Piezoelectric Properties and Morphotropic Phase Boundary of Low-Temperature Sintered PZT Ceramics with BiFeO$_3$ and Ba(Cu$_{0.5}$W$_{0.5}$)O$_3$

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1. Introduction

Lowering a sintering temperature of Pb(Zr,Ti)O$_3$ ceramics is urgently required to avoid the volatilization of PbO which leads to the compositional fluctuation and the environmental contamination. The low temperature sintering of Pb(Zr,Ti)O$_3$ ceramics has been reported by many researchers using different methods. The authors have also reported that the sintering temperature above 1200°C of MnO$_2$-added Pb(Zr,Ti)O$_3$ ceramics is lowered down to 935°C by the simultaneous addition of BiFeO$_3$ and Ba(Cu$_{0.5}$W$_{0.5}$)O$_3$.

Jaffe et al. have found the highest piezoelectric coupling as well as the maximum dielectric susceptibility for the morphotropic phase boundary (MPB) of Pb(Zr,Ti)O$_3$ system. It has been reported that this MPB prepared by a solid-state reaction among the constituent oxides, PbO, TiO$_2$, and ZrO$_2$ always shows both tetragonal (Ti-rich composition) and rhombohedral (Zr-rich composition) phases. The complex oxides added to Pb(Zr,Ti)O$_3$ ceramics may generally cause a shift of the MPB resulting in the deterioration of electric properties. The previous measurements further indicated that the simultaneous addition of the complex oxides described above succeeded in the lowering of sintering temperature without the deterioration of electric properties. These results suggest that the MPB still remains in the coexistence region of the tetragonal and rhombohedral phases in the case of Pb(Zr,Ti)O$_3$-BiFeO$_3$-Ba(Cu$_{0.5}$W$_{0.5}$)O$_3$ system. In this report, the effects of the addition of the complex oxides on the behavior of the MPB and the piezoelectric properties has been discussed in the MnO$_2$-added Pb(Zr,Ti)O$_3$ ceramics.

2. Experimental

Powders of Pb$_3$O$_4$, ZrO$_2$, TiO$_2$, BaCO$_3$, CuO, WO$_3$, Bi$_2$O$_3$, Fe$_2$O$_3$, and MnO$_2$ (>99.0%) were used and 0.5 wt% MnO$_2$-added Pb(Zr$_{0.53}$Ti$_{0.47}$)O$_3$ (indicated as PZT hereafter) and Ba(Cu$_{0.5}$W$_{0.5}$)O$_3$ (abbreviated as BCW) were separately synthesized by heating at 870°C for 2 h. All PZT, BCW.
Bi$_2$O$_3$, Fe$_2$O$_3$, and CuO were weighed in \[(1-x-y)\text{PZT}-x\text{BF}-y\text{BCW}\] + z wt% of CuO (BF is the abbreviation of BiFeO$_3$) proportion. Disk samples with 10 mm in diameter and 3 mm in thickness were formed at the pressure of 800 kg/cm$^2$ and sintered isothermally at a temperature between 870°C and 1250°C for 30 min.

The electric properties of samples were measured after being polarized under 3-4 kV/mm bias at 120°C in a silicone oil bath for 15 min. The dielectric properties were examined at 1 kHz.

A detailed XRD profile was obtained to determine the phases of the ceramics. The XRD profiles of (002) and (200) planes of the tetragonal phase and that of (200) plane of the rhombohedral phase were chosen to observe the change of MPB.

3. Results

Firstly, the amount of BCW was fixed on 5 mol% to the PZT ceramics and the effect of BF on the sintering temperature and electric properties was investigated. The optimum amount of BF was selected to be 5 mol% based on the better dielectric and piezoelectric properties. Secondly, the amount of BF was fixed on 5 mol% and the optimum amount of BCW was selected to be 3 mol%, as in the case of BF addition. Accordingly, 0.92PZT-0.05BF-0.03BCW (abbreviated as PZT-C hereafter) ceramics was determined as the optimum composition, which can be sintered at 935°C for 30 min.

Since the reaction of CuO in the synthesis of BCW was not easily proceeded, the effect of extra CuO addition was investigated. Table 1 is the comparison of the electric properties among PZT, PZT-C and PZT-C' (a abbreviation of 0.92PZT-0.05BF-0.03BCW + 0.08 wt% CuO). It shows that the addition of the complex oxides causes a drastic reduction in the sintering temperature, the properties of PZT-C became better than those of PZT except for $K_p$, $d_{33}$, and $\varepsilon''_{33}/\varepsilon_0$, and that the extra addition of CuO (PZT-C') improved the properties evidently.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sintering temp., time</th>
<th>$\varepsilon''_{xy}/\varepsilon_0$</th>
<th>tan $\delta$ (%)</th>
<th>$T_c$ (°C)</th>
<th>$K_p$ (%)</th>
<th>$Q_m$</th>
<th>$d_{33}(\times10^{11} \text{C/N})$</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT</td>
<td>1250°C, 30 min</td>
<td>910</td>
<td>1.2</td>
<td>362</td>
<td>51.7</td>
<td>314</td>
<td>210</td>
<td>7.59</td>
</tr>
<tr>
<td>PZT-C</td>
<td>935°C, 30 min</td>
<td>847</td>
<td>1.1</td>
<td>290</td>
<td>41.0</td>
<td>670</td>
<td>201</td>
<td>7.65</td>
</tr>
<tr>
<td>PZT-C'</td>
<td>935°C, 30 min</td>
<td>850</td>
<td>1.0</td>
<td>290</td>
<td>47.0</td>
<td>950</td>
<td>236</td>
<td>7.66</td>
</tr>
</tbody>
</table>

In order to determine the MPB in the PbZrO$_3$-PbTiO$_3$ solid solution, the XRD profiles were obtained for the PZT-C ceramics of various compositions with different ratios of Zr/Ti. Figure 1 shows the XRD profiles of (200) and (200) planes of 0.92Pb(Zr$_{1-x}$Ti$_x$)O$_3$-0.05BF-0.03BCW ceramics. For the composition of x=0.55, only one peak was observed which corresponds to the (200)
plane of the rhombohedral phase. On the other hand, two XRD profiles of the tetragonal phase appeared together with the rhombohedral phase when the Ti-rich composition of $x=0.51$ was selected.

![XRD profile of (002) and (200) planes](image)

**Fig. 1.** XRD profiles of (002) and (200) planes of 0.92Pb(Zr$_x$Ti$_{1-x}$)O$_3$-0.05BF-0.03BCW ceramics sintered at 935°C for 30 min. T: tetragonal phase, R: rhombohedral phase.

### 4. Discussion

In order to explain the behavior of BF and BCW in the PZT, the ceramics of different compositions were characterized by XRD and DTA. Figure 2 shows XRD profile of 0.60PZT-0.20BF-0.20 BCW ceramics which consists of the larger amount of BF and BCW. No XRD profile originating from BF or other compounds including Bi and/or Fe was observed. This result indicates that the BF forms a solid solution with the PZT ceramics even for the larger amount of BF addition. On the other hand, the XRD profile corresponding to BaWO$_4$ was observed in Fig. 2. In the case of the larger amount of BCW addition, an additional phase, BaWO$_4$ tends to be formed besides the PZT phase. The additional phase seems to play a very important role for lowering the sintering temperature of the PZT ceramics.

![XRD profile of 0.60PZT-0.20 BiFeO$_3$-0.20Ba(Cu$_{0.5}$W$_{0.5}$)O$_3$](image)

**Fig. 2.** XRD profile of 0.60PZT-0.20 BiFeO$_3$-0.20Ba(Cu$_{0.5}$W$_{0.5}$)O$_3$ ceramics sintered at 870°C for 30 min.

In the present study, the simultaneous addition of the two complex oxides, BiFeO$_3$ and Ba(Cu$_{0.5}$W$_{0.5}$)O$_3$, to the PZT ceramics was very effective for not only lowering the sintering temperature but improving the electric properties. Usually, there is a possibility to cause a shift of the MPB in the
Pb(Zr,Ti)O₃ system by the addition of other compound. The deviation from the MPB composition leads to the deterioration of the electric properties. In the Pb(Zr,Ti₁₋ₓ)O₃ system, the MPB between tetragonal and rhombohedral phases lies in the vicinity of x=0.535. It has been also reported⁷ that this MPB prepared by a solid-state reaction among the constituent oxides always results in the coexistence of tetragonal and rhombohedral phases. Therefore, no deterioration of the electric properties in the present study suggests that the MPB of the 0.92Pb(Zr,Tiₓ)₀.₃₋ₓ₀.₀₅BF₀.₀₃ SCW ceramics still exists around x=0.535. The XRD profiles in Fig. 1, however, indicates that the ceramics with x=0.55~53 gives only profile of (200) planes of the rhombohedral phase. On the other hand, when the x reaches 0.51, two profiles of (002) and (200) planes of the tetragonal phase appear together with the profile of (200) plane of the rhombohedral phase. The MPB of the PZT-C ceramics shifted presumably towards the Ti-rich composition. More detailed relation between the lattice parameters and the compositions for the 0.92Pb(Zr,Tiₓ)₀.₃₋ₓ₀.₀₅BF₀.₀₃SCW solid solution is necessary for the interpretation of the present results, and it may lead to the determination of the optimum composition for the preparation of PZT ceramics of better electric properties.

5. Conclusion

Low temperature sintering of 0.5 wt% MnO₂-added Pb(Zr₀.₅₃Ti₀.₄₇)O₃ ceramics is desirable for suppressing the volatilization of PbO. The addition of two complex oxides, BiFeO₃ and Ba(Cu₀.₅W₀.₅)O₃, lowered the sintering temperature and improved the electric properties of the PZT ceramics. Further addition of CuO improved the piezoelectric properties, particularly Qₘ. A 0.92PZT-0.05BiFeO₃-0.03Ba(Cu₀.₅W₀.₅)O₃ + 0.08 wt% CuO ceramics was sintered at 935°C for 30 min and gave the following characteristics: Kₑ=47.0%, Qₘ=950, d₃₃=236×10⁻¹² C/N, ε₃₃/ε₀=850, tan δ=1.0%. Tₑ=290°C, and bulk density =7.66 g/cm³. Furthermore, it has been proved that the simultaneous addition of BiFeO₃ and Ba(Cu₀.₅W₀.₅)O₃ causes a shift toward the Ti-rich composition in the MPB of the Pb(Zr,Ti)O₃ system.

References