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Effect of PbO on Microwave Dielectric Properties of $(Pb,Ca)(Fe,Nb,Sn)O_3$ Ceramics

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The influence of PbO additive on dielectric properties and sintering behavior of $(Pb_{0.45}Ca_{0.55})$ $\{(Fe_{1/2}Nb_{1/2})_{0.9}Sn_{0.1}\}O_3$ ceramics has been investigated. The incorporation of a limited excess PbO ($\leq$2.0 wt. %) in the starting materials is quite beneficial for densification in the temperature range of 1150~1175°C in air. At a small doping level (0.8 wt. %) the ceramics prepared from powders calcined at 900°C showed the best dielectric properties. The dielectric constants (ε_r) and Q · f were found to be 85.5~86.5 and 8530~8600 GHz, respectively. The temperature coefficient of resonant frequency (τ_f) varied in the range of -2~4 ppm/°C. Examination of the microstructure as well as analysis of the second phases in these materials revealed the presence of the pyrochlore-type phase which is detrimental to the dielectrics.

Key words : Pbo additive, Densification, Dielectric constant (ε_r), Q · f value, Temperature coefficient of vesonant frequency (τ_f), Pyrochlove phase

I. Introduction

Recently it has been found that $(Pb_{1-x}Ca_x)\{(Fe_{1/2}Nb_{1/2})_{1-y}Sn_y\}O_3$ ceramics, where $0.5 \leq x \leq 0.55$, y=0.05, 0.1, show good microwave characteristics, having relatively high dielectric constants (ε_r=86~90), low dielectric loss (Q · f$\geq$8000 GHz) and a temperature stable resonant frequency ($\tau_f \leq |10|$ ppm/°C).[1] These ceramics can be produced at low sintering temperature of 1150°C for 3 h in air. The τ_f nearly 0 ppm/°C was realized at x=0.55. This materials can be used as a resonator component in microwave devices.[2,3] During calcination and sintering steps of PbO-containing ceramics, care must be taken to avoid the PbO loss that is detrimental to electrical properties.[4] However, it makes the technological process *more complex and expensive.*

It is also difficult to fully density SnO_2-doped materials without additives if the powder is prepared by a solid state reaction.[5] It has been shown for other microwave dielectrics that the dielectric constant is affected by density. A higher relative sintered density results in a higher dielectric constant. The temperature coefficient of *resonant frequency (τ_f) is dependent on composition and* the presence of other phases. The quality factor (Q) is mostly affected by additives.[6]

The purpose of present work was to investigate the influence of excess PbO in the starting $(Pb_{0.45}Ca_{0.55})\{(Fe_{1/2}Nb_{1/2})_{0.9}Sn_{0.1}\}O_3$ composition on dielectric properties of ceramics sintered at different temperatures in order to optimize the sintering process.

II. Experimental Procedure

The powders were prepared by a conventional solid-state reaction technique as described previously.[1] Reagent-grade PbO (High Purity Chemical Ltd., 99.9%) $CaCO_3$, Nb_2O_5, SnO_2 (all Aldrich, 99.9%) and Fe_2O_3 (Shinyo Pure Chemical Co. Ltd., 99.9%) were used as starting raw materials. Experimental results showed that the powder of the composition $(Pb_{0.45}Ca_{0.55})\{(Fe_{1/2}Nb_{1/2})_{0.9}Sn_{0.1}\}O_3$ lost 0.8 and 1.1 wt. % of PbO during calcination at 900 and 1000°C for 4 h, respectively. Two kinds of ceramics with the above composition doped with 0.8 and 2.0 wt. % of PbO were prepared. The appropriate materials were mixed and ground in distilled water for 24 h in a ball mill with zirconia balls. The mixtures were dried and calcined at 900 and 1000°C for 4 h, then milled again for 12 h. Disks 10 mm in diameter and 5~6 mm thick were pressed by isostatic pressing at 200 Mpa. The green pellets were sintered at different temperatures (1150~1185°C for 3 h) in air. The bulk densities of samples were measured using the Archimedes method. The PbO deficiency of every pellet was determined from the cumulated weight *losses during calcination and sintering steps.* Sintered pellets were examined by X-ray diffraction (Philips PW 1820) analysis with CuKα radiation. The relative amounts of perovskite and pyrochlore phases were calculated from the ratio of $I_{per}(110)/I_{pyr}(222)+I_{per}(110)$, where $I_{per}(110)$ and $I_{pyr}(222)$ were the diffraction peak intensities of the perovskite phase (110) and pyrochlore phase (222), *respectively. The polished surfaces of ceramics were also*

investigated with a scanning electron microscope (JXA-8600, Jeol), equipped with electron probe microanalyzer (EPMA).

Dielectric properties at microwave frequencies (5.5~6.0 GHz) were measured by the dielectric rod resonator method using a network analyzer (HP8720C).[7] The temperature coefficient of resonant frequency τ_f at microwave frequencies was measured in the temperature range of -20 to 80°C.

III. Results and Discussion

The properties of ceramics investigated in this work are summarized in Table 1. The prepared ceramic samples show a change in color from brown to dark brown with an increase in PbO additive content and sintering temperature. The PbO additive improves the compaction. The green density increases with increase in PbO excess as shown in Fig. 1. The cumulated PbO weight loss at different sintering temperature is presented in Fig. 2. The weight loss steadily increased with increasing temperature from 1150°C to 1185°C. Surprisingly, the PbO loss for sinterd samples doped with 2.0 wt. % of PbO and calcined at 1000°C was found to be lower than that for 900°C. On the other hand, the weight loss of samples containing 2.0 wt. % of PbO and calcined at 1000°C were about 1.8~2.0 % higher than that of undoped samples

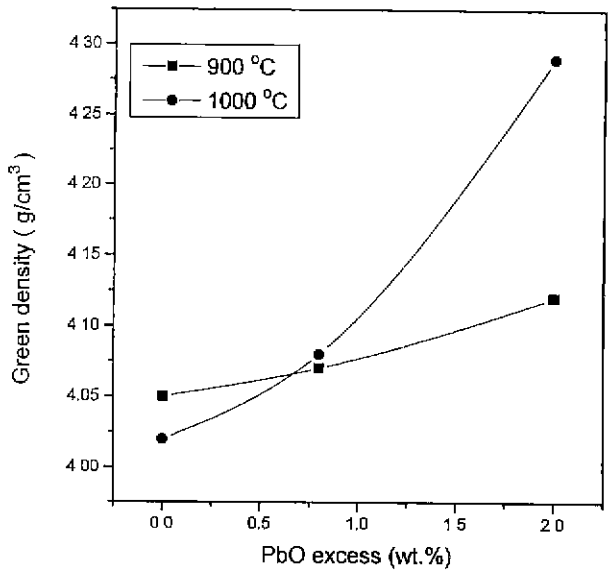

Fig. 1. Green density as a function of PbO doping amount for the calcination temperatures.

calcined at 900°C and sintered in the range of 1150~1185°C. The relative sintered density of ceramics steadily increased with increasing sintering temperature. In general, it was easier to densify samples calcined at 900°C than those at 1000°C. The behavior of ε_r with the density variation was evaluated at different sintering

Table 1. Dielectric Properties and Sintering Conditions for Undoped and PbO-doped $(Pb_{0.45}Ca_{0.55})\{(Fe_{1/2}Nb_{1/2})_{0.9}Sn_{0.1}\}O_3$ Ceramics

No	P, wt.%	T_1, °C	d_g, g/cm^3	T_2, °C	D, g/cm^3	ε_r	Q · f, GHz
1	0	900	4.05	1150	6.09	82.8	8490
2				1165	6.21	84.7	8470
3				1175	6.27	85.6	8370
4				1185	6.28	86.0	7840
5	0.8	900	4.07	1150	6.22	85.5	8530
6				1165	6.28	86.3	8600
7				1175	6.28	86.5	8530
8				1185	6.31	86.6	8185
9	2.0	900	4.12	1150	6.28	85.4	8620
10				1165	6.28	85.7	8550
11				1175	6.29	86.0	8505
12				1185	6.29	85.8	8350
13	0	1000	4.02	1150	5.81	77.0	8350
14				1165	6.10	82.8	8660
15				1175	6.22	84.5	8420
16				1185	6.26	85.4	8170
17	0.8	1000	4.08	1150	5.88	77.9	8450
18				1165	6.14	83.4	8640
19				1175	6 20	84.6	8520
20				1185	6.22	85.4	8270
21	2.0	1000	4.29	1150	5.94	79.1	8620
22				1165	6.16	84.1	8700
23				1175	6.21	85.1	8580
24				1185	6.25	85.1	8500

P : PbO excess, T_1 : calcination temperature, d_g : green density, T_2 : sintering temperature.

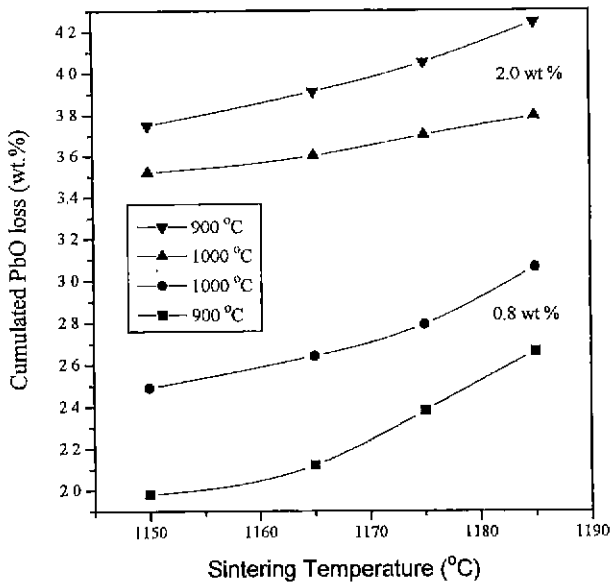

Fig. 2. PbO deficiency as a function of sintering temperature for the ceramics calcined at 900 and 1000°C.

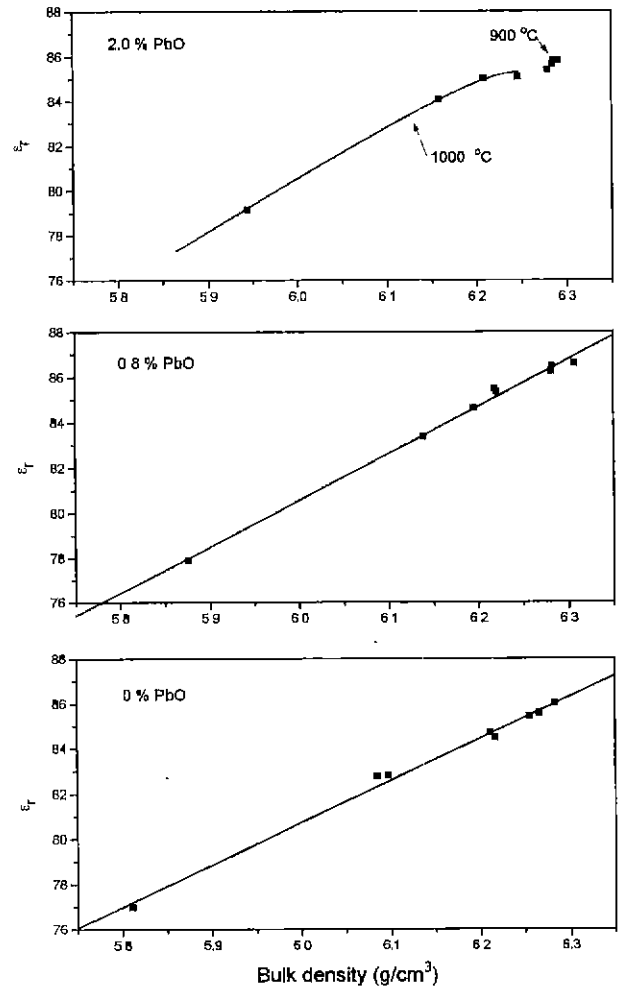

Fig. 3. Dielectric constant of $(Pb_{0.45}Ca_{0.55})\{(Fe_{1/2}Nb_{1/2})_{0.9}Sn_{0.1}\}O_3$ ceramics as a function of bulk density at the different doping amount.

temperatures.

The undoped and doped with 0.8 wt. % PbO ceramics showed nearly linear behavior independent of calcination temperature (Fig. 3). At the same time, the deviation from linearity was found for ceramics doped with 2.0 wt. % of PbO.

Fig. 4 shows ε_r and $Q \cdot f$ as a function of sintering temperature for samples calcinad at 900°C for 4 h. It is seen that ε_r for all samples increases with sintering temperature despite of the increased PbO loss. This means that the PbO evaporation mostly takes place from surface area. PbO additive remarkably improves the dielectric constants of ceramics prepared at 1150°C. Highest ε_r value was obtained in the case of 0.8 wt. % of Pbo excess. This composition is close to the stoichiometric one after calcination at 900°C. Further increase in PbO

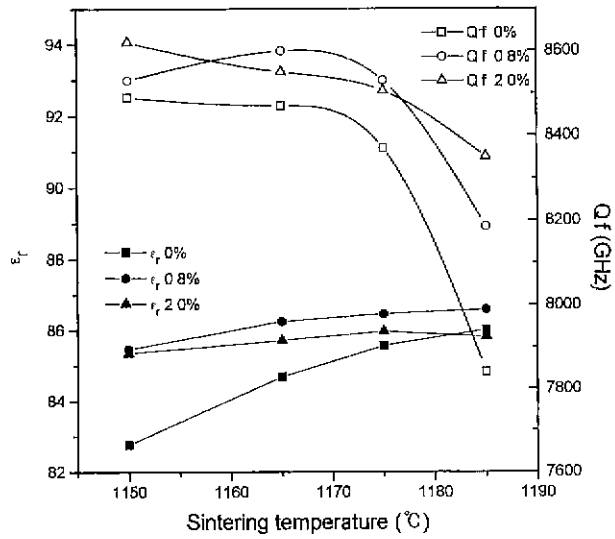

Fig. 4. Dielectric properties of $(Pb_{0.45}Ca_{0.55})\{(Fe_{1/2}Nb_{1/2})_{0.9}Sn_{0.1}\}O_3$ ceramics prepared from the powders calcined at 900°C.

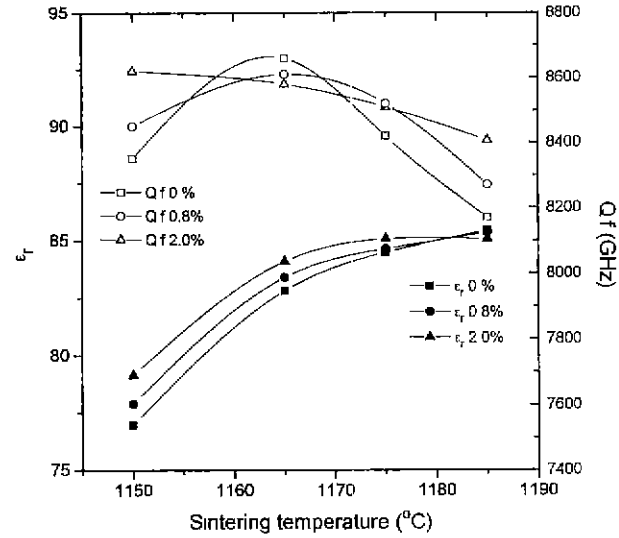

Fig. 5. Dielectric properties of $(Pb_{0.45}Ca_{0.55})\{(Fe_{1/2}Nb_{1/2})_{0.9}Sn_{0.1}\}O_3$ ceramics prepared from the powders calcined at 1000°C.

content produces lower dielectric constants in the whole temperature range. Significant differences are not observed in the products Q · f in the range of 1150~1175°C. The values vary from 8370 to 8600 GHz. The highest Q · f value was obtained for 0.8 wt. % of PbO doped sample was found to be above 1175°C.

Fig. 5 shows ε_r and Q · f as a function of sintering temperature for samples calcinad at 1000°C. It is worth noting that the dielectric constants show a similar saturated behavior with the increase in sintering temperature but their values are lower as compared with samples calcined at 900°C. The best result was shown by highly doped samples. The variation of Q · f values with sintering temperature were also found to be low. The product Q · f slightly increases in the range of 1150~1165°C forming maximum then slowly decreases. The temperature coefficient of resonant frequency for all ceramics varied in the range of -2~4 ppm/°C.

To understand the difference in the loss quality of ceramics sintered at 1185°C the SEM investigation was undertaken as shown in Fig. 6. The EPMA analysis of polished section of ceramics prepared revealed a presence of a pyrochlore phase and other unknown phase enriched in Ca and Fe in the perovskite matrix. It appears that for the same sintering temperature, the stability of the perovskite phase is better at PbO contents. On the other hand, the amount of unknown second phase having the chemical composition of $Ca_{1.83\pm0.03}Pb_{1.2=0.01}Fe_{1.53=0.04}Nb_{0.43\pm0.03}Sn_{0.97-1.03}O_{7.5-5}$ increase with increasing in PbO excess especially at 1185°C. This composition of the pyrochlore phase was found to be $(Pb_{1.26\pm0.01}Ca_{0.70\pm0.02})Nb_{1.44=0.03}Fe_{0.11=0.01}Sn_{0.44\pm0.02})O_{7-\delta}$. The results of EPMA analysis of the perovskite phase in ceramics obtained at 1185°C are given in Table 2. The comparison of the result shows that the Pb/Nb and Sn/Nb ratios increase with increase in PbO excess. The perovskite phase composition for ceramics doped with 2.0 wt. % of PbO is very close to stochiometric $(Pb_{0.45}Ca_{0.55})\{(Fe_{1/2}Nb_{1/2})_{0.9}Sn_{0.1}\}O_3$. At the same time for ceramics prepared from the powder calcinated at 1000°C a small increase in Pb/Ca ratio was detected with increase in PbO doping amount.

For comparison, the X-ray diffraction patterns for ceramics sintered at 1185°C are shown in Fig. 7. The results also show that the amount of pyrochlore phase increases with calcination temperature and decrease with PbO excess in the starting composition. For example, the pyrochlore content for undoped composition was found to be 3.5 and 5% at 900 and 1000°C, respectively. No pyrochlore phase was detected by X-ray diffraction in the sample doped with 2.0 wt. % of PbO. This suggests

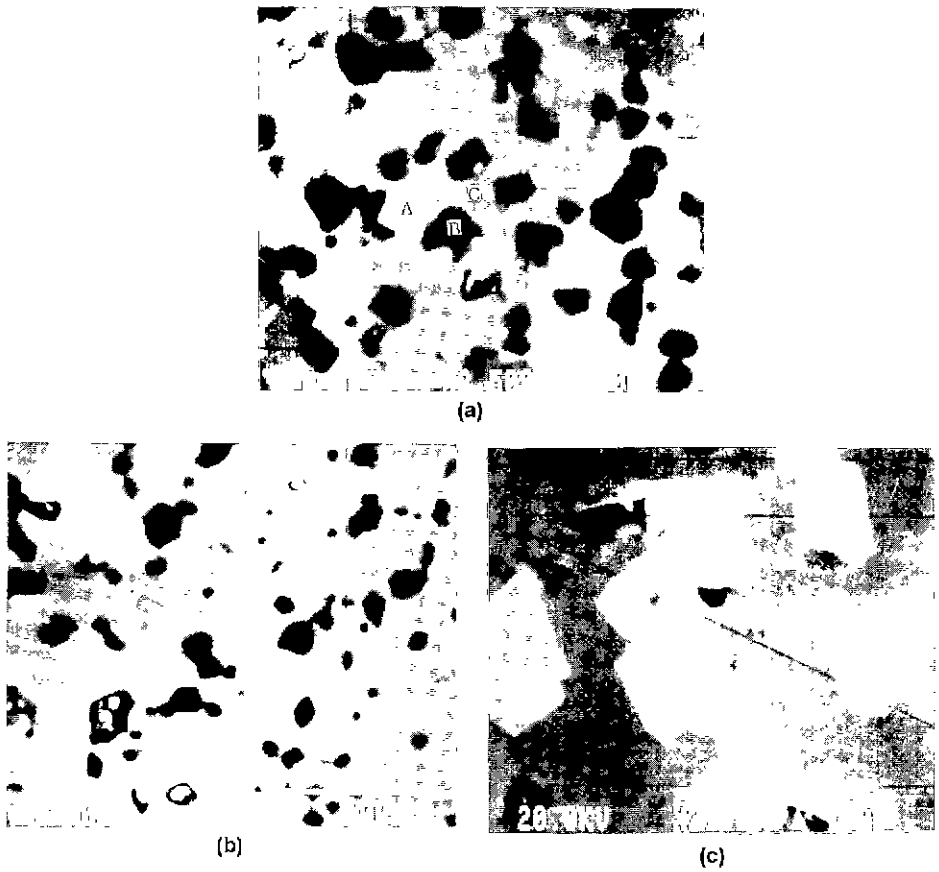

Fig. 6. EPMA photographs of PbO-doped $(Pb_{0.45}Ca_{0.55})\{(Fe_{1/2}Nb_{1/2})_{0.9}Sn_{0.1}\}O_3$ ceramics (A: unknown phase, B: pyrochlore phase, C: perovskite phase). a) 0%, b) 0.8%, c) 2.0 %

Table 2. EPMA Analysis of the Perovskite Phase for Ceramics Sintered at 1185°C

No	Calcination temperature, °C	PbO excess, wt.%	Element content, mol.%				
			Pb	Ca	Fe	Nb	Sn
1	900	0	22.1	27.2	22.1	24.0	4.6
2		0.8	22.9	26.6	21.5	23.7	5.3
3		2.0	23.3	27.1	21.3	23.1	5.2
4	1000	0	21.6	27.7	22.1	24.5	4.1
5		0.8	23.3	26.9	20.8	24.0	5.0
6		2.0	24.0	26.1	21.4	23.0	5.5
7*			22.5	27.5	22.5	22.5	5.0

*Calculated for $(Pb_{0.45}Ca_{0.55})\{(Fe_{1/2}Nb_{1/2})_{0.9}Sn_{0.1}\}O_3$.

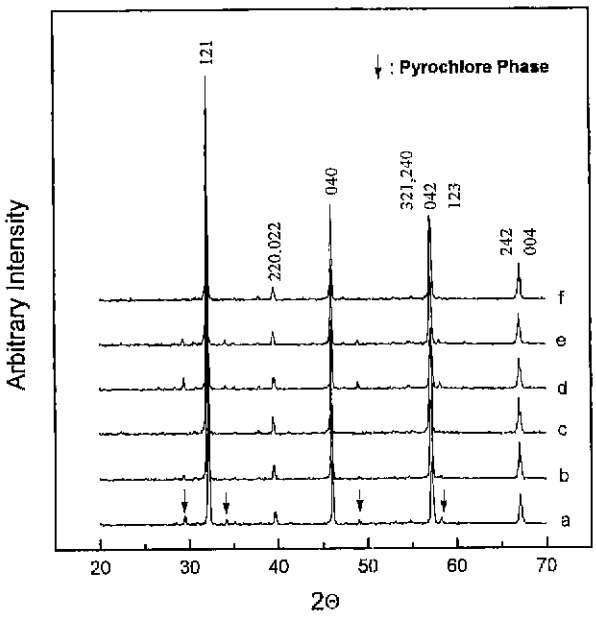

Fig. 7. X-ray patterns of the polished sections of PbO-doped $(Pb_{0.45}Ca_{0.55})\{(Fe_{1/2}Nb_{1/2})_{0.9}\ Sn_{0.1}\}O_3$ ceramics calcined at 900°C [a) 0%, b) 0.8%, c) 2.0%] and 1000°C [d) 0%, e) 0.8%, f) 2.0%] and sintered at 1185°C.

that PbO volatilization promotes the formation of pyrochlore phase. In fact, it seems reasonable to propose that the appearance of the pyrochlore phase can increase the dielectric losses in our case. This observation is in agreement with those reported by Kato et al. for other (Pb,Ca)(Me,Nb)O_3 materials.[8]

IV. Conclusions

The effect of PbO additive on sintering behavior and dielectric properties of $(Pb_{0.45}Ca_{0.55})\{(Fe_{1/2}Nb_{1/2})_{0.9}Sn_{0.1}\})O_3$ was investigated. Doping with PbO (<2.0 wt. %) improves the compaction and the green density increase with PbO concentration especially in the case of powders calcined for 4 h at 900°C. The additive is good for densification purpose in air. The optimum sintering temperature was found to be 1165°C independent of powder calcination temperature. At small doping level (0.8 wt. %) the ceramics prepared from powders calcined at 900°C showed the best dielectric properties in the sintering range of 1150~1175°C. The dielectric constants and products Q · f were found to be 85.5~86.5 and 8530~8600 GHz respectively. The dielectric constants of undoped and doped with 0.8 wt. % of PbO ceramics shows a linear relation with density independent of preparation condition. PbO excess (<2.0 wt. %) does not affect the Q · f value significantly in the range of 1150~1175°C. PbO loss becomes detrimental to dielectric properties above 1175°C due to increase in pyrochlore phase content.

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