Phase transformation and microwave dielectric properties of BiPO$_4$ ceramics

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Abstract Monazite-type compounds, BiPO$_4$ polymorphs were prepared by the solid-state reaction method. The phase transformation and microwave dielectric properties of sintered ceramics were investigated using the X-ray powder diffraction (XRD) and a network analyzer, respectively. The low-temperature phase of BiPO$_4$ has monoclinic structure, and was transformed into the high-temperature phase with a slight distortion of monoclinic when it is heated above 600°C. The effect of the transformation on the microwave dielectric properties was examined. It was found that the dielectric properties of each phase were significantly different. In particular, the high-temperature phase sintered at 950°C has good microwave dielectric properties; the relative dielectric constant (ε_r) = 22, the quality factor ($Q \times f$) = 32,500 GHz and the temperature coefficient of resonant frequency (τ_f) = −79 ppm/ °C.

Keywords Bismuth phosphate · Polymorphs · Microwave dielectric properties · Phase transformation

1 Introduction

Bismuth phosphate with Bi/P ratio of 1:1 has two polymorphic phases [1]. The most stable phase of BiPO$_4$ is the monazite-type structure (LBP, low-temperature monoclinic phase). The other phase (HBP, high-temperature monoclinic phase) is obtained by heating LBP at high temperature. The crystal structure of BiPO$_4$ has been studied by many researchers [2, 3]. X-ray diffraction studies of BiPO$_4$ showed that the HBP has a slight distorted structure of LBP. The crystal structure parameters of the two crystal phases from the previous works are listed in Table 1. The nature of the phase transformation of BiPO$_4$ is not clear at present. According to Mooney-Slater, the transformation from LBP to HBP is reversible and spontaneous at room temperature. However, Masse and Durif reported this transformation is first order and irreversible.

On the other hand, bismuth phosphates are reported to be the good catalysts in different reactions. Bismuth phosphate, pure or doped with molybdenum, catalyzes the synthesis of butyraldehyde from 1-butanol and nitriles from formamides [4, 5]. The bismuth phosphate has also been studied as catalyst of the synthesis of benzene and acrolein form propylene [6, 7].

Apart form the investigation of crystal structure and catalytic characterization, to the best of our knowledge, the microwave dielectric properties of BiPO$_4$ have not been reported, yet. In our present study, the phase transformation and the microwave dielectric properties of BiPO$_4$ were investigated.

2 Experimental procedure

BiPO$_4$ powders were prepared using conventional solid-state reaction method. Bi$_2$O$_3$ (99.9%, High purity Cemical, Japan) and (NH$_4$)$_2$HPO$_4$ (99%, Junsei, Japan) were used as raw materials. Bi$_2$O$_3$ and (NH$_4$)$_2$HPO$_4$ were mixed using a ball-mill for 24 h and the mixture was calcined at 600°C and

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Table 1 The crystal structure parameters of BiPO₄ polymorphs

BiPO₄	Unit cell parameter					Space group	Z	$\rho_{th.}$ (g/cm³)
	a(Å)	b(Å)	C(Å)	β(°)	V_{cell}(Å³)			
LBP	6.7626	6.9516	6.4822	103.736	296.02	P2₁/n	4	6.82
HBP	4.871	7.073	4.709	96.24	161.28	P2₁/m	2	6.22

850°C for 2 h to obtain low-temperature phase (LBP) and high temperature phase (HBP), respectively. The calcined powders were milled again, uniaxially pressed into pellets at a pressure of 1000 kg/cm². The pellets were sintered at 950–1100°C for 2 h with a heating rate of 5°C/min.

The quantitative analysis of transformed phase in the calcined and sintered samples was identified by X-ray powder diffraction (XRD: Model M18XHF, MacScience Instruments, Japan). The bulk density of the sintered specimens was evaluated by Archimedes' method. The microwave dielectric properties of the sintered samples were measured using a network analyzer (Model HP8720C, Hewlett Packard, USA) in the frequency range of 8–12 GHz. The quality factor ($Q \times f$) was measured by the transmission cavity method using a Cu cavity and a Teflon supporter [8]. The dielectric constant (ε_r) was measured using the post resonator method [9] and the temperature coefficient of the resonant frequency (τ_f) was measured using an Invar cavity in the temperature range of 20 to 70°C [10].

3 Results and discussion

3.1 Phase transformation and sintering of BiPO₄

Figure 1 shows X-ray powder diffraction (XRD) patterns of BiPO₄ calcined at 600–900°C for 2 h. It shows that the powder calcined at 600°C exhibits only the low-temperature phase [LBP]. With increasing the calcination temperature, the reflection of a high-temperature phase [HBP] was detected. A single phase of HBP was obtained when it was calcined at 850°C. However, above 900°C, the reflection of LBP was appeared again and even at the prolonged heating (∼48 h) LBP still remained.

The LBP and HBP were sintered at various temperatures to obtain dense sintered samples. The XRD patterns of the LBP sintered at 600–1100°C were shown in Fig. 2(a). It can be seen that a small fraction of the LBP was transformed into the HBP when it is sintered at 700°C. And when the LBP was sintered at 950°C, a large fraction of LBP was transformed into HBP. Therefore, other sintering method was needed to obtain a dense single phase of LBP. To obtain a dense sintered sample of the LBP, the conventional hot pressing method was used at 600°C for 2 h. However, the sintering density was not increased even increasing the pressure. The XRD patterns of the HBP sintered at 900–1100°C were shown in Fig. 2(b).
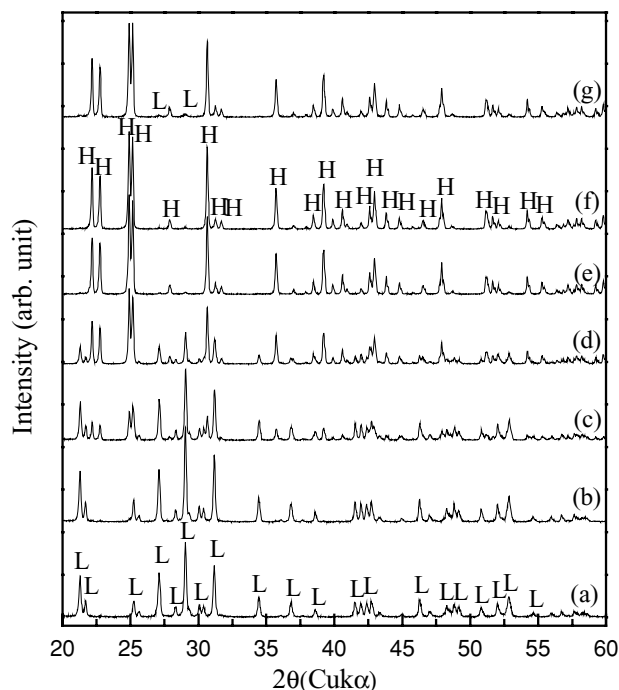
Fig. 1 The XRD patterns of BiPO₄ calcined at (a) 600°C, (b) 650°C, (c) 700°C, (d) 750°C, (e) 800°C, (f) 850°C, and (g) 900°C for 2 h. (H: HBP, L: LBP)
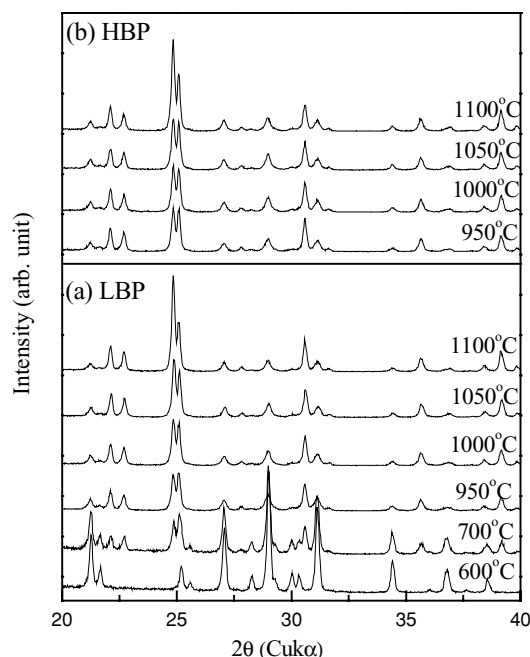
Fig. 2 The XRD patterns of LBP and HBP samples sintered at various temperatures
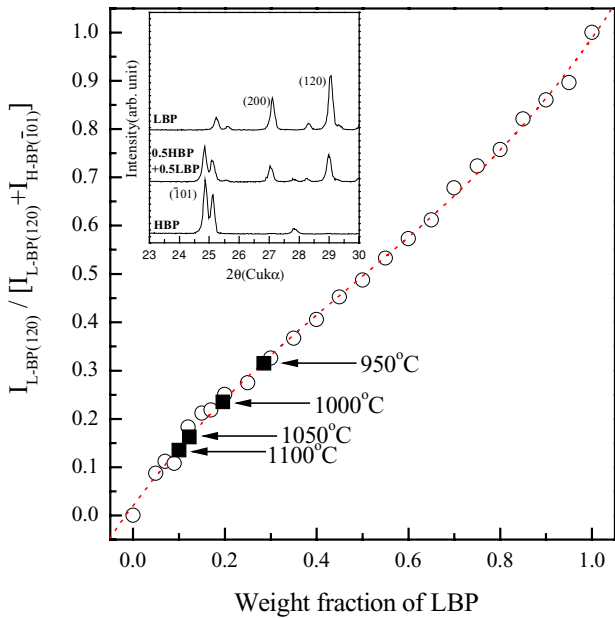
Fig. 3 The relative integrated intensities of LBP (120) and HBP ($\bar{1}$01) of the mixture and sintered samples. The inset shows a magnified view of XRD patterns for LBP, HBP and their mixture of weight ratio 1:1

Table 2 The transformed weight fraction of LBP and HBP samples sintered at various temperatures

Process parameters		Weight fraction	
Calcined powder	Sintering temperature (°C)	LBP	HBP
LBP	950	0.34	0.66
	1000	0.25	0.75
	1050	0.24	0.76
	1100	0.10	0.90
HBP	950	0.29	0.71
	1000	0.20	0.80
	1050	0.12	0.88
	1100	0.10	0.90

were about ~95%, while those of LBP samples were 90–92%. The HBP samples had more higher the sintered density than the LBP samples. Using the HBP samples, therefore, the microwave dielectric properties of $BiPO_4$ were examined as a function of weight fraction of LBP.
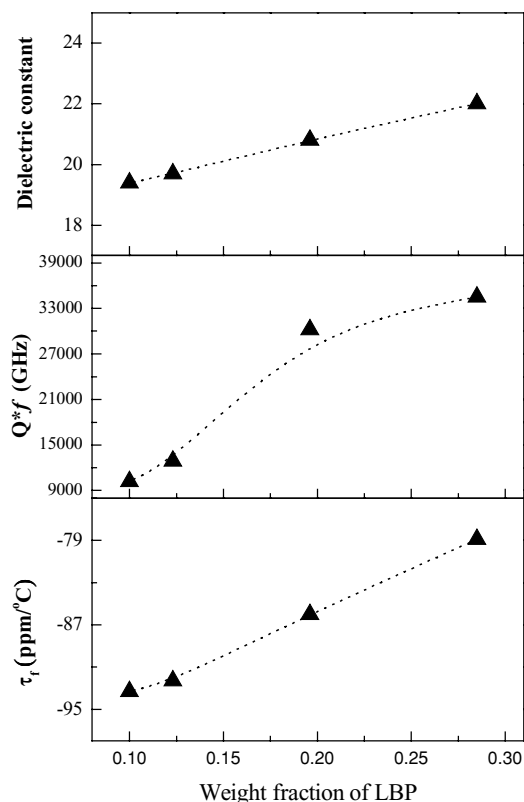
3.2 The microwave dielectric properties of $BiPO_4$

The microwave dielectric properties of HBP samples as a function of a weight fraction of LBP were illustrated in Fig. 5. As mentioned above, with increasing sintering temperature in HBP samples, the transformed weight fraction of LBP decreased from 0.29 to 0.10, while the relative density was not vary with sintering temperature.

The dielectric constant of the HBP samples sintered at 1100°C was 19.4 and tended to increase with decreasing sintering temperature. That is, the dielectric constant of the HBP sample was increased with increasing of the weight fraction of LBP.

A small fraction of HBP transformed into LBP when it was sintered at 950–1100°C. Consequently, when both the single phase of LBP and that of HBP were sintered at above 950°C, the mixed phases of LBP and HBP were observed.

A quantitative analysis based on the relative integrated intensities of the LBP and HBP mixtures was conducted for the calculation of the amount of each phase in sintered samples. The relative integrated intensities of LBP (120) and HBP ($\bar{1}$01) peaks for mixed samples were plotted as a function of LBP weight fraction in Fig. 3. The data points represented by the open circles in Fig. 3 were obtained from the known weight fractions of single phase LBP and HBP mixture. The inset shows a magnified view of XRD patterns for LBP, HBP and 0.5LBP-0.5HBP. We in turn obtained the transformed weight fraction of the HBP samples sintered at 950–1100°C from the relative integral intensities marked by arrows.

Also, the transformed weight fraction of sintered samples was given in Table 2, in detail. In the LBP sample sintered at 950°C, a 66 wt% LBP was transformed into the HBP. At the higher sintering temperature, the transformed weight percentage of HBP was increased. In case of HBP sample sintered at 950°C, a 29 wt% LBP was observed and the transformed weight fraction of LBP was decreased at the higher sintering temperature. However, no more decrease of LBP was observed, even at the elevated temperature and prolonged holding time.

Figure 4 shows the relative density of the LBP and HBP samples as a function of sintering temperature. The LBP samples had relatively lower sintered density than the HBP samples. The relative densities of all sintered HBP samples

Fig. 4 The relative density of the LBP and HBP samples as a function of the sintering temperature from 950 to 1100°C

Fig. 5 The microwave dielectric properties of the HBP samples, as a function of the transformed weight fraction of LBP

At microwave frequencies, the total dielectric polarizability is the sum of both ionic and electronic component. Here, both of the electronic and the ionic polarizability are related to the bonding character of the material. Shannon suggested that molecular polarizabilities of complex substances can be estimated by summing the polarizabilities of constituent ions [11]. Shannon's suggestion is expressed as

$$\alpha_D(ABO_4) = \alpha_D(A^{3+}) + \alpha_D(B^{5+}) + 4\alpha_D(O^{2-}) \qquad (1)$$

where α_D is polarizability. With the aid of estimated polarizability and the Clausius-Mosotti relation shown in Eq. (2), the mean static dielectric constants of $BiPO_4$ can be calculated.

$$\varepsilon_s = (3V_m + 8\pi\alpha_D)/(3V_m - 4\pi\alpha_D) \qquad (2)$$

where, V_m is molar volume. The calculated dielectric constants of LBP and HBP were shown in Table 3. The calculated dielectric constant of LBP was 22.2, which is higher than that of HBP (12.9). Therefore, the increasing tendency of dielectric constant of HBP samples as increasing the weight fraction of LBP is due to the high dielectric constant value of LBP.

Table 3 The calculated dielectric constant of $BiPO_4$ polymorphs from dielectric polarizability of ions

$BiPO_4$	V_m	α_D	$\varepsilon_{r(\text{calc})}$
LBP	73.54	15.38	22.2
HBP	80.695	15.38	12.9

The $Q \times f$ value of the HBP samples was increased from 10,200 to 34,500 GHz with increasing the weight fraction of LBP. It is well known that losses in microwave dielectrics consist of intrinsic and extrinsic losses. The intrinsic loss is related to the crystal structure and bonding character of the materials. And the extrinsic loss is mainly related to the defects, grain size and porosity, etc. [12]. According to Masse et al., the HBP has a slight distorted structure with the small rotated tetrahedra because of adopting a more symmetric arrangement. Since the HBP has a slight distorted structure, a lower Q value should be expected for HBP than the LBP. Thus, as a result of the lower Q value in the HBP, the $Q \times f$ value is seemed to decrease with increasing the weight fraction of HBP (the lower the weight fraction of LBP). And nonlinear increase of $Q \times f$ value with increasing LBP weight fraction is due to the effect of extrinsic factor such as the improvement of the sinterability."

In the mixture region, a linear compositional dependence of the τ_f value was reported by other studies [13, 14]. The τ_f value of HBP samples was negative and also increased linearly with increasing the weight fraction of LBP. The τ_f value of HBP sample sintered at 950°C was −78.9 ppm/°C.

4 Conclusion

The phase transformation and microwave dielectric properties of $BiPO_4$ ceramics were examined. The low-temperature phase of $BiPO_4$ was transformed into the high-temperature phase when it is heated above 600°C. When the LBP sample was sintered at 950°C, a large fraction of LBP was transformed into the HBP, while a small fraction of HBP was transformed into LBP in HBP samples.

From a quantitative analysis based on the relative integrated intensities of LBP and HBP mixture, the amount of transformed phase was calculated and the dielectric properties of $BiPO_4$ ceramics with varying the LBP phase fraction were investigated. With increasing sintering temperature of the HBP sample, the transformed weight fraction of the LBP was varied from 29 to 10. For the increased weight fraction of the LBP, the ε_r value was increased, which is due to the higher dielectric constant of the LBP than that of HBP. The $Q \times f$ value was affected by the structural distortion of the HBP. And the HBP sample sintered at 950°C had a 29 weight fraction of LBP and microwave dielectric properties: $\varepsilon_r = 22.0$, $Q \times f = 32,500$ GHz and $\tau_f = -79$ ppm/°C.

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