

Microwave dielectric properties of $(1-x)\text{CaO}-x\text{BaO}-\text{Li}_2\text{O}-(1-y)\text{Sm}_2\text{O}_3-y\text{Nd}_2\text{O}_3-\text{TiO}_2$ ceramics system

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The $\text{CaO}-\text{Li}_2\text{O}-\text{Sm}_2\text{O}_3-\text{TiO}_2$ system has been reported having a high dielectric constant and good temperature stability. Based on the composition of $\text{CaO}:\text{Li}_2\text{O}:\text{Sm}_2\text{O}_3:\text{TiO}_2 = 16:9:12:63$, the modifications of CaO and Sm_2O_3 were investigated. In this paper, CaO has been partially substituted by BaO and Sm_2O_3 by Nd_2O_3 . It was found that the introduction of BaO leads the modified ceramics to be mixtures of two phases. The fQ value has been significantly promoted, while the dielectric constant can remain higher than 90. To obtain a higher dielectric constant, Sm_2O_3 has been further partially replaced by Nd_2O_3 . The sintering temperatures for the property change were also studied. The temperature coefficient of resonant frequency could be varied from a positive value to a negative value according to the different sintering temperatures. Excellent dielectric properties of $\epsilon_r = 103$, $fQ = 7200$ and $\tau_f = +2$ ppm/ $^\circ\text{C}$ were obtained with a composition of $\text{CaO}:\text{BaO}:\text{Li}_2\text{O}:\text{Sm}_2\text{O}_3:\text{Nd}_2\text{O}_3:\text{TiO}_2 = 14:4:8:10:2:63$ (molar ratio) and sintered at 1350°C for 3 h.

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1. Introduction

With the recent progress in the microwave communication system, microwave dielectric ceramics with a high dielectric constant become more important for the miniaturization of microwave device such as filters, duplexers, voltage-controlled oscillators, and down converters. These ceramics are required for a high dielectric constant (ϵ_r), high Q value and small temperature coefficient of resonant frequency (τ_f). Especially when they are used in UHF and SHF band, they should have a high ϵ_r , since then the guided-wavelength in the medium is rather long as compared to other higher frequency bands. In the past years, many microwave dielectrics, such as $(\text{Pb},\text{Ba})\text{O}-\text{Nd}_2\text{O}_3-\text{TiO}_2$ [1] and $(\text{Ba},\text{Sr})\text{O}-\text{Sm}_2\text{O}_3-\text{TiO}_2$ [2] were developed and widely used. However, the dielectric constants of these materials were not higher than 100.

Generally, a dielectric material with a high dielectric constant has a large positive temperature coefficient for the resonant frequency [3]. With the concept of compensation for the temperature coefficient, K. Ezaki *et al.* [4] combined CaTiO_3 [5] having a large positive τ_f and $(\text{Li}_{1/2}\text{Sm}_{1/2})\text{TiO}_3$ [6] having a large negative on to obtain a high dielectric material with good temperature stability for the resonant frequency. The $\text{CaO}-\text{Li}_2\text{O}-\text{Sm}_2\text{O}_3-\text{TiO}_2$ system was then developed. The authors proposed the non-stoichiometric composition of $\text{CaO}:\text{Li}_2\text{O}:\text{Sm}_2\text{O}_3:\text{TiO}_2 = 16:9:12:63$ as a temperature stable dielectric material for the dielectric resonator use. In their study, CaO was further replaced

by SrO . When SrO is 1 mol%, the dielectric constant increased to 110, the fQ value was slightly lowered down to 4500 GHz, and the τ_f was 7 ppm/ $^\circ\text{C}$. The successive investigation for different lanthanide element substitutions for Sm was reported [7]. They successfully improved the ϵ_r and maintained the temperature stability. Unfortunately, the fQ value was poor. In this paper, the fQ value is promoted from the BaO substitution for CaO . The degradation of ϵ_r has been prevented using Nd_2O_3 to partially replace Sm_2O_3 . In the experiment, the microwave dielectric properties were measured; X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis were also employed to investigate the crystal structure and the microstructure. The following sections will introduce the experimental procedure and discuss the effects of replacing BaO for CaO and Nd_2O_3 for Sm_2O_3 . Moreover, the effects of the sintering temperature are also considered.

2. Experimental procedure

2.1. Sample preparation

High-purity raw material CaCO_3 , BaCO_3 , LiCO_3 , Sm_2O_3 , Nd_2O_3 and TiO_2 (over 99.9% purity) were weighed according to their molar ratio. They were mixed in a plastic jar, ball-milled with agate balls for 16 h in distilled water, dried, and calcined at 1000°C for 3 h in air. The calcined powders were remilled, dried, granulated with PVA and sieved. The sieved powders were then uniaxially pressed into cylindrical disks with

11 mm in diameter and 5 mm in height. After being fired to remove the organic binder, these disks were sintered at 1300–1400°C for 3 h in air.

2.2. Measuring method

The dielectric constant ϵ_r and the fQ value at microwave frequencies were determined by the method proposed by Hakki and Coleman [8], and improved by Kobayashi and Katoh [9].

The disks were, in turn, placed between two parallel conductor plates. Then, the TE_{011} and TE_{012} modes were measured using HP8510B network analyzer. The dielectric constant was calculated from the resonant frequency of the TE_{011} mode of the cylindrical disk. For the Q_d measurement, the conductor loss resulting from the eddy currents around the conductive plate surfaces must be subtracted so as to obtain the dielectric quality factor. For this purpose, two disks with different height were prepared, one is for TE_{011} mode and the other is for TE_{012} mode, where the disk for the TE_{012} mode measurement has 2 times height as that of the disk for the TE_{011} mode. The temperature dependence of resonant frequency was measured in the temperature range of 0–80°C. The crystal phases of the sintered specimen were determined by X-ray diffraction. The microstructures of the as-sintered surfaces were observed by scanning electron microscopy (SEM).

3. Results and discussion

3.1. Effect of BaO replacement for CaO

The CaO-Li₂O-Sm₂O₃-TiO₂ system with composition of CaO : Li₂O : Sm₂O₃ : TiO₂ = 16 : 9 : 12 : 63 was first modified by introducing some amount of BaO to replace CaO. X-ray diffraction analyses of the CaO-BaO-Li₂O-Sm₂O₃-TiO₂ system were examined in Fig. 1.

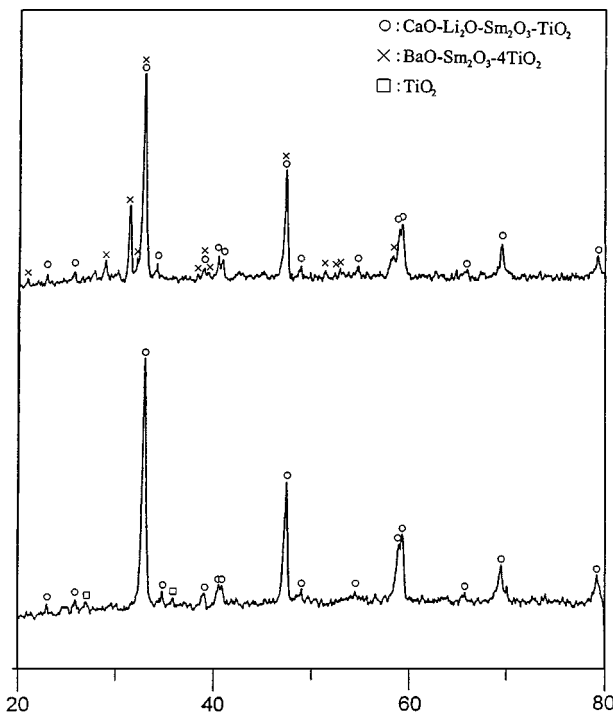


Figure 1 X-ray diffraction patterns of the $(0.16-x)\text{CaO}\cdot x\text{BaO}\cdot 0.09\text{Li}_2\text{O}\cdot 0.12\text{Sm}_2\text{O}_3\cdot 0.63\text{TiO}_2$ system at (a) $x=0$ (b) $x=0.03$.

TABLE I Dielectric properties of the (Ca, Ba)O-Li₂O-Sm₂O₃-TiO₂ ceramics

No.	CaO	BaO	Li ₂ O ₃	Sm ₂ O ₃	TiO ₂	ϵ_r	fQ	D (g/cm ³)	τ_f
1	16	0	9	12	63	104	4280	4.78	+9
2	13	3	9	12	63	92	6230	5.05	-26
3	14	4	8	12	63	96	7580	5.15	-6

It is found that the modified ceramic contains two mixed phases. One phase consistent with the previous report [4] has been identified as CaO-Li₂O-Sm₂O₃-TiO₂, while the other peaks were identified as that of BaO·Sm₂O₃·4TiO₂ with JCPDS #43-0235. As compared to CaO-Li₂O-Sm₂O₃-TiO₂, it is obvious that the small amount of TiO₂ disappeared and a secondary phase of BaO·Sm₂O₃·4TiO₂ formed in the BaO modified ceramics. Due to the presence of the secondary phase, the dielectric properties were changed. The lowered value of the dielectric constant can be explained by the logarithmic mixture rule. The microwave characteristics of the modified system are listed in Table 1. When the substituted amount of BaO is 3 mol% (sample No. 2), the dielectric properties: the ϵ_r of 92, the fQ value of 6230 GHz and the τ_f value of -26 ppm/°C were obtained. Since the BaO-Sm₂O₃-TiO₂ system has a high Q value, but a lower ϵ_r and a negative τ_f value, it is reasonable for the degradation of ϵ_r , the improvement of the fQ value and a negative shift of the τ_f value in the modified system.

The microphotograph of the as-sintered surface from SEM observation is shown in Fig. 2a. The microphotographs of the CaO-Li₂O-Sm₂O₃-TiO₂ system and BaO·Sm₂O₃·4TiO₂ are also shown in Fig. 2b and c for comparison. In Fig. 2a, the microphotograph of CaO-BaO-Li₂O-Sm₂O₃-TiO₂ shows that there coexist two different grains in the specimen. One has a cuboid shape similar to that of CaO-Li₂O-Sm₂O₃-TiO₂, while the other one has a bar shape similar to that of BaO·Sm₂O₃·4TiO₂. It is assumed that the cuboid-shaped grain of CaO-Li₂O-Sm₂O₃-TiO₂ becomes Li-rich, since some Sm₂O₃ and TiO₂ have been extracted for the formation of BaO·Sm₂O₃·4TiO₂.

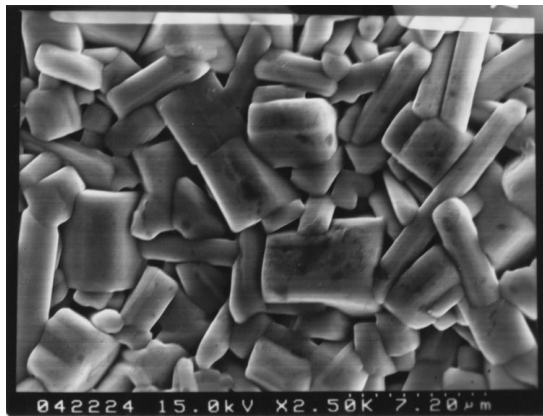
For the calculation of the temperature coefficient of resonant frequency, the τ_f is defined as follows.

$$\tau_f = \frac{(f_{T_2} - f_{T_1})/f_0}{T_2 - T_1}$$

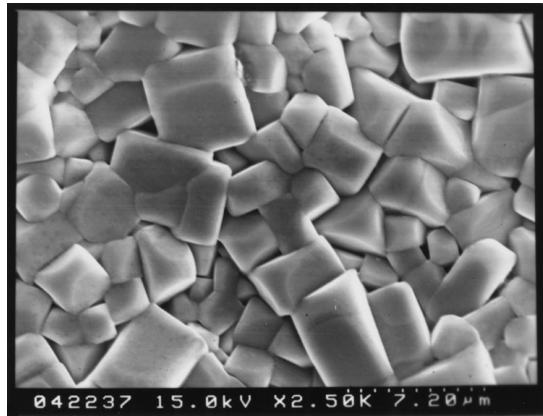
where f_0 , f_{T_1} , and f_{T_2} are the resonant frequencies at 20°C, 0°C and 80°C, respectively.

Since the dielectrics in the CaO-BaO-Li₂O-Sm₂O₃-TiO₂ system are the mixtures of two phases, the τ_f should be also attributed to the resulting volume fraction of each phase. Since the $(\text{Li}_{1/2}\text{Sm}_{1/2})\text{TiO}_3$ phase has a large negative τ_f value, the CaO-Li₂O-Sm₂O₃-TiO₂ phase with Li-rich would result in a negative τ_f value. It is believed that the increment of the secondary phase BaO·Sm₂O₃·4TiO₂ accompanying with the CaO-Li₂O-Sm₂O₃-TiO₂ phase which has a negative τ_f value make the τ_f negatively shift.

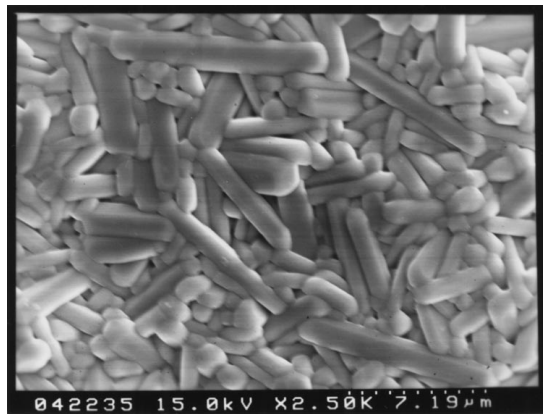
In order to obtain a material with a higher ϵ_r , a higher fQ value and a small τ_f value, the amount of each



(a)



(b)



(c)

Figure 2 SEM microphotographs of the as-sintered surfaces of (a) $0.13\text{CaO}\cdot 0.03\text{BaO}\cdot 0.09\text{Li}_2\text{O}\cdot 0.12\text{Sm}_2\text{O}_3\cdot 0.63\text{TiO}_2$; (b) $0.16\text{CaO}\cdot 0.09\text{Li}_2\text{O}\cdot 0.12\text{Sm}_2\text{O}_3\cdot 0.63\text{TiO}_2$; (c) $\text{BaO}\cdot \text{Sm}_2\text{O}_3\cdot 4\text{TiO}_2$.

component in the $\text{CaO}\text{-BaO}\text{-Li}_2\text{O}\text{-Sm}_2\text{O}_3\text{-TiO}_2$ system has been slight adjusted. The amounts of CaO and BaO were intuitively lifted by 1 mol% for a higher ϵ_r and a higher fQ value, respectively, while the decrease in the Li_2O content was for the compensation of the temperature stability. The adjustment of sample No. 3 gives a moderate ϵ_r of 96, a high fQ value of 7580 GHz and a small τ_f value of -6 ppm/ $^\circ\text{C}$.

3.2. Effect of Nd_2O_3 replacement for Sm_2O_3
Based on the above results, a further study on the dielectric constant was proceeded in this paper. In the previous

study [7], the authors have investigated the tendency for the partial replacement of Ln_2O_3 for Sm_2O_3 , where Ln is the lanthanide element. They found that the ionic radius of Ln would influence the polarization. With an increment in the ionic radius of Ln, the ϵ_r increases almost linearly. However, the fQ value was degraded. Therefore, we started with the BaO modified system and replaced some amount of Ln_2O_3 for Sm_2O_3 to improve the ϵ_r .

3.2.1. Different replacement amount of Nd_2O_3

Table II illustrates the variation of dielectric properties with different amounts of Nd replacement. The specimens were all sintered at 1350°C for 3 h. It is found that the measured results agree with the predicted tendency. The ϵ_r increases, the fQ value falls down and the τ_f value becomes positive with the increasing Nd_2O_3 . The temperature dependence of the resonant frequency is illustrated in Fig. 3. The more the amount of Nd_2O_3 , the more the curve bends up. Excellent properties of $\epsilon_r = 103$, $fQ = 7200$ GHz and $\tau_f = +2$ ppm/ $^\circ\text{C}$ were obtained when the replacement amount of Nd_2O_3 for Sm_2O_3 is 0.17. Since the radii of Sm and Nd are similar to each other, Nd might enter the sites of Sm without changing the structure much. This assumption has been demonstrated in Fig. 4, in which

TABLE II Dielectric properties of the $(\text{Ca}, \text{Ba})\text{O}\text{-Li}_2\text{O}\text{-(Sm}_{1-y}, \text{Nd}_y)_2\text{O}_3\text{-TiO}_2$ ceramics with the composition of $\text{CaO}:\text{BaO}:\text{Li}_2\text{O}:(\text{Sm}, \text{Nd})_2\text{O}_3:\text{TiO}_2 = 14:4:8:12:63$

y	ϵ_r	fQ	τ_f
0	96	7580	-6
0.17	103	7200	+2
0.33	106	6620	+22
0.50	111	5490	+47

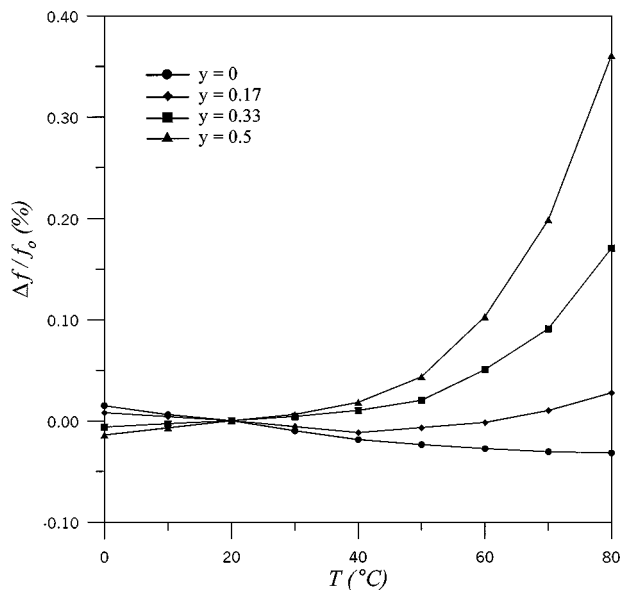


Figure 3 Temperature change of the resonant frequency of the $0.14\text{CaO}\cdot 0.04\text{BaO}\cdot 0.08\text{Li}_2\text{O}\cdot 0.12(\text{Sm}_{1-y}, \text{Nd}_y)_2\text{O}_3\cdot 0.63\text{TiO}_2$ system as a function of y .

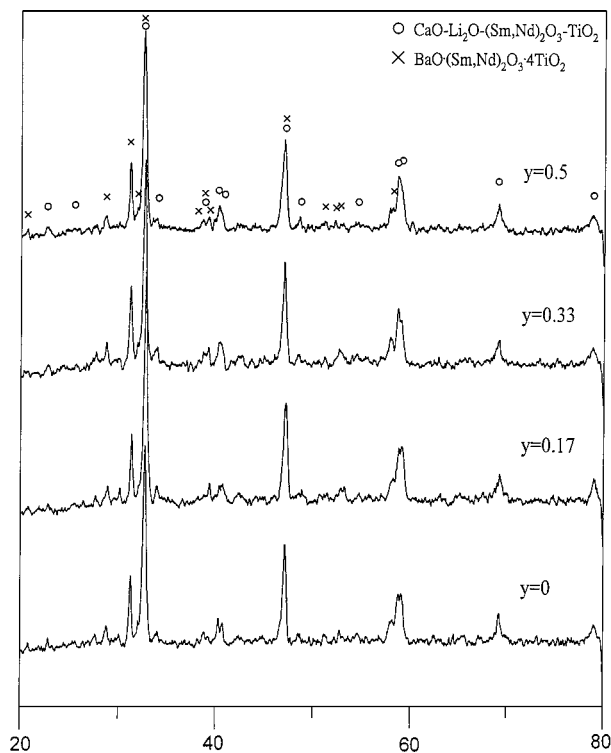


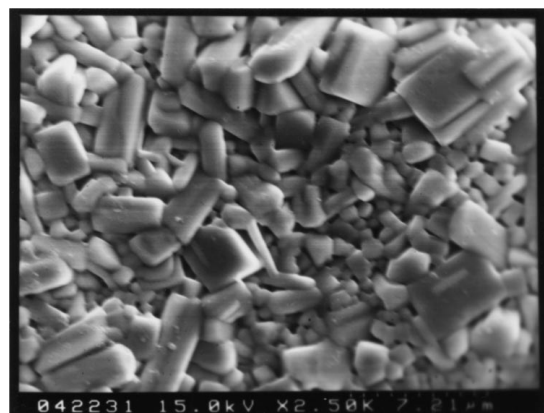
Figure 4 XRD patterns of the 0.14CaO-0.04BaO-0.08Li₂O-0.12(Sm_{1-y}, Nd_y)₂O₃-0.63TiO₂ system.

the peaks for the different amounts of Nd replacement are almost the same as that of (Ca, Ba)O-Li₂O-Sm₂O₃-TiO₂. However, the main peaks shift to lower angles due to the fact that Nd³⁺ > Sm³⁺. The SEM observations of the two-phase system with different sintering temperature are shown in Fig. 5. As can be seen, the grains are as same as those of the Ba modified system. Thus, the cuboid-shaped grains and the bar-shaped grains are recognized as CaO-Li₂O-(Sm,Nd)₂O₃-TiO₂ and BaO-(Sm, Nd)₂O₃-TiO₂, respectively.

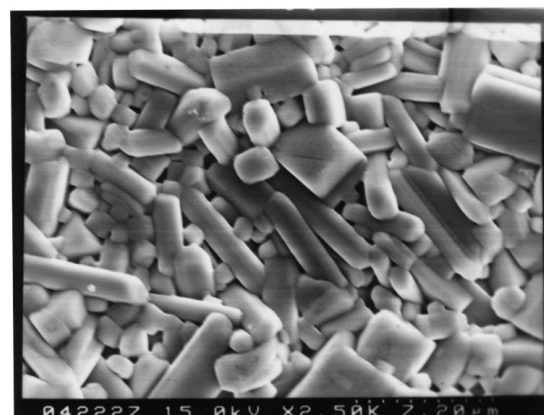
3.2.2. Different sintering conditions

The effects of the sintering temperature to the dielectric properties were then investigated with the composition of CaO : BaO : Li₂O : Sm₂O₃ : Nd₂O₃ : TiO₂ = 14 : 4 : 8 : 10 : 2 : 63. The sintering temperature (T_s) was varied from 1300°C to 1400°C in this work, while the dwell time maintained at 3 h. The variations of the dielectric properties (ϵ_r , fQ and τ_f) and the apparent density are illustrated in Fig. 6. With the increasing T_s , the ϵ_r decreases linearly, the fQ value increase rapid at first and tends to saturate when $T_s > 1350^\circ\text{C}$, the τ_f value goes toward negative, while the density reaches a maximum value at 1375°C, and then falls down slightly.

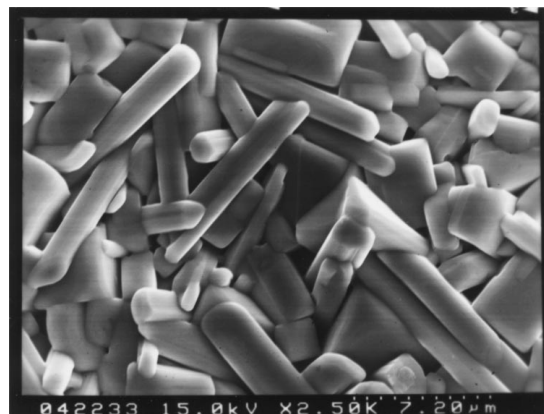
In general, the ϵ_r is proportional to the density of the sintered body. However, it is failed in this two-phase system, thus the decrease of ϵ_r might result from the grain growth condition. The SEM microphotographs with different sintering temperatures as previously shown in Fig. 5 indicates that the grains grow up with the increasing sintering temperature. When the sintering temperature is low, the CaO-Li₂O-(Sm,Nd)₂O₃-



(a)



(b)



(c)

Figure 5 SEM observations of the as-sintered surfaces of 0.14CaO-0.04BaO-0.08Li₂O-0.12(Sm_{0.83}, Nd_{0.17})₂O₃-0.63TiO₂ sintered at (a) 1300°C; (b) 1350°C; (c) 1400°C.

TiO₂ phase dominates in the specimen, thus the highest ϵ_r , the lowest fQ value and the largest positive τ_f value are obtained. As the sintering temperature gets higher, the grains of BaO-(Sm,Nd)₂O₃-TiO₂ grows more rapidly than that of CaO-Li₂O-(Sm,Nd)₂O₃-TiO₂ that would lower the τ_f value although the sintered body becomes denser, the τ_f value shifts negatively, and the fQ value increases rapidly. The successive increment of sintering temperature results in more formation of BSNT, which degrades that ϵ_r , leads the τ_f to a negative value, and promotes the fQ value. The most balanced properties were obtained when sintered at 1350°C for 3 h.

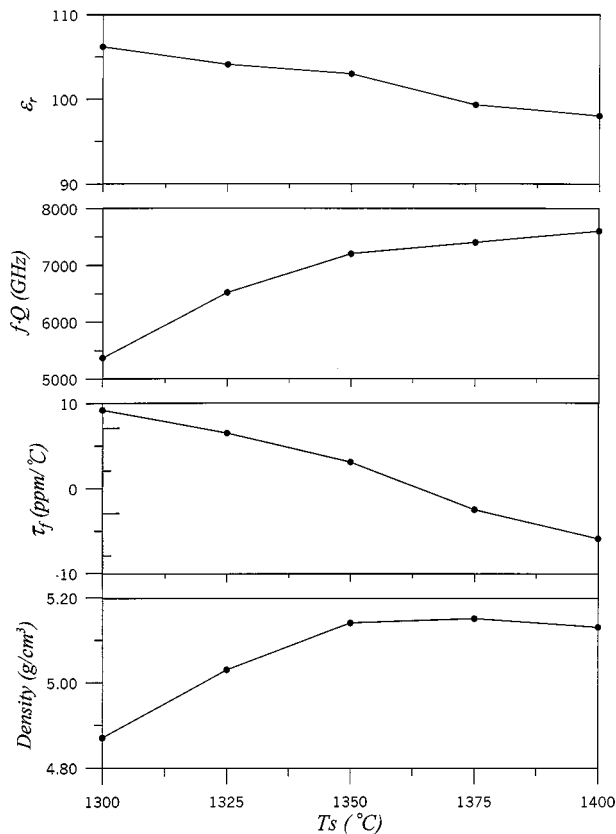


Figure 6 Microwave characteristics and bulk density of 0.14CaO-0.04BaO-0.08Li₂O-0.12(Sm_{0.83}, Nd_{0.17})₂O₃-0.63TiO₂ as functions of the sintering temperature.

4. Conclusion

The substitution of BaO for CaO causes the presence of the secondary phase BaO·Sm₂O₃·4TiO₂. In addition to the main phase CaO-Li₂O-Sm₂O₃-TiO₂, the secondary phase of BaO·Sm₂O₃·4TiO₂ plays an important role in the system. The main contribution of the BaO·Sm₂O₃·4TiO₂ phase is the improvement of the higher fQ value. Because of the extractions of Sm and

Ti for the formation of BaO·Sm₂O₃·4TiO₂, the phase of CaO-Li₂O-Sm₂O₃-TiO₂ becomes Li-rich, which might be considered to have a negative τ_f value. The slight adjustment has effectively improved the negative τ_f .

The further replacement of Nd₂O₃ for Sm₂O₃ can increase the ϵ_r . XRD patterns show that the crystal structures have no apparent changes with the different replacement amounts. The sintering temperature has influences on the density, the ϵ_r , the fQ value, and the τ_f value.

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