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Journal of the European Ceramic Society 23 (2003) 2583–2587
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Effect of sintering method on the microwave dielectric properties of $(Pb_{0.45}Ca_{0.55})(Fe_{0.5}Nb_{0.5})O_3$ ceramics

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Abstract

The microwave dielectric properties of $(Pb_{0.45}Ca_{0.55})(Fe_{0.5}Nb_{0.5})O_3$ (PCFN) were investigated for different sintering methods, double crucible and Pt crucible. For both sintering methods, a single phase PCFN with perovskite structure was obtained for the specimens sintered at 1100 °C. There was no difference in the relative density and dielectric constant for the specimens sintered at 1100 °C prepared by both sintering methods. However, the Qf value of the specimens prepared by Pt crucible method was higher than that of the specimens prepared by double crucible. The change of Qf values was studied by infrared reflectivity spectra from 50 to 4000 cm^{-1}, and investigated in terms of Kramers–Kronig method and classical oscillator model.

Keywords: IR reflectivity spectra; Microwave ceramics; Dielectric properties; $(Pb,Ca)(Fe,Nb)O_3$; Pt crucible; Sintering

1. Introduction

Microwave dielectric materials with a high dielectric constant make the greatest reduction in a resonator size and are preferably employed at low frequencies in mobile communication systems.[1] Much attention has been paid to Pb-based ceramics with the complex perovskite structure, because of their superior dielectric properties which are required for microwave devices. In particular, $(Pb_{0.45}Ca_{0.55})(Fe_{0.5}Nb_{0.5})O_3$ has a high dielectric constant of 91, Qf of 4950 GHz, and a small temperature coefficient of resonant frequency (TCF) of 2.2 ppm/°C.[2]

However, volatile PbO has a deleterious effect on dielectric properties in Pb-based ceramics due to the decrease of density and the lattice defects resulting from the deficiency of lead. Up until now, many researches have attempted to prevent the lead loss and improve the dielectric properties. Lu et al.[3] reported the covered alumina crucible method for $Pb(Mg_{1/3}Ta_{2/3})O_3$ (PMT) ceramics, but the formation of a pyrochlore phase, that was associated with the loss of PbO still prevented the sintering of the ceramics to high density. In another attempt, the Pt crucible method[4] was recently reported to effectively inhibit lead loss in Pb-based ceramics, and the double crucible method has been commonly used to reduce the loss of volatiles in ceramics.

The effect of lattice anharmonicity behavior (ascribed to lattice defects) on dielectric properties can be estimated by far-infrared reflectivity. Far-infrared reflectivity of ceramics is sensitive to intrinsic factors and lattice anharmonicity due to extrinsic factor, such as grain boundaries and porosity.[5]

In this study, the effect of sintering method (double crucible and/or Pt crucible) on microwave dielectric properties of $(Pb_{0.45}Ca_{0.55})(Fe_{0.5}Nb_{0.5})O_3$ (PCFN) was investigated using the far-infrared reflectivity.

2. Experimental procedure

The specimens of $(Pb_{0.45}Ca_{0.55})(Fe_{0.5}Nb_{0.5})O_3$ (PCFN) ceramics were prepared by the conventional mixed oxide method with high purity oxides (>99.9%) via the columbite route.[6] The starting materials were mixed according to the desired compositions and ground with ZrO_2 ball for 24 h in distilled water. The mixtures were dried and calcined at 900 °C for 4 h, and then isostatically pressed into pellets under a pressure of 1450 kg/cm^2. The pressed specimens were sintered from 1075 °C to 1150 °C for 3 h in Pt crucible and/or double crucible, respectively (Fig. 1).

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doi:10.1016/S0955-2219(03)00176-6

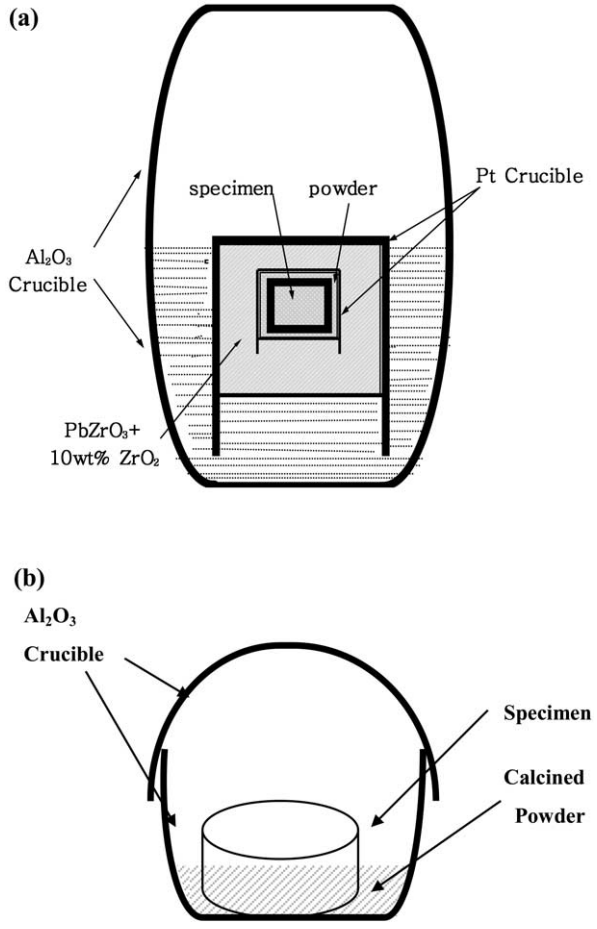

Fig. 1. Schematic diagram of sintering methods: (a) Pt crucible method, and (b) double crucible method.

Powder X-ray diffraction analysis (D/Max-3C, Rigaku, Japan) was used to determine the crystalline phases in the calcined and the sintered specimens. Polished surfaces of the sintered specimens were observed using scanning electron microscopy (Jeol, JSM 820, Japan). The dielectric constant, and unloaded Q value of the specimens were measured by the post resonant method at 5–6 GHz.[7] The temperature coefficient of resonant frequency (TCF) was measured by the cavity method[8] in the temperature range from 25 to 80 °C at 9–11 GHz. The reflectivity spectra were taken at room temperature by FTIR (Bomen DA 8.12, Canada) with frequency resolution of 4 cm^{-1}. The measurement was carried out over the 50–4000 cm^{-1} range.

3. Results and discussion

Fig. 2 shows the X-ray diffraction patterns of $(Pb_{0.45}Ca_{0.55})(Fe_{0.5}Nb_{0.5})O_3$ (PCFN) specimens sintered from 1075 to 1150 °C for 3 h. For both sintering methods, a single phase perovskite structure was obtained.

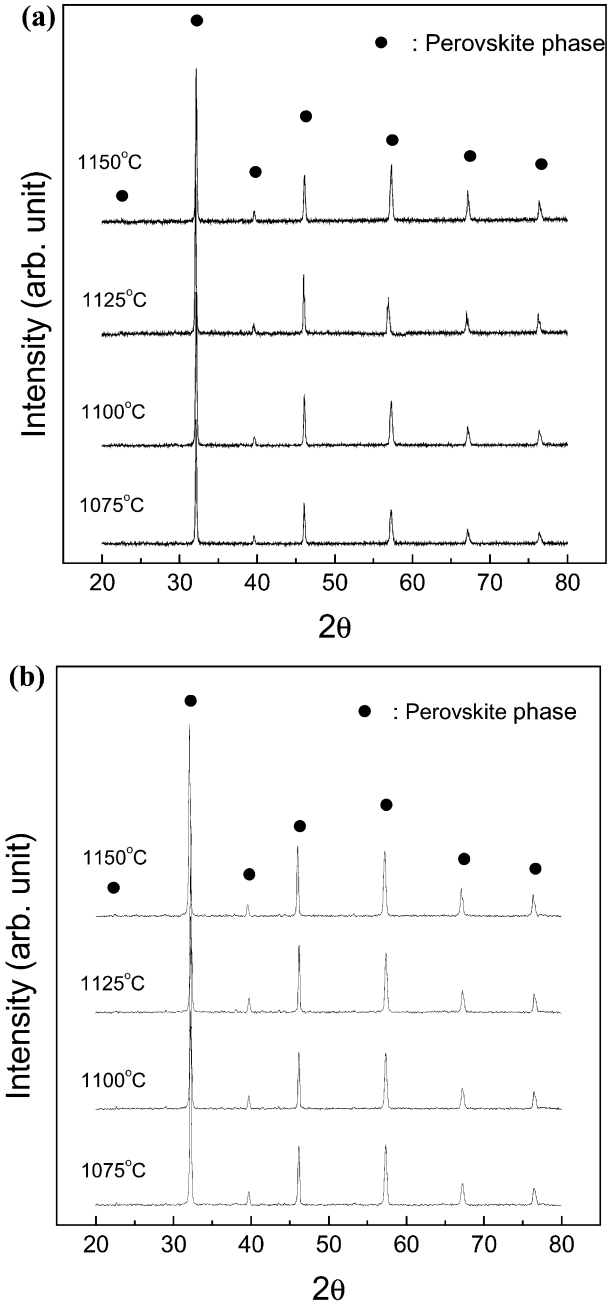

Fig. 2. X-ray diffraction patterns of $(Pb_{0.45}Ca_{0.55})(Fe_{0.5}Nb_{0.5})O_3$ specimens for different sintering methods: (a) Pt crucible method, and (b) double crucible method.

The dielectric constant (K) and the relative density of PCFN specimens are shown in Fig. 3. Dielectric constant of the specimens prepared by Pt crucible method increased remarkably at sintering temperatures up to 1100 °C [Fig. 3(a)], and then showed constant value. However, the dielectric constant of the specimens prepared by double crucible method decreased with an increase of sintering temperature, consistent with the relative density change due to the loss of PbO [Fig. 3(b)]. There was no significant difference in the relative

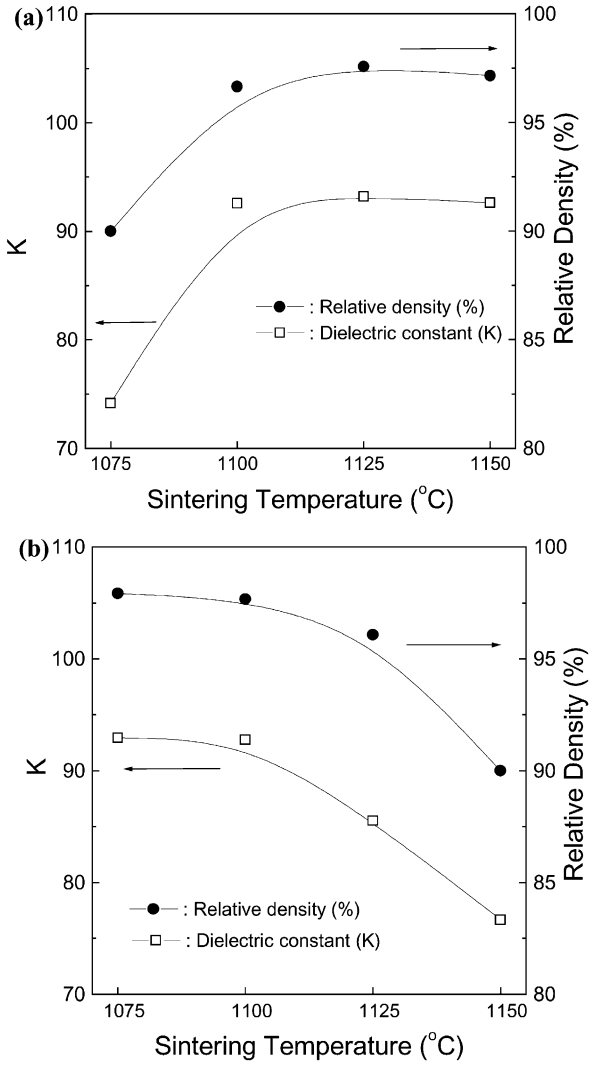

Fig. 3. The dielectric constant (K) and the relative density of $(Pb_{0.45}Ca_{0.55})(Fe_{0.5}Nb_{0.5})O_3$ specimens for different sintering methods: (a) Pt crucible method, and (b) double crucible method.

density and dielectric constant for the specimens prepared by both sintering methods when sintered at 1100 °C.

Fig. 4 shows Qf values of PCFN specimens as a function of sintering temperature. The Qf value of the specimens prepared by Pt crucible method was significantly higher than that by the double crucible method. In general, the Qf values depend on extrinsic factors such as the density, secondary phase, and intrinsic.[9] For the specimens sintered at 1100 °C for 3 h, the effect of secondary phase and density on Qf values of PCFN could be neglected, because there was no secondary phase in either sintering methods and the relative density was higher than 95%,[10] as shown in Figs. 2 and 3, respectively. Therefore, the difference in Qf values achieved by the sintering methods could be explained in terms of differences in intrinsic loss due to the lattice anharmonicity resulting from the loss of PbO during the sintering processes.

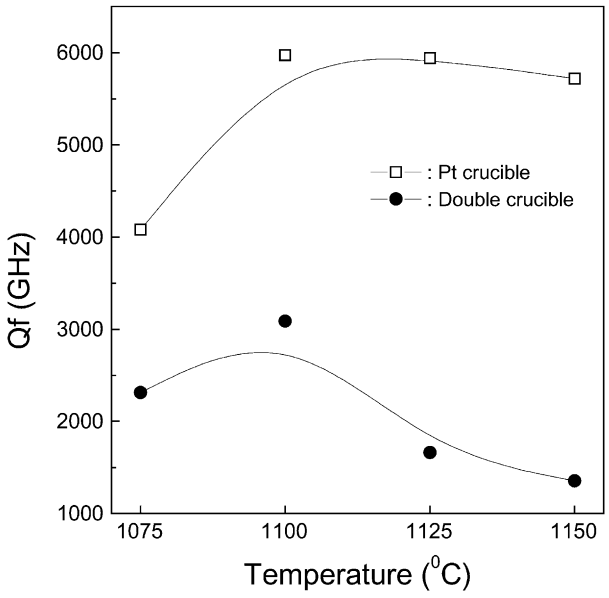

Fig. 4. Qf value of $(Pb_{0.45}Ca_{0.55})(Fe_{0.5}Nb_{0.5})O_3$ specimens for different sintering methods: (a) Pt crucible method, and (b) double crucible method.

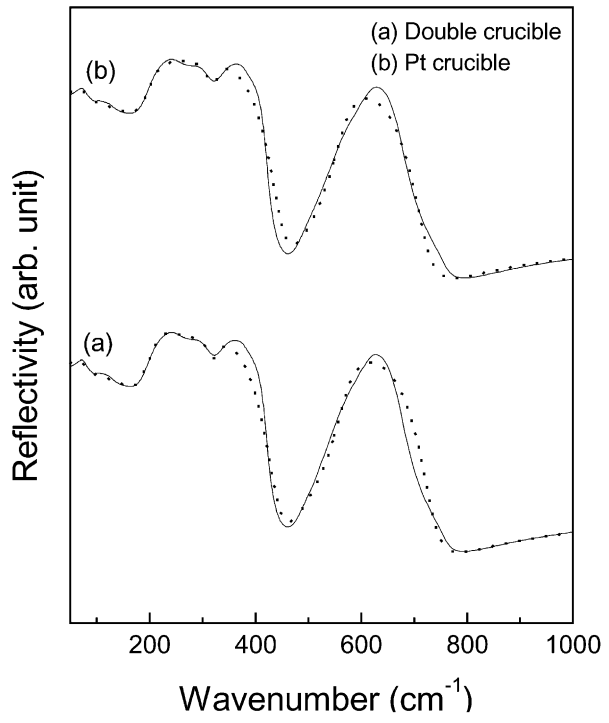

Fig. 5. The far-infrared reflectivity spectra of $(Pb_{0.45}Ca_{0.55})(Fe_{0.5}Nb_{0.5})O_3$ specimens sintered at 1100 °C for 3 h for different sintering methods. (· · ·, measured; ——, calculated).

Fig. 5 shows the infrared reflectivity of the specimens prepared with different sintering methods. The dielectric constant and dielectric loss can be calculated from details of these reflection patterns, particularly peak position, half width of peak and peak height. The real part and imaginary part of complex dielectric function can be obtained from the infrared reflectivity spectra.

Table 1
Dispersion parameters of $(Pb_{0.45}Ca_{0.55})(Fe_{0.5}Nb_{0.5})O_3$ specimens sintered at 1100 °C for 3 h, obtained from the best fit to the reflectivity data

j	Double crucible				Pt crucible			
	ω_j (cm^{-1})	λ_j (cm^{-1})	$\Delta\varepsilon_j$	Tanδ_j ($\times10^{-4}$)	ω_j (cm^{-1})	λ_j (cm^{-1})	$\Delta\varepsilon_j$	Tanδ_j ($\times10^{-4}$)
1	70	40	40	7.1298	70	36.5	44.3	6.1827
2	103.88	40	2	1.0266	93.139	14.424	3.33	0.1013
3	115.84	50	14	2.3136	104.49	14.245	2.7	0.0603
4	152.92	70	10	0.7391	124.01	32.464	8.5	0.2771
5	207.86	42.962	16.8	0.2989	149.89	38.379	4.77	0.1475
6	261.62	93.136	2.26	0.0524	168.29	30.383	1.14	0.0222
7	326.31	30.042	0.32	0.0016	206.52	50	20	0.4021
8	419.18	99.539	0.03	0.0030	272.07	69	1.8	0.0258
9	565	45	1.7	0.0023	326.51	40	0.4	0.0034
10					552.31	48.212	1.25	0.0033
11					577.04	51.297	0.59	0.0492
12					724.61	76.7	0.06	0.0001
			$\varepsilon_\infty = 5.64$				$\varepsilon_\infty = 5.05$	

Fig. 6 shows the imaginary part of the complex dielectric function. The infrared reflectivity spectra for the PCFN can be divided into three wavenumber regions, corresponding to those for the simple cubic structure. The modes appearing below 150 cm^{-1} are thought to be due to the vibration between the A-site cations and BO_6 octahedra. The modes in 150–500 cm^{-1} mainly corresponds to B–O–B bending modes, and the modes above 500 cm^{-1} can be assigned to B–O stretching modes. The difference in the infrared spectra between the specimens prepared by the Pt crucible method and those by double crucible method was found in the lowest frequency range below 150 cm^{-1}, which correspond to the vibration between the A-site cations and BO_6 octahedra.[11] Therefore, the changes of infrared spectra below 150 cm^{-1} could be attributed to the PbO loss during the sintering process.

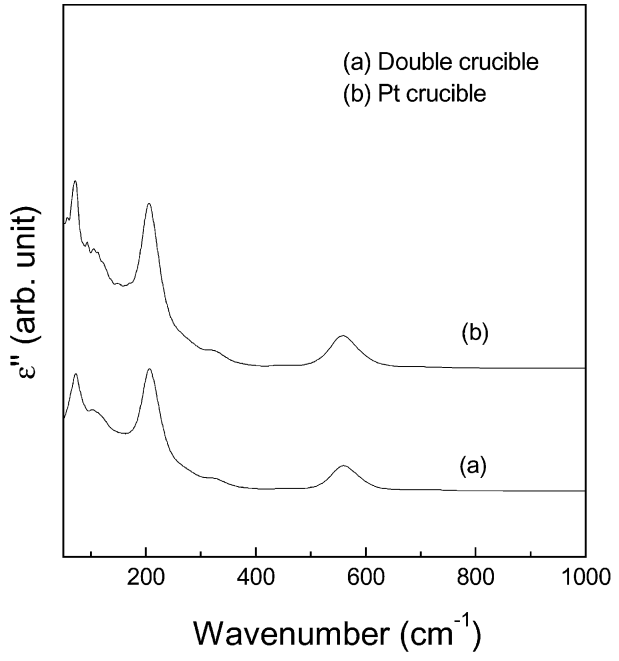

Fig. 6. Imaginary part of the dielectric function of $(Pb_{0.45}Ca_{0.55})(Fe_{0.5}Nb_{0.5})O_3$ specimens sintered at 1100 °C for 3 h for different sintering methods.

Table 1 summarizes the dispersion parameters obtained from the best fit to the reflectivity data, which were determined by Kramer–Kronig analysis and the classical oscillator model; nine phonon modes were available for the best fit of reflectivity data. The contribution to the dielectric loss (tan δ_j) denoted by the first lowest mode at ~70 cm^{-1} and the second lower modes at ~200 cm^{-1} were much higher than the contribution of other modes in PCFN ceramics. Therefore, the Qf value of the specimens prepared by Pt crucible method are higher than for the double crucible method due to the lattice anharmonicity related to the lattice vibration between A-site cations and BO_6 octahedra, and bending angle of B–O–B bond in BO_6 octahedra resulting from the loss of PbO.

The measured and calculated dielectric properties of PCFN specimens obtained from the dispersion parameters are shown in Table 2. The calculated dielectric constant agreed well with the measured values. For all specimens, the calculated Qf values were higher than the measured ones, because the measured Qf values at microwave frequencies included extrinsic loss effects, such as porosity and the grain boundary nature of the specimens.[4]

Table 2
Measured and calculated dielectric properties of $(Pb_{0.45}Ca_{0.55})(Fe_{0.5}Nb_{0.5})O_3$ specimens sintered at 1100 °C for 3 h with different sintering methods

Sintering method	Measured		Calculated	
	K	Qf (GHz)	K	Qf (GHz)
Double crucible	92.6	3088	92.74	4281
Pt crucible	92.77	5972	92.55	6988

4. Conclusion

The effect of sintering method such as double crucible and Pt crucible on microwave dielectric properties of $(Pb_{0.45}Ca_{0.55})(Fe_{0.5}Nb_{0.5})O_3$ (PCFN) was investigated using far-infrared reflectivity. A perovskite single phase was obtained in both sintering methods. For the dielectric constant (K) and relative density, there was no significant difference between the specimens prepared by Pt crucible method and double crucible method when the specimens were sintered at 1100 °C. Due to the difference of the lattice anharmonicity resulting from the loss of PbO, the Qf value of the specimens prepared by Pt crucible was higher than for the specimens prepared by double crucible method.

Acknowledgements

This work was supported by the Korea Science and Engineering Foundation, under Grant (No. R01-2001-000-00262-0).

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