부분수산법에 의한 PZT 세라믹스의 저온소성과 전기적 제특성

Electrical Properties of PZT Ceramics Fabricated by Partial Oxalate Method at Low Sintering Temperature

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Abstract

Pb(Zr,Ti)O$_3$ powders were synthesized by the partial oxalate method and the modified partial oxalate method, where the difference between the two is the use of pre-reacted (Zr,Ti)O$_2$ in the former method. When compared with conventional mixed oxide method, calcination temperature can be reduced to less than 700 °C by both partial oxalate methods, and the resulting particle size was finer and more uniform. Using partial oxalate-derived PZT powders, sintering temperatures can also be reduced 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 ceramics with almost the same physical and electrical properties, so that the step of producing ZTO powder does not seem to be necessary.
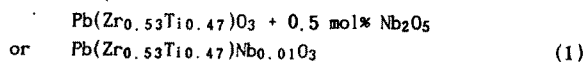
1. Introduction

Today, most of PZT ceramics are still fabricated from PZT powder obtained by calcining PbO, ZrO$_2$, and TiO$_2$ powder mixture, although PZT powder from 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 resulting PZT powder. The fine and uniform powder synthesized by such chemical methods is advantageous in many engineering applications as lower firing temperature and improved reproducibility of properties can be realized. However, such chemical synthesis is not suitable for mass production due to low yield and high cost of powder.

Recently, Yamamoto et al.[1] 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, Zr$_0.53$Ti$_0.47$O$_2$ is used as starting material with lead oxalate prepared from lead nitrate and oxalate solution.

In this paper, the synthesis and low temperature firing of fine PZT powder is presented. We have used both the partial oxalate method which was originally proposed by Yamamoto and the modified partial oxalate method to synthesize PZT powder, and have investigated the dielectric and piezoelectric properties of PZT ceramics. The reaction mechanisms for the formation of PZT powder through the partial oxalate method are being proposed. Finally, the piezoelectric properties of PZT ceramics prepared by both the partial oxalate methods and the conventional mixed oxide method are compared as well as the firing temperatures.

2. Experimental Procedure

The chemical composition used in this study is given below. Raw materials were high purity PbO, ZrO$_2$, TiO$_2$, Pb(NO$_3$)$_2$, (COOH)$_2 \cdot$2H$_2$O and Nb$_2$O$_5$ chemicals.

$$Pb(Zr_{0.53}Ti_{0.47})O_3 + 0.5 \text{ mol\% } Nb_2O_5$$
$$\text{or} \quad Pb(Zr_{0.53}Ti_{0.47})Nb_{0.01}O_3 \quad \quad (1)$$

In the partial oxalate method, the first of three methods tried in this study, weighed ZrO$_2$ and TiO$_2$ powders in molar proportion of 0.53 : 0.47 were mixed for 6 hours by wet ball milling, followed by calcination at 1300°C for 3 hours to form (Zr$_0.53$ Ti$_0.47$)O$_2$ solid solution (ZTO). In addition, ZrO$_2$ and TiO$_2$ powder mixture doped with 0.5 mol % Nb$_2$O$_5$ powder was also calcined at 1300°C (NZTO). Instead of PbO, lead oxalate prepared by mixing lead nitrate and oxalic acid aqueous solution was used in this method.
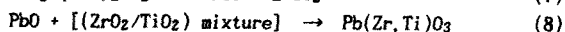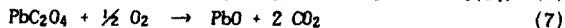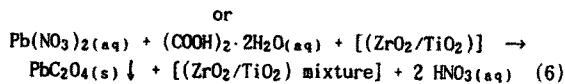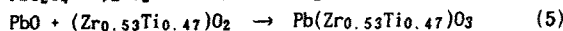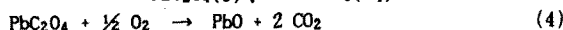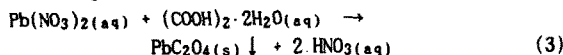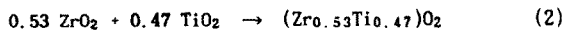
At first, ZTO or NZTO powder was dispersed in 1 mol oxalic acid aqueous solution, and 1 mol lead nitrate solution was dropped into the solution to form fine lead oxalate particles which precipitated onto rather large ZTO particles. Then, ZTO precipitates coated with lead oxalate was washed with distilled water until NO$_3^{2-}$ ion was not detected in washing liquid, followed by drying and calcining at 650 ~ 750°C for the formation reaction of PZT. The ball-milling of calcined PZT agglomerates was necessary to obtain fine PZT powder.

The modified partial oxalate method was devised to eliminate energy-consuming reaction of ZTO or NZTO production. In this method, the mixture of ZrO_2, TiO_2 and/or Nb_2O_5 particles replace ZTO or NZTO of the partial oxalate method. The detailed explanation of two processes are shown in Fig. 1.

The third method to obtain PZT powder was the well-known solid state reaction technique of mixed oxides. The powder produced by this method was used to make PZT ceramic in order to compare its properties with those prepared by partial oxalate methods.

3. Results and Discussion

In order to study the decomposition and/or phase transformation reactions for lead oxalate obtained from mixing lead nitrate and oxalic acid, thermogravimetric and differential thermal analysis were made, and the results are shown in Fig. 2. An exothermic peak at 425 ℃ is due to the formation of free PbO, and an endothermic peak at 900℃ is due to melting of PbO. Above 900℃ weight loss due to evaporation of PbO is evident from TGA curve. Therefore, the PZT formation in partial oxalate methods may be postulated as the series of following reactions.

$$0.53\ ZrO_2 + 0.47\ TiO_2 \rightarrow (Zr_{0.53}Ti_{0.47})O_2 \qquad (2)$$
$$Pb(NO_3)_{2(aq)} + (COOH)_2 \cdot 2H_2O_{(aq)} \rightarrow$$
$$PbC_2O_{4(s)} \downarrow + 2\ HNO_{3(aq)} \qquad (3)$$
$$PbC_2O_4 + \frac{1}{2}\ O_2 \rightarrow PbO + 2\ CO_2 \qquad (4)$$
$$PbO + (Zr_{0.53}Ti_{0.47})O_2 \rightarrow Pb(Zr_{0.53}Ti_{0.47})O_3 \qquad (5)$$

or
$$Pb(NO_3)_{2(aq)} + (COOH)_2 \cdot 2H_2O_{(aq)} + [(ZrO_2/TiO_2)] \rightarrow$$
$$PbC_2O_{4(s)} \downarrow + [(ZrO_2/TiO_2)\ mixture] + 2\ HNO_{3(aq)} \qquad (6)$$
$$PbC_2O_4 + \frac{1}{2}\ O_2 \rightarrow PbO + 2\ CO_2 \qquad (7)$$
$$PbO + [(ZrO_2/TiO_2)\ mixture] \rightarrow Pb(Zr,Ti)O_3 \qquad (8)$$

From Fig. 2, one can see that reactions (4) and (7) occurred at about 425℃, whereas PZT formation reactions (5) and (8) start to occur at 600℃, which was confirmed by the endothermic peak of DTA curve for the same system reported by Yamamoto et al. In addition, as can be seen in Fig.3, XRD patterns revealed the formation of PZT perovskite phase for partial oxalate methods started to occur in the temperature range of 650 ～ 700℃. This is much lower than the temperature range for mixed oxide method, where typical value is in the range of 850 ～ 900℃.
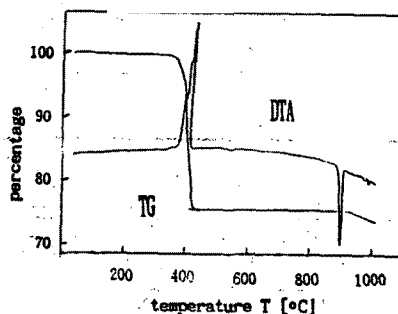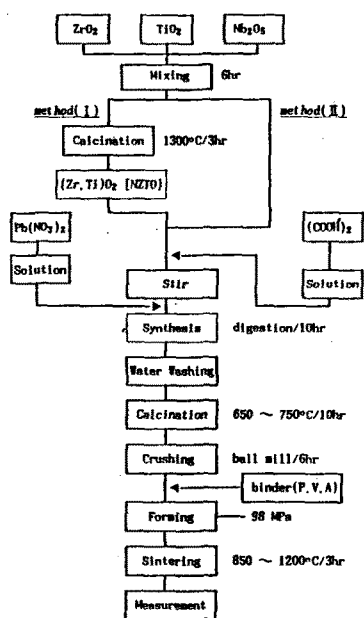

Fig.2. DTA and TGA curves of lead oxalate powder.

Fig.1. Flow chart of PZT powder preparation by the partial oxalate method(I) and the modified partial oxalate method(II).
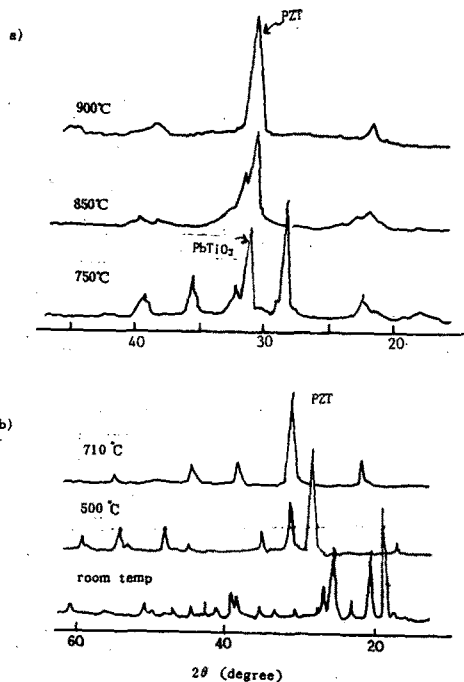

Fig.3. XRD patterns of PZT powders pepared by a) conventional method and b) partial oxalate method

The lowering of PZT formation temperature in partial oxalate methods can be explained by the following. First of all, in mixed oxide method, as temperature increases, $PbTiO_3$ tends to be formed as an intermediate product[2], which then reacts with remaining ZrO_2 to form PZT at a higher temperature. On the other hand, in the partial oxalate method, ZTO powder is used to avoid the formation of $PbTiO_3$, and therefore PZT is formed at a lower temperature. In addition, the use of ultra fine PbO powder produced by the pyrolysis of lead oxalate powder may lower the calcination temperature, since the diffusion path is reduced in a great deal.

In Fig. 4, the temperature dependence of bulk densities of ceramics fired over the temperature range of 850 ～ 1200℃ is demonstrated for various preparation methods. In Fig. 4 and the following figures, same symbols are used to denote various powder preparation routes. Solid dot, open square and triangle represent mixed oxide [PZT], partial oxalate [PZT(1)] and modified partial oxalate-derived powders [PZT(2)], respectively. PZT powders synthesized by two partial oxalate methods show similar sintering behavior, whereas the powder obtained by mixed oxide method shows much 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℃ for partial oxalate-derived powder, whereas the same density is possible at above 1050℃ for 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.
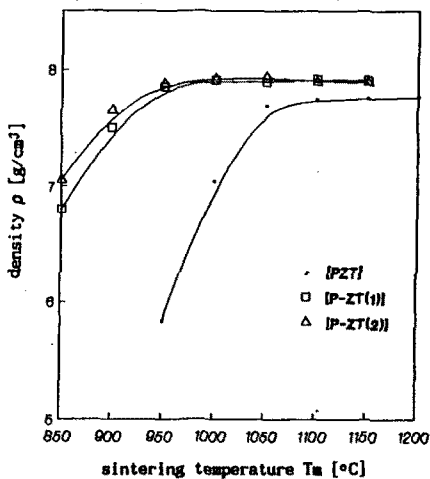
For the sintered samples prepared using three types of PZT powders, the sintering temperature dependence of relative permittivity at room temperature is illustrated in Fig. 5. For two types of partial oxalate methods, relative permittivity reaches maximum at about 1050℃ whereas, for mixed oxide method, the same happens at 1150℃. This result is in accord with Fig. 4, where bulk density values for three methods shows similar trend. The fact that relative permittivity and bulk density show similar temperature dependence can be interpreted due to 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, two partial oxalate methods appear to be better than mixed oxide method since the maximum values of the former happen at about 100℃ lower than that of the latter. This trend is similar to that of dielectric constant, and is again the consequence of 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 can be more adequate in practical applications than mixed oxide method. The sintering temperature for the former can be as low as 950℃, whereas that for the latter must be higher than 1050℃.

Piezoelectric constants d_{33} for three types of samples are shown in Fig. 7, which is important in actuator application. The results also show the similar sintering temperature dependence as relavive permittivity and electromechanical coupling factor.

Fig.4. Bulk density of PZT ceramics as a function of sintering temperature for powders derived by different methods.
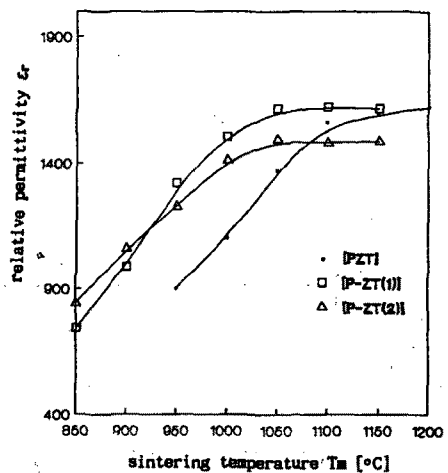

Fig.5. Relative permittivity as a function of sintering temperature for three types of samples.

Remanent polarization from D-E hysteresis loops for samples sintered at four different temperatures using three types of powders is plotted in Fig. 8. It shows that remanent polarization increase with sintering temperature. This temperature dependence again resembles those in relative permittivity and bulk density. From the figure, the saturated values of remanent polarization are $25 \sim 30 \mu m$ /cm^2. In addition, from Figs. 6 and 8, one can find that remanent polarization is proportional to the planar coupling factor.

4. Conclusions

From the results found in this study, it can be concluded that two partial oxalate methods are better techniques to produce fine, homogeneous PZT powder than the mixed oxide method accompanied by ball-milling. Using partial oxalate-derived PZT powders, sintering temperatures can be reduced as low as 950°C without sacrificing desired dielectric and piezoelectric properties, such as relative permittivity, electromechanical coupling factor, and piezoelectric constant. Two partial oxalate methods yield ceramics with almost the same physical and electrical properties, so that the step of producing ZTO powder does not seem to be necessary.
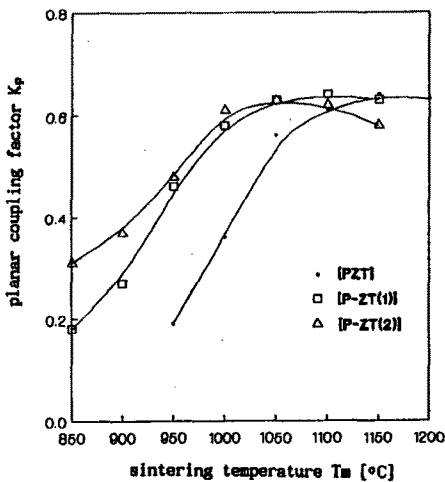
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2. Matso, Y., and Sasaki, H. : "Formtion of lead zirconate-lead titanate solid solution", J. Amer. Ceram. Soc., 48, 289-296(1989).
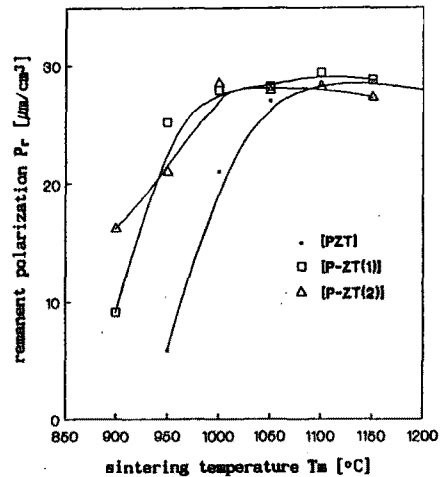
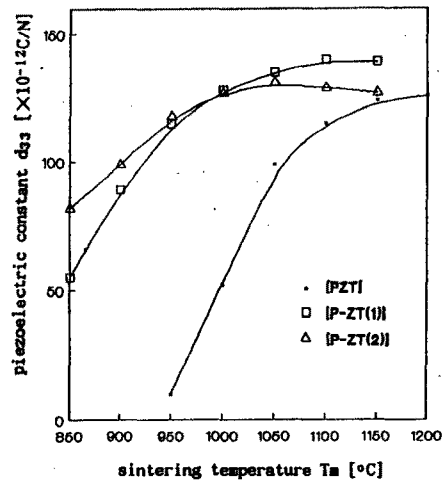Fig. 7. Piezoelectric constant d_{33} as a function of sintering temperature for three types of samples.

Fig. 6. Planar coupling factor as a function of sintering temperature for three types of samples.

Fig. 8. Remanent polarization as a function of sintering temperature.