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Dielectric properties of SiAlON ceramics

Do Kyung Kim[1a], Ha Neul Kim[1b], Young-Hoon Seong[1c],
Seung-Soo Baek[2], Eul-Son Kang[2] and Yong-Gi Baek[2]

[1]Department of Materials Science and Engineering, KAIST,

335 Gwahangno, Yuseong-gu, Daejeon, 305-701, Korea

[2]Agency for Defense Development (ADD), 462 Jochiwongil, Yuseong-gu, Daejeon, Korea
[a]dkkim@kaist.ac.kr, [b]joeperry@kaist.ac.kr, [c]eric_1999@kaist.ac.kr

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Abstract. The dielectric properties of β-SiAlON and various cations doped α-SiAlON bulk ceramics prepared by a hot-press method were investigated. The dielectric properties (dielectric constant and tangent loss) were characterized by a post-resonator method (Hakki-Coleman method) at room temperature in the microwave frequency range. The effect of z-values about β-SiAlON was examined, and also the effects of various interstitial cations on dielectric properties of α-SiAlON were studied. Dielectric properties of α-SiAlON were compared with those of Si_3N_4 and β-SiAlON and their relationship between the dielectric properties and the cationic species of SiAlON were discussed.

Introduction

SiAlON is a solid solution of Si_3N_4 by partial substitution of Si and N elements with Al and O, respectively. SiAlON shows superior mechanical properties and high temperature stability compared to Si_3N_4, which enables SiAlON to be a promising material for high temperature structural applications such as metal extrusion dies, metal cutting tools and heat engines. SiAlON is also considered as a good candidate material for the microwave window application that requires low dielectric constant and dielectric loss. [1-4] Hampshire et al. have reported that the thermal and mechanical properties for the glasses of Ln doped SiAlON (Ln = Y, Ce, Nd, Sm, Eu, Dy, Ho and Er), generally appear to vary linearly with the cationic field strength (CFS) or ionic size of the rare-earth cations. [5] In addition, they have reported that the observed variation in Young's modulus of Ln doped SiAlON glasses (Ln = La, Ce, Gd, Eu, Dy, Er, Yb, and Y) with increasing CFS is quite significant and increases from 90 GPa for Eu to 160 GPa for the Yb-based glass composition. As a result, it indicates the existence of an increasing linear trend as the atomic number increases, with the exception of the Eu-ion. [6] Thus, mechanical and chemical properties of SiAlON have been widely studied from room temperature to high temperature, but there have been only limited reports on the microwave dielectric properties of SiAlON ceramics.

Dielectric measurement techniques at radio and microwave frequencies have been an important subject within a wide range of scientific and engineering applications. Conventionally, the measurements have been made in the frequency domain using cavity, waveguide, stripline or coaxial transmission line. [7-9] They are basically destructive in nature and required tedious sample preparation conditions. In addition, there is a limitation in the maximum temperature region.

Therefore, this study has implemented a novel resonant cavity measurement and the wave-guide measurement techniques for *in-situ* measurements of the complex permittivity of low dielectric material at elevated temperatures. Dielectric constant and tangent loss of β-SiAlON and various cations doped α-SiAlON ceramics up to 1200 °C were measured by the perturbation method [10,11] and up to 800 °C were measured by the wave-guide method.

Experimental Procedure

Commercially available α-Si_3N_4 (UBE-SN-E10, Ube chemical, Japan, average particle size ~0.3μm), β-Si_3N_4 (SN-F1, Denka silicon nitride, Japan, average particle size ~3μm), Al_2O_3 (AKP-50, Sumimoto, Japan), AlN (grade F, Tokuyama, Japan), La_2O_3 (99.99%, Aldrich, America), Nd_2O_3 (99.99%, Aldrich, America), Sm_2O_3 (99.9%, Aldrich, America), Y_2O_3 (99.99%, Aldrich, America) and Yb_2O_3 (99.99%, Aldrich, America) were used for the preparation. The β-$Si_{6-z}Al_zO_zN_{8-z}$ with various z-values (0.5, 4.0) and the five various cations doped α-$Me_{0.6}Si_{9.3}Al_{2.7}O_{0.9}N_{15.1}$ powders were prepared. In order to reduced the particle size and increase homogenous nature, the powders were ball milled in 2-propanol for 24 h using alumina balls. The dispersed powder mixtures in solvent were dried in convection oven at 80 °C for 24 h to remove the solvent and granulated. Thus, obtained powders were hot-pressed (Thermal Technology Inc, Astro Hot Press) in BN-coated graphite dies under N_2 to 1800 °C with an average heating rate of ~20 °C/min and maintained at that temperature for 2 h under uniaxial load of 25MPa.

Dielectric properties of doped α-SiAlON and β-SiAlON were characterized by the post-resonator method (Hakki-Coleman method) at room temperature and the β-$Si_{6-z}Al_zO_zN_{8-z}$ with various z-values was characterized by the perturbation method at high temperatures. The pellet dimensions of β-SiAlONs were 3.5φ x 12mm. The pellets were heated in box furnace at 1200 °C and dielectric properties were measured in steps of 100 °C at 2.45 GHz. Dielectric constant and tangent loss were calculated using eqn. 1.

$$\varepsilon_r' = 1 - 2C'\frac{f_1 - f_0}{f_1}, \quad \varepsilon_r'' = C''\left(\frac{1}{Q_2} - \frac{1}{Q_1}\right)$$

f_o : the resonant frequeny of empty holder,

f_1 : the resonant frequeny of holder within specimen

Q_1 : the quality factor of empty holder,

Q_2 : the quality factor of holder within specimen

C', C'' : the permittivity of specimen (Hakki-Coleman)

Eqn.1. Equation of dielectric measurement (Perturbation Theory)

Result and discussion

β-SiAlON. The X-ray diffraction patterns (XRD) have confirmed the pure single phase crystalline of β-SiAlON. The lattice parameters of β-SiAlON increased with z-values and were confirmed from the characteristic peaks shift. The room temperature dielectric properties were measured by Hakki-Coleman method to confirm the effect of z-values. Measured dielectric constant and loss were slightly lower than those of Si_3N_4. Dielectric constant decreased slightly as z-value increased, but dielectric loss was independent of z-value. The high temperature dielectric constant of β-SiAlON was measured by the perturbation and the wave guide methods. Fig. 1 shows the measured dielectric constant of β-SiAlON using the waveguide and the perturbation methods at various temperatures. From Fig. 1, it is evidently observed that β-SiAlON had lower dielectric constant than Si_3N_4 in the entire temperature range. Dielectric constant of z = 4.0 specimen had higher rate of increase than that of z = 0.5 specimen through both measurements. In addition, dielectric properties of β-SiAlON with different grain sizes were measured to confirm the effect of grain size. Different grain sizes were obtained due to the size difference of starting precursor powders. Dielectric constant and loss had slight difference between fine grain β-SiAlON and coarse grain β-SiAlON. Therefore, it can be concluded that the dielectric properties are independent of its grain size.

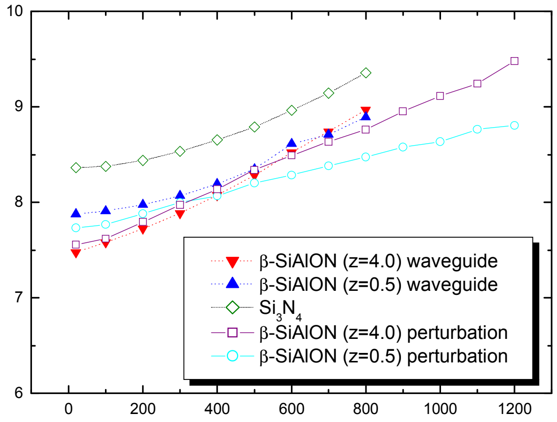

Fig.1. Measured dielectric constant as a function of temperature by waveguide and perturbation method.

α-SiAlON. Various cations doped α-SiAlONs ($Me_{0.6}Si_{9.3}Al_{2.7}O_{0.9}N_{15.1}$) using La_2O_3, Nd_2O_3, Sm_2O_3, Y_2O_3 and Yb_2O_3 were prepared by a hot-press method. The XRD patterns have confirmed the pure single phase crystalline of Y_2O_3, Yb_2O_3 and Sm_2O_3 doped α-SiAlON. On the other hand, La_2O_3 and Nd_2O_3 doping resulted in β-SiAlON and secondary phase formations. Some of the secondary phases were identified as an oxynitride phase and the other phase formations were unidentified. Microstructural analysis by SEM revealed equiaxed grains shape for Sm, Y and Yb doped α-SiAlON. But elongated grains were observed in La_2O_3 and Nd_2O_3 doped α-SiAlON materials. Table 1 summarized cation radius, phases and dielectric properties of cations doped α-SiAlON. The measured dielectric constant of doped α-SiAlON was ranged from 8.618 to 10.263 and dielectric loss was ranged from 1.06×10^{-3} to 9.03×10^{-3}. Yb, Y, and Sm doped α-SiAlON showed lower dielectric constant and loss than La, Nd doped-SiAlON due to single alpha phase solid solution.

Table 1. Cation radius and dielectric properties and phase of SiAlONs

	Cation	Dielectric properties		Phase
	r (Å)	ε'	tan δ	
La-SiAlON	1.172	10.263	5.59 X 10^{-3}	b+2nd phases
Nd-SiAlON	1.123	9.355	9.03 X 10^{-3}	b+2nd phases
Sm-SiAlON	1.098	8.938	1.68 X 10^{-3}	α
Y-SiAlON	1.04	8.681	1.06 X 10^{-3}	α
Yb-SiAlON	1.008	8.618	1.53 X 10^{-3}	α

It can be observed from Table 1 that the dielectric constant increased with radius of cations. Dielectric loss of Y, Yb, and Sm doped α-SiAlON was lower than La, Nd doped α-SiAlON, and also even lower than the sintered Si_3N_4 ceramics. It seems that the electronic polarization effect of the interstitial cation has a relation with the dielectric property of doped α-SiAlON. As a result, it can be concluded that the dielectric constant decreased with increase in the value of CFS. Dielectric loss of Sm, Y, and Yb doped α-SiAlON was almost independent of CFS.

Summary

The β-SiAlON and cations doped α-SiAlON were prepared successfully by a hot-press method. XRD analysis revealed the single phase crystalline β-SiAlON and Y_2O_3, Yb_2O_3 and Sm_2O_3 doped α-SiAlON materials. On the other hand, for La_2O_3 and Nd_2O_3 doped α-SiAlON materials revealed the formation of impurity β-SiAlON phase and secondary phase. Dielectric properties of β-SiAlON exhibited slightly decreased dielectric constant with increased z-values. The β-SiAlON had lower dielectric constant than Si_3N_4 over entire temperature range. Dielectric constant of $z = 4.0$ had higher rate of increase than that of $z = 0.5$ specimen. The cations influence the dielectric properties of α-SiAlON, and small cations have advantage of phase stability as well as dielectric constant in α-SiAlON. Further work is under progress to demonstrate the concrete relationship between dielectric properties and CFS with more experiments by varying the value of CFS.

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SiAlONs and Non-oxides

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