



Effects of BaCu(B₂O₅) addition on phase transition, sintering temperature and microwave properties of Ba₄LiTa₃O₁₂ ceramics

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ABSTRACT

Polycrystalline sample of Ba₄LiTa₃O₁₂ is synthesized in the temperature range of 1300–1350 °C by the conventional solid state reaction method, and a phase transition from cubic to hexagonal perovskite is observed between 1300 °C and 1350 °C. Hexagonal phase of Ba₄LiTa₃O₁₂ obtained at 1350 °C could be stabilized at considerably lower temperature (~925 °C) with BaCu(B₂O₅) (BCB) addition. BCB addition effectively improves the densification of Ba₄LiTa₃O₁₂ ceramic at low temperature and induces only a limited degradation of the microwave dielectric properties. A dense ceramic with a ϵ_r of 25.5, a high $Q \times f$ of 32,600 GHz, and a low τ_f of 23.6 ppm/°C is obtained for the 4 wt.% of BCB-added Ba₄LiTa₃O₁₂ sintered at 925 °C. Moreover, Ba₄LiTa₃O₁₂ ceramics added 1–5 wt.% of BCB have a chemical compatibility with silver electrode at 925 °C, which might be an attractive promising candidate for LTCC application.

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1. Introduction

The rapid growth of the wireless communication industry has created a high demand for the development of ceramic microwave components such as resonators, filters and oscillators. These materials are required to a high relative permittivity (ϵ_r) for miniaturization, a high quality factor ($Q \times f$) for better selectivity and a near-zero temperature coefficient of resonant frequency (τ_f) for stability, but in addition, low cost and minimization of components are two crucial requirements in commercial applications [1–4]. However, contemporary commercial resonator materials such as Ba(Mg_{1/3}Ta_{2/3})O₃, (Zr,Sn)TiO₄, and CaTiO₃–NdAlO₃ had the sintering temperatures higher than 1300 °C [4–9], which limits their applications in low-temperature cofired ceramic (LTCC) microwave devices. As a promising material for LTCC application, the sintering temperature of the ceramics should be lower than the melting point of silver (~960 °C) [10,11].

In order to reduce the sintering temperature, much attention has been paid to Li-containing compounds such as Li_{0.5}Sm_{0.5}WO₄ [12], Li₂MgSiO₄ [13], and Li₂ATi₃O₈ (A = Zn, Mg) [14,15] due to their relatively low sintering temperatures and excellent microwave dielectric properties. Recently, Borisevich [16] reported that both phase transitions (LT → HT, HT → disordered) of A(Li_{1/4}Ta_{3/4})O₃

(A = Ca, Sr) ceramics were found to be reversible, and the HT → LT transition was very slow which was relative to significant diffusion and redistributions of the B-site ions into the different ordered structure. LT polymorph had a previously unreported type of 1:3 order, while the HT polymorph may have a combination of layered 1:3 order with a different type of octahedral tilt system. A(Li_{1/4}Ta_{3/4})O₃ (A = Ca, Sr) ceramics can form a stable cubic perovskite structure at 1300 °C and below, but the sintering conditions of SrLi_{1/4}Ta_{3/4}O₃ are not fully investigated and the microwave dielectric properties of CaLi_{1/4}Ta_{3/4}O₃ are relatively low (ϵ_r of 27, $Q \times f$ of 30,000 GHz and τ_f of 76 ppm/°C) [16]. Thereafter, the microwave dielectric properties of the twinned 8H hexagonal perovskite Ba₄LiTa₃O₁₂ ceramics have been reported by Fang et al. [17] with a moderate ϵ_r of 28, a high $Q \times f$ of 104,000 GHz and a positive τ_f of 25 ppm/°C. Compared with cubic perovskite ceramics, hexagonal perovskite ceramics have a fairly high quality factor. However, the τ_f of hexagonal Ba₄LiTa₃O₁₂ ceramic is a little large and its sintering temperature (around 1450 °C) is still too high to meet the requirement of practical LTCC applications, so it is necessary to reduce the sintering temperature of Ba₄LiTa₃O₁₂ ceramic so that it can be cofired with silver electrode.

BaCu(B₂O₅) (BCB) is generally chosen as a candidate sintering aid because of its low melting point (850 °C), and the favorable microwave dielectric properties ($\epsilon_r \sim 7.4$, $Q \times f \sim 50,000$ GHz, $\tau_f \sim -32$ ppm/°C) [18], which was successfully applied in lowering the sintering temperatures of several ceramics, such as Ba(Zn_{1/3}Ta_{2/3})O₃, Ba(Zn_{1/3}Nb_{2/3})O₃, Ba₄LiNb₃O₁₂ ceramics [18–20]. Moreover, it is reported that the τ_f of Ba₄LiNb₃O₁₂ ceramic could be decreased from 65 to 11.8 ppm/°C with BCB addition due

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to its negative τ_f (-32 ppm/ $^{\circ}\text{C}$) [20]. Therefore, the addition of BCB might be a good method to not only reduce the sintering temperature of $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ ceramics, but also tune τ_f by mixtures of dielectrics. In the present paper, the effects of BCB addition as low-temperature sintering aid on phase transition, sintering temperature and microwave dielectric properties of $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ ceramics have been investigated. The chemical compatibility of hexagonal $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ with Ag electrode has also been discussed.

2. Experimental procedures

High purity powders of BaCO_3 (>99.9%, Huaxin Chemical Reagents Co. Ltd., Baoding, China), Ta_2O_5 (>99.99%, Conghua Tantalum and Niobic Chemical Reagents Smelting Plant, Conghua, China) and Li_2CO_3 (>99.9%, Dongpeng Chemical Engineering Co. Ltd., Xinyu, China) were mixed according to the composition of $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$. The mixture was ball milled in alcohol medium for 4 h in a plastic bottle. The wet mixture was rapidly dried and calcined for 4 h in the temperature range of 1300–1350 $^{\circ}\text{C}$. To synthesize BCB, stoichiometric amounts of high purity BaCO_3 (>99.9%, Huaxin Chemical Reagents Co. Ltd., Baoding, China), CuO (>99.0%, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) and B_2O_3 (>99.99%, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) were weighed and mixed for 4 h and then calcined at 700 $^{\circ}\text{C}$ for 4 h. The powder of $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ calcined at 1300 $^{\circ}\text{C}$ for 4 h was ground with 1–5 wt.% of BCB. The resultant powder was mixed with 5 wt.% of polyvinyl alcohol and pressed into cylindrical disks of 13 mm diameter and 6–8 mm height by uniaxial pressing under a pressure of 200 MPa. The samples were heated at 550 $^{\circ}\text{C}$ for 4 h to remove the organic binder and then sintered at 850–975 $^{\circ}\text{C}$ for 2 h at a heating rate of 5 $^{\circ}\text{C}/\text{min}$.

The bulk densities of the sintered ceramics were measured by the Archimedes method. The phase composition of calcined powders and sintered samples were determined using an X-ray diffractometer (XRD) ($\text{CuK}\alpha_1$, 1.54059 Å, Model X'Pert PRO, PANalytical, Almelo, Holland). The sintered samples were polished and thermally etched at temperature 50 $^{\circ}\text{C}$ lower than their respective sintering temperature for 30 min. The surface micrographs of the samples were examined using a scanning electron microscope (SEM, Model JSM6380-LV, JEOL, Tokyo, Japan). The microwave dielectric properties were obtained using a network analyzer (Model N5230A, Agilent Co., Palo Alto, Canada) and a temperature chamber (Delta 9039, Delta Design, San Diego, CA). The relative permittivity was calculated using TE₀₁₁ mode under the end-short condition using the method suggested by Hakkiani Coleman and modified by Courtney [21,22]. The temperature coefficients of resonant frequency τ_f were calculated by the formula as following:

$$\tau_f = \frac{f_T - f_0}{f_0(T - T_0)} \quad (1)$$

where f_T , f_0 were the resonant frequencies at the measuring temperature T (85 $^{\circ}\text{C}$) and T_0 (25 $^{\circ}\text{C}$), respectively.

3. Results and discussion

The room temperature XRD patterns of the $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ powders calcined in the temperature range of 1300–1350 $^{\circ}\text{C}$ for 4 h are shown in Fig. 1. Cubic $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ phase were formed (matched with PDF files No. 04-006-0073) when samples calcined below 1300 $^{\circ}\text{C}$, while samples calcined between 1300 $^{\circ}\text{C}$ and 1350 $^{\circ}\text{C}$ were comprised of a mixture of cubic and hexagonal phases. In addition, the amount of hexagonal $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ phase increases with increasing calcination temperature. Single-phase hexagonal $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ were formed (matched with PDF files No. 00-027-1216) for samples calcined above 1350 $^{\circ}\text{C}$. The XRD patterns of $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ ceramics added with 1–5 wt.% BCB sintered at 925 $^{\circ}\text{C}$ for 2 h are illustrated in Fig. 2. It is notable that hexagonal phase of $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ obtained at 1350 $^{\circ}\text{C}$ could be stabilized at much lower temperature ($\sim 925^{\circ}\text{C}$) with BCB addition. The diffraction patterns are similar and matched well with the hexagonal phase of $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ (PDF files no. 00-27-1216). All peaks are also indexed, and no peak of secondary phase including BCB phase is observed. It is possible that the BCB liquid phase is not crystallized in the $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ ceramic during cooling and remained as the amorphous phase [18].

Fig. 3 presents the bulk densities of the BCB-added $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ ceramics as a function of sintering temperature from 850 $^{\circ}\text{C}$ to 975 $^{\circ}\text{C}$ for 2 h. The bulk densities of the samples increase with increasing both sintering temperature and BCB content. When 1–2 wt.% of BCB is added, the bulk densities are very low, but

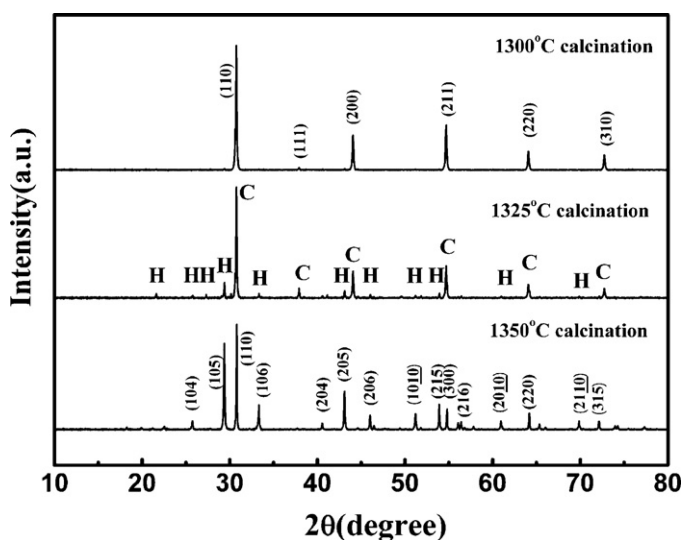


Fig. 1. XRD patterns of $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ calcined in the temperature range 1300–1350 $^{\circ}\text{C}$ for 4 h.

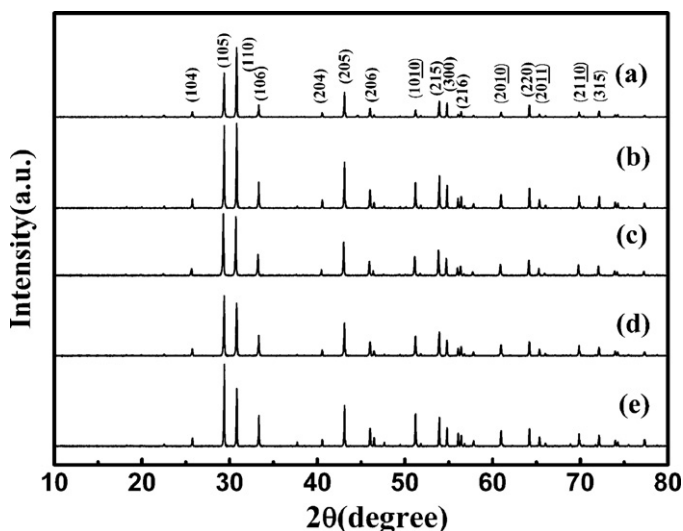


Fig. 2. XRD patterns of $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ ceramics with x wt.% of BCB sintered at 925 $^{\circ}\text{C}$ for 2 h: (a) $x = 1$; (b) $x = 2$; (c) $x = 3$; (d) $x = 4$; (e) $x = 5$.

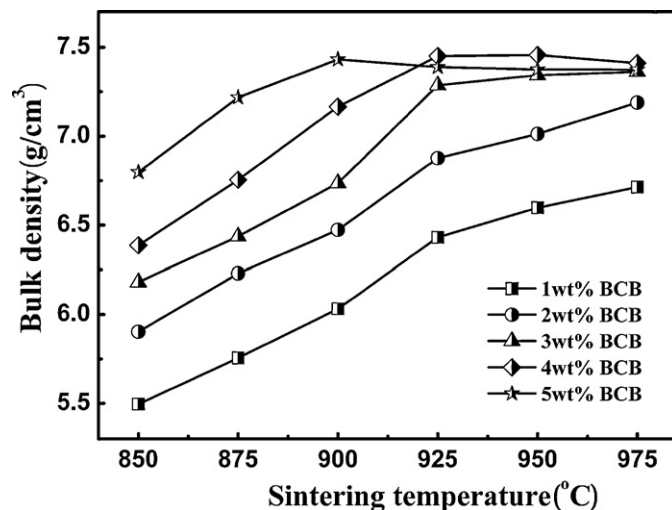


Fig. 3. Bulk densities of $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ ceramics with various BCB additions as a function of sintering temperatures.

Table 1Sintering temperatures, relative densities, and microwave dielectric properties of the $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ ceramics and BCB ceramic.

Material	Sintering temperature ($^{\circ}\text{C}$)	Relative density (%)	ϵ_r	$Q \times f$ (GHz)	τ_f (ppm/ $^{\circ}\text{C}$)	Ref
$\text{Ba}_4\text{LiTa}_3\text{O}_{12}$	1450	95.7	28	103 617	25	[15]
$\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ + 1 wt.% BCB	925	82.8	20.02	26 300	34.7	–
$\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ + 2 wt.% BCB	925	88.5	22.09	29 400	33.8	–
$\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ + 3 wt.% BCB	925	93.8	23.70	31 100	32.4	–
$\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ + 4 wt.% BCB	925	96	25.52	32 600	23.6	–
$\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ + 5 wt.% BCB	925	95.1	25.69	30 800	22.5	–
BCB	810	96	7.4	50 000	–32	[16]

they increase with increasing BCB content and the saturated value ($\sim 7.46 \text{ g/cm}^3$) which are equivalent to a relative density of about 96% is obtained for samples with 4 wt.% of BCB sintered at 925°C for 2 h. Above this temperature a slight decrease is observed, which should be attributed to the BCB volatilization and decomposition. Therefore, for $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ ceramics with 4 wt.% of BCB, 925°C is regarded as the optimum sintering temperature because of the higher relative density. Compared with the pure $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ samples (summarized in Table 1 [17,18]), it is proposed that BCB

effectively lowers sintering temperature and improves the densification of $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ ceramic. This may be ascribed to the low melting temperature ($\sim 850^{\circ}\text{C}$) of BCB. When sintered above 850°C , BCB exists as a liquid phase and assists in the densification of the ceramics.

Microstructures of BCB added $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ ceramics sintered at 925°C for 2 h are illustrated in Fig. 4(b)–(f). When 1 wt.% of BCB is added, the amount of the liquid phase is insufficient for densification of the $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ ceramics and a porous microstructure

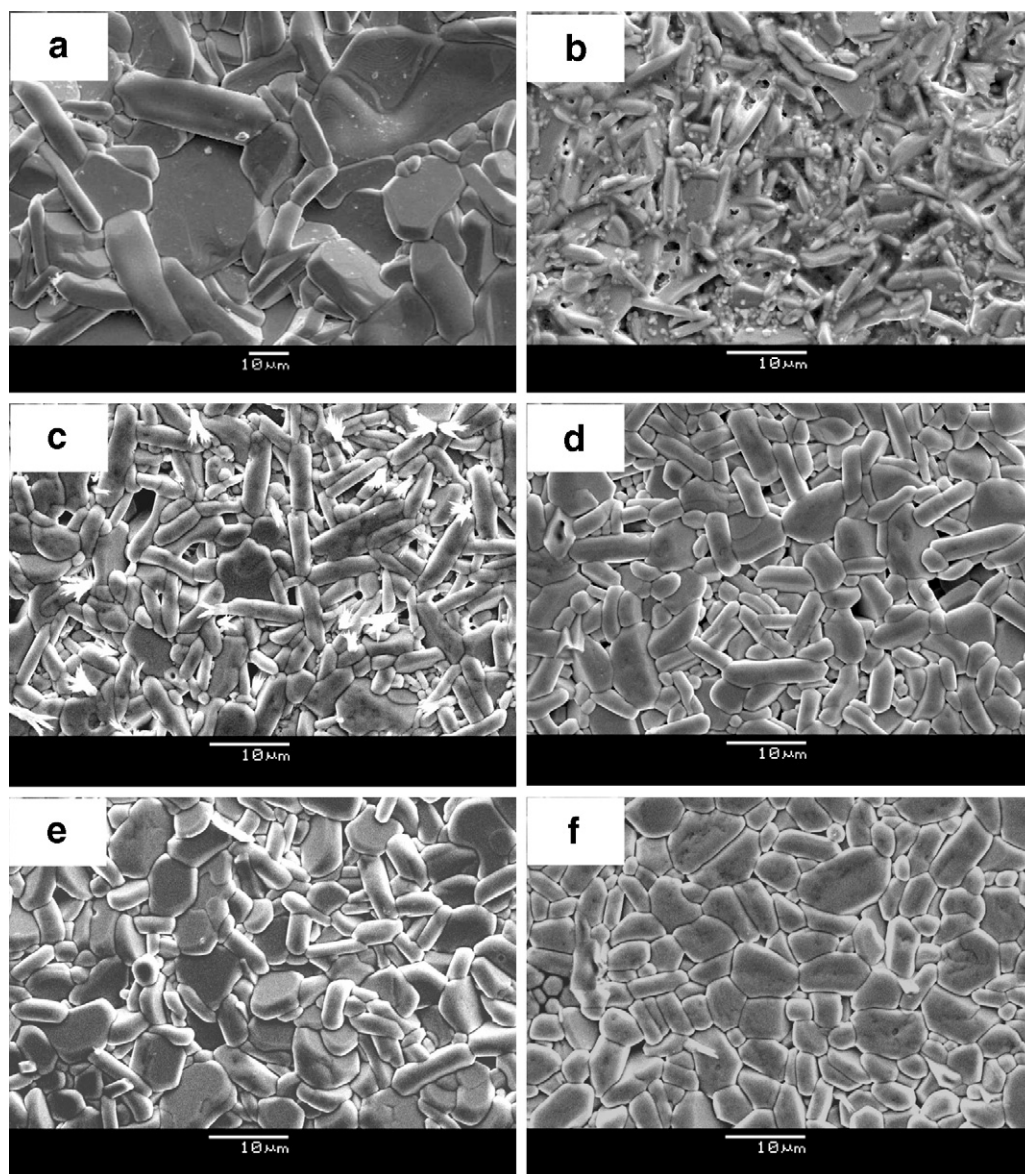


Fig. 4. Scanning electron micrographs of the $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ samples added with different amounts of BCB sintered at 925°C : (a) pure, sintered at 1450°C , (b) 1 wt.%, (c) 2 wt.%, (d) 3 wt.%, (e) 4 wt.%, (f) 5 wt.%.

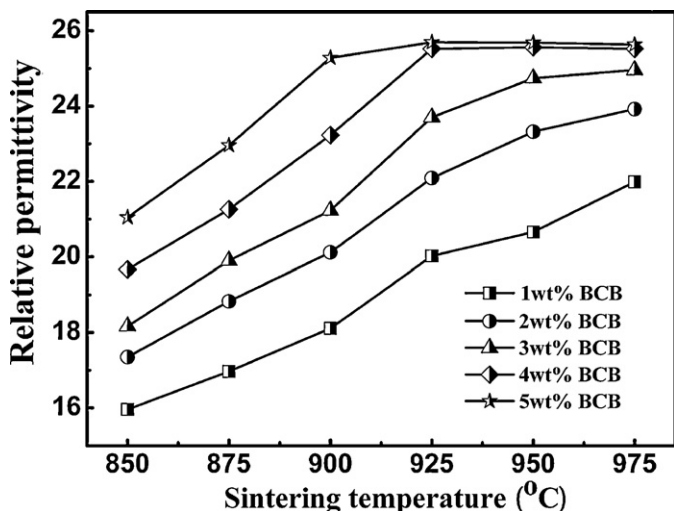


Fig. 5. The relative permittivity of Ba₄LiTa₃O₁₂ ceramics with BCB additions as a function of sintering temperature.

is obtained, as shown in Fig. 4(b). The microstructure becomes denser with increasing BCB contents and the Ba₄LiTa₃O₁₂ ceramics added with 4 wt.% of BCB exhibit the densest microstructure, as shown in Fig. 4(e). Compared with the pure Ba₄LiTa₃O₁₂ ceramics (as shown in Fig. 4(a)), the grain size of the specimens with BCB addition is also much smaller than that of pure Ba₄LiTa₃O₁₂ ceramics. However, further increasing BCB content results in pores in the Ba₄LiTa₃O₁₂ ceramics, which is in accordance with the decrease of bulk densities.

Fig. 5 shows the variation of relative permittivity as a function of sintering temperature for the samples with x wt.% ($x = 1-5$) BCB additions. The permittivities of samples with $x = 1$ and 2 increase rapidly with the increase of sintering temperature due to the increase of relative density. For the samples with $x = 3-5$, the permittivities initially increase with sintering temperature up to 925 °C, and then keep almost constant with further increasing sintering temperature. Generally, the relative densities of the sintered ceramics determine, to some extent, the relative permittivity of the sintered ceramics, due to the low relative permittivity of pores (~ 1.0). In addition, the relative permittivity increases as the BCB content increases even though BCB is reported to have a small ϵ_r (~ 7.4). The relative permittivity changes in our specimens are not very well in accordance with logarithmic rule, which is confirmed by a comparison of experimental and calculated (considering and not considering the effect of pores on relative permittivity) values. Besides, it is noted that the saturated relative permittivity is lower than that of pure compound ($\epsilon_r \sim 28$), which is in agreement with the report of Santha and Sebastian [23].

The $Q_u \times f$ of Ba₄LiTa₃O₁₂ ceramics with BCB additions as a function of sintering temperature is shown in Fig. 6. The $Q_u \times f$ first increases with increasing BCB addition and density. As the sintering temperature increases to 925 °C, the maximum $Q_u \times f$ of 32,600 is obtained for the specimen with 4 wt.% of BCB. Thereafter, the $Q_u \times f$ slightly decreases as the sintering temperature increases. Generally, the $Q_u \times f$ includes not only intrinsic losses that are mainly caused by the lattice vibration modes, but also extrinsic losses dominated by densification or porosity, grain size, and oxygen vacancies, etc.

The τ_f of the low-firing Ba₄LiTa₃O₁₂ ceramics sintered at 925 °C for 2 h as a function of BCB content is shown in Fig. 7. The temperature coefficient of resonant frequency significantly decreases from 34.7 to 22.5 ppm/°C with increasing BCB content, though the τ_f of the 1–3 wt.% BCB-added ceramics are higher than the pure ceramics, which is deeply related to that low densities of the ceramics

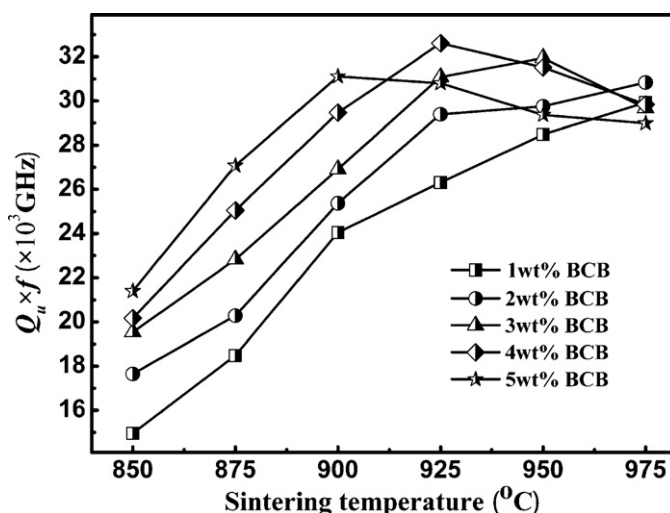


Fig. 6. The $Q_u \times f$ of Ba₄LiTa₃O₁₂ ceramics with BCB additions as a function of sintering temperature.

lead the wide drifts in the resonant peak frequency in the temperature range 25–85 °C [24]. It is reported that the τ_f can be tuned by formation of solid solution or mixtures of dielectrics with opposite τ_f . According to the previous report, Ba₄LiTa₃O₁₂ and BCB exhibit opposite τ_f (28 ppm/°C for the former and –32 ppm/°C for the latter), so the addition of BCB could effectively improve τ_f of Ba₄LiTa₃O₁₂ ceramics.

Ag is generally used as the electrode in LTCC devices because of its high conductivity and low cost. Thus, it is important to study the reaction between Ag electrode and BCB-added Ba₄LiTa₃O₁₂ ceramics. In order to evaluate the chemical compatibility of BCB-added Ba₄LiTa₃O₁₂ ceramic with silver, the mixtures of 5 wt.% of BCB-added Ba₄LiTa₃O₁₂ powders with 20 wt.% Ag (>99.95%, 1.0 μm , Aladdin Reagent Co. Ltd., Shanghai, China) powders and 4 wt.% BCB added Ba₄LiTa₃O₁₂/Ag sample are cofired and analyzed to detect interactions between the low-fired samples and electrodes. The X-ray powder diffraction pattern (XRPD) and the backscattered electron image analysis and EDS analysis of 4 wt.% BCB added Ba₄LiTa₃O₁₂/Ag sample cofired at 925 °C for 6 h are also shown in Fig. 8. Since only peaks for the Ba₄LiTa₃O₁₂ ceramics and Ag are

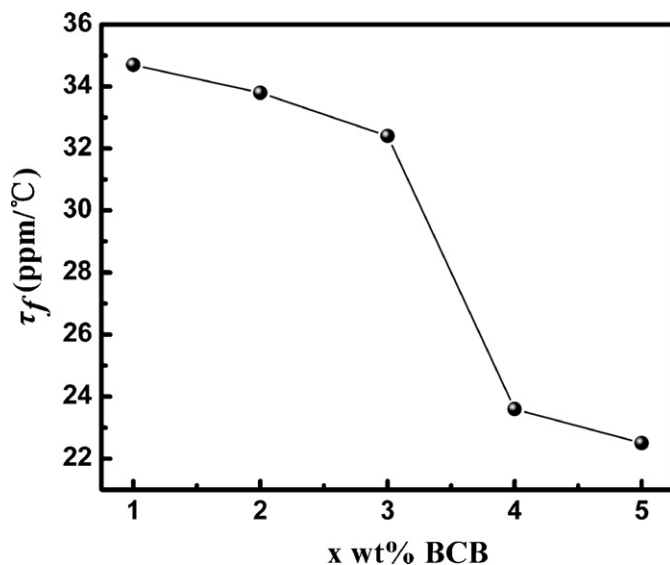


Fig. 7. The τ_f of the low-firing Ba₄LiTa₃O₁₂ ceramics sintered at 925 °C for 2 h as a function of BCB content.

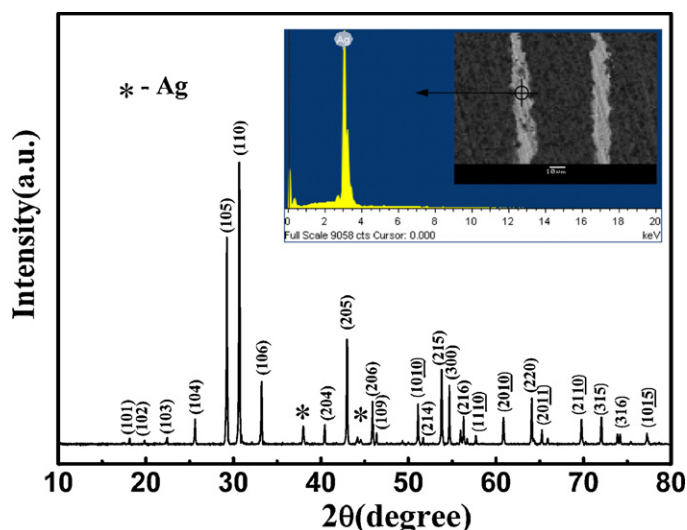


Fig. 8. XRD patterns of the 5 wt.% BCB-added $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ ceramics sintered with 20 wt.% Ag metal at 925 °C for 6 h. Inset shows a backscattered electron image and EDS analysis of 4 wt.% BCB added $\text{Ba}_4\text{LiTa}_3\text{O}_{12}/\text{Ag}$ sample cofired at 925 °C for 6 h.

observed without any peaks for the second phase, and the backscattered electron image analysis and EDS analysis of 4 wt.% BCB added $\text{Ba}_4\text{LiTa}_3\text{O}_{12}/\text{Ag}$ sample cofired at 925 °C for 6 h reveal no chemical reaction to form new phases after firing, it is considered that the $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ compound has a chemical compatibility with silver.

4. Conclusions

The effects of BCB addition on phase transition, the microwave dielectric properties and the microstructure of the $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ ceramic are investigated. A phase transition from cubic to hexagonal $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ is observed in the range of 1300–1350 °C. It is noted that hexagonal $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ obtained at 1350 °C could be stabilized at considerably lower temperature (~925 °C) with BCB added. The small additions of BCB to $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ ceramics enable a reduction in sintering temperature from 1450 to 925 °C, and the temperature coefficient of resonant frequency (τ_f) could be effec-

tively improved. The $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ ceramics sintered with 4 wt.% BCB addition at 925 °C, have ϵ_r of 25.5, $Q_u \times f$ of 32,600 GHz and τ_f of 23.6 ppm/°C. In addition, BCB-added $\text{Ba}_4\text{LiTa}_3\text{O}_{12}$ ceramics show a good compatibility with the Ag electrode at 925 °C, which is a promising candidate material for LTCC application.

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