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Journal of the European Ceramic Society 25 (2005) 2871–2875
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Microwave dielectric properties of $Mg_4Nb_2O_9$–3.0 wt.% LiF ceramics prepared with $CaTiO_3$ additions

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Abstract

A family of low-temperature co-fired ceramics (LTCC) based on mixtures of $Mg_4Nb_2O_9$–3.0 wt.% LiF (MNLF) and $CaTiO_3$ ceramics has been investigated for microwave applications. In this study, it was found that, when increasing amounts of $CaTiO_3$ additions from 0 to 10 wt.%, the temperature coefficient of resonant frequency (τ_f) extremely varied from −71.5 to 39.9 ppm/°C. The dielectric constants (ε_r) increased from 12.3 to 18.3 and the quality factor ($Q{\cdot}f$) drastically decreased from 118,989 to 11,119 GHz. From these results, the MNLF–6 wt.% $CaTiO_3$ ceramic sintered at 950 °C for 10 h was shown to be the appropriate dielectric properties: $\varepsilon_r = 15.7$, $Q{\cdot}f = 22{,}098$ GHz, and $\tau_f = -3.3$ ppm/°C. As for the chemical compatibility of MNLF–6 wt.% $CaTiO_3$ ceramic with Ag, any secondary phase was not recognized from the XRPD profile of the samples heat-treated at 920 °C for 10 h. Thus, it was considered that the MNLF–*x* wt.% $CaTiO_3$ ceramics are applicable to the multilayer devices with silver.

Keywords: Niobates; Dielectric properties; X-ray methods; Electron microscopy; Powders-solid state reaction

1. Introduction

Recently, a variety of low-temperature sintered dielectric ceramics which are co-fired with high conductivity metals such as Ag or Cu have been studied in order to enable the fabrication of multilayer microwave devices; therefore, the much attention has been paid to develop the low-temperature co-fired ceramics (LTCC). The sintering temperatures of commercially developed microwave dielectric materials were too high to use an electrode such as silver (mp = 960.5 °C) and then low-melting point compounds such as B_2O_3, Bi_2O_3, CuO and V_2O_5 were used as the sintering aids.[1–4] In most of the low-temperature sintered ceramics by the addition of sintering aids, however, the $Q{\cdot}f$ value of the ceramics drastically decreased by means of the formation of secondary phase. Although Dai et al.[5] reported the Al_2O_3-based LTCC material with a dielectric constant of 9.1 and a near zero τ_f value, the $Q{\cdot}f$ values are too low to use for the high frequency application; thus, the development of a new LTCC material with the high-$Q{\cdot}f$ value is required. In recent study, the microwave dielectric properties of $Mg_4Nb_2O_9$ ceramic was reported to have a high $Q{\cdot}f$ value which was comparable to that of Al_2O_3;[6] the crystal structure of $Mg_4Nb_2O_9$ ceramic is known to have a corundum-type structure.[7] Also, the microwave dielectric properties of the $Mg_4Nb_2O_9$–3.0 wt.% LiF (MNLF) ceramic sintered at 850 °C have been reported to have a high $Q{\cdot}f$ value and a low dielectric constant ($Q{\cdot}f = 103{,}607$ GHz and $\varepsilon_r = 12.6$); however, the improvement in τ_f value is necessary for the commercial applications because the τ_f value of MNLF was −70 ppm/°C.[8] Thus, in order to tune the τ_f value of MNLF, the effect of $CaTiO_3$ addition to MNLF on the microwave dielectric properties was studied in this study.

2. Experimental procedure

Synthesis of the $Mg_4Nb_2O_9$ and $CaTiO_3$ ceramics were conducted from high purity MgO, Nb_2O_5, $CaCO_3$ and TiO_2 powders, using the standard solid-state methods. Their pow-

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doi:10.1016/j.jeurceramsoc.2005.03.157

ders weighted on the basis of stoichiometric compositions of $Mg_4Nb_2O_9$ and $CaTiO_3$ were mixed and calcined at 1100 °C for 20 h in air. Subsequently, the 2–10 wt.% $CaTiO_3$ and 3.0 wt.% LiF additions to MN were performed. The obtained powders were milled and mixed with a polyvinyl alcohol, and then pressed into a pellet of 12 mm in diameter and 7 mm in thickness under the pressure of 100 MPa. These pellets were sintered at the various temperatures ranging from 850 to 1000 °C for 10 h in air.

The sintering behavior of the ceramics was investigated by the differential thermal analysis (DTA) and the thermogravimetry (TG). The apparent densities of the sintered specimens were measured by using Archimedes method. The crystalline phases were identified by the X-ray powder diffraction (XRPD). Moreover, the morphological changes in the samples were investigated by using a field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray (EDX) spectroscopy. The dielectric constants and the quality factors were measured at the frequency range of 9–11 GHz by the Hakki–Coleman method.[9] The τ_f values were determined from the difference between the resonant frequencies obtained at the two temperatures of 20 and 80 °C.

3. Results and discussion

Fig. 1a and b show the effect of $CaTiO_3$ additions to MNLF ceramics on the DTA and TG curves, respectively. In the case of MNLF, the exothermic reaction took place at the temperature of approximately 850 °C, whereas that of MNLF–6 wt.% $CaTiO_3$ did at the temperatures of approximately 675 and 1100 °C. When comparing with the TG curves, these temperatures are substantially consistent with those beginning on the weight losses; therefore, it is considered that these exothermic reactions may be primarily related to the decompositions of $CaTiO_3$ and LiF compounds, respectively.

The bulk densities of MNLF ceramics sintered at various temperatures are shown as a function of $CaTiO_3$ additions in Fig. 2; those of MNLF ceramics range from 4.037 to 4.185 g/cm^3. The bulk densities of the samples sintered at 850, 900 and 950 °C decreased with increasing the amount of $CaTiO_3$ additions, whereas those of samples sintered at 1000 °C were almost constant as shown in Fig. 2.

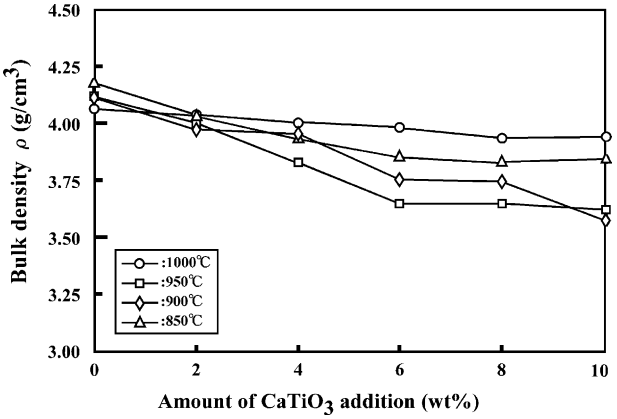

Fig. 2. Effect of $CaTiO_3$ addition on bulk densities of MNLF as a function of amount of $CaTiO_3$ additions.

The microwave dielectric properties of MNLF–*x* wt.% $CaTiO_3$ are shown in Figs. 3 and 4. The dielectric constants of MNLF ceramics with and without the $CaTiO_3$ additions sintered at the various temperatures are shown in Fig. 3a; these values are increased from 12.3 to 18.3 with increasing the amount of $CaTiO_3$ additions. Although it is considered that the $CaTiO_3$ additions to MNLF lead to an increase in the dielectric constant of MNLF, the remarkable increase in the dielectric constant by the $CaTiO_3$ additions was not recognized because of the formation of secondary phases, which arises from the decomposition reaction between the $CaTiO_3$ and MNLF ceramics. In addition, the dielectric constants slightly increased with increasing the sintering temperature; these increases in the dielectric constant were attributed to the presence of the secondary phases. The alternative $Q{\cdot}f$ values of the samples drastically decreased from 118,989 to 11,119 GHz with increasing the amount of $CaTiO_3$ additions as shown in Fig. 3b; these decreases in the $Q{\cdot}f$ values are primary related to the decomposition reaction between MNLF and $CaTiO_3$ ceramics as mentioned above. The effect of $CaTiO_3$ additions on the τ_f value of MNLF sintered at 950 °C was shown in Fig. 4; the τ_f values of MNLF–*x* wt.% $CaTiO_3$ ceramics varied from negative to positive values, ranging from −71.5

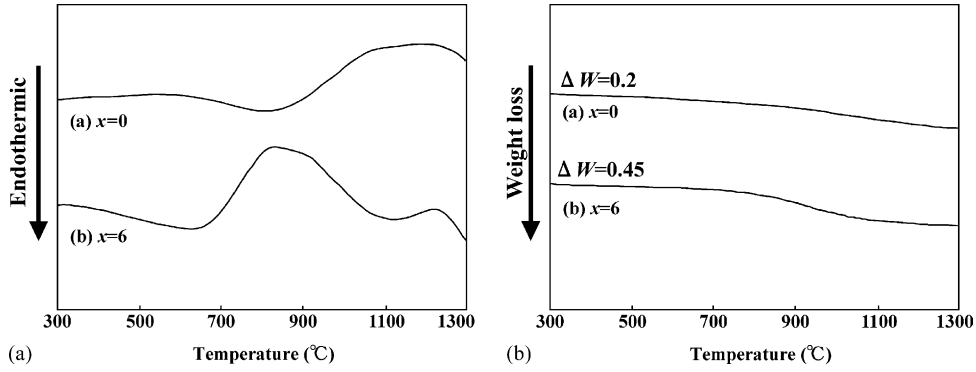

Fig. 1. DTA-TG curves of the MNLF–*x* wt.% $CaTiO_3$ ($x = 0$ and 6) ceramics: (a) DTA and (b) TG curves.

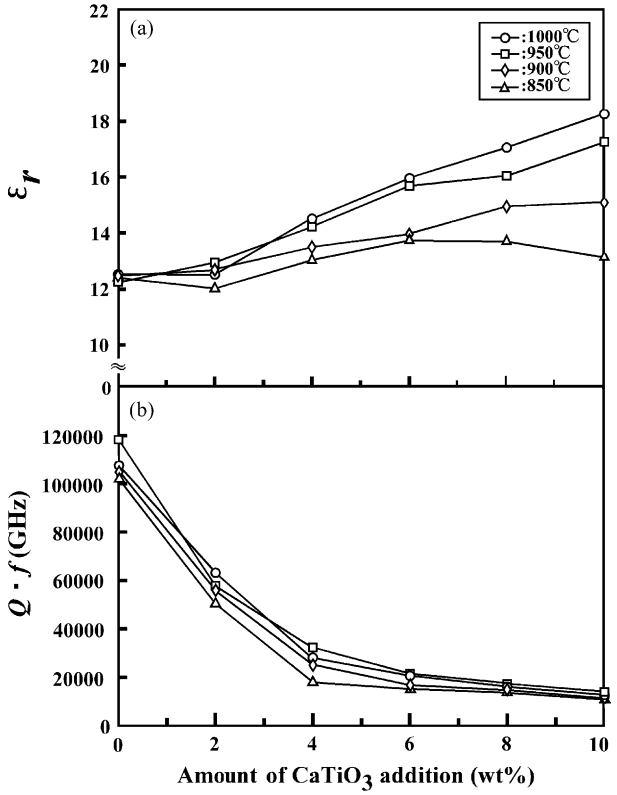

Fig. 3. Variations in dielectric constant (ε_r) and quality factor ($Q{\cdot}f$) of MNLF–x wt.% $CaTiO_3$ ceramics sintered at various temperatures.

to 39.9 ppm/°C. As a result, a dielectric constant of 15.7 and a $Q{\cdot}f$ value of 22,098 GHz with a τ_f value of −3.3 ppm/°C were obtained when the 6 wt.% $CaTiO_3$ addition to MNLF was performed. The variations in the microwave dielectric proper-

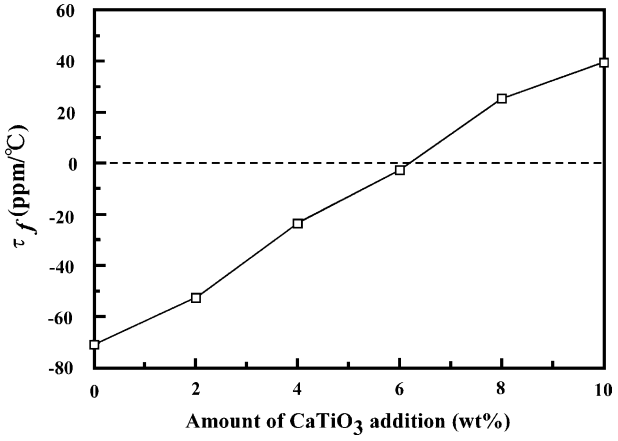

Fig. 4. Relationship between temperature coefficient of resonant frequency (τ_f) of MNLF–x wt.% $CaTiO_3$ ceramics sintered at 950 °C and amount of $CaTiO_3$ additions.

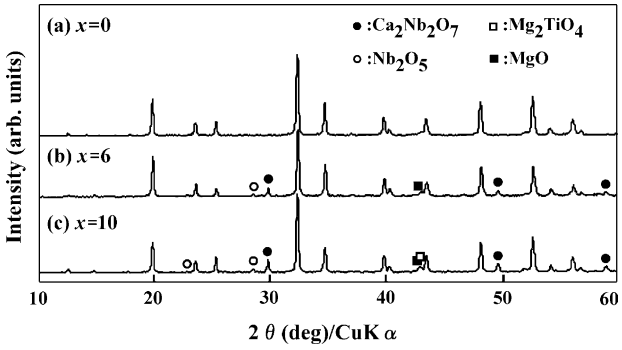

Fig. 5. XRPD patterns of MNLF–x wt.% $CaTiO_3$ (x = 0–10) ceramics sintered at 950 °C for 10 h in air.

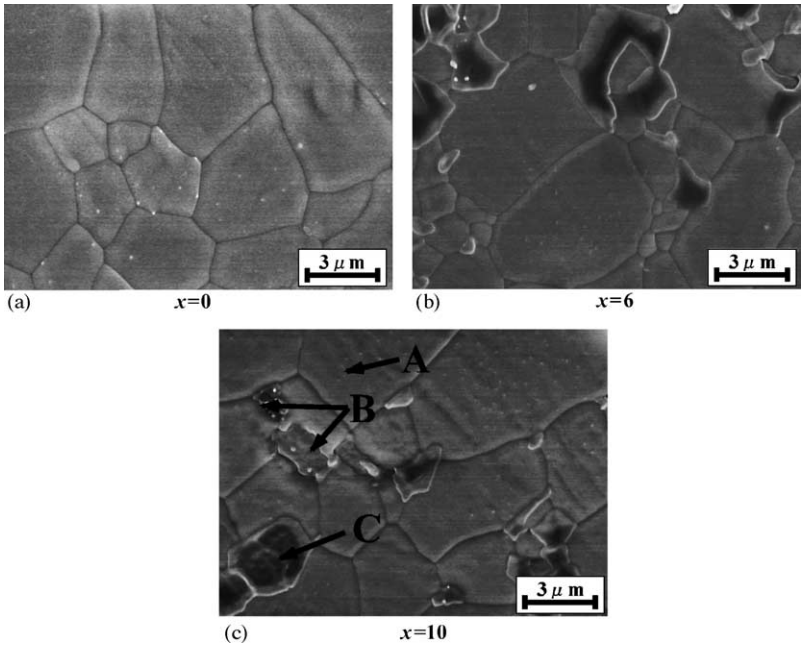

Fig. 6. FE-SEM photographs of MNLF–x wt.% $CaTiO_3$ (x = 0, 6, and 10) ceramics sintered at 950 °C for 10 h in air.

ties of MNLF–*x* wt.% $CaTiO_3$ ceramics are considered to be strongly effected by the formation of secondary phase; thus, in order to clarify the relationship between the secondary phase and microwave dielectric properties of MNLF–*x* wt.% $CaTiO_3$ ceramics, the crystalline phases in the samples sintered at 950 °C were characterized in terms of XRPD.

Fig. 5 shows the XRPD patterns of MNLF with the different amounts of $CaTiO_3$ sintered at 950 °C for 10 h in air. The XRPD patterns of the samples showed the four secondary phases, i.e., $Ca_2Nb_2O_7$, Mg_2TiO_4, Nb_2O_5 and MgO; the presence of $CaTiO_3$ was not recognized in these XRPD patterns. Thus, it was found that the addition of $CaTiO_3$ to MNLF ceramic formed the secondary phases, which resulted in the decomposition reaction between MNLF and $CaTiO_3$; such a formation of secondary phase exerts an influence on the variations in the microwave dielectric properties.

The microstructural changes in the MNLF–*x* wt.% $CaTiO_3$ ceramics were investigated by using the FE-SEM and EDX in order to reveal the effects of $CaTiO_3$ additions on the morphologies of MNLF; the FE-SEM photographs of MNLF–*x* wt.% $CaTiO_3$ ceramics sintered at 950 °C for 10 h were shown in Fig. 6. The large grains were observed in the MNLF without the $CaTiO_3$ ceramic sintered at 950 °C for 10 h as shown in Fig. 6a. However, the increase of the dark and bright colored secondary phases was observed with increasing the amount of $CaTiO_3$ addition. From these results, it is suggested that the changes in the microwave dielectric properties of the samples may be concerned with these secondary phases. The EDX result in the grain marked 'A' exhibited the stoichiometric composition of MNLF ceramic. On the other hand, the concentrations of Ca and Nb in the grain marked 'B' were substantially recognized to be the stoichiometric composition of $Ca_2Nb_2O_7$ ceramics, which was also detected in the XRPD patterns. Also, the grain marked *C* was found to be primarily consistent with the elements of Mg and O which resulted in the decomposition reaction between the MNLF and $CaTiO_3$ ceramics; the volumes of these secondary phases increased with an increase in the amounts of $CaTiO_3$ additions. From these results, it was considered that the formation of secondary phases exerts an influence on the variations in microwave dielectric properties of MNLF–*x* wt.% $CaTiO_3$ ceramics; the relationship between the microwave dielectric properties and the $CaTiO_3$ addition to MNLF was clarified in terms of the XRPD and microstructural analyses.

When the MNLF–6 wt.% $CaTiO_3$ ceramic was sintered at 950 °C for 10 h, although a near zero τ_f value ($\tau_f = -3.3$ ppm/°C) was obtained, it is necessary to have a high $Q{\cdot}f$ value; as well known, the grain growth of the microstructure by the variations in the sintering time is effective in improving the $Q{\cdot}f$ values. Thus, the sintering time dependence of microwave dielectric properties of the MNLF–6 wt.% $CaTiO_3$ ceramic sintered at 950 °C was studied. Fig. 7 shows the dielectric constants and $Q{\cdot}f$ values of the samples sintered for various sintering times at 950 °C; the dielectric constants of samples were increased with increasing the sintering times. The $Q{\cdot}f$ values of the samples increased

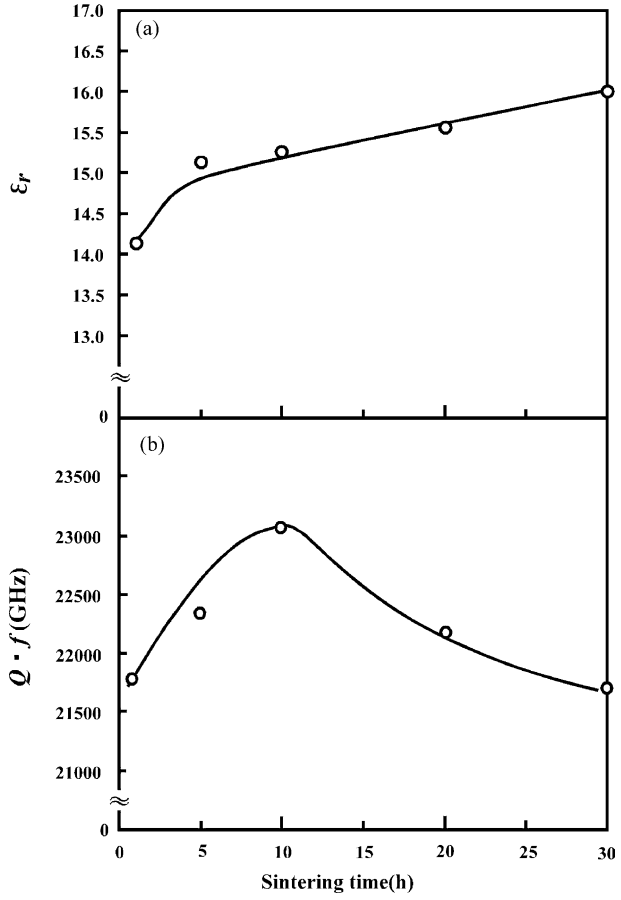

Fig. 7. Sintering time dependence of dielectric constant and $Q{\cdot}f$ value of MNLF–6 wt.% $CaTiO_3$ ceramics sintered at 950 °C.

from 20,831 to 22,801 GHz when the samples were sintered for 1–10 h; the maximum $Q{\cdot}f$ value was obtained at the sintering time of 10 h. Moreover, with increasing the sintering time from 10 to 30 h, the $Q{\cdot}f$ values of samples linearly decreased from 22,801 to 21,741 GHz. The increase in the $Q{\cdot}f$ values of the samples in the sintering time range of 1–10 h is primarily attributed to the grain growth of the microstructure; this result agrees with that of the sintering time dependence in the $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics reported by Kawashima et al.[10] On the other hand, the τ_f values of the samples were found to be independent of the sintering time; a near zero τ_f value was obtained in the sintering times for 2–30 h as shown in Fig. 8. Thus, from these results, in order to improve the $Q{\cdot}f$ values, an appropriate sintering time which exerts an influence on the grain growth of microstructure is necessary, through the τ_f values of the samples were not effected by the variations in the sintering time as mentioned above.

In the case of LTCC materials, which are applicable to multilayer devices, the interfacial reaction between the dielectric materials and electrode materials such as Ag and Cu should be minimized. The heat-treated dielectric ceramics/electrode mixtures are usually investigated by using XRPD in order to know whether the interfacial reaction between these powders takes place or not.[11,12] Thus, the mix-

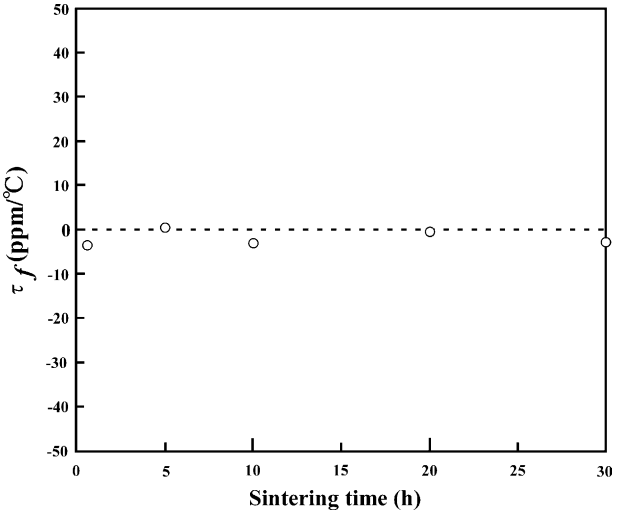

Fig. 8. Variations in temperature coefficient of resonant frequency (τ_f) of MNLF–6 wt.% $CaTiO_3$ ceramics sintered at 950 °C as a function of sintering time.

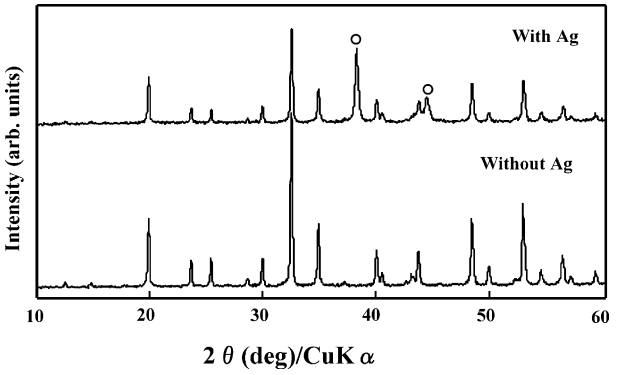

Fig. 9. XRPD patterns of MNLF–6 wt.% $CaTiO_3$ ceramic and mixture of MNLF–6 wt.% $CaTiO_3$ ceramic and Ag heat-treated at 920 °C for 10 h in air.

tures of MNLF–6 wt.% $CaTiO_3$ ceramic with Ag powders were heat-treated at 920 °C for 10 h in air and the chemical compatibility of MNLF–6 wt.% $CaTiO_3$ ceramic with Ag was analyzed by using XRPD as shown in Fig. 9. Since any formation of the secondary phase was not observed in the XRPD pattern, it may be possible to utilize Ag as an electrode material in the case of MNLF–6 wt.% $CaTiO_3$ dielectric ceramics.

4. Conclusions

The effects of $CaTiO_3$ addition on the microwave dielectric properties of MNLF–x wt.% $CaTiO_3$ (x = 2–10) ceramics were investigated in order to clarify the possibility of a development of new LTCC material. It was found that the temperature coefficient of resonant frequency of the samples was increased with increasing the amount of $CaTiO_3$ additions. The dielectric constant and temperature coefficient of resonant frequency of the MNLF–6 wt.% $CaTiO_3$ ceramic sintered at 950 °C were 14.7 and −3.3 ppm/°C, respectively. However, the $Q{\cdot}f$ values were drastically decreased with increasing the amount of $CaTiO_3$ additions; the $Q{\cdot}f$ value of MNLF–6 wt.% $CaTiO_3$ ceramic sintered at 950 °C for 10 h was 22,801 GHz. It was considered that the changes in these microwave dielectric properties are related to the presence of the secondary phases induced by increasing the amount of $CaTiO_3$ additions from 2 to 10 wt.%. Moreover, it was observed that the dielectric constant of samples increases with increasing the sintering time and the $Q{\cdot}f$ value of 22,801 GHz was obtained in the sample sintered at 950 for 10 h. Moreover, it was recognized that the τ_f value of samples remains approximately zero.

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