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Structure and Properties for 28 GHz Microwave Sintered PZT Nanocomposites

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Dense Pb(Zr, Ti)O_3(PZT)/Al_2O_3 nanocomposites were prepared by the 28 GHz microwave heating method and conventional electric furnace sintering. Electrical and mechanical properties of the composites were investigated. The fracture strength of the PZT composites with 0.1 vol% Al_2O_3 was significantly improved in both sintering methods. Smaller grain size and effective reinforcement of the PZT matrix by the second phase were considered to be responsible for the excellent fracture strength. Planar electromechanical coupling factor Kp of the composites sintered by 28 GHz microwave heating was higher than that of the materical prepared by the conventional route. It seemed that the control of the reaction between PZT and Al_2O_3 by the microwave rapid sintering resulted in the high piezoelectric properties.

Key words : PZT, Microwave sintering, Fracture strength, Microstructure, Coupling factor

I. Introduction

Microwave-aided sintering of ceramic materials has been studied by many researchers.[1-4] A lot of benefits of the microwave sintering are reported, e.g. low temperature and short time sintering, rapid heating rates for processes, and fine or bimodal microstructures, Another feature of the method is that it produces a selective heating effect due to the difference in dielectric loss factor between the matrix and second phase.

Lead zirconate titanate (PZT) and its related materials are widely used as actuators and resonators because of their excellent piezoelectric properties. However, piezoelectric ceramics based on PZT have low reliability and poor mechanicl properties, such as, fracture toughness and strength. Therefore, the improvement of the mechanical properties for PZT ceramics is strongly required. Recently, a novel method has been developed to improve the mechanicl property of structural and electronic ceramics. It involves reinforcement by a nano-scale particles 'nanocomposites'.[5,6] Good mechanical properties can be expected in PZT ceramics reinforced by nano particles. In the present study, Al_2O_3, which has lower dielectric loss factor and higher Young's modulus than PZT, was selected as the second phase for the improvement of mechanical properties. Furthermore, by microwave heating, with the selective heating or rapid sintering, and by minimizing the second phase additive content, it could be expected that the control of the reaction between PZT and Al_2O_3 would prevent the decreasing the electrical properties of PZT/Al_2O_3 nanocomposites.

The purpose of this study was to fabricate PZT/Al_2O_3 nanocomposites by the microwave and conventional processing, and to investigate the effect of the second phase and microwave processing on the electrical and mechanical properties for the PZT/Al_2O_3 nanocomposites.

II. Experimental Procedure

As a starting PZT powder, Pb($Zr_{0.52}Ti_{0.48}$)O_3 (Sakai Chemical Industry Co. Ltd., PZT5248) composition which shows the highest electric properties in the $PbZrO_3$-$PbTiO_3$ solid-solution systems was selected. This PZT powder was fabricated by a hydrothermal synthesis, and its average particle size is 0.3 μm. PZT and High purity (>99.9%) Al_2O_3 (TMDA-R, Taimei Chemical Co. Ltd., Japan) powder (0.1, 0.5, 1.0 vol%) were wet-milled in a polyethylene pot using isopropyl alcohol and ZrO_2 balls for 24 h. Mixed slurries were dried with a rotary evaporator. Green pellets were molded by uniaxial pressing at 5 MPa and followed by cold isostatic pressing (CIP) at 200 MPa. The dimensions of green pellets were 17 mm in diameter and 2.5 mm in thickness. Microwave sintering was carried out by 28 GHz power generated by a Gyrotron oscillator. Green pellets were placed on a zirconia plate in the 99.5 % high purity alumina crucible; alumina fiber board was used for thermal insulation (Fig. 1). The sintering profile was 5 mm holding time at 1200°C with 50°C/min heating rate. The temperature during sintering was measured using a Pt sheathed K-type thermocouple. For comparison,

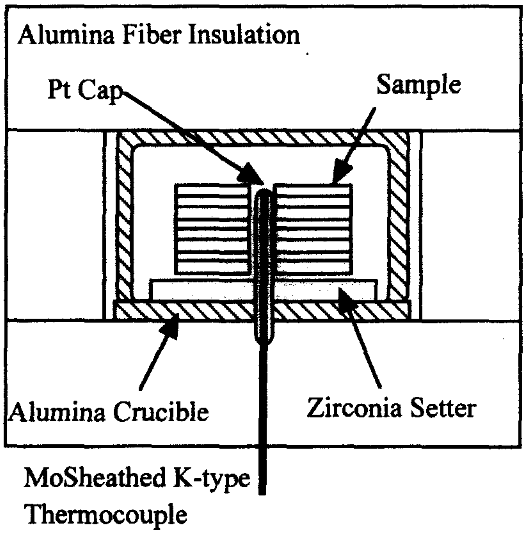


Fig. 1. Sample case of PZT composites for microwave sintering.

samples were fired by the electrical furnace under a PbO controlled atmosphere in the same alumina crucible. The sintering profile was 1200°C and 2 hours holding time with 5°C/min heating rate.

The sintered bodies were ground and polished to a thickness of 1.7 mm by a 400-grit resin-bond diamond wheel and 9, 3 and 0.5 μm diamond pastes. For electric property measurement, Ag-paste was printed on both sides of the disk, and then fired at 600°C for 10 min. The poling treatment was carried out in silicon oil at 120°C for 30 min with an electric field of 2 kV/mm.

Bulk density was determined by the Archimedes method in water, and then relative density was calculated by using the theoretical density. Fracture strength was measured by the piston-on-ring biaxial flexure test.[7-9] Hardness and fracture toughness were measured by the indentation fracture method and calculated using the equation proposed by Niihara *et al.*[10] Young's modulus was measured by the pulse echo method. Fracture surfaces and microstructures were observed with a scanning electron microscope (SEM). The dielectric constant (εr) at 1 kHz and the frequency characteristics were measured by an impedance analyzer (HP4194A). The planar electromechanical coupling factor Kp was calculated as described in literature.[11]

III. Results and Discussion

The relative density of PZT composites prepared by 28 GHz microwave heating and conventional sintering is shown as a function of Al_2O_3 content in Table 1. Although relatively short sintering times were used, the relative densities of the monolithic PZT prepared by the microwave sintering were much higher than those prepared by conventional sintering. However, with the addition of 0.1 vol% Al_2O_3, the relative density of conventional sintering was slightly increased and on the other hand, that of microwave sintering was decreased drastically. Furthermore, the relative densities of PZT composites were of almost similar values in the same composition regardless of sintering methods.

The average grain size calculated by the intercept method using SEM photographs is also given in Table 1. The addition of Al_2O_3 resulted in a reduction of the average grain size of the composites in both cases. This behavior suggests that the microwave processing can promote the sintering of PZT, however, the addition of Al_2O_3 inhibited the grain growth of PZT strongly. It is considered that the lead aluminate created by the reaction between Al_2O_3 and PZT during sintering hinders the matrix grain growth. In addition, the incorporation of Al^{+3} ions into the PZT lattice effectively modifies the surface energy of PZT and as a consequence, homogeneous grain structure with a fine grain size was realized in the nanocomposites.

Fracture strength measured by a biaxial flexure test, hardness and fracture toughness, measured by indentation fracture (I.F.) method, are shown in Fig. 2 and 3. In both sintering conditions, the strength of the monolithic PZT was 70~80 MPa. The strength of the nanocomposites increased with increasing Al_2O_3 content. The nanocomposite with 0.5 vol% Al_2O_3 shows a maximum strength value, (110~120 MPa). Furthermore, the hardness of the composites was significantly improved by 0.1 vol% Al_2O_3 addition in both sintering methods. Fracture toughness of the composites was almost the same or slightly decreased with the addition of Al_2O_3.

In order to analyze improvement of the strength, the

Table 1. Characterisitic and Properties for PZT/Al_2O_3 Composites

Al_2O_3 Content (vol%)	Sintering Method	Relative Density (%)	Mean Grain Size (μm)	Unpoled Dielectric Constant*	Poled Dielectric Constant*	Kp (%)
0	Microwave	100.0	4.5	1152	1411	48.6
0.1	Microwave	97.8	4.9	1037	1120	46.2
0.5	Microwave	97.2	1.5	1024	971	37.6
1.0	Microwave	97.8	1.2	831	781	39.8
0	Conventional	97.2	7.6	1128	1379	41.4
0.1	Conventional	97.6	2.4	1093	1078	20.0
0.5	Conventional	97.7	1.1	1093	1045	12.2
1.0	Conventional	97.0	0.9	1029	1028	10.1

*Measurement at 1 kHz.

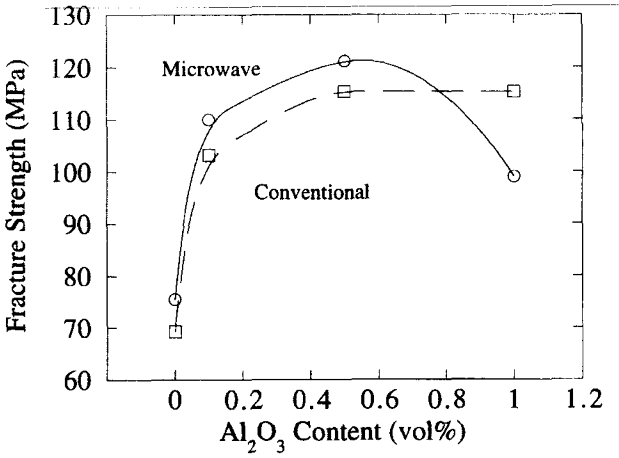


Fig. 2. The fracture strength of PZT/Al_2O_3 composites.

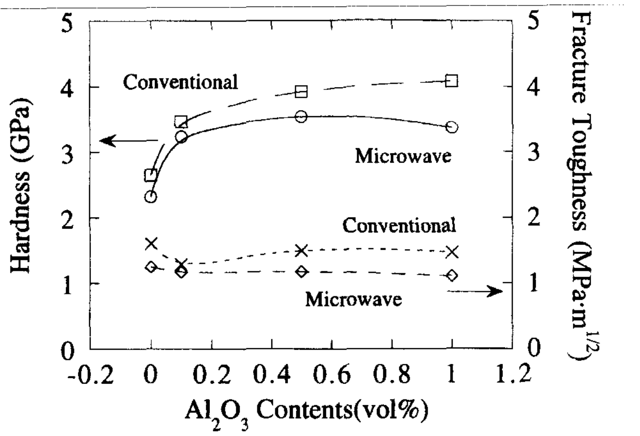
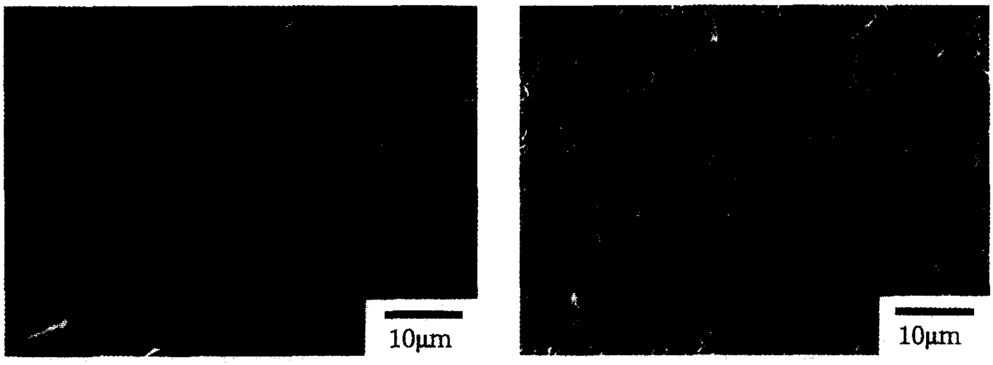


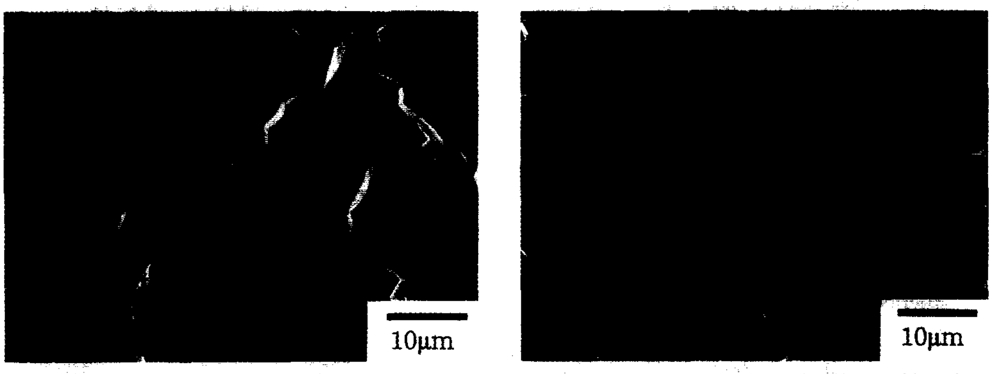
Fig. 3. The hardness and fracture toughness of PZT/Al_2O_3 composites.

microstructure of sintered bodies was observed by SEM. SEM images of the fracture surfaces for monolithic PZT and 0.5 vol% Al_2O_3 added composites sintered by microwave and commercial sintering are shown in Fig. 4. The fracture mode was completely intergranular in monolithic PZT, whereas, it changed from intergranular to intra and intergranular with Al_2O_3 addition. These microstructural observations suggest that the PZT grain boundary was reinforced by the small quantity of Al_2O_3 addition. It is considered that this grain boundary reinforcement and grain size reduction improved the fracture strength and hardness of the composites. A little degradation of fracture toughness of composites is considered to result in the decrease of crack deflection effect due to the intragranular fracture. From the further microstructure observation by SEM, the second phase were homogeneously dispersed in the PZT matrix. The grain size of the dispersed phase was estimated to be 100~500 nm. As mentioned previously, small quantity of the dispersed particles is enough to prevent grain growth and to effectively reinforce PZT matrix.

The relative dielectric constant before and after poling



(a) Conventional Heating Monolithic PZT (b) Conventional Heating PZT/0.5vol%Al_2O_3



(c) Microwave Heating Monolithic PZT (d) Microwave Heating PZT/0.5vol%Al_2O_3

Fig. 4. SEM photographs showing the microstructure change of PZT composites by Al_2O_3 addition.

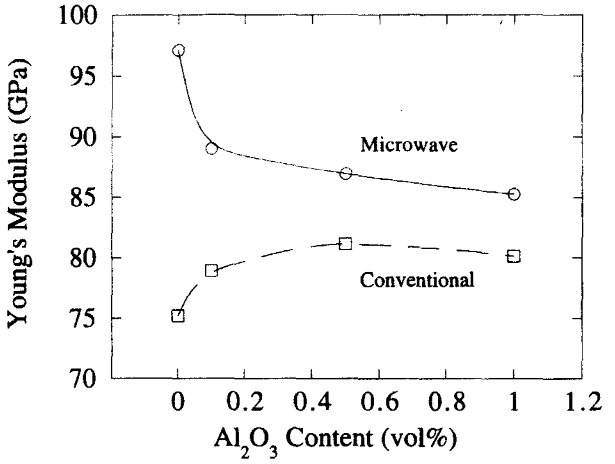


Fig. 5. Effct of the second phase dispersoids on the Young's modulus of PZT/Al_2O_3 composites.

treatment and Kp of the composites were given in Table 1. The dielectric constant of the poled PZT/Al_2O_3 composites decreased with increasing second phase content. However, a very small change of the dielectric constant with Al_2O_3 content was found for the unpoled materials. This phenomenon suggests that the intergranular second phases prevent domain switching. Since the contribution by domain switching to the dielectric constant was decreased in the composites, the dielectric constant of the composites after poling decreased with Al_2O_3 content. Kp of the composites was also decreased by Al_2O_3 addition in both sintering methods.

Another feature that is observed in Table 1 is that the sintering method causes a different dielectric behavior in the composites. The Kp degradation with Al_2O_3 content in the composites prepared by microwave sintering was a small in comparison to conventional sintering. It would be considered that extremely rapid sintering, which is one of the characteristics of the microwave sintering can control the reaction between the PZT matrix and Al_2O_3. From the result of Young's modulus measurement, as shown in Fig. 5, the Young's modulus of the composites sintered by microwave heating was higher than that by conventional one in the same compositions. It is suggested that the effect of the matrix reinforcement by the dispersoids is much greater in microwave-sintered composites than conventional processing due to the controlled reaction between the matrix and dispersoids.

IV. Conclusion

High strength PZT nanocomposites with 0.1~1.0 vol% Al_2O_3 were successfully prepared by 28 GHz microwave heating or conventional heating methods. The fracture strength of 0.5 vol% Al_2O_3 added PZT nanocomposites was about two times higher than monolithic PZT. Al_2O_3 had a significant influence on the microstructure development of PZT ceramics in both sintering methods. The composites prepared by microwave sintering show higher Kp than that for conventional heating. It was found that microwave sintering might control the reaction of Al_2O_3 with PZT.

Acknowledgments

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