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Low-temperature sintering and microwave dielectric properties of $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics using glass addition of oxides

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Abstract

The microstructures and microwave dielectric characteristics of complex perovskite $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics with $60P_2O_5$–15ZnO–$5La_2O_3$–$5Al_2O_3$–$5Na_2O$–5MgO–$5Yb_2O_3$ (PZLANMY) additions (1–4 wt%) prepared through the conventional solid-state route were investigated. It was found that $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics can be sintered at 1210 °C owing to the sintering aid of PZLANMY-glass addition. At 1300 °C, $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics with 1 wt% of PZLANMY-glass addition possess a dielectric constant (ε_r) of 27, a $Q\times f$ value of 64,000 GHz and a temperature coefficient of resonant frequency (τ_f) of -29 ppm/°C. The PZLANMY-glass doped $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics can find applications in microwave devices that require low sintering temperature.

Keywords: $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics; $60P_2O_5$–15ZnO–$5La_2O_3$–$5Al_2O_3$–$5Na_2O$–5MgO–$5Yb_2O_3$ glass ceramics; Microwave dielectric properties

1. Introduction

The demand for the development of microwave dielectric materials is increasing with the rapid progress in modern communication systems. Dielectric resonators that are fabricated by microwave dielectric materials provide a compact, low-cost, and highly reliable choice as resonator elements in microwave system modules and recently these components replace the metallic cavity more frequently. Microwave dielectric materials with high quality factor ($Q\times f$), high dielectric constant (ε_r) and zero temperature coefficient of resonant frequency (τ_f) for use as dielectric resonators and microwave device substrates have also been developed by many researchers. High dielectric constant material can effectively reduce the size of the resonators since the wavelength (λ) in dielectrics is inversely proportional to $\sqrt{\varepsilon_r}$ of the wavelength (λ_0) in vacuum, and the inverse of the dielectric loss ($Q=1/\tan\delta$) has to be high for achieving prominent frequency selectivity and stability in microwave transmitter components.

Complex perovskite ceramic ($Nd(A_{1/2}Ti_{1/2})O_3$) compositions with a measured quality factor ($Q\times f$) in excess of 140,000 GHz and dielectric constants between 27 and 32 are widely used as substrate for microwave devices as they provide low dielectric loss, excellent lattice matching and good matching for thermal expansion [1–3]. In addition, $Nd(A_{1/2}Ti_{1/2})O_3$ compositions have a non-cubic symmetry and a $GdFeO_3$-type structure [4,5]. One of the $Nd(A_{1/2}Ti_{1/2})O_3$ compositions, $Nd(Co_{1/2}Ti_{1/2})O_3$ sintering at 1440 °C for 4 h, has a dielectric constant (ε_r) of 27, a quality factor ($Q\times f$) of 140,000 GHz and a temperature coefficient of resonant frequency (τ_f) of –46 ppm/°C. Owing to these properties, it is used as a dielectric resonator in microwave communication module applications [5]. However, the sintering temperatures of conventional microwave dielectric ceramics used in passive communication devices are typically 1200–1400 °C. For practical applications, the sintering temperature of $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics must be reduced. Adding glass with a low melting temperature, chemical processing and small particle size of the starting materials generally help to reduce the sintering temperature of the dielectric materials [6–9]. The $60P_2O_5$–15ZnO–$5La_2O_3$–$5Al_2O_3$–$5Na_2O$–5MgO–$5Yb_2O_3$ glass addition

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(PZLANMY-glass addition) makes it possible to decrease the sintering temperature because it has a low melting temperature (about 1300 °C) and a transition temperature (about 499 °C). In this paper, $60P_2O_5$–15ZnO–$5La_2O_3$–$5Al_2O_3$–$5Na_2O$–5MgO–$5Yb_2O_3$ glass addition (PZLANMY-glass addition) is added to lower the sintering temperature further. The microstructures and microwave dielectric properties of $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics with the PZLANMY-glass additions were investigated.

2. Experimental procedures

A sample of $Na(Co_{1/2}Ti_{1/2})O_3$ was prepared using the solid-state method from individual high-purity oxide powders (> 99.9%): Nd_2O_3, CoO and TiO_2. The starting materials were mixed according to a stoichiometric ratio to synthesize the $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics. The powders were ground in distilled water for 12 h in a ball mill with agent balls. The mixture was dried at 100 °C, and thoroughly milled before it was calcined at 1250 °C for 2 h. The calcined powder $Nd(Co_{1/2}Ti_{1/2})O_3$ was ground and sieved through a 100-mesh screen. The PZLANMY-glass powders were prepared from the above-mentioned high purity oxide chemicals of $NH_4H_2PO_4$, ZnO, La_2O_3, Al_2O_3, Na_2CO_3, MgO, and Yb_2O_3. These oxides were weighed stoichiometrically and mixed for 12 h by using distilled water as the medium. They were dried, melted in an alumina crucible at 1350 °C for 1 h, quenched and powdered. The calcined powders with different amounts of PZLANMY-glass additions were then re-milled for 12 h with PVA solution as a binder. The milled powders were pressed into a disk of 11 mm in diameter and 5 mm in thickness. A pressing pressure of 2000 kg/cm^2 was used for all the samples. The pellets were sintered at temperatures ranging from 1210 °C to 1330 °C for 4 h in air.

The X-ray diffraction (XRD, Siemens D5000) data of powder and bulk samples were collected using Cu Kα radiation (at 30 kV and 20 mA). The microstructural observations and analysis of the sintered surface were performed using scanning electron microscopy (SEM, Philips XL-40FEG). The density of the sintered specimens, as a function of sintering temperature, was measured by the liquid Archimedes method using distilled water as the liquid. On the other hand, the dielectric constants (ε_r) at microwave frequencies were measured using the Hakki–Coleman dielectric resonator method, as modified and improved by Courtney [10,11]. Microwave dielectric properties of the sintered samples were measured by a HP 8757D network analyzer and a HP 8350B sweep oscillator.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics with various PZLANMY-glass additions formed at different sintering temperatures (1210–1330 °C). A homogeneous $Nd(Co_{1/2}Ti_{1/2})O_3$ phase with a monoclinic structure belongs to the $P2_1/n$ space group, such that a 1:1 order in the B site could be obtained. Similar X-ray diffraction patterns were obtained from the $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics at various sintering temperatures (1210–1330 °C). Unknown phases were not observed on PZLANMY-addition since the detection of a minor phase by X-ray is extremely difficult.

Fig. 2 shows photographs of the microstructure of the surface of the PZLANMY-glass doped $Nd(Co_{1/2}Ti_{1/2})O_3$ sintered at temperatures of 1210–1330 °C. The grain size increased with the increase of sintering temperature as well as the amount of PZLANMY-glass additions due to the sintering aid. At the 1 wt% PZLANMY-glass addition level, porous specimens were observed at sintering temperatures between 1210 °C and 1240 °C. However, rapid and abnormal grain growth of the $Nd(Co_{1/2}Ti_{1/2})O_3$ specimen occurred on PZLANMY-glass addition at higher sintering temperatures. These changes may directly affect the microwave dielectric properties of the $Nd(Co_{1/2}Ti_{1/2})O_3$ samples.

The density of the $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics with various PZLANMY-glass additions at different sintering temperatures are shown in Fig. 3. Initially, the density increased with an increase of sintering temperature at 1 wt% PZLANMY-glass addition. After reaching the maximum density at 1300 °C with 1 wt% PZLANMY-glass addition, it slightly decreased owing to the rapidly abnormal grain growth. It seemed that the PZLANMY-glass did attribute to the densification of the $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics at low temperatures. In addition, the density also increased with increasing amounts of PZLANMY-glass additions and the sintering temperature. The higher the PZLANMY-glass doping level and the sintering temperature the higher was the densification as evidenced by the abnormal grain growth as observed in Fig. 2. The maximum density was found to be 6.5 with 4 wt% of PZLANMY-glass addition at 1240 °C.

Fig. 4 plots the dielectric constant of the $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics with different amounts of PZLANMY-glass additions as a function of sintering temperature. The relationships between dielectric constant and sintering temperature reveal the same trend as those between density and sintering temperature since a higher density represents a lower porosity. A higher density causes the increase in the dielectric constant. The 4 wt% PZLANMY-glass doped $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics at 1240 °C had the highest dielectric constant. The dielectric constant slightly decreased as the PZLANMY glass content increased. At 4 wt% added, $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics sintered at 1240 °C had an ε_r of 27.2. The variation in ε_r was related mainly to the density of the specimen.

Fig. 5 presents the quality factor ($Q \times f$) of the PZLANMY-glass doped $Nd(Co_{1/2}Ti_{1/2})O_3$ at various sintering temperatures. The microwave dielectric loss is caused not only by the lattice vibrational modes, but also by the pores and the second phases [12]. With 1 wt% of PZLANMY-glass addition, the $Q \times f$ increased from 32,000 GHz to 64,000 GHz as the sintering temperature

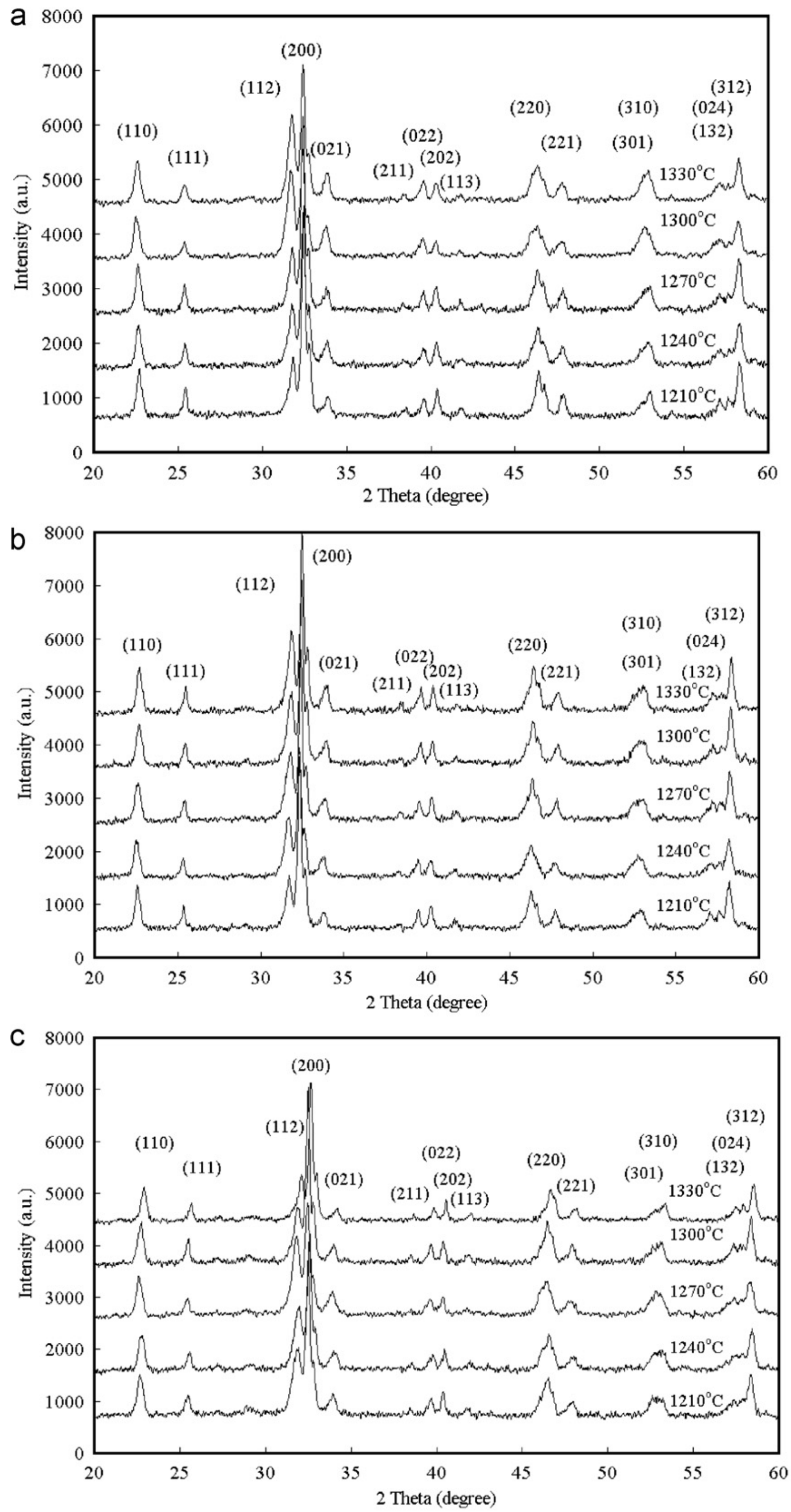

Fig. 1. X-ray diffraction patterns of $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics at various PZLANMY-glass additions and sintering temperatures. (a) 1wt%, (b) 2wt% and (c) 4wt%.

increased from 1210 °C to 1300 °C for 4 h, and thereafter it decreased. The decrease in $Q \times f$ was caused by the rapid grain growth, as presented in Fig. 2. Larger grains and higher porosities were associated with poorer $Q \times f$ values of the as-sintered samples with added PZLANMY-glass at high sintering temperatures. The decrease in $Q \times f$ may also

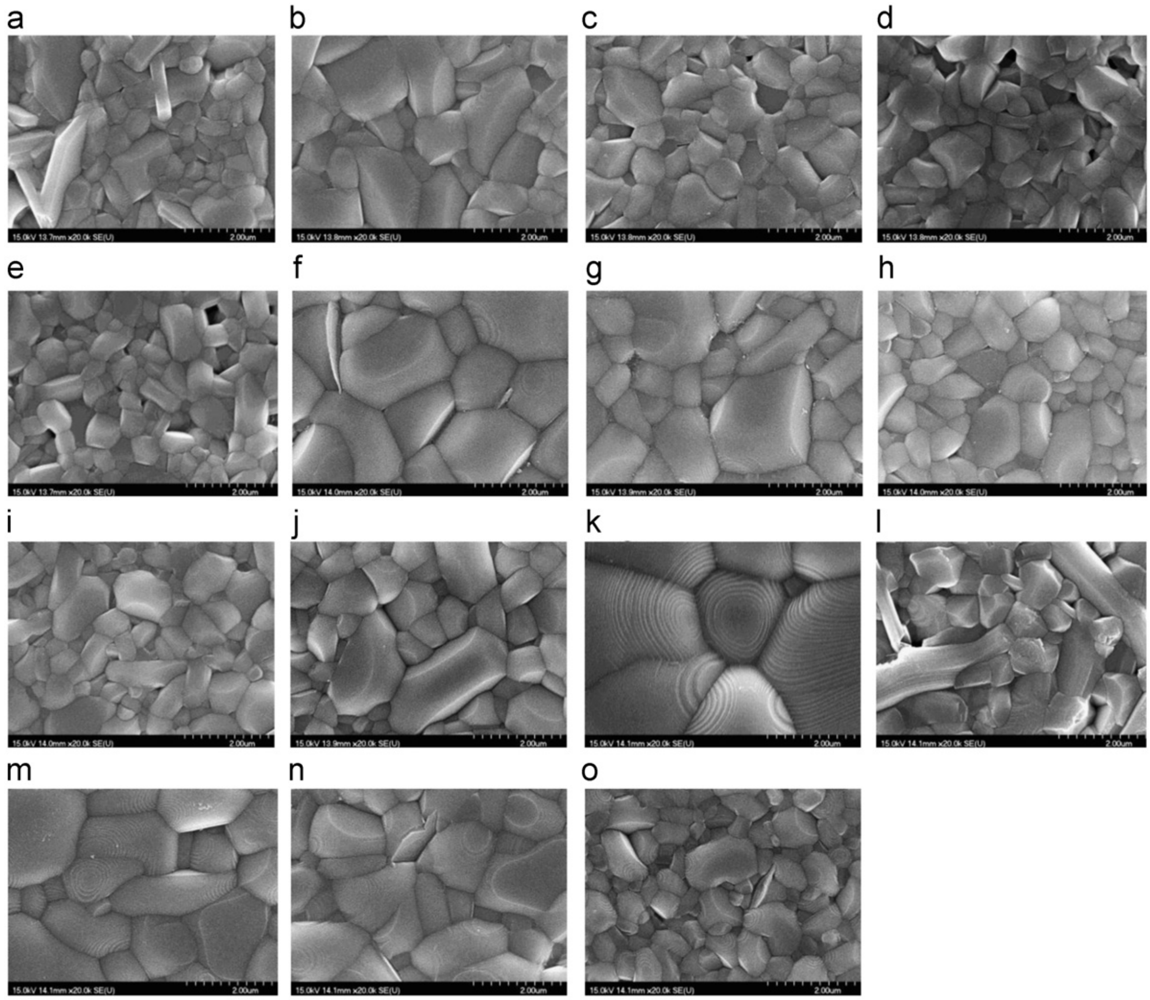

Fig. 2. SEM photographs of $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics with various PZLANMY-glass additions and sintering temperatures. (a) 1wt%; 1330 °C, (b) 1wt%; 1300 °C, (c) 1wt%; 1270 °C, (d) 1wt%; 1240 °C, (e) 1wt%; 1210 °C, (f) 2wt%; 1330 °C, (g) 2wt%; 1300 °C, (h) 2wt%; 1270 °C, (i) 2wt%; 1240 °C, (j) 2wt%; 1210 °C, (k) 4wt%1330 °C, (l) 4wt%1300 °C, (m) 4wt%1270 °C, (n) 4wt%1240 °C and (o) 4wt%1210 °C.

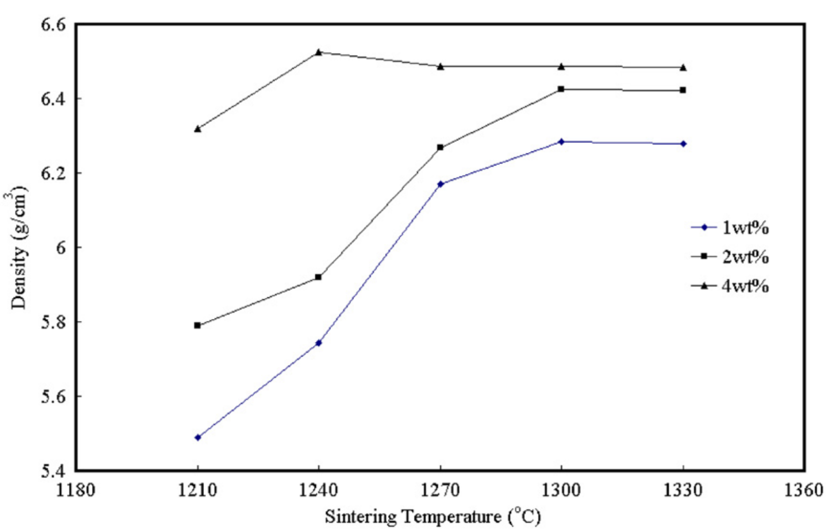

Fig. 3. Dependence of density on sintering temperature for $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics at various PZLANMY-glass additions.

have been associated with the porous specimens at lower sintering temperatures. However, the relationship between the $Q \times f$ values and the sintering temperature follows that between the density and the sintering temperature. The relative density also plays an important role in controlling the dielectric loss, as has been demonstrated for other

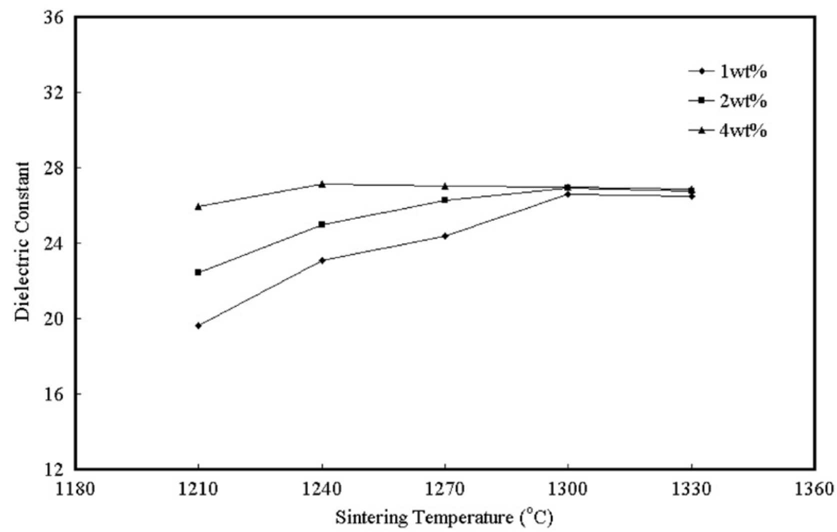

Fig. 4. Dependence of dielectric constant on sintering temperature for $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics at various PZLANMY-glass additions.

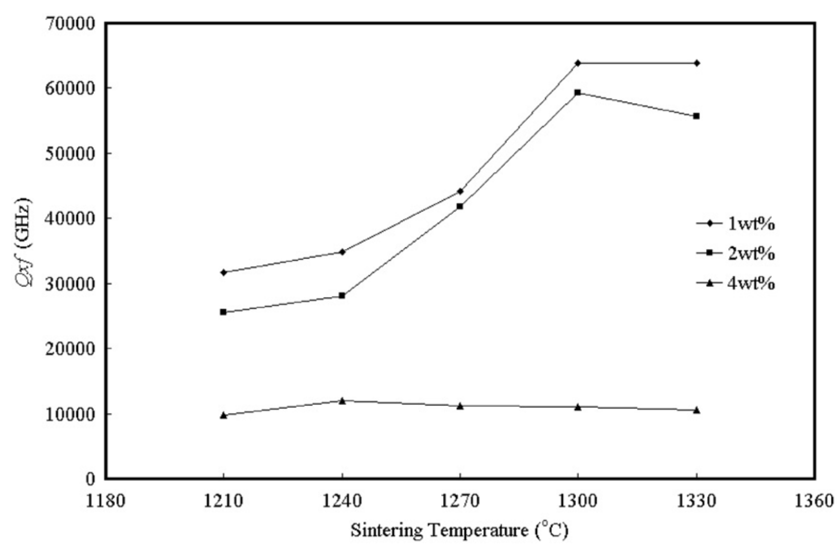

Fig. 5. Dependence of $Q \times f$ value on sintering temperature for $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics at various PZLANMY-glass additions.

microwave dielectric materials. The $Q \times f$ value of $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics decreases as the PZLANMY-glass content increases over 1 wt% since the grain boundary phases and abnormal grains were produced in relatively large quantities at higher sintering temperatures, as observed in Fig. 2. Additionally, the sintering temperatures associated with the optimum $Q \times f$ value for various PZLANMY-glass additions decreased as the PZLANMY-glass content increased, because the sintering temperature associated with the optimum $Q \times f$ value, which corresponds to the optimal density and uniformity of grain size, decreased as the PZLANMY-glass content increased, as also shown in Fig. 2. Since not only were the observed grains in the $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics with 1 wt% PZLANMY-glass addition more uniform than the others but also the lattice imperfections and dielectric loss were lower; the decrease in the $Q \times f$ values for highly PZLANMY-glass doped $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics resulted from the grain morphology and the low $Q \times f$ of the liquid phase. This fact explains the decrease in the $Q \times f$ values of $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics as the amount of PZLANMY-glass added increased. With 1 wt% added, the maximum $Q \times f$ value, 64,000 GHz, was obtained for $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics sintered at 1300 °C. The quality factor of the PZLANMY-glass doped $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramic at low-sintering temperatures exceeded that of the pure $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics because the grain sizes were more uniform.

Fig. 6 plots the temperature coefficients of resonant frequency (τ_f) of PZLANMY-glass doped $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics at different sintering temperatures. The temperature coefficient of the resonant frequency is well known to be related to the composition, the additives and the second phase of the material. The τ_f is a function of the PZLANMY-glass content. It varied from -53 to -21

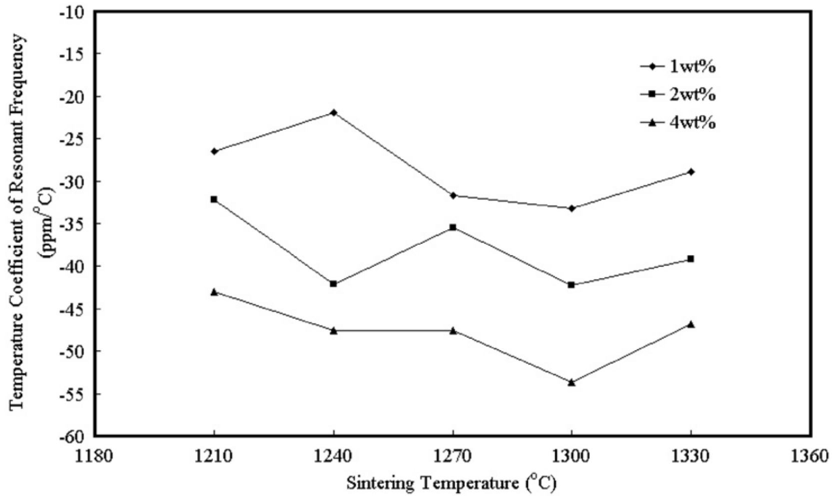

Fig. 6. Dependence of τ_f value on sintering temperature for $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics at various PZLANMY-glass additions.

ppm/°C on an average as the amount of the added PZLANMY-glass increased from 1 to 4 wt%. No significant change was observed in the τ_f value with sintering temperature at a fixed amount of added PZLANMY-glass.

4. Conclusion

The dielectric properties of the PZLANMY-glass doped $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics were investigated. PZLANMY-glass was added as a sintering aid to reduce the firing temperature of $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics. A large decrease in the sintering temperature (near 150 °C) can be achieved by adding the PZLANMY-glass to the $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics. Similarly, the temperature coefficient of resonant frequency was significantly improved by adding the PZLANMY-glass to the $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics. With 1 wt% of PZLANMY-glass addition, a dielectric constant of 27, a $Q \times f$ value of 64,000 GHz and temperature coefficients of resonant frequency (τ_f) of –29 ppm/°C were obtained for $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics that were sintered at 1300 °C for 4 h.

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