Low-temperature sintering of alkaline niobate based piezoelectric ceramics using sintering aids

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Three kinds of sintering aids, LiBiO_2 , CuBi_2O_4 and LiBO_2 , were selected as sintering aids for the low temperature sintering of $(\text{Li}_{0.04}\text{K}_{0.52}\text{Na}_{0.44})(\text{Nb}_{0.84}\text{Ta}_{0.1}\text{Sb}_{0.06})\text{O}_3$ (LF4) ceramics and the effects of these compounds on the sintering behavior of the LF4 ceramics was investigated. The addition of LiBiO_2 decreased the sintering temperature of LF4 about 100°C but the effect was limited and the broadening of XRD peaks due to the degradation of crystallinity was observed. The CuBi_2O_4 was also effective to decrease the sintering temperature of LF4 ceramics but a secondary phase was formed when a large amount of CuBi_2O_4 was added. The addition of a small amount of LiBO_2 was very effective to decrease the sintering temperature of LF4 ceramics. By optimizing the sintering conditions, ceramics with the relative density of 95% were obtained at 950°C which was lower than the melting point of Ag. Li ions in LiBO_2 were incorporated into the LF4 lattices, giving rise to the degradation of piezoelectric properties through the change of crystalline phase. The addition of excess Na with LiBO_2 restricted the incorporation of Li ions into the lattice. Ceramics sintered at 950°C showed the relative permittivity of 738 and the d_{33} constant of 138 pC/N at room temperature.

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1. Introduction

Lead zirconium titanium oxide ($\text{Pb}(\text{Zr,Ti})\text{O}_3$, PZT) has been widely used in various piezoelectric devices because of its excellent properties controlled by the chemical modifications.¹⁾ However, PZT contains huge amount of Pb that is environmental burdened materials. Although Pb in electric ceramics is now excluded from the regulation because of the absence of alternative materials to replace PZT-based ceramics,²⁾ lead-free piezoelectric ceramics are desired to be developed and many studies aiming at new lead-free piezoelectric ceramics have been done so far.³⁾⁻⁹⁾

Potassium sodium niobate ($\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$; KNN) is regarded as a candidate material to replace PZT. Saito et al. invented a piezoelectric material represented as $(\text{Li}_{0.04}\text{K}_{0.52}\text{Na}_{0.44})(\text{Nb}_{0.84}\text{Ta}_{0.1}\text{Sb}_{0.06})\text{O}_3$ (LF4) which showed a high piezoelectric d_{33} constant (300 pC/N), and could be fired in air. In addition, grain oriented (textured) LF4 ceramics (LF4T) showed $d_{33} = 416$ pC/N that was comparable to PZT-based ceramics.³⁾ A problem of KNN-based ceramics including LF4 is a compositional control because K and Na easily evaporate in the sintering process. The defects induced by the volatility of K and Na may decrease the piezoelectric properties. The reduction of sintering temperature should suppress the volatility of these alkaline elements and also improve reproducibility of piezoelectric KNN-based ceramics. Furthermore, a low temperature sintering process will provide a benefit in the application of multilayer piezoelectric actuators where ceramics are sintered with internal metal electrodes. In this case, the sintering temperature is hopefully reduced below the melting point of less expensive Ag ($961^\circ\text{C}^{10)}$).

In general, the sintering temperature of the ceramics can be reduced by utilizing low-melting point additives as sintering aids. Hayashi et al. reported that lithium bismuth oxide (LiBiO_2) with a melting point of 700°C was effective for the low-temperature sintering of $(\text{Pb}_{0.86}\text{Ba}_{0.04}\text{Sr}_{0.12})(\text{Zr}_{0.56}\text{Ti}_{0.44}\text{Sb}_{0.02})\text{O}_3$.¹¹⁾ Hasegawa and Otagiri reported that copper bismuth oxide (CuBi_2O_4) with melting point of 600°C was effective for the low-temperature sintering of BaTiO_3 .¹²⁾ Lithium metaborate (LiBO_2), used in the alkali fusion for inorganic analyses, is also expected as a sintering aid though it was not studied so far, because it has a low melting point of $845^\circ\text{C}^{13)}$ and previous report revealed that the addition of Li was promoted the sintering of KNN-based ceramics.¹⁴⁾

In this study, we investigated the effect of LiBiO_2 , CuBi_2O_4 and LiBO_2 -additions on the sintering behavior of the LF4 ceramics, and measured the dielectric and piezoelectric properties of ceramics finally obtained by the low temperature sintering process proposed in this study.

2. Experimental procedure

2.1 Sample preparation

The LF4 ceramics were prepared by a conventional solid state reaction process from the raw powders of K_2CO_3 (Wako Pure Chemical Ind., Ltd., 99.9%), Na_2CO_3 (Wako Pure Chemical Ind., Ltd., 99.9%), Li_2CO_3 (RARE METALLIC Co., Ltd., 99.99%), Nb_2O_5 (RARE METALLIC Co., Ltd., 99.9%), Ta_2O_5 (Kojundo Chemical Laboratory Co., Ltd., 99.9%) and Sb_2O_3 (Kojundo Chemical Laboratory Co., Ltd., 99.99%). These powders were mixed to form the chemical composition of $(\text{Li}_{0.04}\text{K}_{0.52}\text{Na}_{0.44})(\text{Nb}_{0.84}\text{Ta}_{0.1}\text{Sb}_{0.06})\text{O}_3$ by ball milling in dehydration acetone for 24 h. After drying, the mixed powder was calcined at 780°C for 4 h. LiBiO_2 , CuBi_2O_4 or LiBO_2 was added to the LF4 calcined powder as a sintering aid. LiBiO_2 was added to the calcined powder as a mixture of Li_2CO_3 and Bi_2O_3 powders.

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CuBi_2O_4 was first prepared by firing CuO and Bi_2O_3 mixed powders at 720°C for 5 h and added to the LF4 calcined powder. The particle size of the CuBi_2O_4 was $2\text{--}5\ \mu\text{m}$. As for LiBO_2 , a commercial powder (Kojundo Chemical Laboratory Co., Ltd., 99%) with the particle size of a few μm was added to the calcined powder. After mixing these sintering aids, the LF4 powders were crushed and mixed by ball milling in dehydration acetone for 24 h. After drying, these powders were pressed to pellets using the cold-isostatically press (CIP) at 100 MPa and were sintered in air for 1–2 h at $880\text{--}1150^\circ\text{C}$ with a temperature rising rate of $2\text{--}10^\circ\text{C}/\text{min}$.

2.2 Characterization of ceramics

The crystalline phases formed in the ceramics were verified by x-ray diffraction (XRD: Rigaku Co., Rint2000) at room temperature. The relative densities of ceramics were evaluated by the Archimedes' method. The microstructure of ceramics was observed by a scanning electron microscopy (SEM: JEOL, JSM-5310).

The samples used for dielectric and piezoelectric measurement were cut from ceramic discs. After polishing, Au electrodes were deposited to the sample surfaces by the DC sputtering method. The leakage currents of samples were measured as a function of applied electric (E) field up to 1 kV/mm. Temperature dependences of dielectric permittivity (ϵ_r) and dielectric loss tangent ($\tan \delta$) of the samples were measured by an impedance analyzer (Agilent, 4294A) at 100 kHz from 25°C to 500°C . The polarization vs. electric hysteresis curves of samples were measured by a ferroelectric tester (Radiant, RT6000). Before the measurements of piezoelectric properties, the samples were poled in silicone oil at the electric field of 5 kV/mm for 20 min at 100°C .

The piezoelectric properties of samples were measured for 31-resonator made of the samples with an impedance analyzer (Agilent, HP4294A) using resonance and anti-resonance method.¹⁵⁾ The piezoelectric d_{33} constant was measured with a quasistatic piezoelectric coefficient testing meter (Institute of Acoustics, Chinese Academy of Sciences, ZJ-3B/4B d_{33} Meter).

3. Results and discussion

3.1 Selection of suitable sintering aid

Figure 1(a) shows the relative densities of LiBiO_2 -added LF4 ceramics as a function of sintering temperature. The addition of 1.4 wt% LiBiO_2 decreased the sinterability of LF4 ceramics, while the addition of 9.7 wt% was effective to decrease the sintering temperature about 100°C to obtain the same density with the pure LF4 ceramics. The XRD profiles of the LF4 and LiBiO_2 -added LF4 ceramics are shown in Fig. 2(a) and (b), respectively. Broadening of diffraction peaks observed in the LiBiO_2 -added LF4 ceramics in comparison with the pure LF4 indicated that the crystallinity of the LF4 degraded with the addition of LiBiO_2 , which may cause a serious reduction of piezoelectric properties. Furthermore, too much amount of LiBiO_2 should be necessary to reach the sintering temperatures below the melting of Ag. From these results, we concluded that LiBiO_2 was not suitable as a sintering aid of the LF4 though it worked in the sintering of PZT.

Figure 1(b) shows the relative densities of CuBi_2O_4 -added LF4 ceramics as a function of sintering temperature. The addition of 0.5 wt% CuBi_2O_4 did not affect the sinterability of LF4, but a notable effect was observed when 16 wt% CuBi_2O_4 was added. A dense ceramics with a relative density over 95% was obtained by sintering at 980°C which was about 170°C lower than the case of pure LF4-ceramics. The XRD profiles of 16 wt% CuBi_2O_4 -added LF4 ceramics in Fig. 2(c) indicated that a considerable amount of secondary phase was formed. This result indicated that CuBi_2O_4 was not suitable as a sintering aid of the LF4 though it worked in the sintering of BaTiO_3 .

Figure 1(c) shows the relative densities of the LiBO_2 -added LF4 ceramics as a function of sintering temperature. The optimum sintering temperature to obtain maximum density of ceramics decreases with increasing amount of LiBO_2 . The sintering temperature was reduced to 950°C when 4 wt% of LiBO_2 was

Fig. 1. Relative density of ceramics as a function of sintering temperature. (a) LiBiO_2 , (b) CuBi_2O_4 and (c) LiBO_2 .

Fig. 2. XRD profiles of ceramics. (a) LF4 ceramics sintered at 1135°C , (b) 9.7 wt% LiBiO_2 -added LF4 ceramics sintered at 1000°C , (c) 16 wt% CuBi_2O_4 -added LF4 ceramics sintered at 980°C and (d) 4 wt% LiBO_2 -added LF4 ceramics sintered at 950°C .

Fig. 3. SEM images of fracture surfaces of LF4 ceramics added with various amount of LiBO_2 and sintered at 1050°C . (a) 0 wt%, (b) 1.5 wt%, (c) 3 wt% and (d) 4 wt%.

Fig. 4. Current vs. voltage relation of the LF4 ceramics added with different amount of LiBO_2 . (a) 0 wt%, (b) 1.5 wt%, (c) 3 wt% and (d) 4 wt%.

added, which was about 200°C lower than that of pure LF4 ceramics. It was found that the addition of a small amount of LiBO_2 was very effective to reduce the sintering temperature of LF4 ceramics. The XRD profile of 4 wt% LiBO_2 -added LF4 ceramics is shown in Fig. 2(d). Although two weak peaks of a secondary phase are observed, relatively sharp diffraction peaks of the LF4 phase indicates that the crystallinity of the LF4 phase was hardly degraded by the addition of LiBO_2 . It should be noted that the shape of diffraction peak marked by a circle in the figure indicated that the crystalline phase changed from orthorhombic (or morphotropic phase boundary, MPB) to tetragonal, which will be discussed in the later section. **Figure 3** shows the SEM images of fracture surfaces of LiBO_2 -added LF4 ceramics. The addition of LiBO_2 promoted the grain growth of the LF4 ceramics, which was due to the formation of a liquid phase during sintering at temperatures higher than melting point of LiBO_2 (845°C). From these results, we concluded that LiBO_2 is the most suitable

sintering aid in the three compounds tested in this study.

3.2 Optimization of chemical composition and sintering process

The DC current vs. electric field curves LiBO_2 -added LF4 ceramics were shown in **Fig. 4**. The electric insulation of the ceramics increased in the 1.5 wt% LiBO_2 -added LF4 but it decreased when the amount of LiBO_2 increased above 3 wt%. The change of electric insulation is attributable to the incorporation of Li ions into the LF4 lattices. The LF4 ceramics should have K and Na vacancies at the A site of perovskite lattices because of the evaporation of these elements during the sintering. By adding LiBO_2 , the K and Na vacancies are filled with the Li ion in LiBO_2 to increase electric insulation. However, the addition of further amount of Li ions may form other defects in the lattices, giving rise to the decrease of electric insulation as shown in Fig. 4(c) and (d). To obtain high piezoelectric activity, high electric insulation is essentially important to perform the poling process. Therefore, the amount of LiBO_2 should be equal or less than 3 wt%, where the electric insulation was in the same range of the pure LF4.

The purpose of this study is to make LF4-based ceramics which can be sintered below the melting point of Ag. To meet this demand, we chose 3 wt% as a LiBO_2 amount and the sintering process of the 3 wt% LiBO_2 -added LF4 ceramics was optimized finally as follows: increasing temperature at the rate of $10^\circ\text{C}/\text{min.}$ to 950°C and sintering for 2 h. This process enabled us to make ceramics with a relative density of 95% without degrading electric insulation. This sample named as LFLB3 was used in the measurements of dielectric and piezoelectric properties mentioned in the next section.

It was mentioned that the crystalline phase in the LF4 changed from the orthorhombic (or MPB) to the tetragonal by adding LiBO_2 (Fig. 2(d)). The incorporation of Li ions into the LF4 lattices induced this change. Previous report also pointed out that the increase of Li content in the LF4 changed the crystalline

phase to the tetragonal.¹⁴⁾ It is known that the piezoelectric activity has a maximum at the MPB. Therefore, the change of crystalline phase may degrade the piezoelectric activity. To avoid this problem, we added 2 mol% of excess Na to the 3 wt% LiBO₂-added LF4 ceramics. The excess Na did not change the sinterability of the ceramics and a relative density over 95% were obtained at the sintering temperature of 950°C. This sample was named as LFLB3Na. The XRD profiles around (200) diffraction peak of pure LF4, LFLB3 and LFLB3Na were compared in Fig. 5. It is obvious that the XRD profiles of LF4 and LFLB3Na were almost

Fig. 5. XRD profiles of (a) LF4, (b) LFLB3 and (c) LFLB3Na ceramics.

Fig. 6. Polarization vs. electric field hysteresis curves of (a) LF4, (b) LFLB3 and (c) LFLB3Na ceramics.

identical, indicating that the tetragonal phase formed in the LFLB3 was changed to the orthorhombic or the MPB by the addition of 2 mol% excess Na which restricted the incorporation of Li ions in to the LF4 lattices.

3.3 Dielectric and piezoelectric properties

Figure 6 shows the P - E hysteresis curves of pure LF4, LFLB3 and LFLB3Na. The remanent polarization (P_r) of the LF4 was 4.3 $\mu\text{C}/\text{cm}^2$, it increased to 5.2 $\mu\text{C}/\text{cm}^2$ in the LFLB3 and to 7.0 $\mu\text{C}/\text{cm}^2$ in the LFLB3Na. The result indicated that the ferroelectric property of the LF4 did not degrade by the addition of 3 wt% of LiBO₂. Figure 7 shows the temperature dependence of dielectric permittivity (ϵ_r) and loss tangent ($\tan \delta$) of pure LF4, LFLB3 and LFLB3Na ceramics. The Curie temperature (T_c) of LFLB3 at 394°C is about 80°C higher than that of the LF4, which was consistent with the previous report showing that the Li incorporation into the LF4 lattice increased the Curie temperature.¹⁴⁾ The Curie temperature of LFLB3Na decreased in comparison with the LFLB3 because the incorporation of Li ions into the lattices was restricted by the addition of excess Na. The $\tan \delta$ of LFLB3 steeply increased at high temperatures but it was improved in the LFLB3Na. However, the broad maximum of dielectric permittivity in Fig. 6(c) indicated that the addition of LiBO₂ sintering aid was not inert to the LF4 lattices even with the presence of excess Na, which cause the degradation of electric properties as mentioned below.

In Table 1 dielectric and piezoelectric properties of the LF4, LFLB3 and LFLB3Na are listed. The addition of LiBO₂ to LF4 hardly changed s_{11}^E but decreased k_{31} , d_{31} , d_{33} and ϵ_r . The low dielectric and piezoelectric constants are due to the change of the crystalline phase from the orthorhombic (or MPB) to the tetragonal. The properties of LFLB3 were markedly improved in the

Fig. 7. Temperature dependence of dielectric permittivity of (a) LF4, (b) LFLB3 and (c) LFLB3Na ceramics.

Table 1. Dielectric and Piezoelectric Properties of the LF4, LFLB3 and LFLB3Na Ceramics

Sample	$-d_{31}$ (pC/N)	s_{11}^E (pm ² /N)	k_{31} (%)	d_{33} (pC/N)	ϵ_r	T_c (°C)
LF4	76	10.6	21.7	225	1310	316
LFLB3	29	10.7	12.5	93	580	394
LFLB3Na	44	11.5	16.3	138	723	362

LFLB3Na and the d_{33} constant of 138 pC/N was obtained. The chemical modification to approach the MPB is the reason of this improvement, which could be seen in the increase of s_{11}^E indicating the softening of crystal lattices. Although the d_{33} of LFLB3Na ceramics is still much lower than that of the LF4 ceramics, it seems to be acceptable if the low sintering temperature of 950°C is taken into account.

In this study, we found that LiBO_2 would be an effective sintering aid for the LF4 and possibly for KNN-based piezoelectric ceramics. The Li ions in LiBO_2 were incorporated into the LF4 lattices to fill up A site vacancies of perovskite structure, which changed the crystalline phase and electric properties. Further studies to optimize both the composition of the LiBO_2 -based sintering aid and the sintering process should be necessary to minimize the degradation of piezoelectric properties.

4. Conclusion

Three candidates of sintering aids, LiBiO_2 , CuBi_2O_4 , and LiBO_2 , were tested to reduce the sintering temperature of LF4 based ceramics below the melting point of Ag. The addition of LiBiO_2 could reduce the sintering temperature but its effect was limited. A secondary phase was formed by the addition of 16 wt% CuBi_2O_4 to decrease the sintering temperature below 1000°C. In the three candidates, LiBO_2 was the most effective to decrease the sintering temperature of LF4 ceramics. By optimizing sintering conditions, the addition of 3 wt% of LiBO_2 enabled us to sinter ceramics with a relative density of 95% at 950°C which was lower the melting point of Ag. However, the incorporation of Li ions into the LF4 lattices changed the crystalline phase to the tetragonal and degraded the piezoelectric properties. The addition of 2 mol% Na with LiBO_2 restricted the Li ion incorporation in the lattice. Ceramics prepared using sintering aids of LiBO_2 with the excess Na showed the relative permittivity of 738

and the d_{33} constant of 138 pC/N at room temperature.

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