

Influence of V_2O_5 additions to $NdAlO_3$ ceramics on sintering temperature and microwave dielectric properties

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Abstract

The effects of sintering aids addition on the microstructures and microwave dielectric properties of $NdAlO_3$ ceramics were investigated. V_2O_5 was selected as liquid phase sintering aid to lower the sintering temperature of $NdAlO_3$ ceramics. With V_2O_5 addition, the densification temperature of $NdAlO_3$ can be effectively reduced from 1650 °C to 1390~1410 °C. The crystalline phase exhibited no phase differences at low addition level while $Nd_4Al_2O_9$ and $NdAl_{11}O_{18}$ present as second phases as the addition level was over 1 wt.%. The quality factor $Q \times f$ was strongly dependent upon the amount of additions. $Q \times f$ values of 64,000 GHz and 48,000 GHz could be obtained at 1390~1410 °C with 0.25 wt.% and 0.5 wt.% V_2O_5 addition, respectively. During all addition ranges, the relative dielectric constants were not significantly different and ranged from 21.6 to 22.5. The temperature coefficients varies from -31~-43 ppm/°C. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Due to the development in mobile communication, mobile telephone systems, as well as in satellite broadcasting systems was rapidly, how to design the high-quality devices is very important. In order to achieve miniaturization of the dimensions of the devices and for the system work with high efficiency and stability, the materials for microwave resonators are required to be excellent in following three dielectric characteristics.¹⁻³ The first characteristic is high dielectric constant (ϵ_r), because the microwave wavelength is inversely proportional to $\sqrt{\epsilon_r}$ of the dielectric materials ($\lambda = \lambda_0 / \sqrt{\epsilon_r}$), where λ_0 is the wavelength in air. The second one is high Q value, (which is the inverse of the dielectric loss $\tan\delta$). This is required to achieve high frequency selectivity and stability in microwave transmitter and receiver components. The third, temperature coefficient of the resonant frequency (τ_f), is required to be as close to 0 ppm/°C as possible. Several ceramics systems such as $Ba(Mg_{1/3}Ta_{2/3})O_3$, $(Mg, Ca)TiO_3$, $Ba(Zn_{1/3}Ta_{2/3})O_3$, $(Zr, Sn)TiO_4$ have therefore been developed for the

microwave applications.³⁻⁵ The research on the microwave dielectric properties of the rare-earth aluminates was investigated by Cho et. al.⁶ for their valuable characteristics at X-band applications. $NdAlO_3$ ceramics exhibited good microwave dielectric properties of high dielectric constant (~ 21.8) and good quality factor ($Q \times f = 55,000$ GHz). The temperature coefficient of the resonant frequency τ_f is in the vicinity of -34 ppm/°C.⁶⁻⁷ The $NdAlO_3$ ceramics have been used as a substrate for microwave components since it provides a high quality factor, excellent lattice matching and a good matching for thermal expansion.^{7,15} However, $NdAlO_3$ ceramics require a very high sintering temperature (1650 °C) and were difficult to densify without any additions.⁶ For practical manufacturing process, it is desired to reduce the sintering temperatures of $NdAlO_3$ ceramics. Recently, several methods to reduce sintering temperatures of dielectric ceramics were reported.⁸⁻⁹ The liquid-phase sintering by glass addition was found to effectively lower the firing temperature, while it also decreased the microwave dielectric properties of the ceramics due to the low densities with glass aids. Another method applied for lowering the sintering temperature was a novel chemical processing method, which often required a flexible procedure that would

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increase the cost and time in fabrication. In previous researches, liquid phase fluxes such as B_2O_3 , CuO , V_2O_5 and Bi_2O_3 were introduced as sintering aids to low the sintering temperature of ceramics and obtain good dielectric properties.^{10–14} In this study, V_2O_5 was added to $NdAlO_3$ ceramics to lower the sintering temperature for practical applications. The influences of V_2O_5 additions on the sintering temperatures, microstructures and the microwave dielectric properties of $NdAlO_3$ ceramics have been investigated.

2. Experimental procedures

Samples of $NdAlO_3$ were prepared by conventional solid-state methods from individual reagent-grade oxide powders: Nd_2O_3 and Al_2O_3 . The raw powders were weighed according to the desired stoichiometry with various amounts of V_2O_5 additions. The starting mate-

rials were milled in a plastic jar with zirconium balls under pure water for 6 h. The mixtures were dried and forced through a 320-mesh sieve and then calcined at 1200 °C for 2 h, dried, ball-milled and granulated by sieving through 180 mesh. The calcined powders were remilled for 12 h with suitable amount of 3% solution of polyvinyl alcohol (PVA) as the binder and compacted into disks 11 mm in diameter by 5 mm in height. After debinding, the disks were sintered at temperatures from 1370 to 1450 °C in air tmosphere for 2 h with the heating rate 10 °C/min.

The crystalline phases of the calcined powder and the sintered ceramics were identified by X-ray diffraction pattern analysis. Microstructure observations of the sintered surfaces were performed by scanning electron microscopy (SEM). Energy dispersive spectroscopy (EDS) was also performed to identify the existences of second phases. The bulk densities of sintered samples were measured by the Archimedes method. Microwave

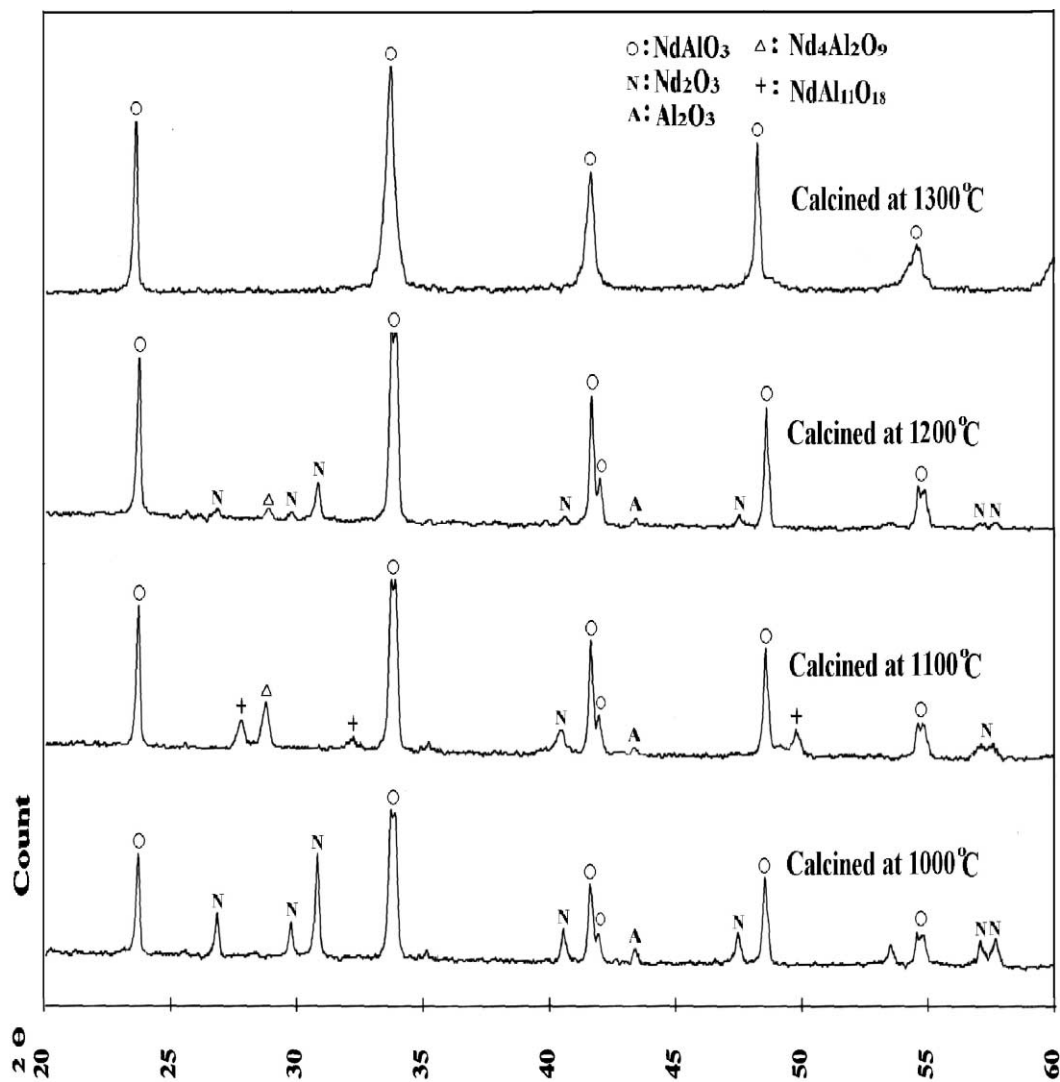


Fig. 1. XRD patterns of $NdAlO_3$ powders calcined at different temperatures for 2 h.

dielectric properties were calculated from the resonant frequency by using the Hakki and Colemans dielectric resonator method under TE_{011} and TE_{018} modes.^{15–16} A cylindrical dielectric resonator was positioned between two brass plates connected to the measuring system. A HP8757D network analyzer and a HP8350B sweep oscillator were employed in the measurement. The dielectric constant ϵ_r was approximated using the values of resonant frequency and the size of the fired disk. Since the shrinkage of all the specimens was not uniform, the Q values were measured at different frequencies (9–9.5 GHz). Temperature coefficient of resonant frequency (τ_f) was also measured by the same method by changing the temperature mainly from 20 to 80 °C and calculated from the equation:

$$\tau_f = \frac{f_{80} - f_{20}}{f_{20} \times 60} \times 10^6 (\text{ppm}/^\circ\text{C}) \quad (1)$$

Where f_T is the resonant frequency of the dielectric resonator at temperature T °C.

3. Results and discussions

In order to examine the chemical properties of calcined NdAlO_3 powders and select a suitable calcining temperature, the starting materials were prepared at 1000, 1100, 1200 and 1300 °C. Fig. 1 shows the XRD pattern of NdAlO_3 powders calcined at different temperatures for 2 h. The phases existing at each calcining temperature were observed as illustrated in the figure. With increase of calcining temperature, the mixed powders reacted more and the intensity of major NdAlO_3 phases was enhanced. Homogeneous NdAlO_3 phase with rhombohedral structure could be obtained above 1000 °C. However, there were second phase coexisting with the major phase and perhaps seriously affect the microwave dielectric properties of NdAlO_3 ceramics. So 1200 °C was selected as calcining temperature.¹⁴ Fig. 2 shows the XRD pattern of NdAlO_3 ceramics with 0.25 wt.% V_2O_5 additions sintered at different temperatures for 2 h. With the increase of sintering temperature, the intensity of NdAlO_3 phase was enhanced. The crystal-

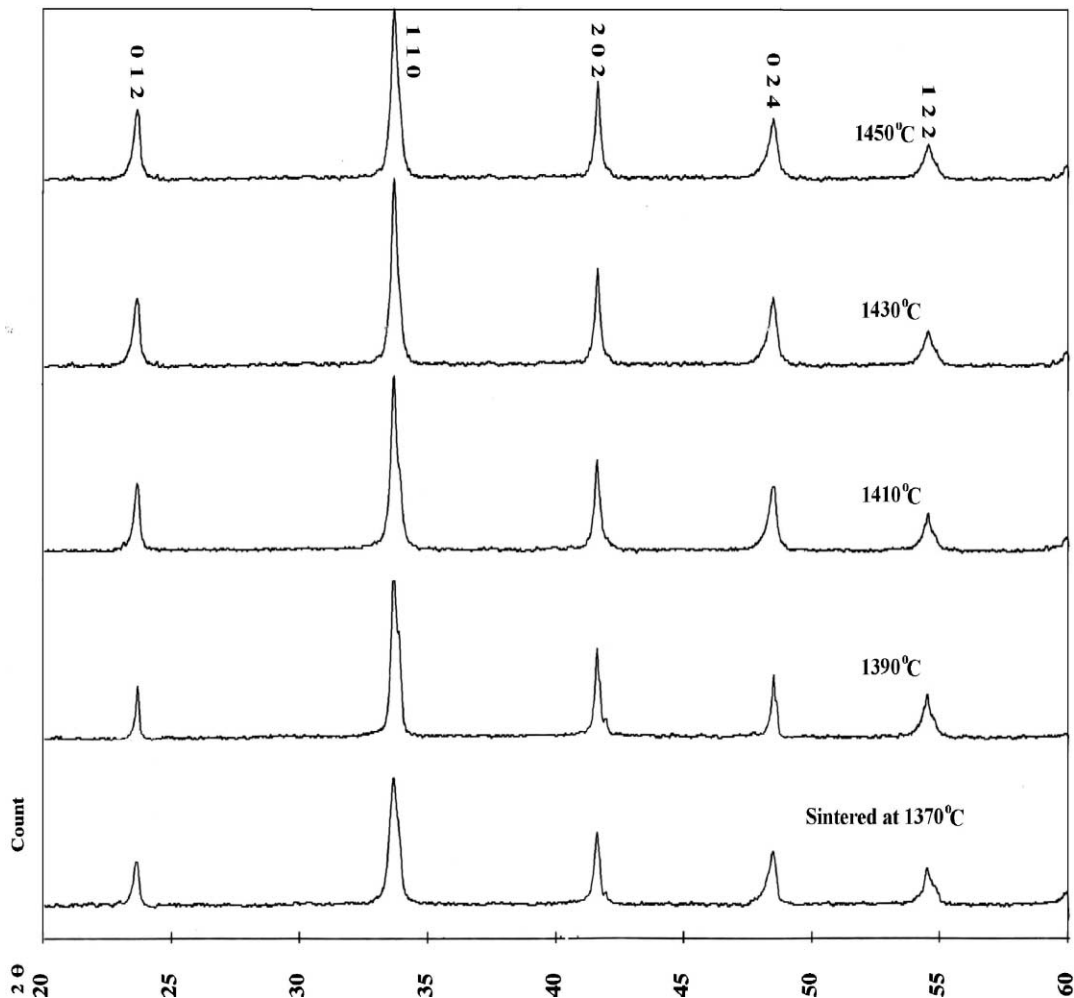


Fig. 2. X-ray diffraction patterns of NdAlO_3 ceramics with 0.25 wt.% V_2O_5 sintered at different temperatures.

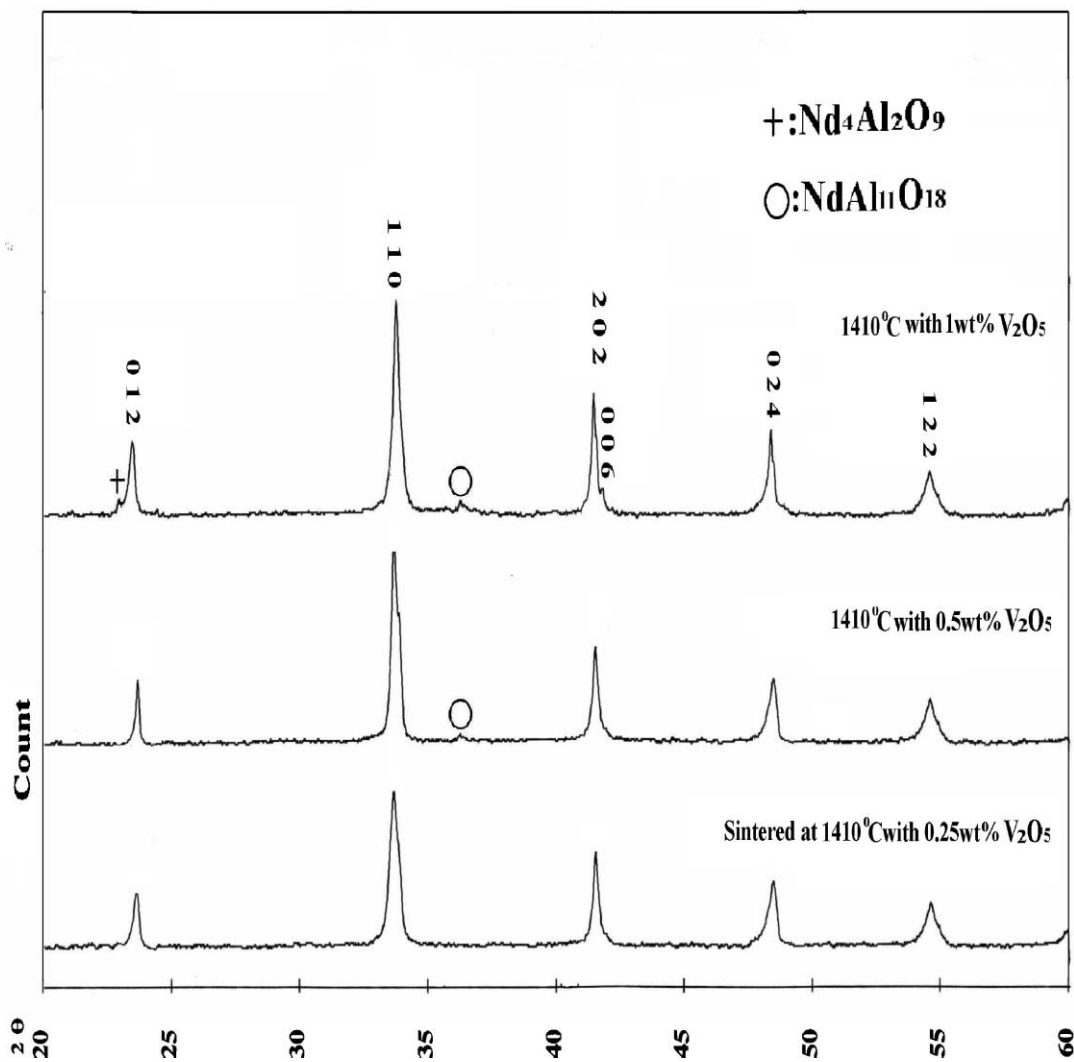


Fig. 3. X-ray diffraction patterns of NdAlO_3 ceramics with various amount of V_2O_5 additions sintered at 1410°C .

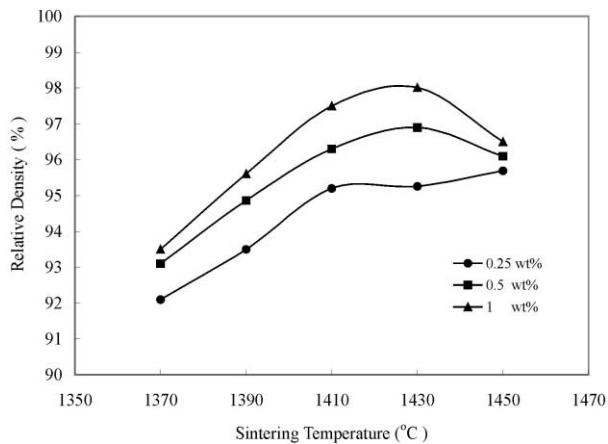


Fig. 4. Relative densities of NdAlO_3 ceramics with various V_2O_5 additions as a function of sintering temperatures.

line phase in NdAlO_3 ceramics prepared with different amounts of V_2O_5 additions sintered at 1410°C for 2h were identified and the XRD diffraction patterns shown in Fig. 3. It showed that almost single phase NdAlO_3 could be obtained with additions of V_2O_5 under 1410°C at the level of 0.25–0.5 wt.% additions. Identification of the minor phase by X-ray diffraction is extremely difficult, partly due to overlapping. However, second phases $\text{NdAl}_{11}\text{O}_{18}$ and $\text{Nd}_4\text{Al}_2\text{O}_9$ were detected (Fig. 3). To prove the existence of the second phases, EDS analysis of NdAlO_3 ceramics with 1 wt.% additions was performed. Since the grain morphology was very similar, the grains of different phases were distinguished by backscattered electron image (BEI). After enough trials, the constituent ratio of Nd and Al were obtained and located at 44.62: 46.17 (%) for the general regions. The second phase was detected by EDS spectra at certain

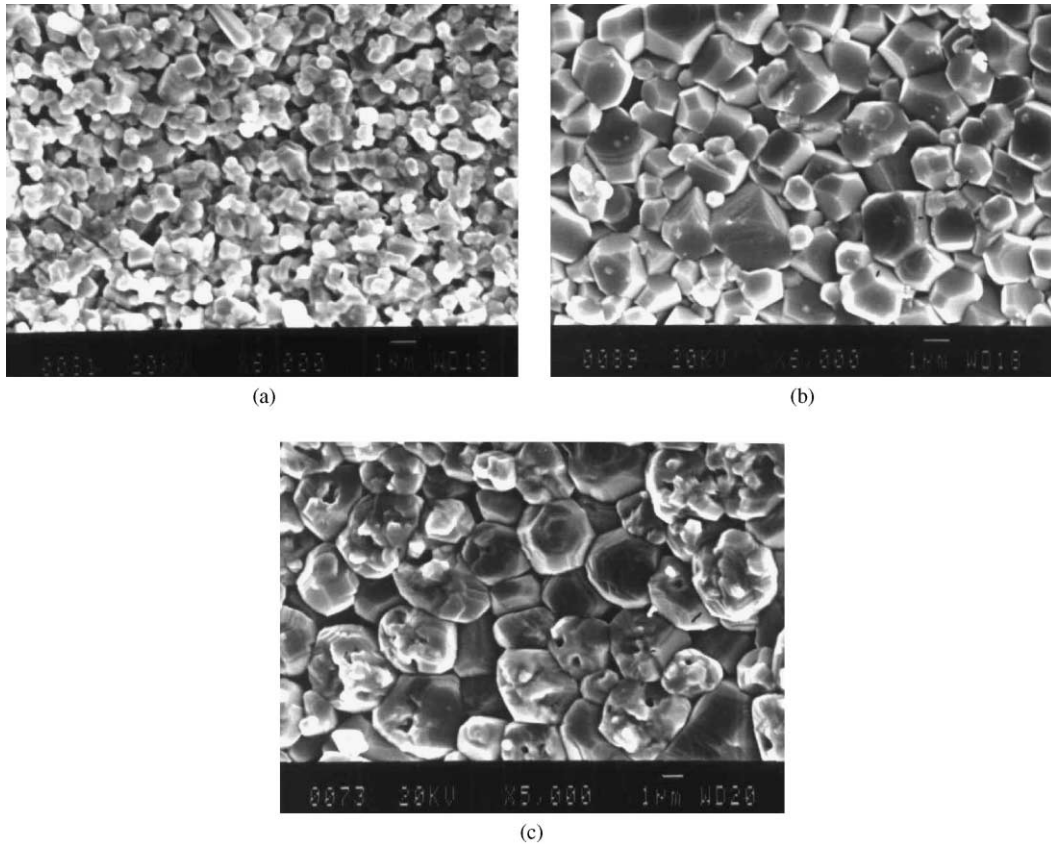


Fig. 5. (a) SEM of NdAlO_3 ceramics sintered at $1410\text{ }^\circ\text{C}$ with 0.25 wt.% V_2O_5 (b) 0.5 wt.% V_2O_5 and (c) 1 wt.% V_2O_5 .

specific grains, and the relative ratio of Nd and Al suggested the existence of second phase $\text{Nd}_4\text{Al}_2\text{O}_9$, and $\text{NdAl}_{11}\text{O}_{18}$.

The relative densities of V_2O_5 -sintered NdAlO_3 ceramics as a function of sintering temperatures are presented in Fig. 4. The densities of NdAlO_3 ceramics increased with increasing V_2O_5 additions up to 1 wt.%. The relative densities (RDs) of NdAlO_3 ceramics with

V_2O_5 sintered at $1410\text{ }^\circ\text{C}$ increased from 95.0 to 98.3% as the additions increased from 0.25 to 1 wt.%. The density increases with the increase of additions might be the result of enlarged grain size as shown in Fig. 5. The relative densities of NdAlO_3 ceramics with 0.25 and 0.5 wt.% V_2O_5 increased from 92.8 to 96.4% and 95.2 to 98.3%, respectively, as the sintering temperature increased from 1370 to $1450\text{ }^\circ\text{C}$. After reaching a max-

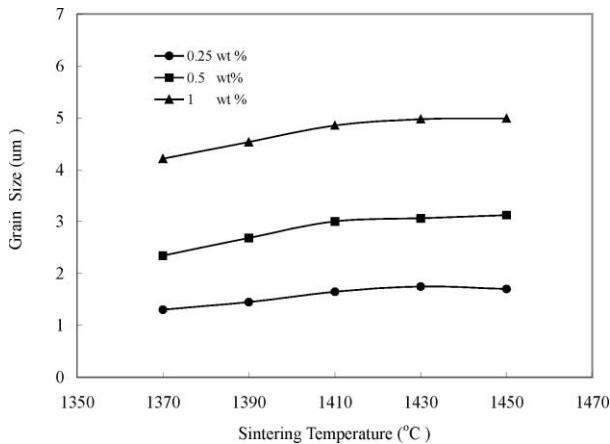


Fig. 6. The grain size of NdAlO_3 ceramics with various amount of V_2O_5 as function of sintering temperatures.

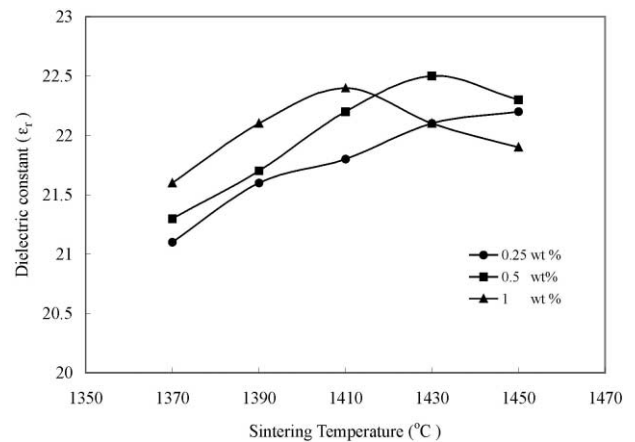


Fig. 7. The relative dielectric constant ϵ_r of NdAlO_3 ceramics with various amount of V_2O_5 as a function of sintering temperatures.

imum value at vicinity of 1390–1430 °C, the RDs of NdAlO₃ decreased with the increase of sintering temperatures. Relative density of 94–98% could easily be obtained with various amount of additions at sintering temperatures 1390–1430 °C. The enhanced densification at a lower sintering temperature was achieved by the liquid phase effect of V₂O₅ additions, via a eutectic reaction.^{12–15} The sintering temperature 1390–1430 °C were selected since that all the samples have densities higher than 95% theoretical.

SEM photographs of NdAlO₃ ceramics sintered at 1410 °C for 2 h with different additions are illustrated in Fig. 5. All samples showed homogeneous grain size. The grain size increased linearly with the amount of additions, which might be the result of the liquid phase effect.^{12–15}

The grain sizes of NdAlO₃ ceramics prepared with different amount of additions as a function of sintering temperature are illustrated in Fig. 6. The grain sizes increased with the increase in additions as shown in Fig. 5. The relationship between grain sizes and sintering temperature showed the same trend as that between relative densities and sintering temperature. Grain sizes of 1.3–4.6 μm were obtained. It was believed that the grain wetting ability was directly dependent on the amount of V₂O₅ additions.

Fig. 7 illustrated the relative dielectric constant of NdAlO₃ ceramics prepared with different additions as function of sintering temperature. The relationships between ϵ_r values and sintering temperatures reveal the same trend with that between densities and sintering temperatures. The increase of ϵ_r could be explained by higher densification and reduction in pore values. The ϵ_r values of well densified NdAlO₃ ceramics exhibited no significant differences with various additions at different sintering temperature and ranged from 21.6 to 22.5.

Many factors believed to affect the microwave dielectric loss and can be divided into two fields, the intrinsic loss and extrinsic loss.^{17,18} The intrinsic losses are

mainly caused by lattice vibration modes while the extrinsic losses are dominated by second phases, oxygen vacancies, grain sizes and densification or porosity. Interfacial polarization was thought to play an important role in porous materials.¹⁹ Fig. 8 illustrated the $Q \times f$ values of NdAlO₃ ceramics prepared with different additions as a function of sintering temperature. The $Q \times f$ values of NdAlO₃ ceramics increase with the increase of sintering temperature. The $Q \times f$ values of V₂O₅-sintered NdAlO₃ maintained good properties at low sintering temperatures. The $Q \times f$ values reached a maximum value of 64,000 GHz at 1410–1430 °C with 0.25 wt.% V₂O₅ additions. The $Q \times f$ value of V₂O₅-sintered NdAlO₃ ceramics decreased with further increase in the addition amount and change from 64,000 GHz (0.25 wt.%) to 16,000 (1 wt.%). In fact, the effects of V₂O₅ additions on microwave dielectric characteristic of NdAlO₃ might depend on the chemical properties of the additions, the related chemistry reactions, second phases during calcining and sintering procedures and the final density. It could be concluded that the $Q \times f$ value of NdAlO₃ ceramics were independent of the densification since the densities of the samples investigated in this studies were higher than 95% RDs. The $Q \times f$ values of NdAl₁₁O₁₈ and Nd₄Al₂O₉ sintered at 1410 °C are less than 13,000 and 10,000, respectively, and seriously affect the characteristic of quality factor. Since the calcining temperature was selected at 1200 °C, not only major NdAlO₃ phase was obtained but also the existence of second phase NdAl₁₁O₁₈ and Nd₄Al₂O₉ could be avoided. As the observations from XRD diffractions and detections of EDS analysis, the second phase appeared at the addition level of 1 wt.% and seriously affected the $Q \times f$ value of NdAlO₃ ceramics. The quality characteristic of V₂O₅-sintered NdAlO₃ ceramics sintered at lower temperature has a large $Q \times f$ value of 64,000 GHz that is better than the properties of previous researches. This was due to the suitable selection of calcining temperature and well controlled the extrinsic loss.¹⁸

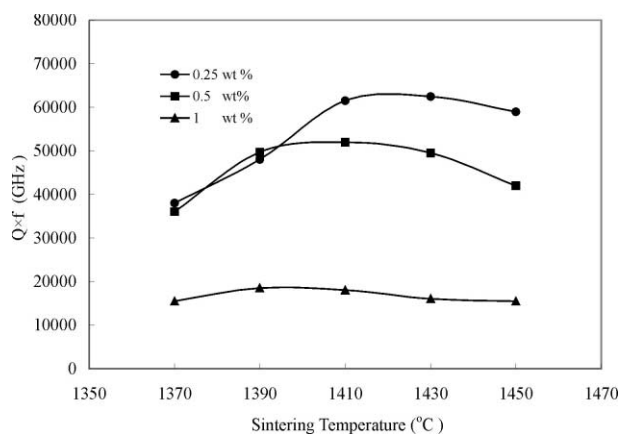


Fig. 8. $Q \times f$ values of NdAlO₃ ceramics with various amount of V₂O₅ as a function of sintering temperatures.

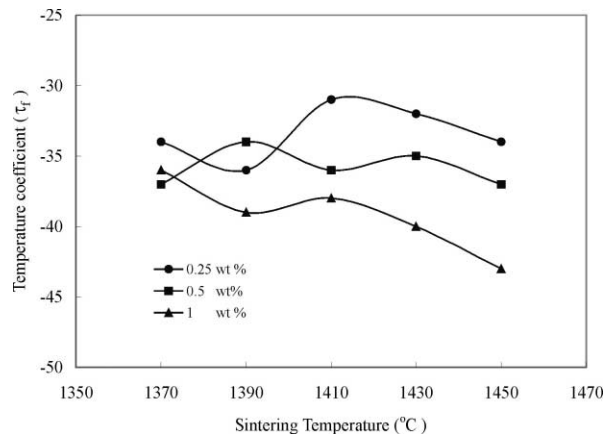


Fig. 9. The composition dependence on τ_r of NdAlO₃ ceramics with various amount of V₂O₅ as function of sintering temperatures.

Fig. 9 shows the composition dependence of τ_f in the NdAlO₃ ceramics sintered at 1410 °C. The τ_f of NdAlO₃ ceramics exhibited no significant differences with the increase of additions. The temperature coefficient ranges from –31 ppm/°C to –43 ppm/°C. For practical applications, a modification in the temperature stability is necessary for NdAlO₃ ceramics.

4. Conclusion

The sintering temperatures of the NdAlO₃ ceramics were effectively reduced from 1650 to 1410–1430 °C. NdAlO₃ ceramics with appropriate V₂O₅ additions can be well sintered to approach 98% theoretical density below 1430 °C due to liquid phase sintering. $Q \times f$ values of 64,000 could be achieved at 1390–1430 °C with 0.25 wt.% V₂O₅. $Q \times f$ values of V₂O₅-sintered NdAlO₃ ceramics decreased with further increase in the addition amount and change from 64,000 GHz (0.25 wt.%) to 16,000 (1 wt.%). As 1200 °C was selected as calcining temperature, not only the homogeneous main phase could be obtained but also the existence of second phase NdAl₁₁O₁₈ could be reduced. At low addition level (0.25–0.5 wt.% V₂O₅), the NdAlO₃ ceramics remained single phase and only presented second phase Nd₄Al₂O₉ with additions at 1 wt.%. The second phase seriously affect the dielectric properties. Since the dielectric constants were related to the densities of NdAlO₃ ceramics, there was no significant difference in dielectric constants with different addition levels. The temperature coefficient of the resonant frequency τ_f remains a large negative value of –31 to –43 ppm/°C.

Acknowledgements

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