TAILORING THE MICROWAVE DIELECTRIC PROPERTIES OF ALKALINE EARTH GEHLENITE TYPE CERAMIC

B. ARUN, K. M. MANU AND M. T. SEBASTIAN*

*Materials Science and Technology Division,
 National Institute for Interdisciplinary Science and Technology,
 Council of Scientific and Industrial Research (CSIR),
 Trivandrum, India – 695019
 Email: arunnair7up@gmail.com*

The effect of glass fluxing and isovalent substitution on the microwave dielectric properties of low permittivity $\text{Sr}_2\text{Al}_2\text{SiO}_7$ (SAS) ceramic has been investigated. X – ray diffraction pattern of all the compositions indicate the formation of tetragonal Gehlenite type ceramics with space group $P4_2/m$ (no. 113). The addition of small amounts of lithium magnesium zinc borosilicate (LMZBS) glass to $\text{Sr}_2\text{Al}_2\text{SiO}_7$ ceramic enhanced the densification. Glass fluxing also improved the quality factor and relative permittivity. A small partial substitution of Al^{3+} and Si^{4+} by Ga^{3+} and Ge^{4+} was found to degrade the dielectric properties of SAS ceramic. The composition $\text{Sr}_2\text{Al}_2\text{SiO}_7 + 1 \text{ wt. \% LMZBS}$ glass showed the best dielectric properties with $\epsilon_r = 7.3$, $Q \times f = 36000 \text{ GHz}$ and $\tau_f = -23.0 \text{ ppm/}^\circ\text{C}$.

Keywords: Silicates, glass fluxing, microwave substrate, quality factor.

1. Introduction

Microwave wireless communication industry has shown an explosive growth in recent years. The wide spread use of high frequency digital devices require low relative permittivity (ϵ_r) dielectric substrates for reducing the signal propagation delay. The ceramic substrate should possess high quality factor ($Q \times f$) or low loss factor ($\tan \delta$) for better selectivity. Low or nearly zero temperature variation of resonant frequency (τ_f), high thermal conductivity and low coefficient of linear thermal expansion are also required for substrate applications¹.

Recent literatures report suitability of various silicate based ceramics for microwave substrate and millimeter wave communications²⁻⁴. Oshato et al², reported the microwave dielectric properties of Forsterite ceramics with a high $Q \times f$ and low ϵ_r . However, the search for new high performance silicates is still continuing with balanced properties. Manu et al.⁴ recently investigated the microwave dielectric properties of $\text{Sr}_2\text{Al}_2\text{SiO}_7$ ceramics and its temperature compensation. It showed a quality factor of 33000 GHz with $\epsilon_r = 7.2$ and $\tau_f = -37 \text{ ppm/}^\circ\text{C}$. In the present investigation, we report the tailoring of

*email: mailadils@yahoo.com

microwave dielectric properties of $\text{Sr}_2\text{Al}_2\text{SiO}_7$ ceramics by substitution of isovalent materials in different sites and the addition of low loss LMZBS glass.

2. Experimental

The $\text{Sr}_2\text{Al}_{2-x}\text{Ga}_x\text{Si}_{1-y}\text{Ge}_y\text{O}_7$ ($x, y = 0, 0.1$) ceramic was prepared by the conventional solid state ceramic route. Stoichiometric amounts of high purity powders of SrCO_3 (99.9 %, Sigma Aldrich, Inc, Milwaukee, WI, U.S.A.), Al_2O_3 (99.7 %, Sigma Aldrich), Ga_2O_3 (≥ 99.99 %, Sigma Aldrich), GeO_2 (99.98 %, Alfa Aesar, Share road, Heysham, Lancs) and SiO_2 (99.6 %, Sigma Aldrich) were weighed and ball milled for 24 hours in distilled water medium. The resultant slurry was dried and calcined at 1350°C for 4 hours. Different weight percentages of LMZBS glass were added to fine powders of SAS ceramic and ball milled in water medium for 24 hours and then dried. Cylindrical pucks of dimensions $11 \text{ mm} \times 6 \text{ mm}$ were made and the sintering was carried out in the temperature range $1450 - 1550^\circ\text{C}$ for 4 hours. The sintered samples were powdered and used to analyze the crystal structure and phase purity by X-ray diffraction (XRD) method (PANalytical X'Pert PRO Diffractometer having Ni filtered $\text{CuK}\alpha$ radiation, Netherlands). The sintered densities of the specimens were measured by the Archimedes method. The microwave dielectric properties were measured in the frequency range 8 - 15 GHz using a vector network analyzer (Agilent, Model No: E5071C, USA). The relative permittivity and unloaded quality factor were measured by Hakki - Coleman method modified Courtney and by the cavity method respectively¹. The temperature variation of resonant frequency was measured in the temperature range $25 - 70^\circ\text{C}$.

3. Results and discussion

Figure 1 (a) – (d) show X – ray diffraction pattern $\text{Sr}_2\text{Al}_{2-x}\text{Ga}_x\text{Si}_{1-y}\text{Ge}_y\text{O}_7$ ($x, y = 0.1$) ceramics and SAS – LMZBS glass composites sintered at their optimized temperatures.

Fig. 1. Powder X – ray diffraction pattern of (a) $\text{Sr}_2\text{Al}_2\text{SiO}_7$ (SAS) + 0.5 wt. % LMZBS sintered at 1500°C for 4 hours (b) SAS + 1 wt. % LMZBS sintered at 1500°C for 4 hours (c) $\text{Sr}_2\text{Al}_{1.9}\text{Ga}_{0.1}\text{SiO}_7$ sintered at 1525°C for 4 hours and (d) $\text{Sr}_2\text{Al}_2\text{Si}_{0.9}\text{Ge}_{0.1}\text{O}_7$ sintered at 1525°C for 4 hours.

All the compositions were indexed according to JCPDS file no: 38 – 1333. The patterns belong to the tetragonal Sr – Gehlenite type ceramics with space group $P\bar{4}2_1m$ (no. 113).

All the patterns are quite similar and the addition of glass did not show any change in the pattern indicating that no considerable reaction has occurred with SAS and LMZBS.

Fig. 2. Variation of densification of SAS – LMZBS composites as a function of sintering temperature.

Fig.2 shows the variation of densification with sintering temperature for SAS + 1 wt. % LMZBS and SAS + 0.5 wt. % LMZBS glass. It can be seen from figure 2 that, densification first increases reaching a maximum value at 1500°C and thereafter decreases. Presence of pores in the microstructure may be the reason for the low densification at lower temperatures¹. As temperature increases, material transport increases thereby enhancing the densification. The low densification at 1525°C can be attributed due to porosity in the microstructure caused by the exaggerated grain growth. The sintering temperatures of all the compositions in the present investigation were optimized in a similar manner as in figure 2 for the highest density. It has been reported that the densification of SAS ceramic is 97.3 % and its optimized sintering temperature is 1525°C for 4 hours⁴. From, figure it can be seen that the densification was improved to 98.5 % with the addition of 1 wt. % LMZBS glass and the sintering temperature was reduced to 1500°C for 4 hours. It is well known fact that suitable amounts of low loss and low melting glasses can act as good sintering aids for enhancing the densification of ceramic by the liquid phase sintering mechanism⁵. The LMZBS glass melts at high temperatures thereby providing a liquid phase in the voids of grains. The melt viscous fluid enhances the material transport through liquid phase sintering there by providing better sinterability at lower temperatures.

The sintering temperatures of all the compositions have been carried out for its best density and best dielectric properties. Figure 3 shows variation of relative permittivity and the quality factor of SAS + 1 wt. % LMZBS glass as a function of sintering temperature. It can be seen from figure 3 that both ϵ_r and Q_{uxf} varies in a manner similar to densification as observed in Figure 2. The microwave dielectric properties are very much depending upon the densification¹. It is a well known fact that the pores in the

Fig. 3. Variation of $Q_0 \times f$ and ϵ_r of SAS + 1 wt. % LMZBS glass composite as a function of sintering temperature.

dielectric sample degrade the quality factor and the relative permittivity⁶. Hence the optimized sintering temperature of SAS + 1 wt. % LMZBS is 1500°C for 4 hours.

Table 1 gives the lattice parameter, cell volume and the theoretical density of $\text{Sr}_2\text{Al}_{2-x}\text{Ga}_x\text{Si}_{1-y}\text{Ge}_y\text{O}_7$ ($x, y = 0, 0.1$) ceramics sintered at their respective optimized sintering temperatures.

Table 1. Lattice parameter, cell volume and the theoretical density of $\text{Sr}_2\text{Al}_{2-x}\text{Ga}_x\text{Si}_{1-y}\text{Ge}_y\text{O}_7$ ($x, y = 0, 0.1$) ceramic.

Compound	Lattice parameter		Cell volume (Å ³)	Theoretical density (g cm ⁻³)
	a(Å)	c(Å)		
Sr ₂ Al ₂ SiO ₇ *	7.833	5.270	323.346	3.799
Sr ₂ Al _{1.9} Ga _{0.1} SiO ₇	7.837	5.278	324.196	3.826
Sr ₂ Al ₂ Si _{0.9} Ge _{0.1} O ₇	7.836	5.281	324.287	3.827

*lattice parameter values are taken from [4]

The lattice parameters and cell volume were calculated using the relation⁷,

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \tag{1}$$

$$V = a^2 \times c \tag{2}$$

where a and c are the lattice parameters, V being the cell volume.

It can be seen from the table 1 that both the lattice parameters and cell volume were found to increase with the substitution of Ga^{3+} and Ge^{4+} in the respective sites of Al^{3+} and Si^{4+} . It can be attributed due to the relatively high ionic radii of Ga^{3+} and Ge^{4+} than that of Al^{3+} and Si^{4+} ¹. The theoretical densities of these compositions were also calculated.

Table 2. Sintering temperature (ST), densification and microwave dielectric properties

Compound	ST (°C)	Densification (%)	ϵ_r	$\epsilon_{r \text{ corr.}}$	$Q_u \times f$ (GHz)	τ_f (ppm/°C)
$\text{Sr}_2\text{Al}_2\text{SiO}_7$ (SAS) + 0.5 wt. % LMZBS	1500	97.7	7.30	7.55	34200	-35.8
SAS + 1 wt. % LMZBS	1500	98.5	7.30	7.46	36300	-23.0
$\text{Sr}_2\text{Al}_{1.9}\text{Ga}_{0.1}\text{SiO}_7$	1525	95.9	7.20	7.66	21500	-41.0
$\text{Sr}_2\text{Al}_2\text{Si}_{0.9}\text{Ge}_{0.1}\text{O}_7$	1525	90.3	6.60	7.66	22900	-28.0

Table 2 gives the densification and the microwave dielectric properties of various compositions. The relative permittivity values of all the compositions were in the range 6.6 – 7.3. Earlier report⁴ shows that the relative permittivity of SAS ceramic is 7.2 at microwave frequencies. The ϵ_r values of glass added composites show a value of 7.3. The enhancement in the ϵ_r values is due to the improved densification.

The relative permittivity values depend on the observed porosity in the compounds. In order to get the exact trend in the ϵ_r values, porosity corrected ϵ_r values ($\epsilon_{r \text{ corr.}}$) were also calculated and are given in table 2. It can be seen that porosity corrected ϵ_r values of glass added compositions are nearly the same of ϵ_r value (porosity corrected) of SAS ceramic reported earlier⁴. However, for $\text{Sr}_2\text{Al}_{1.9}\text{Ga}_{0.1}\text{SiO}_7$ and $\text{Sr}_2\text{Al}_2\text{Si}_{0.9}\text{Ge}_{0.1}\text{O}_7$ ceramics, the porosity corrected ϵ_r values are slightly higher than that of pure SAS ceramic. The increase in the $\epsilon_{r \text{ corr.}}$ values can be attributed due to the relatively high ionic polarizability of Ga^{3+} and Ge^{4+} compared to that of Al^{3+} and Si^{4+} ⁸. Several extrinsic and intrinsic factors contribute to the quality factor of the ceramics¹. In the present investigation, substitutions of higher ionic radii elements like Ga^{3+} and Ge^{4+} in $\text{Sr}_2\text{Al}_2\text{SiO}_7$ ceramic reduced the quality factor. However, the glass fluxing improved the $Q_u \times f$ value. Moreover, the reduction in τ_f values was also observed with glass fluxing and Ge^{4+} substitution in pure SAS ceramic.

In the present investigation, addition of 1 wt. % LMZBS glass enhances the quality factor from 33000 GHz to 36300 GHz with a reduction on τ_f value from -37.0 ppm/°C to -23.0 ppm/°C. The improved dielectric properties make this composite as a potential candidate for high frequency substrate applications.

4. Conclusions

The effect of dopants and isovalent substitution of higher ionic radii elements in different sites on the microwave dielectric properties of $\text{Sr}_2\text{Al}_2\text{SiO}_7$ ceramic has been investigated. All the compounds were prepared by the conventional solid state ceramic route. The solid solution formation with the substitution of Ga^{3+} and Ge^{4+} in Al^{3+} and Si^{4+} sites was confirmed by the powder X – ray diffraction data. The addition of glass was found to improve the dielectric properties and Ga^{3+} and Ge^{4+} substitution degraded the dielectric properties. The composition SAS + 1 wt. % LMZBS glass showed best dielectric properties with $\epsilon_r = 7.3$, $Q_u \times f = 36300$ GHz and $\tau_f = -23.0$ ppm/°C..

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