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Journal of the European Ceramic Society 24 (2004) 1761–1764
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Microwave dielectric properties of low-temperature sintered $Ca[(Li_{1/3}Nb_{2/3}),Ti]O_{3-\delta}$ ceramics

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Abstract

$Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ($0.5 \geqslant x \geqslant 0$) solid solutions with additives were fabricated to develop a new microwave resonator with a low sintering temperature. With the addition of 2.0 wt.% B_2O_3, the maximum densities of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ($0.1 \geqslant x \geqslant 0.3$) ceramics were obtained after sintering at 1000 °C. The $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics exhibit an orthorhombic phase with the 1:2 ordered structure. As the x composition increases from 0 to 0.5, the dielectric constant, ε, increases from 30 to 60, the quality factor, $Q \times f$, decreases from 30 000 to 14 900 *GHz*, and the temperature coefficient of resonant frequency, τ_f, in creases from −17 to 83.6 ppm/°C. Typically, at $x = 0.2$, the specimen shows the optimum dielectric properties: $\varepsilon = 40$, $Q \times f = 20\,500$ GHz (at 8 GHz), and $\tau_f = 4.7$ ppm/°C. Furthermore, the addition of both B_2O_3 and Bi_2O_3 was found to be effective in reducing the sintering temperature of $Ca[(Li_{1/3}Nb_{2/3})_{0.7}Ti_{0.3}]O_{3-\delta}$ ceramics to 920 °C without a significant degradation of the microwave dielectric properties.

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Keywords: Dielectric properties; Niobates; Perovskites; Powder–solid state reaction; Sintering

1. Introduction

The rapid growth of the wireless communication industry has created a high demand for microwave ceramics components. In addition to the requirements of material with a high dielectric constant, ε, *a* high quality factor, $Q \times f$ value, and a zero temperature coefficient of resonant frequency, τ_f, the lower cost and smaller size of the individual components are the crucial requirements for commercial applications. As a consequence, much attention has been paid to developing low temperature-cofired ceramics (LTCC) for microwave applications, because of the design and functional benefits realized upon the miniaturization of multilayer devices with a high electrical performance using the highly conductive internal-electrode metals such as silver, copper, and their alloys. The LTCC materials will contribute much to the integration of electronic components.[1] Generally, most of the commercial dielectric materials used for high-frequency applications show the high quality factor and high dielectric constant, but they have a high sintering temperatures (>1300 °C). Thus, there is a considerable interest in the development of new materials with low sintering temperatures. This led to searching for ceramics with low melting points, such as $BiNb(Ta)O_4$, TiO_2–TeO_2, $ZnTiO_3$.[2–4] Recently, Li-based $Ca(Li_{1/3}Nb_{2/3})O_{3\text{-d}}$ ceramics have received much attention because of the good dielectric properties and low sintering temperature, ~1150 °C.[5] However, the sintering temperature of this material is still too high to use Ag or Cu as an internal electrode in multilayer devices. In addition, The $Ca(Li_{1/3}Nb_{2/3})O_{3-\delta}$ ceramics need to be sintered in a P_t box to control the volatility of Li_2O at such an elevated temperature. Our previous study has shown that the additions of 0.5–4 wt.% B_2O_3 were effective in reducing the sintering temperature of the $Ca(Li_{1/3}Nb_{2/3})O_{3-\delta}$ ceramics from 1150 to 1000 °C without degradation of the microwave dielectric properties.[6] This approach demonstrated that the $Ca(Li_{1/3}Nb_{2/3})O_{3-\delta}$ ceramics might have potential applications for co-fired circuit components. In this paper, the τ_f values of the $Ca(Li_{1/3}Nb_{2/3})O_{3-\delta}$ ceramics (−17 ppm/°C) were improved to that close to 0 ppm/°C by the investigation of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ($0.5 \geqslant x \geqslant 0$) solid solutions. In addition, mixtures of B_2O_3 and Bi_2O_3

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0955-2219/$ - see front matter © 2003 Published by Elsevier Ltd.
doi:10.1016/S0955-2219(03)00549-1

were added in order to prepare $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics at the temperature close to 900 °C.

2. Experimental

High purity (⩾99.9%) oxide powders of $CaCO_3$, Li_2CO_3, TiO_2, Nb_2O_5 were used as the starting powders. The powders were weighed according to the compositions of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ $(0.5 \geqslant x \geqslant 0)$ ceramics, and then milled with ZrO_2 balls for 24 h in ethanol. Mixtures were dried and calcined at 900 °C for 2 h. The calcined powders were re-milled for 24 h again with the additions of B_2O_3 and Bi_2O_3 powders, and then the powders were pressed into pellets with 10 mm in diameter and 5 mm thickness under 1500 kg/cm^2 isostatically. These pellets were subsequently sintered from 900 to 1100 °C for 4 h in air. The crystalline phases were analyzed by X-ray powder diffraction (XRPD) using Cu-K_α radiation of 2θ from 10 to 70°. The microstructure of the etched ceramics surfaces was observed by using scanning electron microscope (SEM). These specimens were mechanically polished, and then, etched at 960 °C for 10 min. The apparent density, (ρ) of the ceramics was measured by the Archimede method. The theoretical density (ρ_{tho}) of the ceramics was obtained using the unit cell volume from the XRD data. The measurement of dielectric constant (ε) and unloaded quality factor (Q) of $Ca(Li_{1/3}Nb_{2/3})O_{3-\delta}$ ceramics were performed on TE_{011} mode at the resonant frequency from 7 to 10 GHz by using the Hakki-Coleman's dielectric resonator method. The temperature coefficient of resonator frequency (τ_f) was calculated at the range between 20 and 80 °C.

3. Results and discussion

3.1. B_2O_3-doped $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ $(0.5 \geqslant x \geqslant 0)$

The apparent densities (ρ) and the relative density (ρ/ρ_{tho}) of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics with the addition of 2.0 wt.%B_2O_3 as a function of sintering temperature are shown in Fig. 1. From Fig. 1, the relative density of the ceramics samples sintered at 1000 °C for 4 h ranged between 97.1% and 98.2%, except the samples with $x=0.5$. For $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics with $0.1 \leqslant x \leqslant 0.3$, the ρ values have the highest values at 1000 °C, and then decrease slightly with an increase of the sintering temperatures up to 1100 °C. A slight decrease of ρ values with the sintering temperatures is considered to be due to a volatility of Li_2O at the elevated temperatures and the formation of the pores in the ceramics. Therefore, the $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ *ceramics* with $0.1 \leqslant x \leqslant 0.3$ can be well sintered at 1000 °C for 4 h. For the samples with $x=0.5$, ρ values increase gradually with an increase of sintering temperature up to 1100 °C, indicating that this composition has a higher sintering temperature >1100 °C. The SEM microstructures of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics sintered at 1000 °C, 4 h (Fig. 2) show a dense grain structure. The grain size of the present materials varies with the×composition. The grain size of specimens with $x=0.2$ and 0.3 is about 1–1.5 μm, which is larger than that of specimens with $x=0.05$ and 0.5, only 0.2–0.5 μm. The reason for the grain growth of Ti-bearing ceramics may be related to the improvement of the sinterability. However, because of the higher sintering temperature of $CaTiO_3$, as a substitution of Ti increases up to $x=0.5$, sinterability is suppressed and the grain size is decreased [shown in Figs. 1 and 2 (d)].

XRD patterns of sintered $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ $(0.05 \leqslant x \leqslant 0.5)$ ceramics with the different × compositions are shown in Fig. 3. All of the XRPD patterns can be identified as a $CaTiO_3$-type orthorhombic structure and no secondary phase is appeared. This demonstrates that the $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics are complete solid solutions over the entire range of x composition. The systematic peak shifts of 2θ from a low angle to a high angle with the increase in×composition indicate a decrease of lattice volume due to the substitution of a smaller ion Ti^{4+} (0.0605 nm, coordination number CN=6) for $(Li_{1/3}Nb_{2/3})^{3.87+}$ (CN=6) with an average ionic radii of 0.068 nm.[7] In addition, the weak peaks at 2θ = 13.1 and 18.67 °C for the specimen with $x=0.1$ can be attributed to the superlattice diffractions of 1:2 order (Li/Nb) in the $Ca(Li_{1/3}Nb_{2/3})O_{3-\delta}$ compound. Furthermore, the intensity of the superlattice diffractions decreases with an increase of x composition, and the peaks of superlattice diffractions disappear for the $Ca[(Li_{1/3}Nb_{2/3})_{0.5}Ti_{0.5}]O_{3-\delta}$ ($x=0.5$) shown in Fig. 3(e).

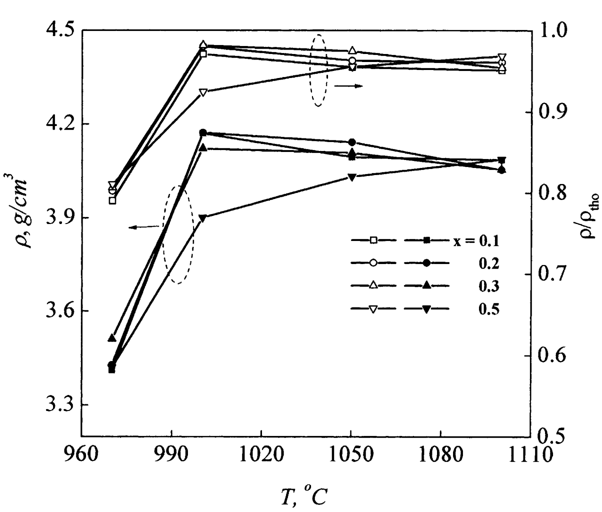

Fig. 1. Apparent densities (ρ) and relative density (ρ/ρ_{tho}) for $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ($x=0.1$, 0.2, 0.3, 0.5) ceramics doped with 2.0 wt.% B_2O_3 as a function of sintering temperatures.

The microwave dielectric properties of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics as a function of x composition are shown in Fig. 4. As the x composition changes from 0 to 0.5, the ε values increase linearly from 30 to 60, the $Q\times f$ values decrease from 30 000 to 14 900 GHz, and the τ_f values increase from −17 to 83.6 ppm/°C. At $x=0.2$, the specimen shows the optimum dielectric properties: $Q\times f=20\,500$ GHz, $\varepsilon=40$, and $\tau_f=4.7$ ppm/°C. These data are comparable to those of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics with $x=0.2$ sintered at 1150 °C in a *Pt* box.[6] Therefore, it was believed that 2.0 wt.% B_2O_3 was effective in reducing the sintering temperature of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ $(0.3 \geqslant x \geqslant 0)$ ceramics from 1150 to 1000 °C without the degradation of microwave dielectric properties. This good result is related to the enhancement of the apparent density of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics at the low temperatures obtained by a liquid sintering process.[6]

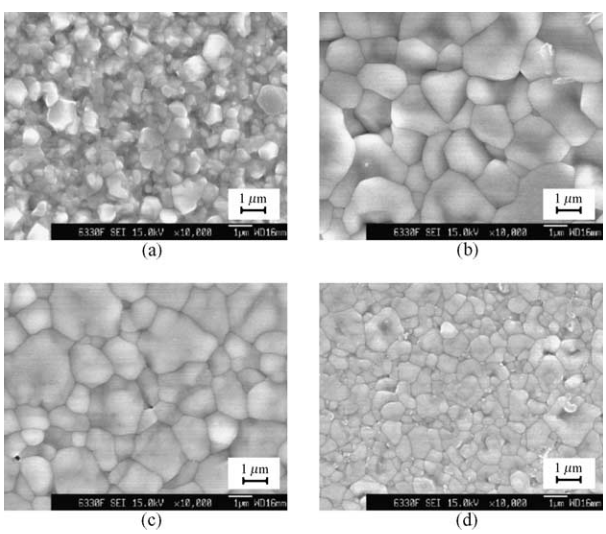

Fig. 2. SEM micrographs of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics doped with 2.0 wt.% B_2O_3 and sintered at 1000 °C for 4 h, (a) $x=0.05$, (b) 0.2, (c) 0.3, (d) 0.5.

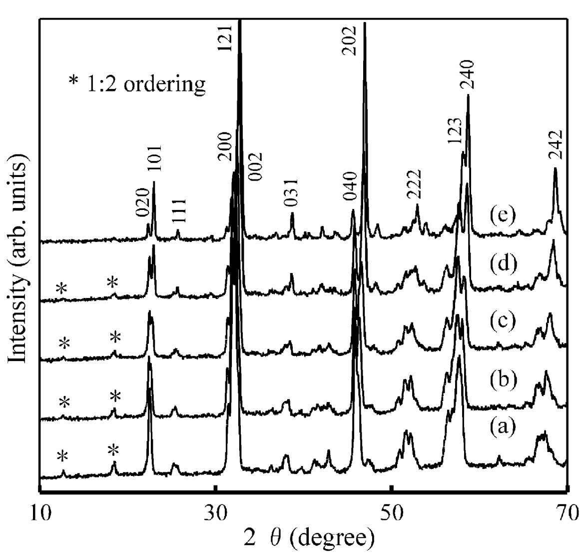

Fig. 3. XRD spectra for $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics doped with 2.0 wt.% B_2O_3 and sintered at 1000 °C for 4 h, (a) $x=0.1$, (b) 0.15, (c) 0.2, (d) 0.3, (e) 0.5.

3.2. B_2O_3 and Bi_2O_3-doped $Ca[(Li_{1/3}Nb_{2/3})_{0.7}Ti_{0.3}]O_{3-\delta}$

Even though $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}(x=0.2)$ shows excellent microwave dielectric properties, this ceramics can not be co-fired with the Ag electrode, which requires a low sintering temperature ~900 °C. In this section, the mixtures of B_2O_3 and Bi_2O_3 were added in order to sinter the ceramics at the temperature close to 900 °C. Regarding the sinterability and the τ_f values of the $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ solid solutions, the composition with $x=0.3$ was chosen as the basic materials. In addition to the consideration of the low melting points of Bi_2O_3 (825 °C) and B_2O_3 (462 °C), the additives were selected because a series of eutectic phases with a low melting point might be formed between Bi_2O_3 and B_2O_3.[8]

Table 1 shows the density and microwave dielectric properties of $Ca[(Li_{1/3}Nb_{2/3})_{0.7}Ti_{0.3}]O_{3-\delta}$ ceramics doped with the mixtures of 2.0 wt.% B_2O_3 and Bi_2O_3 (1.0–6.0 wt.%) and sintered at the temperatures from 920 to 980 °C. It was found that the mixtures of B_2O_3 and Bi_2O_3 were effective in reducing the sintering temperatures close to 900 °C. The relative density above 98% was obtained for the specimens doped with a

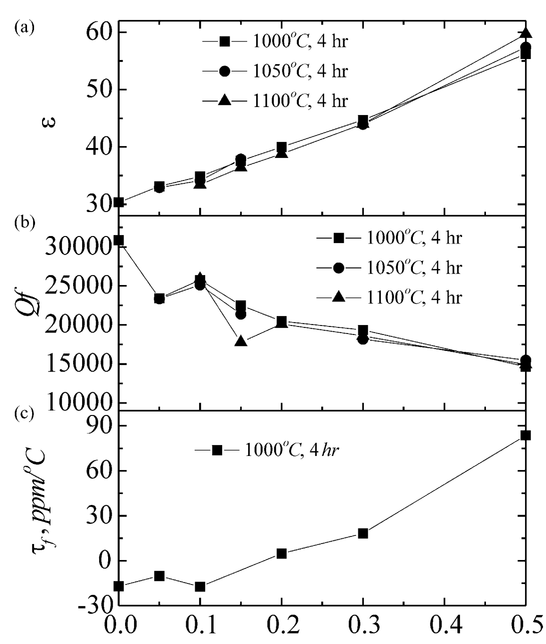

Fig. 4. The dielectric constant, ϵ (a), quality factor, $Q\times f$ (b), and temperature coefficient of resonant frequency, τ_f (c) of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ $(0.0 \leqslant x \leqslant 0.5)$ ceramics doped with 2.0 wt.% B_2O_3 as a function of composition x.

Table 1
The apparent density and microwave dielectric properties of $Ca[(Li_{1/3}Nb_{2/3})_{0.7}Ti_{0.3}]O_{3-\delta}$ ceramics doped with a combination of 2.0 wt.% B_2O_3 and Bi_2O_3 (1.0–6.0 wt.%) and sintered at temperatures from 920 to 980 °C

Bi_2O_3 (wt.%)	T (°C)	ρ (g/cm^3)	f_0 (GHz)	Q	ε	$Q\times f$ (GHz)	τ_f (ppm/°C)
1.0	920	3.321	8.73	414	31.4	3600	
	940	3.758	7.839	510	39.5	4000	
	960	4.021	7.637	2167	43.9	16 600	35.5
	980	4.116	7.642	2114	45.3	16 200	
3.0	940	4.035	7.73	1667	43.1	12 900	53.7
	980	4.29	7.703	1674	41	12 900	
6.0	920	4.211	7.684	1380	43.1	10 600	10.7
	940	4.215	7.682	1529	43.4	11 700	
	960	4.227	7.738	1543	44.4	12 000	
	980	4.205	7.631	1323	43.4	10 100	

combination of 2.0 wt.% B_2O_3 and 6.0 wt.% Bi_2O_3 and sintered at 920 °C for 4 h. At the optimum sintering temperatures for each composition, the slight increase of ρ values with an increase of Bi_2O_3 content is due to some of Bi^{3+} ions with higher weight remaining in the ceramics, forming a solid solution or secondary phase. The mixtures of B_2O_3 and Bi_2O_3 have no detrimental effect on the dielectric constant as listed in Table 1. However, a minor degradation of the quality factor $Q\times f$ on Bi_2O_3 addition was observed: ~14% per 1.0 wt.% Bi_2O_3, 31% per 3.0 wt.% Bi_2O_3, and ~35% per 6.0 wt.% Bi_2O_3, respectively. In addition, the τ_f values could be modified with the mixtures of B_2O_3 and Bi_2O_3. With the addition of 2.0 wt.% B_2O_3 and 6.0 wt.% Bi_2O_3, the $Ca[(Li_{1/3}Nb_{2/3})_{0.7}Ti_{0.3}]O_{3-\delta}$ ceramics show the superior dielectric properties: $\varepsilon = 43.1$, $Q\times f = 10600$ *GHz*, and $\tau_f = 10.7$ ppm/°C after sintering at a temperature as low as 920 °C. The microwave dielectric properties and sinteriability of the studied ceramics are comparable to those of V_2O_5–CuO-doped $BiNbO_4$ compound,[3] indicating that Li-based ceramics have potential applications as co-fired circuit components.

4. Conclusions

1. The nonstochiometric $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ $(0.5 \geqslant x \geqslant 0)$ solid solutions exhibited an orthorhombic phase over an entire x composition range. With the addition of 2.0 wt.% B_2O_3, the sintering temperatures of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ $(0.3 \geqslant x \geqslant 0)$ ceramics were reduced from 1150 to 1000 °C without the degradation of the microwave dielectric properties. The temperature coefficient of resonant frequency, τ_f, increased from −17 to 83.6 ppm/°C as the x composition increased from 0 to 0.5. At $x = 0.2$, the ceramics sintered at 1000 °C possesses a dielectric constant $\varepsilon \sim 40$, a $Q\times f$ value ~20 500 GHz (at 8 GHz), and a τ_f value ~4.7 ppm/°C.
2. By the combination of 2.0 wt.% B_2O_3 and 6.0 wt.% Bi_2O_3, a new kind of LTTC materials with the superior dielectric properties of $\varepsilon = 43.1$, $Q\times f = 10\,600$ *GHz*, and $\tau_f = 10.7$ ppm/°C was obtained in $Ca[(Li_{1/3}Nb_{2/3})_{0.7}Ti_{0.3}]O_{3-\delta}$ ceramics after sintering at a temperature as low as 920 °C.

References

1. Kagata, H., Inoue, T., Kameyama, X. and Ishizaki, T., Low-fire microwave dielectric ceramics and multilayer devices with silver internal electrode, Ceramics Transactions. In *Dielectric Ceramics Proceding, Properties, and Applications*, ed. K. M. Nair, J. P. Guha and A. Okamoto. American Ceramic Society, Westerville, OH, 1993, pp. 81–90.
2. Kagata, H. T. and Inoue, K. J., Low-fire Bismuth-based dielectric ceramics for microwave use. *Jpn. J. Appl. Phys.*, 1992, **31**, 3152–3155.
3. Udovic, M., Valant, M. and Suvorov, D., Dielectric characterization of ceramics from TiO_2–TeO_2. *Journal of European Ceramic Society*, 2001, **21**, 1735–1738.
4. Kim, H. T., Kim, S. H., Nahn, S. N. and Byun, J. D., Low-temperature sintering and micowave dielectric properties of zinc metatitanate–rutile mixtures using boron. *Am. Ceram. Soc.*, 1999, **82**, 3043–3048.
5. Choi, J. W., Kang, C. Y., Yoon, S. J., Kim, H. J. and Juang, H. J., Microwave dielectric properties of $Ca[(Li_{1/3}Nb_{2/3})_{1-x}M_x]O_{3-\delta}$ (M = Sn, Ti) ceramics. *J. Mater. Res.*, 1999, **14**, 3567–3570.
6. Liu, P., Kim, E. S. and Yoon, K. H., Low-temperature sintering and microwave dielectric properties of $Ca(Li_{1/3}Nb_{2/3})O_{3-\delta}$ ceramics. *Jpn. J. Appl. Phys.*, 2001, **40**, 5769–5773.
7. Shannon, R. D., Revised effective ionic radii and systematic studies of interatomic distance in hilides and chalcogenides. *Acta. Cryst.*, 1976, **A32**, 751–767.
8. Daniel, E. M. and Levin, C. L., Phase diagram between B_2O_3 and Bi_2O_3. *J. Am. Ceram. Soc.*, 1962, **45**, 355–360.