 and 16,667 GHz, respectively. The low $Q \times f$ values should be originated from the low relative densities and the presence of the secondary phase. The temperature coefficients of resonant frequency τ_f of $SrLaGaO_4$ and $SrNdGaO_4$ ceramics ranged from −40 to −30 ppm/°C and from 6.6 to 11.5 ppm/°C, respectively (Table 1). According to Cockbain,[12] the temperature coefficient of dielectric constant can be approximately expressed as the following when $\varepsilon \geq 10$ and $\tan\delta \leq 0.1\%$:

$$\tau_\varepsilon \approx G - \alpha(\varepsilon + 1) \tag{3}$$

$$G = \frac{\varepsilon}{3\alpha_m}\left(\left(\frac{\partial\alpha_m}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial\alpha_m}{\partial T}\right)_V\right) \tag{4}$$

where α is the linear expansion coefficient, α_m the polarizability of a macroscopic small sphere of volume V, and T the temperature. Combining Eqs. (1) and (3), the τ_f value should be in direct proportion to the product of α and ε, and so does the product of cell volume and dielectric constant for the linear expansion coefficient will increase with increasing cell volume. The dependency of τ_f on sintering temperature has almost the same tendency of that of the product of cell volume and dielectric constant on sintering temperature. The different τ_f of $SrLaGaO_4$ and $SrNdGaO_4$ ceramics should originate from the different stress states,[2,10,11] and the details will be involved in our further work.

4. Conclusions

$SrLaGaO_4$ and $SrNdGaO_4$ ceramics with minor $Sr_3Ga_2O_6$ secondary phase had been obtained by sintering at 1250–1350 °C. The dielectric constant varied slightly with sintering temperature and the variation rule was consistent with that of the density. The $Q \times f$ values of $SrLaGaO_4$ and $SrNdGaO_4$ ceramics increased initially with increasing sintering temperature and then decreased. The dependence of τ_f on sintering temperature had almost the same tendency as that of the cell volume and dielectric constant product on sintering temperature. The good microwave dielectric properties such as $\varepsilon = 20.3$, $Q \times f = 16{,}219$ GHz, and $\tau_f = -33.5$ ppm/°C for $SrLaGaO_4$ and $\varepsilon = 21.4$, $Q \times f = 16{,}650$ GHz, and $\tau_f = 7.1$ ppm/°C for $SrNdGaO_4$ were achieved.

Acknowledgements

This work was supported by National Science Foundation of China under grant number 50272058, National Science Foundation for Distinguished Young Scientists under grant number 50025205 and Chinese National Key Project for Fundamental Researches under grant number 2002CB613302.

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