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Microwave dielectric properties of forsterite-based solid solutions

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Abstract

Recently forsterite has been reported as an excellent dielectric material for millimeter wave application. However, its temperature variation of the resonant frequency (τ_f) is relatively large which precludes its immediate use in practical applications. In this paper, we report the effect of substituting Ca and Mn for Mg on the microwave dielectric properties of forsterite. The composition $0.975Mg_2SiO_4$–$0.025Mn_2SiO_4$ showed excellent $Q \times f$ value of 180,000 GHz with a τ_f of −71 ppm/°C. The end member Mn_2SiO_4, showed a $Q \times f$ of 50,000GHz, ε_r of 8.52 and $\tau_f = -90$ ppm/°C. In the case of Ca substitution for Mg, τ_f shifted to high negative value with increasing amount of Ca. However, $Q \times f$ did not show much change in its value. It is suggested that the increase of τ_f towards a more negative value is related to the ionic radii of the substitutes.

Keywords: Silicates; Dielectric properties; Forsterite

1. Introduction

Recently various telecommunication and radar systems are developed for kilometer-wave to centimeter-wave applications. The increase in the amount of information to be transported necessitated the need for new low loss dielectric materials for high frequency communication. Millimeter-wave telecommunication can transmit a large amount of information at a very high speed. This is important in intelligent transport systems (ITS), ultra high speed wireless LAN and satellite broadcasting. The important characteristics required for a dielectric material used in millimeter-wave telecommunication systems are: (a) high quality factor ($Q \times f$) to achieve high selectivity; (b) low dielectric constant (ε_r) to reduce the delay time of electronic signal transmission and (c) nearly zero temperature coefficient of resonant frequency (τ_f) for frequency stability. This limits the number of materials available for millimeter wave communication.[1–4] Silicates build on silica tetrahedron with about 55% of covalent bonding. Hence, silicates are expected to have low ε_r and suggested as suitable dielectric materials for millimeter-wave communication.[2] Recently, Tsunooka et al.[3] reported that forsterite (Mg_2SiO_4) show excellent microwave dielectric properties. Silicates with olivine structure, which is the same as that of forsterite are expected to have superior microwave dielectric properties. In the present paper, we report the preparation, characterization and properties of $(1-x)Mg_2SiO_4$–xCa_2SiO_4 and $(1-x)Mg_2SiO_4$–xMn_2SiO_4 dielectric ceramics.

2. Experimental procedures

High purity chemicals such as MgO (99.99%), $CaCO_3$ (99.9%) or MnO (99.9%) and SiO_2 (99.9%) powders were weighed in stoichiometric ratios and mixed and ball milled using ZrO_2 balls for 24 h. After drying the powder for $(1-x)Mg_2SiO_4$–xCa_2SiO_4 ceramics was calcined at 1150 °C for 3 h in air. The calcined powder was ball milled again for 24 h and dried. The powder was pressed into cylindrical shape under a uni-axial pressure of 7.84 MPa and CIP of 200 MPa. The pellets were then sintered at 1400 °C for 2 h in air. The $(1-x)Mg_2SiO_4$–xMn_2SiO_4 for $x = 0$–0.15 were calcined at 1150 °C for 3 h in air and sintered at 1400 °C for 2 h in air. The samples of composition $x = 1.0$ was calcined at 1100 °C 3 h in air and sintered at 1300 °C for 2 h in air. The samples of composition $x = 2.0$ was calcined at 1050 °C 3 h in N_2 gas and sintered at 1100 °C for 2 h in N_2 gas. In order to know the effect of valency change of Mn, the compositions with $x = 0.05$ and 0.1, was also calcined and sintered in N_2 gas. The crystalline phase of the samples was identified by powder X-ray diffraction. Lattice parameters were refined using the computer program WPPF for whole-powder-pattern.[5] Microwave dielectric properties were measured by Hakki and Colemans' method[6] using the TE_{011} mode with a network analyzer.

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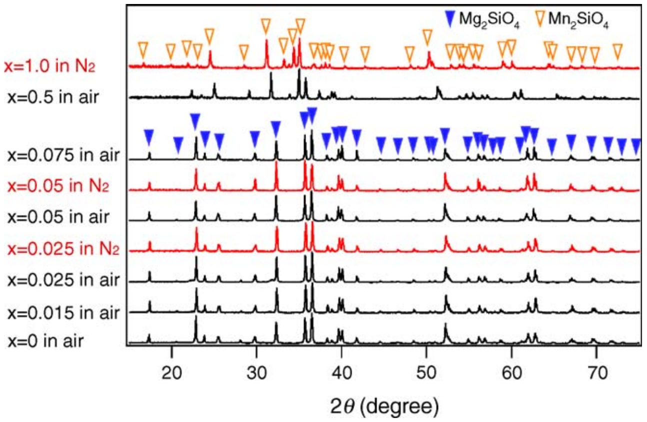

Fig. 1. Powder-XRD patterns of $(1-x)Mg_2SiO_4$–xMn_2SiO_4 solid solutions.

3. Results and discussion

Fig. 1 shows powder-XRD patterns of $(1-x)Mg_2SiO_4$–xMn_2SiO_4 solid solutions. A study of the XRD patterns indicates the formation of solid solution in the whole range of x with no secondary phases. The composition $x = 1.0$ could be prepared by calcining and sintering in air, however the composition with $x = 2.0$ could not be prepared by heating in air. When it was calcined in air, SiO_2 and MnO did not react to form the solid solution but the MnO changed to Mn_2O_3. However, the solid solution was formed on calcining and sintering the samples in N_2 gas. Fig. 2 shows the results of the refinement of the lattice parameters of $(1-x)Mg_2SiO_4$–xMn_2SiO_4 solid solutions. All the crystallographic axes expanded with increase of x which was caused by substitution of Mn for Mg. The rate of expansion along the a-axis was the largest. No difference in the value of lattice parameters observed between samples sintered in air and N_2 gas.

The microwave dielectric properties of $(1-x)Mg_2SiO_4$–xMn_2SiO_4 solid solutions are shown in Fig. 3 as a function of composition (x). At $x = 0.025$, the solid solution phase showed the highest value of $Q \times f$ of 180,000 GHz. In the range of $x = 0.025$–0.05, the samples both sintered in air and N_2 gas showed a high $Q \times f$ over 100,000 GHz. The ε_r of $(1-x)Mg_2SiO_4$–xMn_2SiO_4 solid solutions increased with x. The larger dielectric polarizability[7] of 6 coordinated Mn^{2+} than Mg^{2+}caused the ε_r to increase. In the solid solution series τ_f showed a tendency to shift towards a more negative value with increase of x. The τ_f of samples sintered in N_2 gas are found to be more on the negative side as compared to those sintered in air.

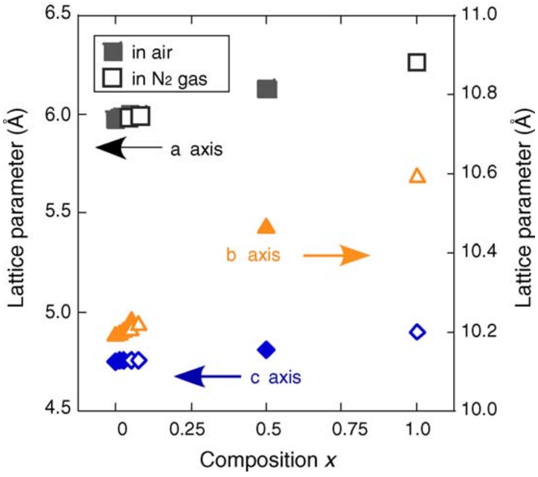

Fig. 2. Lattice parameters of $(1-x)Mg_2SiO_4$–xMn_2SiO_4 solid solutions.

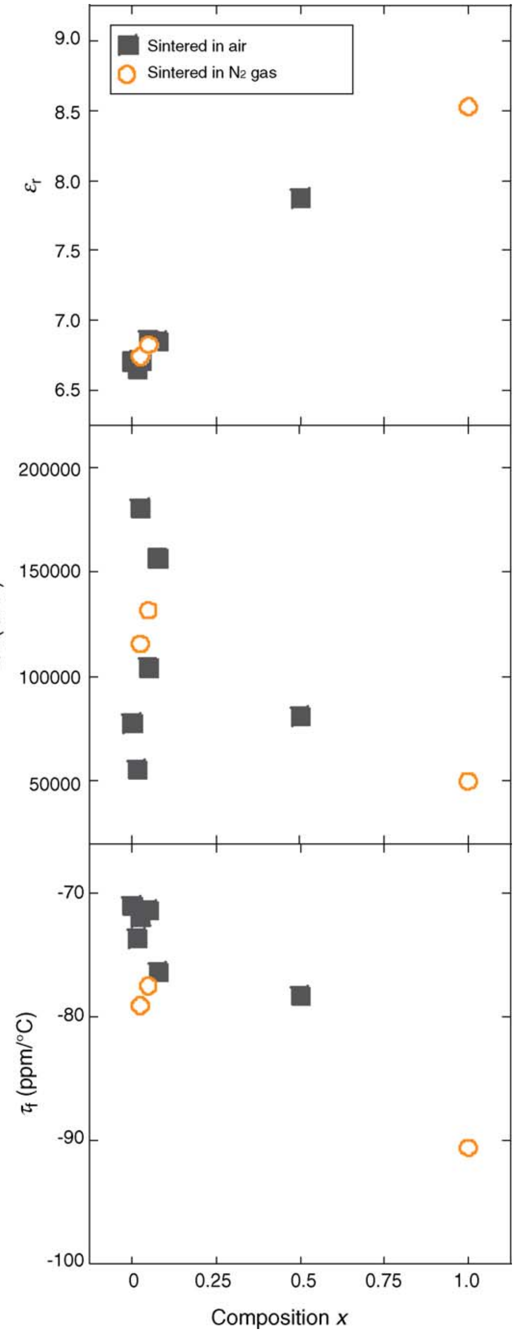

Fig. 3. Microwave dielectric properties of $(1-x)Mg_2SiO_4$–xMn_2SiO_4 solid solutions.

Fig. 4 shows the powder XRD patterns of the $(1-x)Mg_2SiO_4$–xCa_2SiO_4 ceramics sintered at 1400 °C for 2 h as a function of composition x. For $x = 0$–0.075, the XRD peaks corresponding to that of Mg_2SiO_4 are observed and that

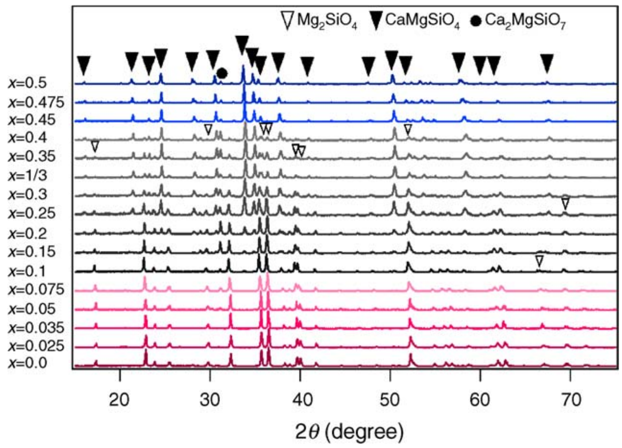

Fig. 4. Powder-XRD patterns of the $(1-x)Mg_2SiO_4$–xCa_2SiO_4 ceramics.

of Ca_2SiO_4 is not seen. XRD peaks corresponding to that of $Ca_2MgSi_2O_7$ phase are found for the compositions in the range, $x = 0.05$–0.5. For $x = 0.15$ and 0.2, the diffraction peaks of $Ca_2MgSi_2O_7$ phase appeared strongly. For the composition of $x > 0.1$, peaks of $CaMgSiO_4$ began to appear. Hence, it is evident that $(1-x)Mg_2SiO_4$–xCa_2SiO_4 solid solutions is formed only for $x < 0.1$. In the range of composition $x = 0.1$–0.4, coexistence of Mg_2SiO_4 and $CaMgSiO_4$ phases are observed. At the composition of $x = 0.45$, the powder-XRD patterns of Mg_2SiO_4 disappeared completely and in the range of $x = 0.45$–0.5 the diffraction peaks are shifted to low angles indicating the formation of Ca_2SiO_4 based solid solutions. The results of refining lattice parameter of $(1-x)Mg_2SiO_4$–xCa_2SiO_4 ceramics are shown in Fig. 5. In the range of $x = 0$–0.075 and $x = 0.45$–0.5, all the crystallographic axes increased with increase of x and the formation of solid solutions are confirmed. The rate of expansion of b-axis was larger than the others. The lattice parameter of c-axis hardly increased in the range $x = 0.45$–0.5.

Microwave dielectric properties of $(1-x)Mg_2SiO_4$–xCa_2SiO_4 ceramics are shown in Fig. 6. At the composition $x = 0.025$, $Q \times f$ showed the highest value (105696 GHz) in the series. In the range $x = 0.2$ and 0.4, $Q \times f$ and ε_r show non-linear variation. This is due to the coexistence of Mg_2SiO_4 and Ca_2SiO_4 based solid solutions. In the extent of forming Mg_2SiO_4 based solid solutions ε_r increased linearly with x. However, in the extent of forming Ca_2SiO_4 based solid solutions microwave dielectric properties hardly exhibit any changes. In this study sintering temperature of $(1-x)Mg_2SiO_4$–xCa_2SiO_4 ceramics were fixed at 1400 °C. Melting point of Mg_2SiO_4 is 1890 °C and that of Ca_2SiO_4 was 1485 °C. This sintering temperature was suitable to Mg_2SiO_4 solid solutions, however it was too high for Ca_2SiO_4 solid solutions to sinter. Ca_2SiO_4 based solid solutions sintered in optimized conditions are expected to exhibit higher $Q \times f$. The

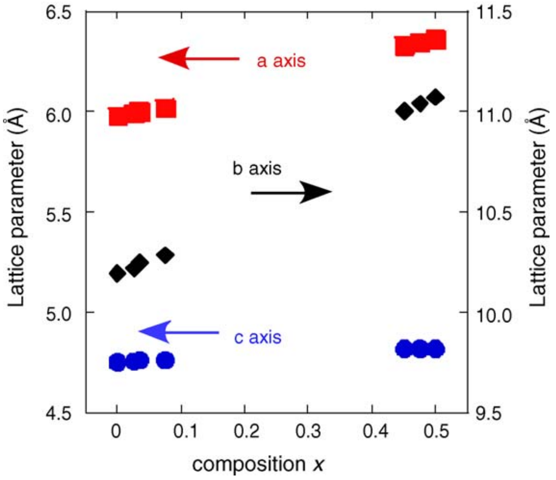

Fig. 5. Lattice parameter of $(1-x)Mg_2SiO_4$–xCa_2SiO_4 ceramics.

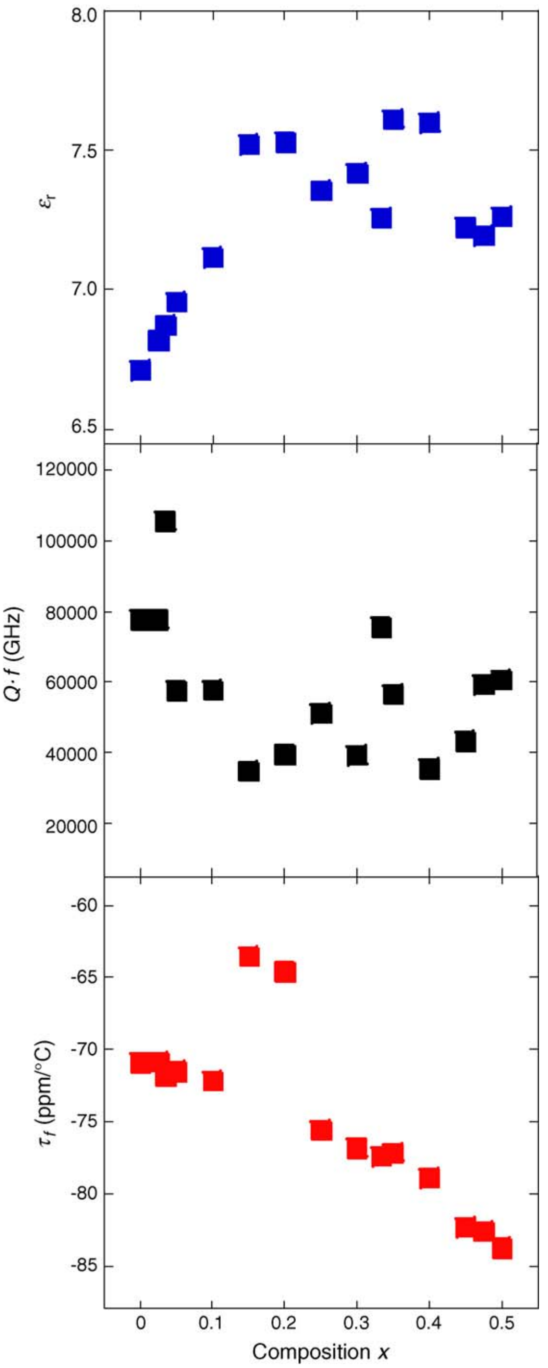

Fig. 6. Microwave dielectric properties of $(1-x)Mg_2SiO_4$–xCa_2SiO_4 ceramics.

τ_f of $(1-x)Mg_2SiO_4$–xCa_2SiO_4 ceramics had a tendency to shift to negative side with increase of x, except $x = 0.15$ and 0.2. At $x = 0.15$ and 0.2 formation of $Ca_2MgSi_2O_7$ phase affected the microwave dielectric properties. This tendency was found to be the same for $(1-x)Mg_2SiO_4$–xMn_2SiO_4 solid solution also. It is suggested that τ_f is related to ionic radii of cations, and by adopting smaller cations it may be possible to make τ_f close to 0 ppm/°C in silicates with olivine structure.

4. Conclusion

$Mg_{2-x}Mn_xSiO_4$ solid solutions showing excellent microwave dielectric properties were prepared. The composition with $x = 0.025$ showed $Q \times f = 180{,}000$ GHz, $\varepsilon_r = 6.71$, $\tau_f = -71.2$ ppm/°C. The $(1-x)Mg_2SiO_4$–xCa_2SiO_4 ceramics with the composition $x = 0.07$ showed good microwave dielectric properties of $Q \times f = 105{,}000$ GHz, $\varepsilon_r = 6.87$ and $\tau_f = -71.8$ ppm/°C. The ε_r showed a tendency to increase with increase of Mn or Ca content. This is due to the higher dielectric polarizability of Mn^{2+} and Ca^{2+} as compared to Mg^{2+}. In $(1-x)Mg_2SiO_4$–xMn_2SiO_4 solid solutions and $(1-x)Mg_2SiO_4$–xCa_2SiO_4 ceramics τ_f showed a tendency to shift to more negative values with the increase of cation ionic radius. In silicates with olivine structure τ_f may be shifted to 0 ppm/°C by adopting smaller cation.

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