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Fabrication of fine-grain piezoelectric ceramics using reactive calcination

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Fine-grain piezoelectric ceramics with the formula $Pb(Zr_{0.53}Ti_{0.47})O_3$(PZT) were prepared by a reactive calcination process. Using conventional materials and processing techniques, highly reactive powders of PZT were achieved by calcining to or near the point of maximum volume expansion, whereby associated morphological changes resulted in highly reactive powder. Upon milling, powders $<0.3\ \mu m$ were readily obtained allowing densification at temperatures $<1000\ ^\circ C$. The B-site precursor method, whereby the ZrO_2 and TiO_2 oxides were pre-reacted prior to reaction with PbO, further enhanced reactivity by eliminating intermediate reactions and subsequent phase(s) which can hinder densification and overall homogeneity. Highly dense piezoceramics with grain sizes ~ 1 to $2\ \mu m$ exhibiting dielectric and piezoelectric characteristics comparable to conventionally prepared large grain size materials were obtained.

1. Introduction

Modified lead zirconate titanate (PZT) ceramics are choice materials still widely used for various piezoelectric applications [1–4]. In general, conventionally prepared PZT ceramics are calcined and sintered at relatively high temperatures, ≥ 900 and $1200\ ^\circ C$, respectively, to ensure complete phase formation and the desired piezoelectric properties. Problems associated with the high processing temperatures include PbO loss through volatilization and hence poor overall uniformity. In recent applications, such as multilayer actuators [5, 6] it is desirable to use lower sintering temperatures to incorporate less costly internal electrodes, as well as to achieve finer grain-size structures. The latter are particularly important in high-frequency devices such as biomedical transducers [7].

Processing methods employed to enhance the reactivity of PZT have included various chemical techniques (sol–gel, molten salt, and hydrothermal) to prepare homogeneous and fine powders, as well as high-energy milling, and hot pressing [1–3, 8–13]. Although the above methods have been successful in reducing the firing temperature and subsequent grain size, they are in general expensive and not amenable to large-scale production.

Previous investigations on the role of calcination and its effect on sintering of PZT ceramics found that densification could be enhanced by partially reacting the component powders near the point of maximum volume expansion, an effect generally observed in the formation of lead based $Pb(B)O_3$ perovskites [14]. The enhanced densification was attributed to a reactive sintering process, associated with the completion of the PZT formation reaction. (The term “reaction sintering” is herein defined as a process by which densification is enhanced as the result of an accompanying phenomenon, e.g. a chemical reaction, which is greatly beneficial to diffusion and the overall sintering phenomenon.)

The reaction sequence of PZT, however, is quite complex with several intermediate phases being formed. Associated with these phases, which include $PbTiO_3$, are volume expansions and morphological transformations that may actually hinder or lead to inhomogeneous densification if the oxide mixture is not properly processed. Based on the work by Swartz and Shrout [15] on related lead-based perovskites, it was proposed that by pre-reacting the B-site oxides TiO_2 and $ZrO_2 \rightarrow ZrTiO_4$ prior to reaction with PbO, only a single reaction step and subsequent volume expansion would occur and thus lead to more homogeneous densification.

In this study, the concept of reactive sintering in conjunction with conventional materials and processing techniques was proposed to prepare highly reactive PZT powder and fine-grain piezoelectric ceramics. Reactive sintering was investigated for both mixed oxide and B-site precursor powder methods. The dielectric, piezoelectric, and physical characteristics were determined for both systems.

2. Experimental procedure

2. Powder preparation

The PZT composition selected for this study, being

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near the morphotropic phase boundary, was $Pb(Zr_{0.53}Ti_{0.47})O_3$. Raw materials used for the experiments were reagent grade PbO (Hammond Lead Products, Inc., PbO (yellow, 99%) Hammond, Indiana, USA); TiO_2 (Whittaker, Clark & Daniels, TiO_2 Grade (99%) Pittsburgh, Pennsylvania, USA); and ZrO_2 (Harshaw/Filtrol, ZrO_2 (electronic grade) Cleveland, Ohio, USA). The powders were weighed in a nalgene container and vibratory milled (Sweco, Inc., Model M-18-5, Florence, Kentucky, USA) for 24 h with ethyl alcohol using ZrO_2 milling media. A small amount of dispersant was added to provide efficient milling. The slurry was dried in an oven at 80 °C and calcined near the point of maximum volume expansion described in the next section. To further increase the reactivity of the powder, approximately one-half of the calcined powder was vibratory milled. The materials were designated PZT–AS (as-calcined) and PZT–M (milled).

A PZT mixture was also prepared using zirconate titanate (ZT) powder, where ZT was prepared from ZrO_2 and TiO_2 in the ratio of 53:47. The mixture was prepared as above and calcined at 1400 °C for 4 h. The calcined ZT powder was hammer-milled and sieved through 60 mesh, followed by the addition of PbO and calcined again near the point of maximum volume expansion. Again, part of the powder was milled, designated ZTP–M and ZTP–AS (for the as-calcined material).

2.2. Calcination and sintering studies

To determine the optimum calcination temperature, powders of uncalcined PZT–AS and ZTP–AS were pressed (~ 34 MPa) into discs 1.25 cm in diameter and 3 to 4 mm thick. The discs were heated in an electric furnace up to 1000 °C with a heating rate of $2\,°C\,min^{-1}$, with samples removed from the furnace at 50 °C intervals. The sample dimensions were measured to determine volume expansion and/or shrinkage. X-ray powder diffraction (XRD) of the samples was used to characterize the completion of the reaction sequences. The calcination temperature used for the large batches (~ 1 kg) was selected to be ~ 50 °C less than the point of maximum expansion of the discs to allow for differences due to kinetics. The PZT and ZTP powders were calcined at 725 °C for 4 h. As stated, halves of the two batches were vibratory milled subsequent to calcination to further enhance reactivity. The powders were again characterized for specific surface area, particle size and agglomeration. For comparison of particle size(s) and the degree of agglomeration, scanning electron microscope (SEM) photomicrographs of the powders were taken. Discs were prepared using a 3 wt % PVA being pressed into a disc of 1.25 cm diameter at ~ 70 MPa. The green densities of all the discs were in the range of 4.5 to $4.8\,g\,cm^{-3}$. After binder burnout, the pellets were sintered at 850 to 1200 °C in closed alumina crucibles for 1 h. A PbO atmosphere was maintained using $PbZrO_3$ powder. The pellets were characterized for geometric density and grain size as determined on fractured surfaces by SEM.

2.3. Dielectric and piezoelectric properties

Samples with densities greater than 90% theoretical ($\rho_{theo} \sim 8\,g\,cm^{-3}$) were polished and electroded with sputtered-on gold with air-dry silver applied to ensure better contact during poling and electrical property measurements. Discs were poled in a silicon oil bath at 120 °C with an applied field of 50 to $60\,kV\,cm^{-1}$ for 3 to 10 min. Values of the piezoelectric constant, d_{33}, measured using a Berlincourt d_{33} meter, were checked to ensure completion of poling.

The dielectric constant (K) and dissipation factor (DF) (loss) of the ZTP and PZT samples were measured using a Hewlett-Packard (Model 4274A) LCR meter. The piezoelectric planar coupling coefficient (k_p) and mechanical quality factor, Q_m, were determined using a Hewlett-Packard (Model 3577A) network analyser in reference to the IRE standard [16]. Values were measured 24 h after poling.

3. Results and discussion

The volume expansion/shrinkage curves as a function of calcining temperature for P + Z + T and ZT + P mixtures are shown in Fig. 1. As presented, the PZT mixture exhibited two volume expansions near 650 and 750 °C, whereas the ZTP, as anticipated, exhibited only one near 800 °C. As previously reported [14], the two expansion maxima observed for P + Z + T reflect the formation of PT (~ 650 °C) and intermediate PZT phase(s) (~ 750 °C), respectively. The volume expansions are reportedly believed to be due to a molar volume increase of the reaction phase(s) in contrast to the starting oxides. Naturally, the expansion behaviour is dependent on the forming pressure, heating rate, etc. The sequence of XRD patterns shown in Fig. 2a also confirms the formation of the intermediate phases PT and PZT. Above 750 °C, the completion of the perovskite PZT phase began to take place, with the diffraction peak(s) becoming sharper with increasing temperature. In the ZTP case (see Fig. 2b) no reaction took place until ~ 750 °C, where the formation of PZT began and completed at ~ 800 °C as reflected by the strong diffraction peaks.

Simplified reaction sequences of the two types of

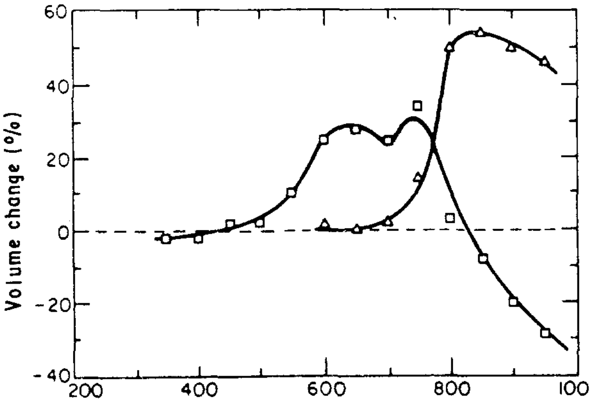

Figure 1 Volumetric expansion/shrinkage characteristics for □ P + Z + T (PZT) and △ ZT + P (ZTP) mixtures as a function of temperature.

PZT mixtures can be summarized in the following:

P + Z + T [PZT–AS]	P + ZT [ZTP–AS]
$PbO + TiO_2 \xrightarrow{\sim 650^\circ C} PbTiO_3$	
$PbO + PbTiO_3 + ZrO_2 \xrightarrow{\sim 750^\circ C} Pb(Zr_xTi_{1-x})O_3$ (intermediate PZT)	$PbO + ZrTiO_4 \xrightarrow{\sim 800^\circ C} PZT$
$PbTiO_3 + Pb(Zr_xTi_{1-x})O_3 \xrightarrow{> 750^\circ C} PZT$	

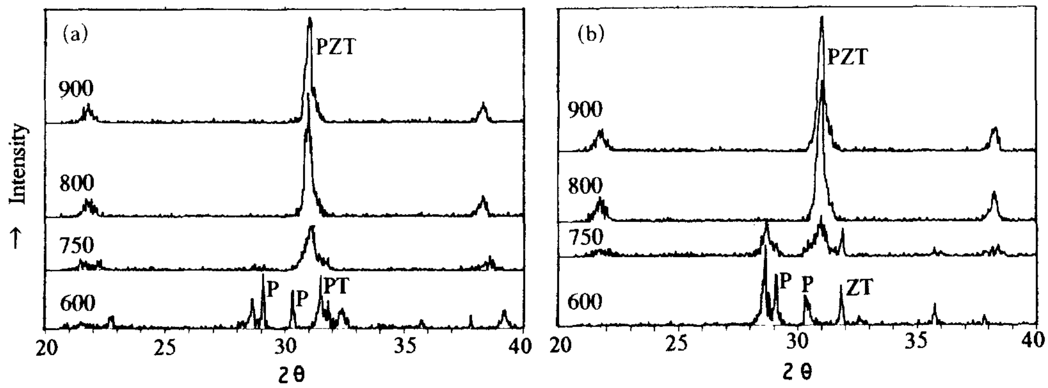

Figure 2 XRD patterns for (a) P + Z + T and (b) ZT + P formation processes.

TABLE I Component and reacted powder characteristics

Component powders	Surface area ($m^2 g^{-1}$)	Equivalent particle size (μm)	Median particle size (μm)*	Average Agglomeration Number (50)
PbO	0.54	1.20	5.9	120
TiO_2	8.40	0.17		
ZrO_2	21.4	0.05	0.9	5800
Reacted powders				
($ZrTiO_3$)-precursor	1.2	1.00	3.5	43
PZT–AS	0.50	1.50	3.8	16
PZT–M	2.97	0.25	1.1	85
ZTP–AS	1.09	0.68	1.8	18
ZTP–M	2.70	0.27	0.8	26

*Micromeretic Sedigraph (model 5000).

Although the reported reaction sequence(s) for P + Z + T are more complex than presented, the importance of the B-site precursor method in eliminating intermediate reactions and associated morphological changes was apparent. This technique helps prevent the possibility of problems associated with unreacted ZrO_2 and competing volume expansions with densification during firing. The single calcines of the PZT–AS and ZTP–AS at 725 °C for 4 h, though below the point of volume expansion(s) shown in Fig. 2, were found to be single-phase perovskite PZT. The process by which powders are reacted at a point of maximum volume expansion due to associated morphological changes is hereafter designated as "reactive calcination".

The powder characteristics of the milled and unmilled reactively calcined PZT and ZTP powders are reported in Table I. Also included are the powder characteristics of the ZT precursor powder. As presented, the equivalent particle size as determined from the surface area, was smaller for the ZTP powder, though both were calcined at the same conditions. Upon milling, a significant reduction in particle size and corresponding increase in surface area was observed with a slight increase in agglomeration. It is interesting to note that the PZT–AS and ZTP–AS powders milled to approximately the same particle size, reflecting the limit of milling efficiency. SEM analysis confirmed the calculated particle sizes and degree of agglomeration.

Densities of the sintered discs as a function of firing temperature (850 to 1200 °C) for the PZT and ZTP materials are plotted in Fig. 3. Almost no increase in density occurred below 900 °C for PZT–AS and milled (PZT–M) powders, whereas densification (> 85% theoretical) occurred as low as 850 °C for ZTP. As expected, milling increased the reactivity of the powders and subsequent densification. Densities > 90%

TABLE II Dielectric and piezoelectric properties of PZT and ZTP

	Firing temperature (°C)	Density ($g\,cm^{-3}$)	Average grain size (μm)	K (RT, 1 kHz)	Dissipation Factor (%)	Piezo d_{33} ($\times 10^{-12}$ C/N)	k_p (%)	Q_m
$Pb(Zr_{0.53}Ti_{0.47})O_3$ [1]	> 1200	7.5	5–10	~ 700	–	~ 200	45	–
PZT–AS	1000	6.3	2.0	–	–	–	–	–
	1200	7.4	2.6	440	1.4	200	46	330
ZTP–AS	1000	7.8	2.1	890	1.6	180	25	240
	1200	7.9	2.8	800	0.7	250	50	380
PZT–M	1000	7.3	0.9	560	1.5	170	29	210
	1200	7.8	1.8	480	0.9	190	46	350
ZTP–M	1000	7.7	1.5	790	2.6	190	34	200
	1200	7.8	2.4	740	1.7	250	49	270

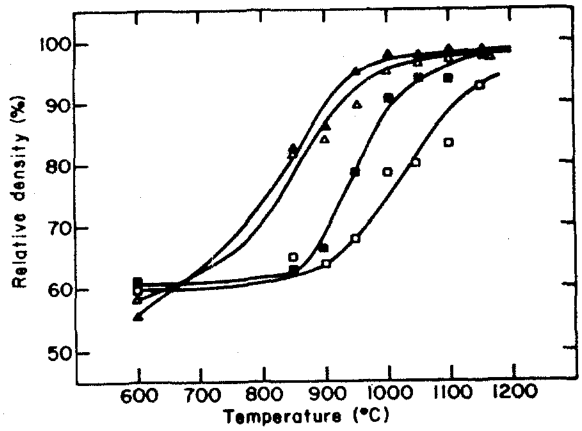

Figure 3 Sintering behaviour of milled and as-calcined PZT and ZTP powders. □, PZT–AS; ■, PZT–M; △, ZTP–AS; ▲, ZTP–M.

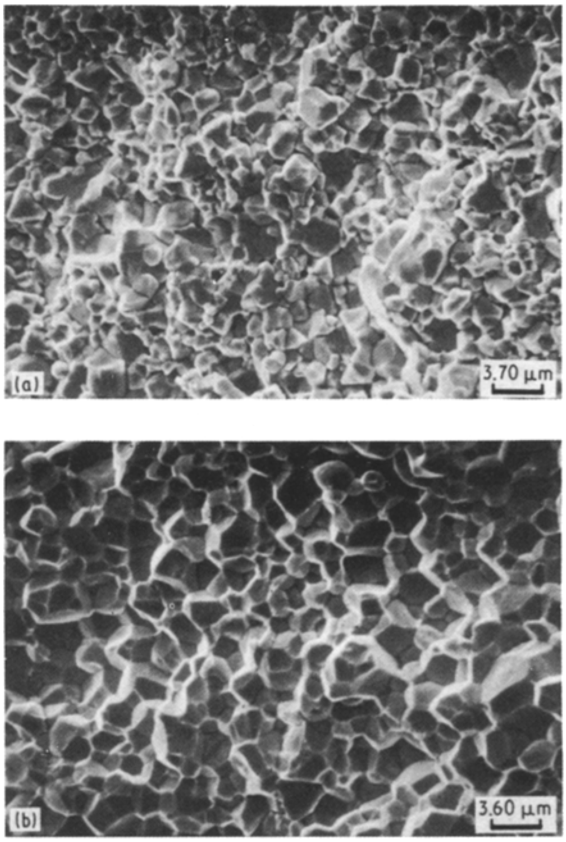

Figure 4 SEM photomicrographs of ZTP–M samples fired at (a) 1000 and (b) 1200 °C, respectively (fracture surfaces).

theoretical were achieved for the ZTP–M material as low as 950 °C, whereas temperatures of 1000 and 1200 °C were required for the PZT–M and PZT–AS, respectively. The average grain sizes for PZT and ZTP samples fired at 1000 and 1200 °C are reported in Table II.

Typical SEM photomicrographs of fractured (intergranular) surfaces of the sintered samples are shown in Fig. 4. Grain sizes for PZT–AS and ZTP–AS samples fired at 1000 °C were found to be ~ 2 μm, increasing in size to ~ 3 μm at the higher firing temperature. Samples processed with the milled powders were found to be somewhat smaller. Grain sizes in the neighbourhood of ~ 1.5 μm with a fired density > 95% theoretical were obtained for the ZTP–M material fired at only 1000 °C for 1 h.

In addition to physical characteristics, the dielectric and piezoelectric properties of PZT–M and ZTP–M ceramics fired at 1000 and 1200 °C are reported in Table II. For comparison, data for conventionally prepared $Pb(Zr_{0.53}Ti_{0.47})O_3$ from Jaffe *et al.* [1] are reported. Okazaki and Nagata [17, 18] found that both the dielectric and piezoelectric properties (K, d_{33}, k_p etc.) increase with density and grain size. This behaviour was also observed where the lower density and finer grain sized materials possessed lower values. However, the largest deviations were found to occur between the PZT and ZTP materials, regardless of density or grain size. The PZT materials, whether originally milled or not, possessed significantly lower dielectric constants and piezoelectric d_{33} values. This difference reflects inhomogeneity in the PZT material in that the properties, such as the dielectric K, are very dependent on the Zr:Ti ratio near the morphotropic phase boundary. Also the piezoelectric properties d_{33} and k_p for the ZTP materials fired at 1000 °C were inferior to those fired at 1200 °C, though possessing similar densities and grain sizes. The lower values are believed to be related to the crystallinity of the materials being less developed. The associated defects thus result in a stiffening out of the extrinsic polarizability (domain wall motion) [19]. As found for other perovskites [20] longer sintering times may anneal out various crystalline defects resulting in less grain-size dependency.

4. Conclusions

Using reagent-grade materials and conventional processing techniques, fine-grain PZT ceramics were fabricated based on reactive calcination. By reacting the component powders (PbO, ZrO_2, and TiO_2) near the point of maximum volume expansion, very fine (< 0.3 µm) and highly reactive powders were readily made. Such powders could be densified at temperatures less than $\sim 1000\,^{\circ}C$. Being fully reacted, enhanced densification was simply due to the reactive nature of fine powders and not due to a reactive sintering process, as originally proposed. The reactive calcination process was further enhanced by first prereacting the B-site oxides (ZrO_2 and TiO_2) prior to reaction with PbO. This step eliminated intermediate phase reactions which hindered densification and resulted in a more homogeneous material.

Highly dense piezoceramics with fine grain size structure < 2 µm exhibiting dielectric and piezoelectric properties comparable to conventionally prepared large grain-size materials were obtained. However, further investigations of the mechanisms and morphological changes which take place during calcination are still required. The role of grain size and associated dependency of the dielectric and piezoelectric properties also needs to be addressed.

References

1. B. JAFFE, W. R. COOK, Jr. and H. JAFFE, "Piezoelectric Ceramics" (Academic Press, New York, 1971).
2. R. C. BUCHANAN, "Ceramic Materials for Electronics" (Marcel Dekker, New York, 1986) p. 154.
3. L. M. LEVINSON, "Electronic Ceramics Properties, Devices, Applications" (Marcel Dekker, New York, 1987) p. 371.
4. T. SHIOSAKI, *Ferroelectrics* **91** (1989) 39.
5. K. UCHINO, *Ceram. Bull.* **65** (1986) 4.
6. W. WERSING, H. WALTH and M. SCHNOLLER, *Ferroelectrics* **87** (1988) 271.
7. W. A. SMITH, A. A. SHAVLOV and B. A. AULD, *ibid.* **91** (1989) 155.
8. L. M. BROWN and K. S. MAZDIYASNI, *J. Amer. Ceram. Soc.* **55** (1932) 541.
9. J. B. BLUM and S. R. GURKOVICH, *J. Mater. Sci.* **20** (1985) 4479.
10. M. SUZUKI, S. UEDAIRA, H. MASUYA and H. TAMURA, "Ceramic Powder Science" IIA edited by G. Messing, E. Fuller, Jr. and H. Hausner (American Ceramic Society, Westerville, OH, 1988) p. 163.
11. J. H. ADAIR, T. R. SHROUT and K. OSSEO-ASARE, Proceedings International Meeting on Advanced Materials, MRS, Tokyo **3** (1989) p. 141.
12. K. C. BEAL, "Advances in Ceramics, Vol. 21: Ceramic Powder Science" (American Ceramic Society, Westerville, OH, 1987) p. 33.
13. S. TASHIRO, N. SASKI, Y. TSUJI, H. IGARASHI and K. OKAZAKI, *Jpn J. Appl. Phys.* **26** (1987) 142.
14. S. VENKATARAMANI, Ph.D. thesis, Pennsylvania State University, 1981.
15. S. L. SWARTZ and T. R. SHROUT, *Mater. Res. Bull.* **17** (1982) 1245.
16. I. R. E. Standards on Piezoelectric Crystals: Measurements of Piezoelectric Ceramics (Institute of Electrical and Electronics Engineers, New York, 1961).
17. O. OKAZAKI and K. NAGATA, "Mechanical Behavior of Materials" (Society of Materials Science, Kyoto, Japan, 1972) p. 404.
18. K. OKAZAKI and K. NAGATA, *J. Amer. Ceram. Soc.* **56** (1973) 82.
19. X. L. ZHANG, X. CHEN, L. E. CROSS and W. A. SCHULZE, *J. Mater Sci.* **18** (1983) 968.
20. T. R. SHROUT, U. KUMAR, M. MEGHERHI, N. YANG and S. J. JANG, *Ferroelectrics* **76** (1989) 479.

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