SrLnAlO$_4$ (Ln=Nd and Sm) Microwave Dielectric Ceramics

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Abstract. SrLnAlO$_4$ (Ln=Nd and Sm) ceramics with K$_2$NiF$_4$ structure were prepared by a solid state reaction approach, and their microwave dielectric characteristics were evaluated together with the microstructures. The single phase dense SrNdAlO$_4$ and SrSmAlO$_4$ ceramics were obtained by sintering at 1450–1475°C and 1475–1500°C, respectively, and the good microwave dielectric characteristics were achieved: (1) $\varepsilon = 17.8$, $Q \cdot f = 25{,}700$ GHz, $\tau_f = -9$ ppm/°C for SrNdAlO$_4$; and (2) $\varepsilon = 18.8$, $Q \cdot f = 54{,}880$ GHz, $\tau_f = 2$ ppm/°C for SrSmAlO$_4$ dense ceramics. The Qf value significantly increased with increasing sintering temperature.

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 K$_2$NiF$_4$-type structure has attracted much scientific attention because of their potential applications as substrates for high-T_c superconductor thin films [1–10]. SrLaAlO$_4$ was reported as the first compound in ABCO$_4$ group by Ruddlesden and Popper [1]. Since then, the structure, crystallization and properties of ABCO$_4$ compounds were investigated by several authors [2–10]. So far, investigations have concentrated on the single crystals of ABCO$_4$ and their substrate application, and there is rarely report on ABCO$_4$ ceramics.

On the other hand, since ABCO$_4$ crystals have a dielectric constant around 20 combined with a very low dielectric loss at microwave frequencies [8, 9], 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$_3$ [11], Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$ [12], and LaAlO$_3$ [13], ABCO$_4$ ceramics may have the merits of easy preparation combined with low cost because of

their lower melt points and using low cost raw materials. However, there is rare report on the preparation and the dielectric properties especially microwave dielectric properties of ABCO$_4$ ceramics.

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.

Experimental Procedure

SrLnAlO$_4$ (Ln=Nd and Sm) ceramics were prepared by a solid-state reaction process using reagent-grade SrCO$_3$ (99.95%), Nd$_2$O$_3$ (99%), Sm$_2$O$_3$ (99.9%), and Al$_2$O$_3$ (99.98%) powders as the raw materials. The weighed raw materials were mixed by ball milling with zirconia media in ethanol for 24 h, and the mixtures were heated at 1200°C in air for 3 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 1400°C–1500°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

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microscopy (SEM), and the crystal phases were determined by powder x-ray diffraction (XRD) using Cu Kα radiation after crushing and grinding. Dielectric constant ε and quality factor Q (the inverse of dielectric loss, tanδ) were evaluated around 10 GHz using the resonator method of Hakki and Coleman [14]. Because Q factor generally varies inversely with the frequency, in the microwave region, the product of Qf was used to evaluate the dielectric loss instead of Q. The temperature coefficient of the dielectric constant, τ_ε was evaluated at 1 MHz, using an LCR meter (Model HP4284A, Hewlett-Packard Co., Palo Alto, CA) equipped with a thermostat. The τ_f value was evaluated from the equation,
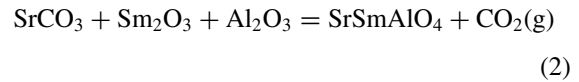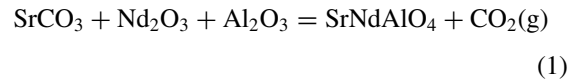
$$\tau_f = -(\tau_\varepsilon/2) - \alpha \qquad (1)$$

where α was the linear expansion coefficient [15]. The value of α was around 8 ppm/$^\circ$C for SrLnAlO$_4$ (Ln=La, Nd and Sm) [8].

Results and Discussion

Both SrNdAlO$_4$ and SrNdAlO$_4$ single phase powders can be synthesized by a solid reaction process at 1200°C in air for 3 hours through the following reactions:

$$SrCO_3 + Nd_2O_3 + Al_2O_3 = SrNdAlO_4 + CO_2(g) \qquad (1)$$

$$SrCO_3 + Sm_2O_3 + Al_2O_3 = SrSmAlO_4 + CO_2(g) \qquad (2)$$

The dense ceramics can be obtained by sintering the powder compacts in air at 1450–1475°C and 1475–1500°C, respectively. The X-ray theoretic density is calculated as 6,227 Kg/m^3 for SrNdAlO$_4$ and

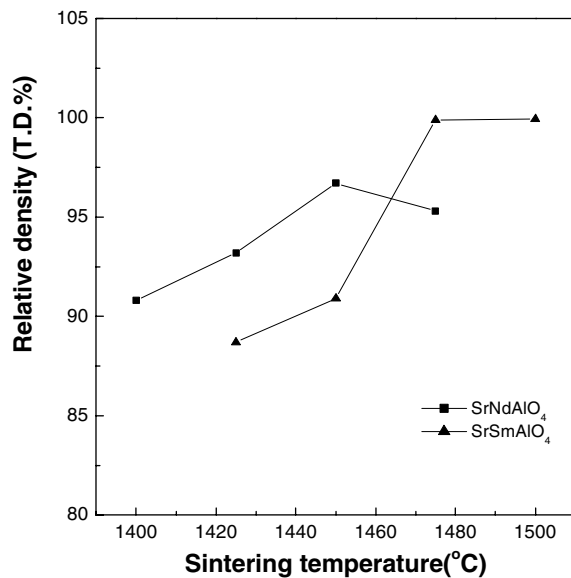*Fig. 2.* XRD patterns of (a) SrNdAlO$_4$ and (b) SrSmAlO$_4$ ceramics sintered at various temperatures.

Fig. 1. Variation of relative density of SrNdAlO$_4$ and SrSmAlO$_4$ ceramics as function of sintering temperature.
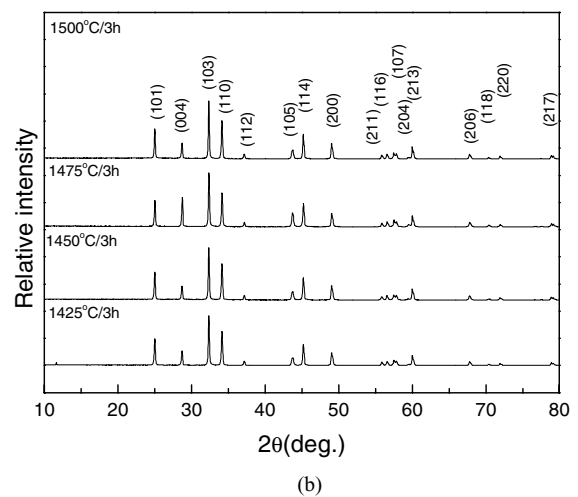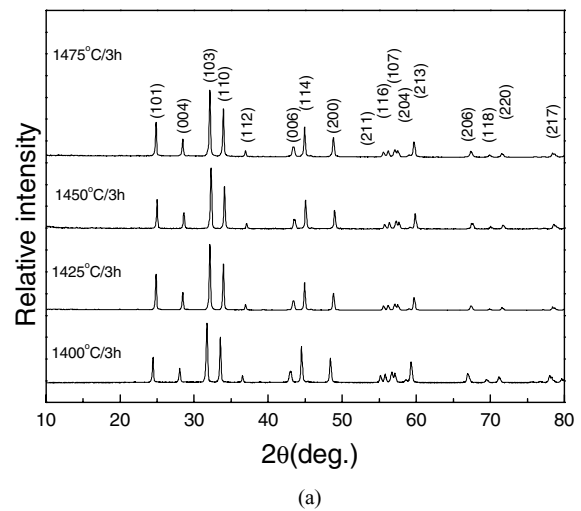
6,387 Kg/m^3 for SrSmAlO$_4$. Figure 1 gives the variation of relative density of SrNdAlO$_4$ and SrSmAlO$_4$ ceramics with sintering temperature. The former has a lower densification temperature, 1450°C, but the maximum relative density is only 97% T.D. (theoretic density). On the other hand, nearly full densification (>99% T.D.) can be achieved in the latter though the densification temperature is higher (1475°C).

XRD patterns of SrNdAlO$_4$ and SrSmAlO$_4$ ceramics are shown in Fig. 2. All peaks can be assigned to SrNdAlO$_4$ (JCPD Card No. 71-0893) and SrSmAlO$_4$ (JCPD Card No. 24-1190) with tetragonal K$_2$NiF$_4$ structure. With varying the sintering temperature, no significant difference can be distinguished in XRD patterns. The SEM micrographs of SrNdAlO$_4$ and SrSmAlO$_4$ ceramics are shown in Figs. 3 and 4, respectively. The obvious grain growth is observed for SrNdAlO$_4$ ceramics sintered at temperatures above 1450°C and for SrSmAlO$_4$ ceramics sintered at temperatures above 1475°C.
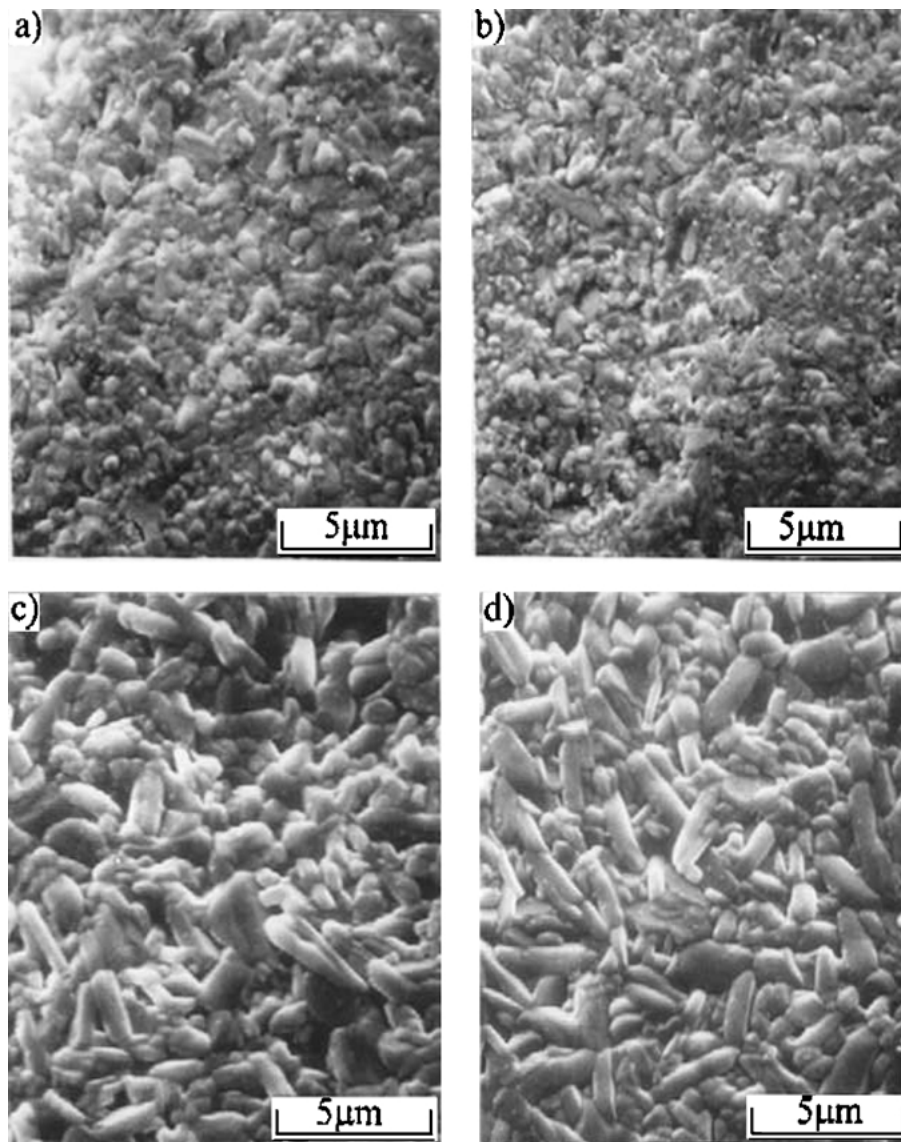

Fig. 3. SEM micrographs of SrNdAlO$_4$ ceramics sintered in air for 3 h: (a) sintered at 1400°C; (b) sintered at 1425°C; (c) sintered at 1450°C; and (d) sintered at 1475°C.
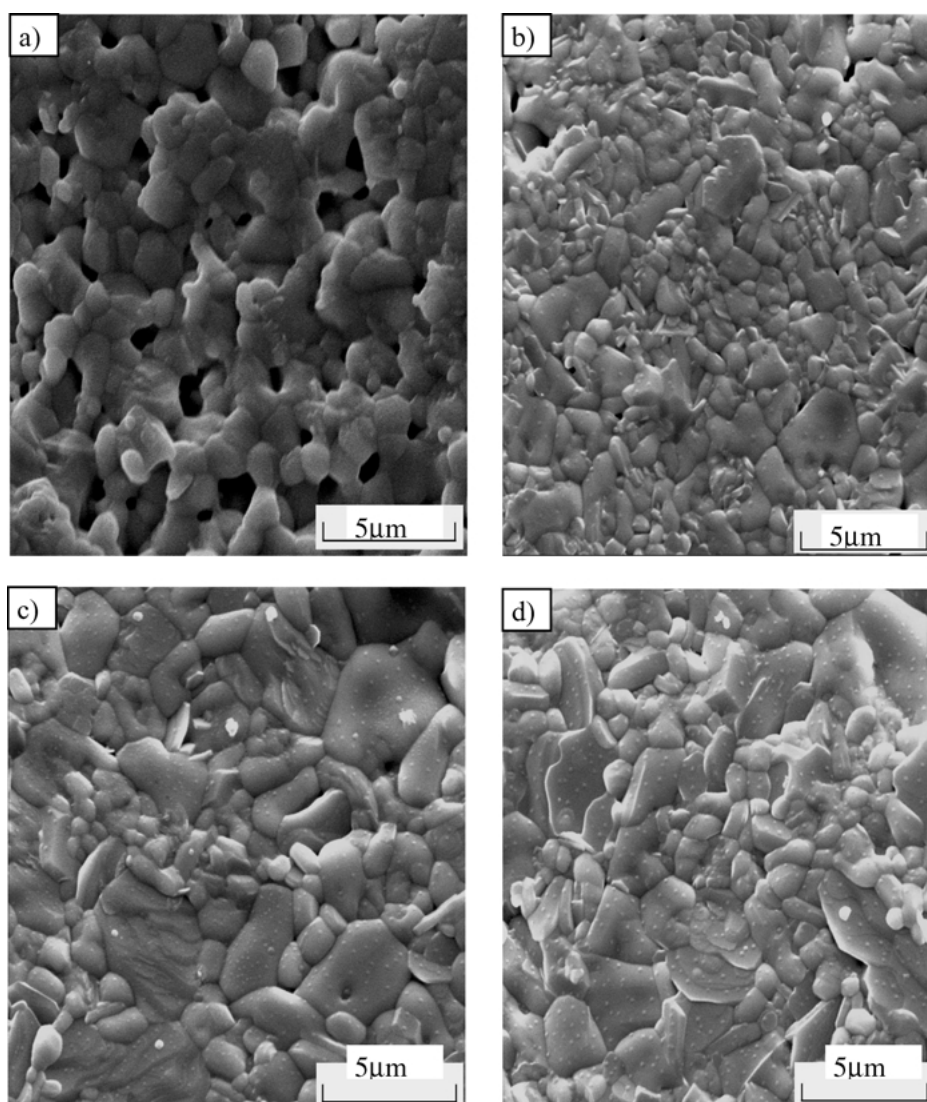
Fig. 4. SEM micrographs of SrSmAlO$_4$ ceramics sintered in air for 3 h: (a) sintered at 1425°C; (b) sintered at 1450°C; (c) sintered at 1475°C; and (d) sintered at 1500°C.

The microwave dielectric properties of SrNdAlO$_4$ and SrSmAlO$_4$ ceramics are listed in Table 1. The dielectric constant is slightly different for the present two ceramics (17.8 for the former and 18.8 for the latter), but the Qf value is significantly different. The latter has a much higher Qf value (54,880 GHz) than the former (25,700 GHz), and this is primarily due to the more ordered state of A-site cations of the latter since the ion radio difference between Sr^{2+} and Sm^{3+} is greater than that between Sr^{2+} and Nd^{3+}. In addition, the higher relative density and less porosity also con-

tribute to the higher Qf value of SrSmAlO$_4$. A very small temperature coefficient of resonant frequency can be obtained in the present ceramics, $-8 - -9$ ppm/°C for SrNdAlO$_4$ and $2-5$ ppm/°C for SrSmAlO$_4$ dense ceramics. The dielectric constant and temperature coefficient change slightly while the Qf value indicates significant variation with varying sintering temperature. The Qf value increases significantly with increasing sintering temperature, and this tendency is more obvious for SrSmAlO$_4$. Since there is almost no change in XRD patterns with sintering temperatures, the

Table 1. Microwave dielectric properties of SrNdAlO₄ and SrSmAlO₄ ceramics sintered at various temperatures

Composition	Sintering condition	f_0 (GHz)	ε	tanδ	Qf (GHz)	τ_f (ppm/°C)
SrNdAlO₄	1425°C/3 h	9.33	17.5	0.00043	21700	−9
SrNdAlO₄	1450°C/3 h	10.34	17.6	0.00045	22980	−8
SrNdAlO₄	1475°C/3 h	10.28	17.8	0.0004	25700	−9
SrSmAlO₄	1450°C/3 h	10.14	17.3	0.00032	31690	5
SrSmAlO₄	1475°C/3 h	9.46	18.2	0.00018	52560	5
SrSmAlO₄	1500°C/3 h	8.78	18.8	0.00016	54880	2

influence of phase constitution and cation ordering is absent. Therefore, the variation of Qf value of the present ceramics with sintering temperature should be primarily related to the variation of grain size. The grain size increases significantly with increasing sintering temperature, and it leads to the decreased amount of grain boundaries, subsequently the density of lattice defects rich in the vicinity of grain boundary decreases, and therefore results in the decreased dielectric loss and increased Qf value. Moreover, the increased relative density and less porosity with increasing sintering temperature are also beneficial to the higher Qf value.

Conclusion

The single phase SrNdAlO₄ and SrSmAlO₄ dense ceramics were obtained by sintering at 1450–1475°C and 1475–1500°C, respectively, and the good microwave dielectric characteristics were achieved: (1) $\varepsilon = 17.8$, $Q \cdot f = 25,700$ GHz, $\tau_f = -9$ ppm/°C for SrNdAlO₄; and (2) $\varepsilon = 18.8$, $Q \cdot f = 54,880$ GHz, $\tau_f = 2$ ppm/°C for SrSmAlO₄. The dielectric constant and temperature coefficient changed slightly with sintering conditions, while the Qf value increased significantly with increasing sintering temperature.

Acknowledgment

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