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Phase formation, sintering behavior and microwave dielectric properties of bismuth and manganese co-doped [(Pb, Ca) La] (Fe, Nb)$O_{3+\delta}$ solid solution

**Ming-Zhe Hu · Jun Qian · Hao-Shuang Gu ·
Yong-De Hao**

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Abstract The phase formation, sintering behavior and microwave dielectric properties of Bi_2O_3 and MnO_2 co-doped [(Pb, Ca) La](Fe, Nb)$O_{3+\delta}$ (PCLFN) ceramics were investigated. The Bi_2O_3 and MnO_2 binary dopants formed stable and low melting temperature solubilities at grain boundary which resulted in an effectively lowered sintering temperature by about 140 °C a more rapid sintering process and enhanced bulk densities. Sintering procedure has significant effect on grain size and porosities in ceramics. With high sintering temperature and time, the evaporation of PbO scaled up from surface toward the bulk and resulted in a Pb^{2+} deficient layer up to 0.25 mm depth under ceramic surface. Investigation of sintering dynamic revealed that either volume diffusion or second-order interface mechanism controlled the grain growth in present system. An optimal microwave dielectric properties of $\epsilon_r = 91.1$, $Q_f = 4{,}870$ GHz and $\tau_f = 18.5$ ppm/°C could be obtained in Bi_2O_3 and MnO_2 co-doped [(Pb, Ca) La](Fe, Nb)$O_{3+\delta}$ ceramics sintered at 1,050 °C for 4 h when the quality ratio of Bi_2O_3/MnO_2 was 1 and the doping content $w = 1$ wt%.

Introduction

Recently multilayer microwave devices have encountered a great development to reduce the size of microwave filters and antenna duplexers in mobile communication system [1]. In multilayer devices, low-temperature sintering ceramics are co-fired with inner low-melting-point conductor such as silver or copper [2, 3]. Lead-based perovskite ceramics have been found to be one of the most effective low temperature co-fired ceramics (LTCCs) due to their high dielectric constant ϵ_r, low dielectric loss (or high quality factor Q_f) and stable temperature properties ($\tau_f \approx 0$). For example, $[(Pb_{0.5}Ca_{0.5})_{1-x}La_x](Fe_{0.5}Nb_{0.5})O_{3+\delta}$ (PCLFN) ceramics possess excellent microwave properties with ϵ_r higher than 100, $Q_f > 5{,}500$ GHz and approaching zero τ_f values [4]. However, its sintering temperature was relatively higher than 1,150 °C which was not suitable for co-firing with Ag (melting-point 961 °C) or Cu (1,064 °C) directly.

In order to lower PCLFN's sintering temperature, additives of Bi_2O_3 and MnO_2 had been doped in our previous work and successfully lowered its sintering temperature to 1,050 °C without significantly degrading the microwave characteristics [M. Z. Hu et al. submitted]. However, it is well known that besides composition, sintering procedure is also the same important factor for deciding the microstructures and sequentially microwave properties of ceramics. So aiming at revealing the optimal processing of Bi_2O_3 and MnO_2 co-doped PCLFN ceramics, in present paper, the influence of sintering parameters on the microstructures and microwave properties of above ceramics was elaborately investigated. Additionally, the sintering

M.-Z. Hu (✉) · J. Qian
Shool of Physics and Electronics, Hubei University,
Xueyuan Road, Wuhan 430062, Hubei, P. R. China
e-mail: mingzhe-hu@163.com

H.-S. Gu
Key Lab of Material Physics and Chemistry,
Hubei University, Xueyuan Road, Wuhan 430062,
Hubei, P. R. China

Y.-D. Hao
Department of Electronics, Hua Zhong University of
Science and Technology, Luoyu Road, Wuhan 430074,
Hubei, P. R. China

characteristics and the relationships between microstructures and microwave properties of Bi_2O_3 and MnO_2 co-doped PCLFN ceramics were also discussed.

Experimental procedure

Commercial purity powders including PbO (>99.5%), $CaCO_3$ (>99.5%), La_2O_3 (>99.5%), Fe_2O_3 (>99.8%), Nb_2O_5 (99.9%) and Bi_2O_3 (>99.0%)/MnO_2 (optical purity) were batched and synthesized by conventional solid-state reaction method to fabricate stoichiometry $[(Pb_{0.5}Ca_{0.5})_{0.92}La_{0.08}](Fe_{0.5}Nb_{0.5})O_{3+\delta}$ + M (M represents Bi_2O_3/MnO_2, wt%) ceramics. After mixing the batched powders with distilled water, the slurry was planetary ball milled in an agate pot for 4 h. The prepared slurry was dried and calcined at 950 °C for 2 h in a closed Al_2O_3 crucible which was followed by another 3 h planetary ball milling. After drying and adding with 5 wt% PVA binder, the powder was pelleted under a uniaxial pressure of 200 MPa into 16 mm diameter and 8–10 mm height cylinder. Then these pellets were sintered at 1,050–1,190 °C for 2.5–4.0 h after debinding in a closed Al_2O_3 crucible with a protecting PbO atmosphere produced by the same calcined powder and $PbZrO_3$ + ZrO_2 (10 wt%) mixing powder.

The bulk densities of ceramics were measured by Achimede method. The phase composition of sintered ceramics was checked by X-ray (RIGAKU,D/Max-3B) diffraction using Cu-Kα radiation and the PbO weight percentage content of the polished ceramic surface was examined by XRF (Shimadzu XRF1800). The SEM and EDS analysis was carried on JEOL, JSM-35C and JMS-5610LV system respectively for observing microstructures and phase formation of the present system. The microwave dielectric properties (ϵ_r and Q) were obtained by means of Hakki-Coleman's rod dielectric resonator method [5] on ADVANTEST R3767C network analyzer in the frequency range of 2.0–4.5 GHz. The temperature coefficient of resonant frequency was obtained by measuring TE_{011} modes resonant frequency at 20–70 °C.

Results and discussion

Figure 1 illustrates the influence of 1 wt% Bi_2O_3, MnO_2 and their combined doping on volume shrinkage of PCLFN ceramics at various temperatures. It was seen that the initial volume shrinkage of doping samples moved toward much lower temperature than the undoped ones. The shrinkage of doped samples appeared to occur rapidly at 1,050 °C indicating a predominant liquid phase sintering mechanism. In contrast, however, the shrinkage for undoped ones did not occur as rapid until 1,150 °C. After 1,150 °C, the shrinkage of doped ones became saturated suggesting the completeness of reactions and in particular, the samples with k = 1value (k was the quality ratio of two dopants, $k = m_{Bi2O3}/m_{MnO2}$) possess the highest initial volume shrinkage of 18.15% at 1,050 °C for 2.5 h.

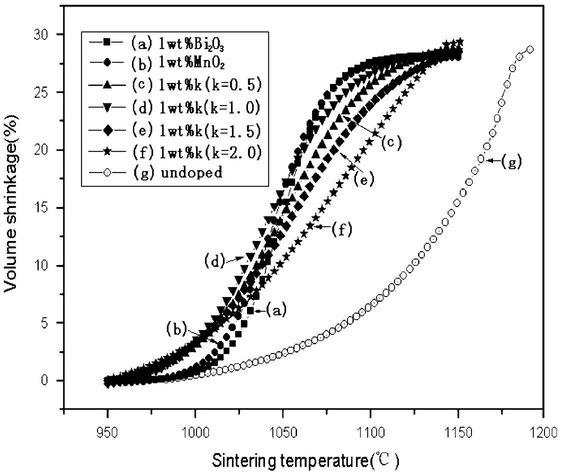

Fig. 1 Variation of the shrinkage with sintering temperature for w = 1 wt% in Bi_2O_3 and MnO_2 doping PCLFN ceramics sintered for 2.5 h

The bulk densities of co-doped PCLFN ceramics (k = 1) related with sintering temperatures at different co-doping content w was shown in Fig. 2. The co-doped samples obtained higher bulk density as well as faster increase at low temperatures and saturated after 1,130 °C, while the bulk density of undoped

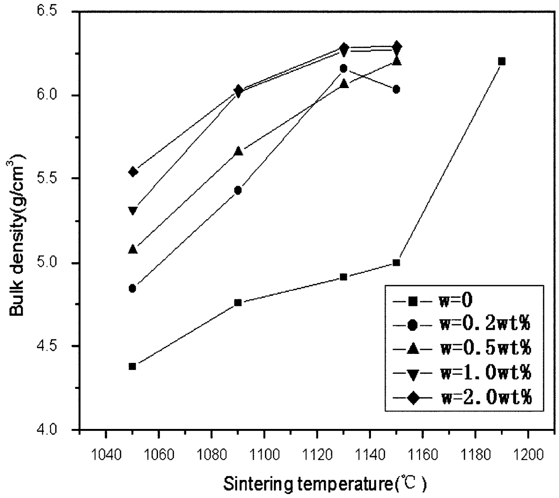

Fig. 2 Variation of the bulk density with sintering temperature for k = 1 in Bi_2O_3 and MnO_2 co-doped PCLFN ceramics sintered for 2.5 h

samples only got its rapid increase in the temperature range of 1,150–1,190 °C. All the bulk densities gradually increased with the increasing of temperature as well as co-doping content. The highest value of 6.296 g/cm^3 was obtained when co-doping content $w = 2$ wt% and sintered at 1,150 °C for 2.5 h.

All the above results indicated that Bi_2O_3 and MnO_2 were effective sintering aids for lowering sintering temperatures of PCLFN ceramics. In order to understand its detailed sintering process and mechanism, EDS analysis was conducted on the $k = 1$ and $w = 1.0$ wt% co-doped PCLFN sample sintered at 1,050 °C for 4 h. As shown in Fig. 3, the specimen exhibited dense and homogeneous microstructure without any trace of second recrystallization. The chemical composition of EDS spectra taken from four points A, B, C and D were listed in Table 1. It revealed that part of Mn^{4+} entered the main phase lattice while Bi^{3+} segregated with its mole ratio to Mn^{4+} equal to about 2:1 at the grain boundary which suggested that a predominant liquid phase sintering dominated the sintering process in the present system. At lower firing temperature MnO_2 and Bi_2O_3 formed a melting chemical compound at grain boundary which could wet the solid particles and bring about the capillary pressure between them. This would accelerate the rearrangement of the solid particles and speed up the dissolving and material transporting process, resulting in a faster sintering process and lowered sintering temperature. During cooling the flux former recystallized and segregated at grain boundary. Meanwhile, part of Mn^{4+} entered into the crystal lattice of matrix phase causing crystal lattice distortion which would also give rise to an activated sintering [6]. The above joint efforts would make the co-doping system being sintered at lower temperature. The elemental analysis of the small grain (point B) as illustrated in Table 1 showed it can be approximately described as $(Pb_{1.65}Ca_{1.16}La_{0.19})(Fe_{0.8}Nb_{3.2})O_{13}$, which satisfied $(M_{Pb} + M_{Ca} + M_{La}):(M_{Fe} + M_{Nb}) = 1.5:2$ or $Pb_3Nb_4O_{13}$ pyrochlore phase that agreed quite well with XRD patterns (Fig. 5).

As for the matrix grain (point A), one could estimate it from Table 1 as $(Pb_{0.38}Ca_{0.54}La_{0.08})(Fe_{0.53}Nb_{0.45}Mn_{0.02})O_3$ which was stoichiometry and balanced both in crystal charge and structure, developing a stable ABO_3 perovskite matrix in the present system.

Figure 4 illustrates the variation of XRF PbO weight percentage content with the distance from

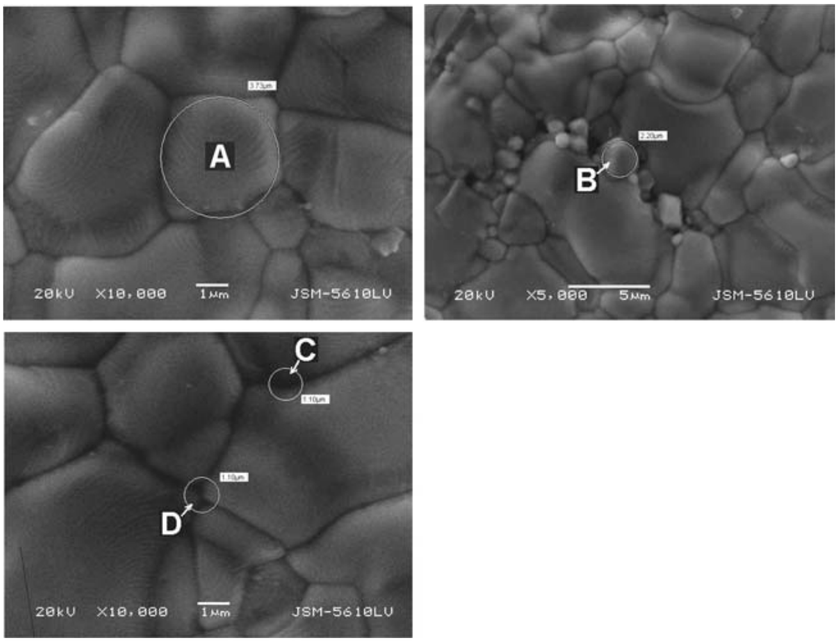

Fig. 3 EDS spectrum of $k = 1$ and $w = 1.0$ wt% co-doped PCLFN ceramic sintered at 1,050 °C for 4 h

Table 1 EDS chemical composition of Bi_2O_3 and MnO_2 co-doped PCLFN ceramic when $k = 1$, $w = 1$ wt% and sintered at 1,050°C for 4 h

Position	Composition (mol%)						
	Pb	Ca	La	Fe	Nb	Mn	Bi
Point A	19	27	4	26.5	22.5	1	–
Point B	23.6	16.6	2.7	11.4	45.7	–	–
Point C	20	26	4	26.5	22.5	1	2
Point D	22	25	3	26	23	1	2

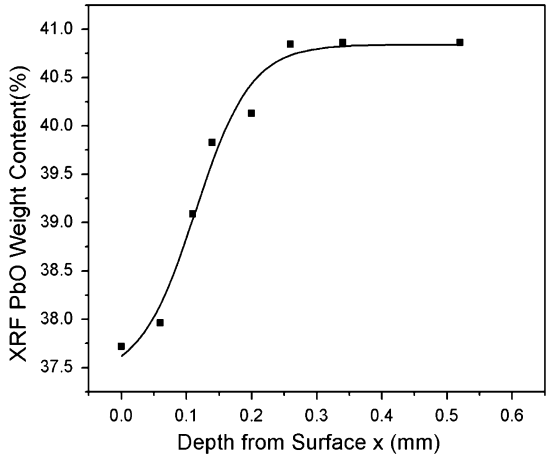

Fig. 4 Variation of XRF PbO weight percentage content with the depth from surface x (mm) in $k = 1$, $w = 1$ wt% sample sintered at 1,150 °C for 4.0 h

surface x (mm) in $k = 1$, $w = 1$ wt% sample sintered at 1,150 °C for 4 h. It can be seen that an almost linear concentration gradient of PbO was formed between the surface and the bulk in the range of $x \le 0.25$ mm, which means the evaporation of PbO initially occurred at the surface and then Pb^{2+} and O^{2-} in the bulk gradually diffused toward surface and evaporated to atmosphere in the sintering process. However, the PbO content became stable at the diffusion depth above $x = 0.25$ mm, which means no Pb^{2+} deficient layer exist. And as well known the PbO deficiency will contribute to the decomposition of perovskite phase into parasitic pyrochlore phase and an inhomogeneous chemical composition. XRD detection of the same sample has also proved that as the evaporization of PbO the relative content of pyrochlore phase (calculated using Eq. (1)) increased from 10.5% in the bulk to 16.0% at the surface, which could be ascribed to the decomposition of PCLFN perovskite phase.

Figure 5 describes one of the XRD patterns of the sample with $k = 1$, $w = 1$ wt% and sintered at 1,090 °C for 2.5 h. It can be seen that besides main phase PCLFN, small amount of $Pb_3Nb_4O_{13}$ pyrochlore phase (JCPDS File no.25-0443) also existed in ceramics which was quite consistent with the EDS spectrum. The volume fraction of pyrochlore phase is calculated from XRD patterns of some samples using the relative intensities of the (222) pyrochlore peak $I_{\mathrm{pyro}}(222)$ and the (110) perovskite peak $I_{\mathrm{pero}}(110)$ in:

$$\varphi\% = \frac{I_{\mathrm{pyro}}(222)}{I_{\mathrm{pero}}(110) + I_{\mathrm{pyro}}(222)} \times 100\% \qquad (1)$$

The result is shown in Table 2.

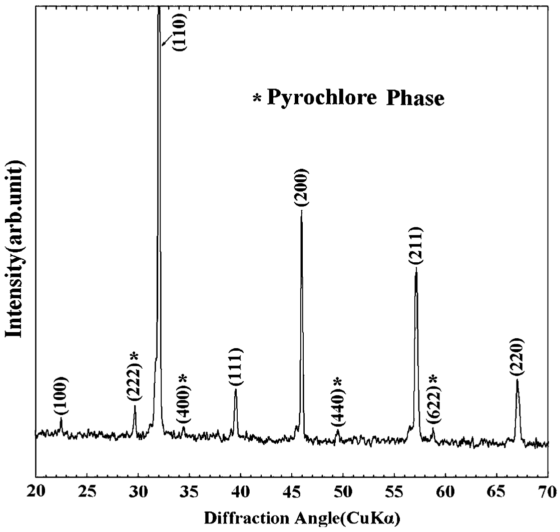

Fig. 5 XRD pattern for $k = 1$, $w = 1$ wt% sample in Bi_2O_3 and MnO_2 co-doping PCLFN ceramics with sintering temperature of 1,090 °C, 2.5 h

Table 2 Relative volume fraction of the pyrochlore phase in MnO_2 and Bi_2O_3 co-doped PCLFN system

Sintering condition	Relative volume fraction of pyrochlore phase φ (%)
1,050 °C /2.5 h	12.60
1,050 °C /4.0 h	12.28
1,090 °C /2.5 h	9.47
1,130 °C /2.5 h	10.60

It can be deduced that pyrochlore phase decreased with the increasing sintering temperature or time which indicated evidently that raising the sintering temperature and time enhances the reaction rate and allows the formation of perovskite phase. What's more, since the relative content of Pb^{2+} in pyrochlore phase was higher than that in perovskite phase (see Table 1), so the dissolution of pyrochlore phase into perovskite phase would increase the relative content of Pb^{2+} in A site of ABO_3 perovskite structure and resulted in the enlarged crystal cell volume which was identified by the systematic shift of the main phase peaks to lower diffraction angle as the increasing of sintering temperature or time.

Figure 6 shows the dielectric properties of co-doped samples ($k = 1$, $w = 1$ wt%) varied with sintering temperature when calcined at 950 °C for 2 h. When sintered at 1,050 °C, microwave properties were poor of $\epsilon_r = 60.5$ and $Q_f = 2{,}010$ GHz with a high positive τ_f value, compared with Figs. 1 and 2, the volume shrinkage and bulk density was 18.15% and 5.319 g/cm^3 respectively, which indicated the chemical reaction was just in the middle stage of sintering procedure

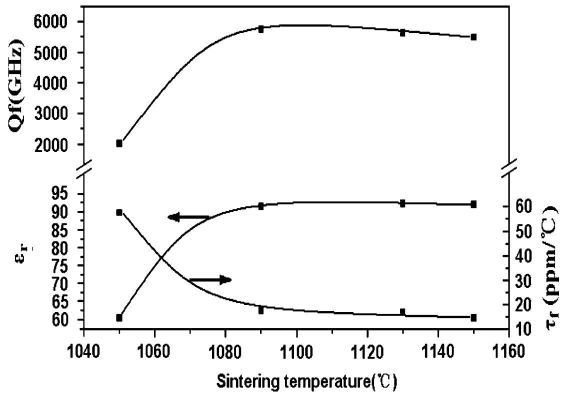

Fig. 6 Variation of the microwave dielectric properties with sintering temperature for $k = 1$, $w = 1$ wt% in Bi_2O_3 and MnO_2 co-doped PCLFN ceramics

and the large relative content of pores and pyrochlore phase deteriorate the microwave dielectric properties. However, when sintering temperature reached 1,090°C, the microwave dielectric properties became stable and the volume shrinkage and bulk density at present were 27.69% and 6.021 g/cm^3 respectively which indicated the completeness of chemical reactions and the relative content of pyrochlore phase became almost certain values and it would not disappear even at higher sintering temperatures [4]. In fact, as the pyrochlore phase dissolved into perovskite phase the tolerance factor t and the electronegativity difference e of the main phase [7, 8] would both increased from 0.970 and 3.873 of $(Pb_{0.38}Ca_{0.54}La_{0.08})(Fe_{0.53}Nb_{0.45}Mn_{0.02})O_3$ phase to 0.973 and 4.048 of $[(Pb_{0.5}Ca_{0.5})_{0.92}La_{0.08}](Fe_{0.5}Nb_{0.5})O_{3+\delta}$, so according to Jang et al., the phase structure should become more stable. However, the higher charge of La^{3+} at A-site, substituting (Pb/Ca)$^{2+}$, would cause the charge unbalance of the system and the stoichiometry of $[(Pb_{0.5}Ca_{0.5})_{0.92}La_{0.08}](Fe_{0.5}Nb_{0.5})O_3$ could not be really produced with pyrochlore phase separating from it which can be simply described by Eq. (2).

$$\begin{aligned}(Pb_{0.46}Ca_{0.46}La_{0.08})(Fe_{0.5}Nb_{0.5})O_{3.04} \rightarrow\ & x\left(Pb_{0.38+\frac{0.04}{x}}Ca_{\frac{0.46}{x}}La_{0.08}\right)\left(Fe_{\frac{0.5}{x}}Nb_{\frac{x-0.5}{x}}\right)O_3 \\ & + \frac{1-x}{4}\left(Pb_{0.84}La_{\frac{0.32}{3}}\right)_3 Nb_4O_{13} + \left(\frac{x}{4} - 0.21\right)PbO \uparrow\end{aligned} \tag{2}$$

However, in the actual reaction, the situation is much more complicated with Ca^{2+} and Fe^{3+} also entering into the pyrochlore phase leading to a more flexible x value.

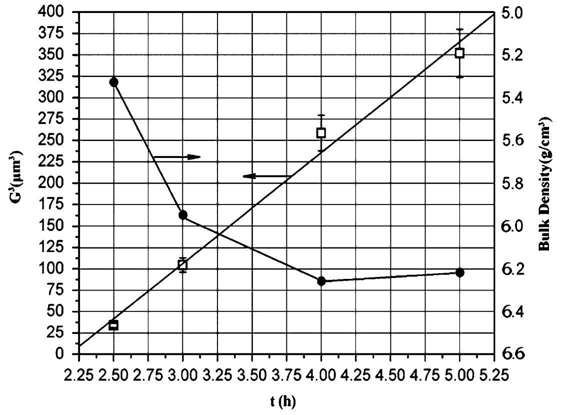

Fig. 7 The cubic order of the grain size G (μm^3) and the bulk density (g/cm^3) varied with sintering time t (h) for $k = 1$, $w = 1$ wt% in Bi_2O_3 and MnO_2 co-doped PCLFN ceramics sintered at 1,050 °C

Figure 7 shows the average grain size (determined by Mendelson method [9]) and the bulk density of co-doped samples sintered at 1,050 °C varied with sintering time t. The average grain size gradually increased with increasing t value. With the growing of grains and the disappearing of porosities, the bulk density rapidly increased and reached its maximal value of 6.259 g/cm^3 when sintered for 4 h. However, it began to decrease when longer sintering time was employed which was due to the large amount of PbO loss during longer sintering time as shown in Fig. 8.

Figure 8 also illustrates the relationships between microwave dielectric properties and the sintering time at 1,050 °C. With the increasing of sintering time the microwave dielectric properties was improved obviously. When sintering time was 4 h, microwave dielectric properties reached the optimal value of $\epsilon_r = 91.1$, $Q_f = 4{,}870$ GHz and $\tau_f = 18.5$ ppm/°C. With longer sintering time ϵ_r and Q_f value decreased instead. Since PbO vaporization loss increased almost linearly with sintering time, so this decrease might stem from the excessive evaporation of Pb ion from crystal lattice which usually causes parasitic pyrochlore phase and open pores in microstructures, which were, as well known, the most usual deteriorative factors to

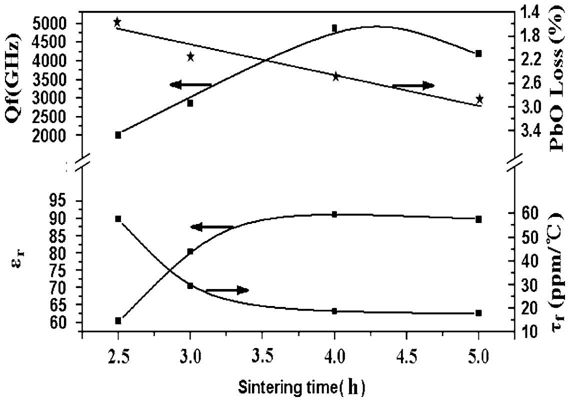

Fig. 8 Variation of microwave dielectric properties and PbO weight loss percentage with sintering time for $k = 1$, $w = 1$ wt% Bi_2O_3 and MnO_2 co-doped PCLFN ceramics sintered at 1,050 °C

the dielectric properties in lead-based ceramics [10, 11].

According to dynamic theory of ceramics growth, the relationship between average grain size G and sintering time t could be approximately described as [6]:

$$G^n = Pt \tag{3}$$

In which G was the average grain size in sintering time t, n was the dynamic growth index of ceramics, commonly in the range of 2–4 and P was constant at a certain temperature.

When inspected the relationship between G^n and t in the present system with different n value, one would find that linearity between them can be well fitted at $n = 3$ as shown in Fig. 7 which indicated the grain growth of the co-doped PCLFN ceramics ($k = 1$) was controlled by either volume-diffusion or second-order interface mechanism [6, 12] with the calculated reaction constant $P = 9.26 \times 10^{-21}$(m^3/s) at 1,050 °C from Eq. (3).

Conclusion

With the investigation of phase formation, sintering behavior and microwave dielectric properties of Bi_2O_3 and MnO_2 co-doped $[(Pb_{0.5}Ca_{0.5})_{0.92}La_{0.08}](Fe_{0.5}Nb_{0.5})O_{3+\delta}$ (PCLFN) ceramics, the following results could be clarified:

1. The sintering behavior of PCLFN ceramics was effectively improved by liquid phase sintering mechanism with Bi_2O_3 and MnO_2 sintering aids. The effectively lowered sintering temperature was resulted from two joint efforts, one is Bi_2O_3 and MnO_2 binary dopants formed stable and lower melting temperature flux at grain boundary, the other is part of Mn^{4+} entered into PCLFN crystal lattice also gave rise to an activated sintering process.
2. Sintering procedure influenced the chemical composition, grain size and porosities in ceramics significantly. With high sintering temperature and time PbO would evaporate from ceramics, causing an almost linear concentration gradient of PbO from the surface toward the bulk and the increase of pyrochlore phase and porosities in microstructure which would deteriorate microwave dielectric properties instead.
3. The investigation of sintering dynamics indicated that the grain growth of Bi_2O_3 and MnO_2 co-doped PCLFN ceramics was controlled by volume-diffusion or second-order interface mechanism with the calculated reaction constant $P = 9.26 \times 10^{-21}$ (m^3/s) at 1,050°C.
4. The PCLFN ceramics co-doped with Bi_2O_3 and MnO_2 could be well sintered at 1,050 °C and an optimal microwave dielectric properties of $\epsilon_r = 91.1$, $Q_f = 4{,}870$ GHz and $\tau_f = 18.5$ ppm/°C could be obtained when $k = 1$ and $w = 1$ wt% and sintered at the optimal time of 4 h, which manifested itself a potential use in future multilayer microwave devices.

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