Low Temperature Firing and Electrical Properties of PZT Ceramics Prepared from Partial Oxalate Method Derived Powders.

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Abstract

Low temperature-fired PZT ceramics and their electrical properties were studied using the fine powders synthesized by two different versions of partial oxalate methods. The sintering behavior of the partial oxalate derived powders was compared to that of the conventional powder formed by the mixed-oxide technique. It was found that the sintering temperature of partial oxalate-derived PZT powder compacts could be reduced to as low as 950°C without sacrificing desired dielectric and piezoelectric properties, such as relative permittivity, electromechanical coupling factor, and piezoelectric coefficient. In particular, two partial oxalate methods yielded PZT ceramics with almost the same physical and electrical properties, so that the step of producing prereacted ZTO powder in the “original” partial oxalate method was found to be unnecessary.

1. Introduction

Today, most of PZT ceramics are still fabricated from PZT powder obtained by calcining PbO, ZrO2, and TiO2 powder mixture\(^1\), although PZT powder from a chemically-derived precursor such as alkoxide, oxalate, or sol-gel is available to some extent. The latter has been developed to improve the uniformity, purity and particle shape, and to obtain smaller particle size and narrow distribution of the resulting PZT powder. The fine and uniform powder synthesized by such chemical methods is advantageous in many engineering applications because lower firing temperature and improved reproducibility of properties can be realized. In addition, the powders from most of chemical solution synthesis methods are adequate for the
study of powder morphology and powder characteristics since there are no mixing or milling processes. However, such chemical synthesis is not suitable for mass production due to the low yield and high cost of powder.

Besides the chemical methods described above, the mechanical milling of coarse agglomerated calcined powder produced by relatively inexpensive mixed oxide route can also be used to obtain fine submicron powder. However, milling process with grinding media such as partially stabilized zirconia balls often results in unwanted and uncontrollable impurity contamination.

All of the foregoing processes share common objectives of achieving homogenous submicron and monosize powder. The pure chemical methods face the problem of poor productivity, while the mechanical milling of conventionally calcined powder meets the challenge of unavoidable contamination of the resulting powder. Therefore, it has been necessary to develop novel processes to combine the advantages and to eliminate the disadvantages of the two techniques. An example of newly developed chemical methods in this respect is the multi-stage coprecipitation method proposed by Watanabe et al. In this method, Mg(NO₃)₂ and Nb₂O₅ are pre-reacted, and PbO is subsequently added to the solution to form chemically homogenous Pb(Mg₁/₃ Nb₂/₃)O₂ powder. The modified mixed oxide method proposed by Swartz et al. involves two step firing processes where MgO and Nb₂O₅ powder are pre-reacted to form columnar phase MgNb₂O₆ by usual mixed oxide technique, and PbO is reacted with the resulting columnite to obtain single phase perovskite. This method was reported to be very effective to avoid the formation of pyrochlore phase such as Pb₂Nb₂O₇, which is known to be detrimental to the desired dielectric properties.

Recently, Yamamoto et al. proposed the partial oxalate method which combined the conventional mixed oxide method and the chemical method for the synthesis of PZT powder. In this method, ZTO(Zr₆/₃Ti₄/₃O₁₉) powder is used as starting material with lead oxalate prepared from lead nitrate and oxalate solution. This approach was attempted to produce the most active parts by the chemical method and bypass the conventional reaction process, and thereby eliminating the formation of PbTiO₃ which is usually formed as an intermediate product during firing of the mixed oxide powder.

In this paper, the low temperature firing behavior of fine PZT powders synthesized by two different versions of partial oxalate methods is presented and compared with that of conventional PZT powder. Then the dielectric and piezoelectric properties of the PZT ceramics obtained from powders prepared by the two partial oxalate methods will be compared with those of the PZT ceramics from the conventional mixed oxide process.

2. Experimental Procedure

The chemical composition used in this study is given in equation (1). Raw materials used to synthesize PZT powders were PbO, ZrO₂, TiO₂, Pb(NO₃)₂, (COOH)₂·2H₂O, and Nb₂O₅ chemicals, whose purities were reagent-grade or better.

\[ \text{Pb}_{(Zr_{0.53}Ti_{0.47})}O_3 + 0.5\text{mol}\% \text{Nb}_2\text{O}_5 \]

or

\[ \text{Pb}_{(Zr_{0.53}Ti_{0.47})}\text{Nb}_{0.50}O_3 \]  

(1)

In this study, the PZT powders prepared by the two different versions of the partial oxalate methods and the conventional solid state reaction method of mixed oxides were used. The full details of the two different versions of the partial oxalate methods are described elsewhere. Therefore, it may be sufficient to mention the difference between the two methods in this communication. The "original" partial oxalate method which was proposed by Yamamoto et al. and the modified partial oxalate method are only different in the elimination of either the use of costly ultrafine NZTO powder or the solid state reaction process of ZrO₂, TiO₂, and Nb₂O₅ to form NZTO powder from the original method. The modified partial oxalate method was devised to eliminate the energy-consuming reac-

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tion of ZTO or NZTO (ZTO doped with Nb₂O₅) production. One of the objectives of this study is, of course, the examination and evaluation of the modified method. In this method, the mixture of ZrO₂, TiO₂, and/or Nb₂O₅ particles replaces ZTO or NZTO of the partial oxalate method. The flow diagram of the two partial oxalate methods are illustrated in Fig.1.

The other method to obtain PZT ceramics was the well-known solid state reaction technique of mixed oxides. The electrical properties and sintering behavior of the resulting PZT ceramic were compared to those of the PZT ceramics prepared by the partial oxalate methods.

Average particle sizes of the calcined and crushed PZT powders used in this study are summarized in Table 1. It is evident that partial oxalate methods yield finer particles than conventional mixed oxide method.

Table 1 Average particle sizes of calcined PZT powders.

<table>
<thead>
<tr>
<th>Preparation Method</th>
<th>Symbol</th>
<th>Calcination Temp. (°C)</th>
<th>Particle Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional Mixed Oxide</td>
<td>PZT</td>
<td>900</td>
<td>1.69</td>
</tr>
<tr>
<td>Partial Oxalate</td>
<td>P-ZT(1)</td>
<td>710</td>
<td>0.71</td>
</tr>
<tr>
<td>Modified Partial Oxalate</td>
<td>P-ZT(2)</td>
<td>710</td>
<td>0.96</td>
</tr>
</tbody>
</table>

Sintering behavior of the powder compacts was examined by pressing the powder into the pellet at 98 MPa and fired at 850~1200°C for three hours. Bulk density, crystal structure, dielectric and piezoelectric properties, and poling behavior of PZT ceramics were then examined in some detail. Fired-on silver paste was applied onto two faces of discs by heat treatment at 800°C for 10 minutes. Poling was performed by immersing the ceramic into silicone oil and applying 3 kV/mm field.

3. Results and Discussion

In Fig.2, the temperature dependence of bulk densities of ceramics fired over the temperature range of 850~1200°C is illustrated for various preparation methods. The same symbols are used in Fig. 2 and in the following figures to denote various powder preparation routes. Solid dot, open square and triangle represent mixed oxide (PZT), partial oxalate (P-ZT(1)) and modified partial oxalate-derived powders (P-ZT (2)), respectively. PZT powders synthesized by two partial oxalate methods shows similar sintering behavior, whereas the powder obtained by the mixed oxide method shows very sluggish sintering kinetics, and as a result, higher temperatures are necessary to obtain the same sintering densities. It is noted that almost full density is realized at as low as 950°C for partial oxalate-derived powder, whereas the same density is possible at above 1050°C for the mixed oxide-derived PZT powder. This result again reflects the fact that the partial oxalate-derived powders are smaller in size and chemically more uniform so that the densification can be
accomplished at lower temperatures.

Average grain sizes determined from the figure by the line intercept method are plotted against the sintering temperature in Fig. 3. It is clear that grain growth occurs at lower temperatures for partial oxalate-derived powder compacts.

The temperature dependence of relative permittivity and Curie temperature for ceramics sintered using modified partial oxalate-derived powder are shown in Fig. 4. It is found that, as sintering temperature increases, Curie temperature decreases whereas the relative permittivity at Curie point increases. This result is in good agreement with the finding by Yamamoto et al. for the similar system. Shrouat et al. also found the same temperature dependences of relative permittivity and Curie temperature for Pb(Mg1/3Nb2/3)O3 ceramic, and interpreted the data in terms of average grain size instead of sintering temperature. However, since average grain size is proportional to sintering temperature as seen in Fig. 3, the results obtained in this study remain consistent with other studies.

For the sintered samples prepared using three types of PZT powders, the sintering
that relative permittivity and bulk density show a similar temperature dependence may be explained by the influence of pores. Electromechanical coupling factors for three types of PZT ceramics are shown in Fig. 6 as a function of sintering temperature. It is noticeable that the coupling factors for all samples generally increase with sintering temperature. However, the two partial oxalate methods appear to be better than the mixed oxide method since the maximum values of the former happen at about 100°C lower than that of the latter. This trend is similar to that of relative permittivity, and is again the consequence of the decrease of sintering temperature for the same bulk density.

Since the coupling factor of 0.55 is sufficient for most piezoelectric applications, two partial oxalate methods are more adequate in practical applications than the mixed oxide method. The sintering temperature for the former can be as low as 950°C, whereas that for the latter must be higher than 1050°C.

Piezoelectric coefficients $d_{31}$ for three types of samples, which are important in actuator application, are shown in Fig. 7. The results also show the similar sintering temperature dependence as relative permittivity and electromechanical coupling factor.

D-E hysteresis loops for samples sintered at different temperatures using three types of powders were measured using Sawyer-Tower Circuits and typical curves are illustrated in Fig. 8. Remanent polarization determined from D-E hysteresis loops
are plotted as a function of sintering temperature in Fig. 9. It is seen that remanent polarization increases with sintering temperature. This temperature dependence again resembles those for relative permittivity and bulk density. From the figure, the saturated values of remanent polarization are 25–30 μC/cm². In addition from Fig. 6 and Fig. 9, one can find that remanent polarization is proportional to the planar coupling factor.

![Graphs](image)

**Fig. 8** D-E hysteresis loops for PZT ceramics sintered using three types of powders. (vertical: 15 μC/cm²/div, horizontal: 500V/mm/div)

**Fig. 9** Remanent polarization as a function of sintering temperature.

4. Conclusions

From the results found in this study, it can be concluded that the PZT powders derived from two different partial oxalate methods showed better sintering behavior than the mixed oxide-derived powder. Using the partial oxalate-derived PZT powders, sintering temperatures could be reduced to as low as 950°C without sacrificing desired dielectric and piezoelectric properties such as relative permittivity, electromechanical coupling factor, and piezoelectric coefficient. Two partial oxalate methods yield PZT ceramics with almost the same physical and electrical properties, so that the step of producing ZTO powder in partial oxalate method (1) was found to be an unnecessary one.

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References


著者紹介

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