부분수산법에 의한 PZT 세라믹스의 저온소성과 전기적 제특성

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

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요 약

두가지 부분수산법, 즉 부분수산법(1)과 수정된 부분수산법에 의해 합성한 미분말을 사용하여 PZT 세라믹스를 저온소성하고 그 전기적 제특성을 조사하였다. 두가지 부분수산법에 의해 합성한 분말의 소결거동을 조사해본 결과 고상반응법보다 훨씬 낮은 소결온도인 950℃에서도 단일상의 페로브스카이트상이 얻어지고 치밀화가 이루어졌을 뿐만 아니라 비유전율, 전기기계 결합계수, 압전정수 등 유전 및 압전특성이 고상반응법에 비해 손색이 없었다. 특히 두가지의 부분수산법에 의해 얻어진 PZT 세라믹스는 물리적 전기적 제특성이 서로 비슷하게 나타났으며, 이 결과로부터 부분수산법(1)에서 수반되는 ZTO 분말을 따로 합성하는 공정이 불필요한 수정된 부분수산법이 편리함을 알았다.

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℃ without sacrificing desired dielectric and piezoelectric properties, such as relative permitivity, 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, ZrO_2, and TiO_2 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

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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 homogenious submicron and monosize powder. The pure chemical methods[2] face the problem of poor productivity, while the mechanical milling of conventionally calcined powder[3] 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.[4] In this method, $Mg(NO_3)_2$ and $Nb_2(NO)_5$ are pre-reacted, and PbO is subsequently added to the solution to form chemically homogenious $Pb(Mg_{1/3}Nb_{2/3})O_3$ powder. The modified mixed oxide method proposed by Swartz et al.[5] involves two step firing processes where MgO and Nb_2O_5 powder are pre-reacted to form columbite phase $MgNb_2O_6$ by usual mixed oxide technique, and PbO is reacted with the resulting columbite to obtain single phase perovskite. This method was reported to be very effective to avoid the formation of pyrochlore phase such as $Pb_2Nb_2O_7$ which is known to be detrimental to the desired dielectric properties.

Recently, Yamamoto et al.[6-7] 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, $ZTO(Zr_{0.53}Ti_{0.47}O_2)$ powder is used as starting materi-

al 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 $PbTiO_3$[8] 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, ZrO_2, TiO_2, $Pb(NO_3)_2$, $(COOH)_2 \cdot 2H_2O$, and Nb_2O_5 chemicals, whose purities were reagent-grade or better.

$$Pb(Zr_{0.53}Ti_{0.47})O_3 + 0.5mol\% \cdot Nb_2O_5$$
$$\text{or}$$
$$Pb(Zr_{0.53}Ti_{0.47})Nb_{0.01}O_3 \qquad (1)$$
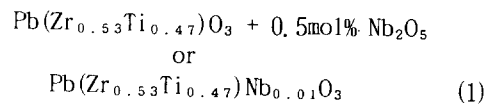
In this study, the PZT powders prepared by the two different versions of the partial oxalate methods and the conventional solid state reaction method of mixed oxides were used. The full details of the two different versions of the partial oxalate methods are described elsewhere.[9] Therefore, it may 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.[6] and the modified partial oxalate method are only different in the elimination of either the use of costly ultra-fine NZTO powder or the solid state reaction process of ZrO_2, TiO_2, and Nb_2O_5 to form NZTO powder from the original method. The modified partial oxalate method was devised to eliminate the energy-consuming reac-

tion of ZTO or NZTO (ZTO doped with Nb_2O_5) 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 ZrO_2, TiO_2 and/or Nb_2O_5 particles replace 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 summerized in Table 1. It is evident that partial oxalate methods yield finer particles than conventional mixed oxide method.

Table 1 Average particle sizes of calci-
ned PZT powders.

Preparation Method	Symbol	Calcination Temp. (℃)	Particle Size (μm)
Conventional Mixed Oxide	PZT	900	1.69
Partial Oxalate	P-ZT(1)	710	0.71
Modified Partial Oxalate	P-ZT(2)	710	0.96

Sintering behavior of the powder compacts was examined by pressing the powder into the pellet at 98MPa and fired at 850~1200℃ 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℃ 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℃ is illustrated for various preparation methods. The same symbols are used in Fig. 2 and in the following figures to denote various
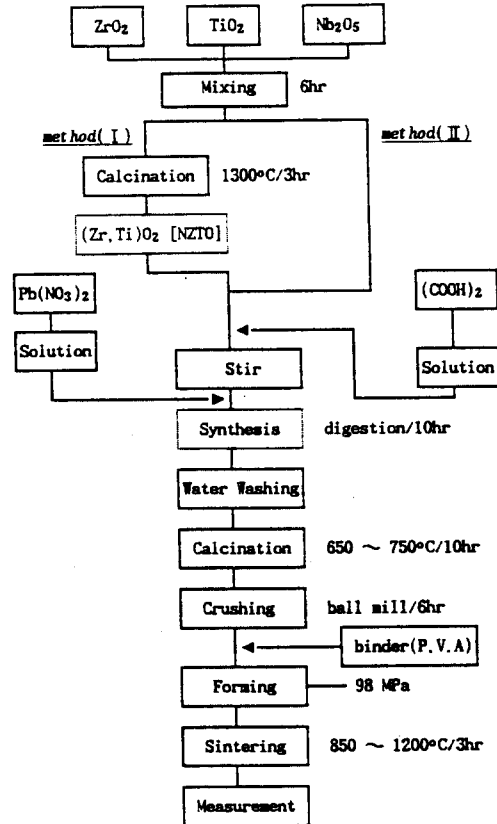

Fig. 1 Flow chart of PZT powder prepara-
tion by the partial oxalate meth-
od(1) and the modified partial
oxalate method(Ⅱ).

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℃ for partial oxalate-derived powder, whereas the same density is possible at above 1050℃ 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 uni form so that the densification can be
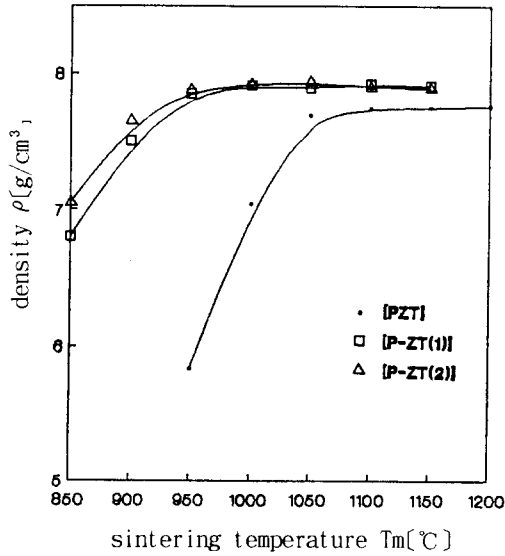
Fig. 2 Bulk density of PZT ceramics as a
function of sintering temperature
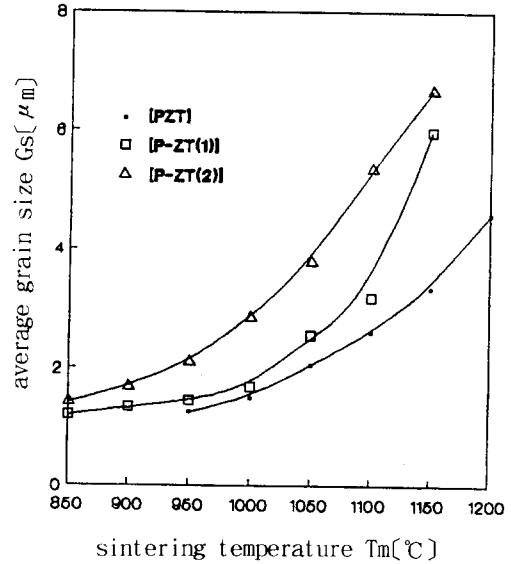for powders derived by different
methods.

Fig. 3 Average grain sizes of PZT ceramics
as a function of sintering tempe-
rature.

Fig. 4 Temperature dependence of relative
permittivity for samples prepared
using modified partial oxalate-
derived PZT powder at various
sintering temperature.

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.[7] for the similar system. Shrout et al.[5] also found the same temperature depen- dences of relative permittivity and Curie temperature for $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramic, and interpreted the data in terms of ave rage grain size instead of sintering temp- erature. 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.

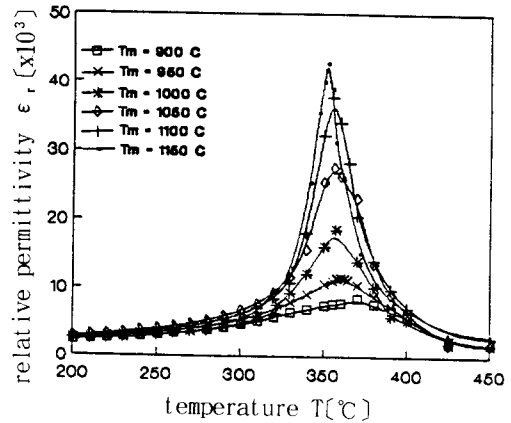For the sintered samples prepared using three types of PZT powders, the sintering

temperature dependence of relative permi- ttivity at room temperature is illustrated in Fig. 5. For two types of partial oxalate methods, relative permittivity reaches the maximum at about 1050℃ whereas, for the mixed oxide method, the maximum occurs at 1150℃. This result is in accord with Fig. 2, where bulk density values for three methods show a similar trend. The fact

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that relative permittivity and bulk densi-
ty 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 tempera-
ture. 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℃ lower than that of the latter.
This trend is similar to that of relative
permittivity, and is again the consequence
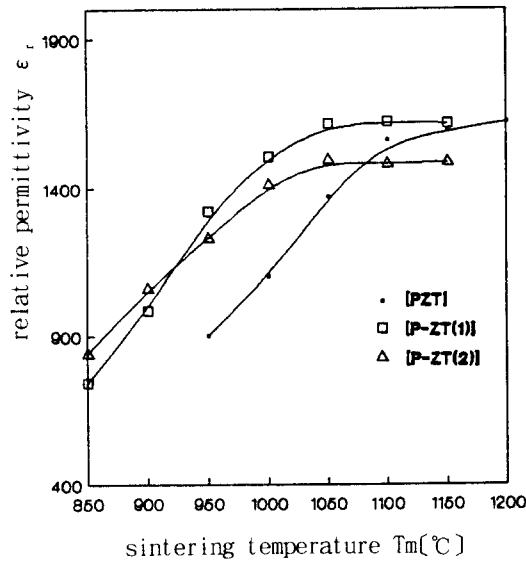of the decrease of sintering temperature

Fig. 5 Relative permittivity as a func-
tion of sintering temperature for
three types of samples.

for the same bulk density.

Since the coupling factor of 0. 55 is
sufficient for most piezoelectric applica-
tions, 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℃, whereas that for the latter must
be higher than 1050℃.

Piezoelectric coefficients d_{31} for three
types of samples, which are important in
actuator application, are shown in Fig. 7.
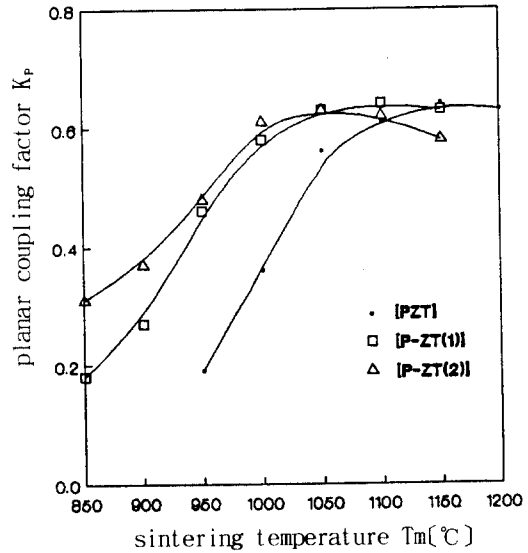The results also show the similar sinteri-

Fig. 6 Planar coupling factor as a func-
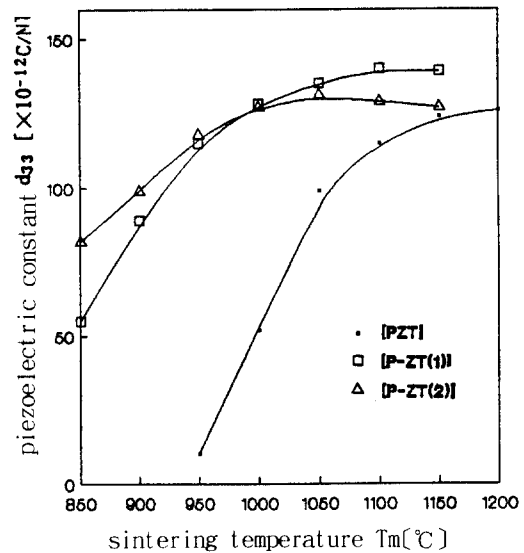tion of sintering temperature for
three types of samples.

Fig. 7 Piezoelectric coefficient d_{31} as a
function of sintering temperature
for three types of samples.

ng temperature dependence as relative
permittivity and electromechanical coupli-
ng factor.

D-E hysteresis loops for samples sinter-
ed at different temperatures using three
types of powders were measured using Sawy-
er-Tower Circuits and typical curves are
illustrated in Fig. 8. Remanent polariza-
tion 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 $25 \sim 30 \mu C/cm^2$. In addition from Fig. 6 and Fig. 9, one can find that remanent polarization is proportional to the planar coupling factor.
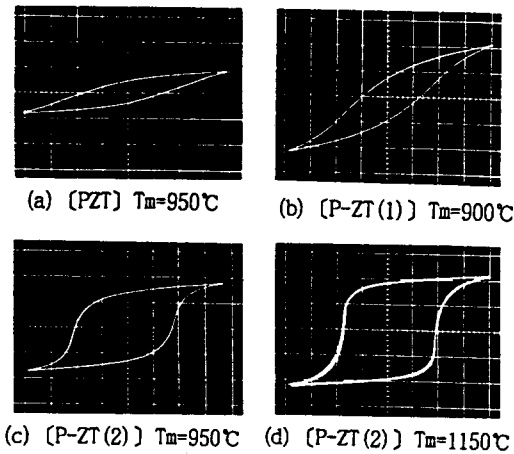
(a) [PZT] Tm=950℃   (b) [P-ZT(1)] Tm=900℃

(c) [P-ZT(2)] Tm=950℃   (d) [P-ZT(2)] Tm=1150℃

Fig. 8   D-E hysteresis loops for PZT ceramics sintered using three types of powders. (vertical: $15 \mu C/cm^2/div$, horizontal: 500V/mm/div)
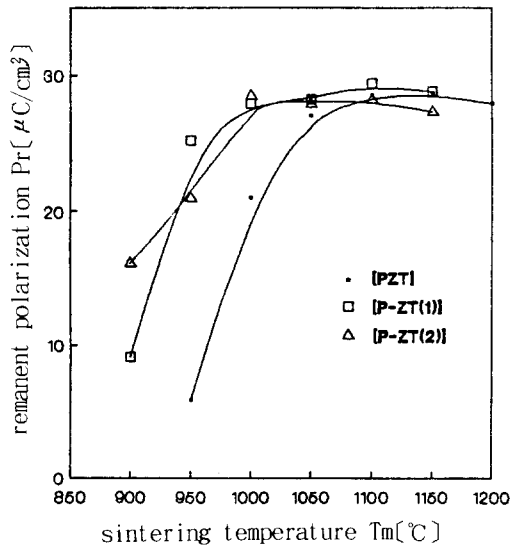
Fig. 9   Remanent polarization as a function of sintering temperature.

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℃ 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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