Fabrication and Piezoelectric Properties of 1-3 Composite Sheets Consisting of Highly Oriented PZT Single Crystal Grains

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Abstract

Cube-shaped PZT single crystals with PZ/PT=55/45 composition were grown in a relatively uniform size distribution around 80μm by a PbO-flux method. The PZT grains obtained were mixed with liquid polyimide resin and rolled on a glass plate to fabricate 1-3-type composite sheet. This rolling process resulted in a high orientation of the PZT grains as the {h00} are parallel to the substrate plane. The degree of grain orientation reached about 90%. After heating at 180°C, the composite sheet showed a well-defined DE hysteresis loop due to the dielectric property of PZT grains. The longitudinal field-induced strain was 0.2% at 120kV/cm.

1. Introduction

Recently single crystals of piezoelectric materials attract much attention for the piezoelectric performance is highly enhanced by a domain operation [1-3]. If PZT exists in single crystal, the physical properties are of interest in connection with the crystallography, but it is very difficult to grow PZT single crystal in a reasonable size, particularly near the morphotropic phase boundary (MPB) composition (PZ/PT=52/48). Anyhow, since the ferroelectric and piezoelectric properties of the MPB PZT is little made clear in connection with the crystallography, it is praised to obtain its single crystal in a certain size. Though a PbO flux method has been attempted to grow MPB PZT single crystals in our laboratory, it resulted in the precipitation of grains as large as no more than several 10μm. The PZT grains thus obtained, though so small, exhibited the feature of single crystals, assuming the habit of cube well-developing the six planes {100}. Because of the cube-habit, these PZT grains should be settled looking the side face upward, when scattered onto a substrate, in a similar manner as a dice is stable in contacting its side face with table plane. If such the oriented state is fixed with a polymer binder into sheet in thickness same as the size of PZT grain, we can see interesting physical properties, possibly like single crystal. This composite sheet is classified as 1-3 type, according to the concept of connectivity of piezoelectric component in the diphasic solid [4]. The 1-3 composites consisting of PZT ceramics are widely studied for ultrasonic transducer application [5, 6], however, the one using PZT single crystal grains, in which they are highly oriented, is of quite new style. If such the composite is realized, it may allow us development of new application.

In this paper, PZT single crystals were grown by a PbO flux method and 1-3 composite sheets were fabricated by using them. Liquid polyimide resin was adopted as matrix, because the handling is relatively easy. As the perovskite composition, PZ/PT=55/45 was chosen aiming at that rhombohedral phase is precipitated, the piezoelectric function is well-remained and the crystals are grown in size at least larger than in the MPB composition. The reason why the rhombohedral crystal was adopted is that the grain-orientation mode is unified, because the {100} are all equivalent. For the 1-3 composite sheets fabricated, the grain-orientation is discussed together with the ferroelectric and

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piezoelectric properties.

2. Experimental

Raw oxides, PbO, ZrO_2 and TiO_2 of reagent grade, were mixed to PbO/perovskite=2/1 composition. The oxide mixture was placed into a platinum crucible, soaked at 1175°C for 5h in an electric furnace and cooled to 800°C at a rate of 2°C /h. The cooled and solidified melt was treated with an acetic acid solution to remove the PbO added in excess. The PZT crystals purified were checked by XRD analysis to be rhombohedral phase with the absence of any secondary phase. For the fabrication of 1-3 composite sheets, the PZT grains sieved to 75 to 100μm size were used.

Figure 1 illustrates the processing scheme for the fabrication of 1-3 composite sheets. A certain amount of liquid polyimide resin was added to the PZT grains, and their mixture was rolled on a glass substrate. By this rolling, the PZT grains are arrayed in one layer with a high orientation. After drying at 120°C for 1h in a drying oven, the resultant composite film was stripped off from the substrate and hot-pressed in a metal mold of punch-die type under 0.2MPa at 180°C for 30min using a heater-press-machine. The temperature 180°C was necessary to make sure the high insulation of polymer. In this hot-pressing treatment, the composite film was sandwiched in between 0.2mm thick Teflon sheets and then put into the machine. The insertion of Teflon sheets is effective for the PZT grains uneven in height expose the heads from the polyimide resin. Since this occurs due to the flow of Teflon and polyimide, it was important to previously cut the composite film and Teflon sheet in size smaller than the punch diameter.

Gold-sputtered films were applied to both the surfaces of composite sheet as electrodes to measure the electrical properties. Against the applied voltage, the dielectric DE hysteresis loop was observed by using a piezoelectric test system (Radiant RT-6000HVS), and the field-induced strain was measured by using a laser-type displacement meter.

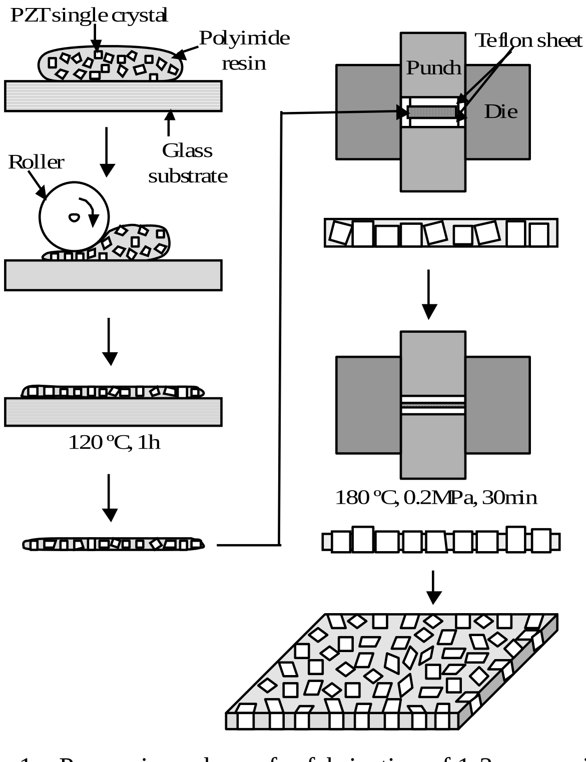

Fig. 1 Processing scheme for fabrication of 1-3 composite sheet consisting of highly oriented PZT single crystal grains.

3. Results and Discussion

3.1. Fabrication of 1-3 Composite Sheets

The PZT crystals obtained by a PbO flux method showed size distribution curve with peak at around 80µm. As a whole, the crystals were grown in size in some extent larger compared to in the MPB composition (PZ/PT=52/48). Figure 2 shows SEM photograph of PZT crystals which are sieved to the range of 75 to 100µm. These crystals assume a habit of discrete dice, seeing with a favorable eye. The XRD analysis revealed that they were of rhombohedral structure. Figure 3 shows an example of as-rolled film with matrix of polyimide resin. It is shown that most of PZT grains look at the side face upward. In this film, the filling fraction of PZT grains goes up to about 50%. As the other results, no matter how high the filling fraction was up to 60% at the highest. In Fig. 4, XRD diagrams are compared between the as-rolled film and the powder sample of the same crystals. It is evident that the PZT crystals are highly oriented as the {h00} is parallel to the film plane. By Lotgering's equation [7], the degree of grain-orientation to the {h00} was estimated to be about 90%. This high grain-orientation is due to a shear effect on the rolling. In the rolling process, however, there was a question that the PZT grains of smaller size are still covered with the polymer.

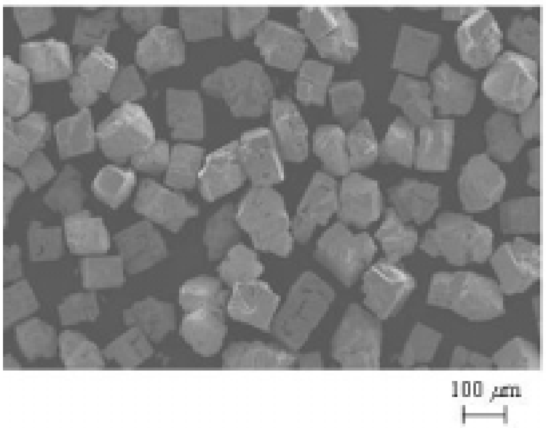

Fig. 2 PZT single crystals obtained by a PbO flux method.
(Composition: PZ/PT=55/45)

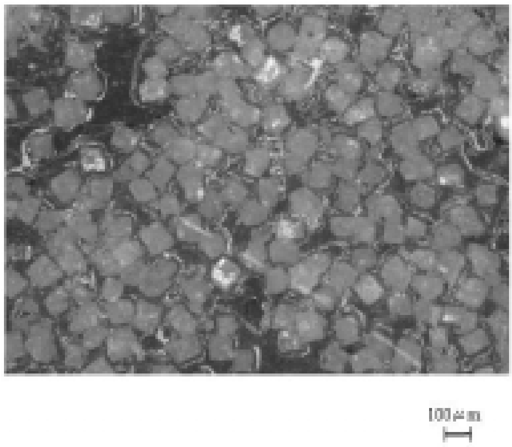

Fig. 3 An example of as-rolled film.

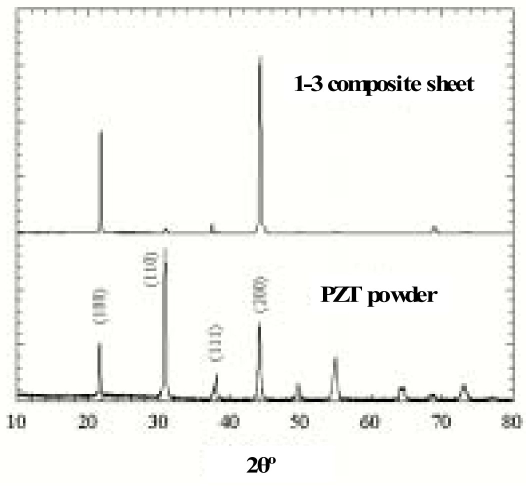

Fig. 4 XRD diagrams of 1-3 composite sheet and PZT powder.

In order to be 1-3 type, it is required to expose the heads of PZT grains from the polymer ensuring the contacts of electrodes. Though polishing is believed to be an effective means to do it, we adopted another method which does not injure the crystals. That is, our method is to sandwich the composite sheet sample with Teflon sheets on the hot-pressing process, as schematically shown in Fig. 1. Since Teflon and polyimide resin are moderately soft under the hot-pressing condition, the PZT grains sink into the Teflon, and as a result the heads of PZT grains are exposed from the polymer, in spite of their different dimensions. In the fabrication of 1-3 composite sheet, anyhow, a key was to eliminate the polymer layer covered the surface of PZT grains for observing desired ferroelectric and piezoelectric behaviors.

3.2. Ferroelectric and Piezoelectric Properties

Figure 5 shows an example of DE hysteresis loop measured at room temperature. A well-defined DE loop is seen. Under the applied electric field 100kV/cm, the coercive field E_c is about 40kV/cm and the remanent polarization P_r is 2.4μC/cm^2. In this 1-3 composite sheet, PZT grains are oriented to the [100] and the filling fraction of PZT grains is about 50%. In the rhombohedral crystal, the remanent polarization along the [100] is originally lower, since the magnitude alters in the order [100]<[101]<[111]. The P_r value is proportional to the filling fraction of ferroelectric component. Even if considering these facts, it is felt that the value 2.4μC/cm^2 is too small. In the case of rhombohedral PZT thin films prepared by a sol-gel method, which have texture of preferred orientation to the {100}, the P_r is observed to be 30μC/cm^2 when 60kV/cm is applied [8]. On the other hand, tetragonal PZT films epitaxially deposited onto single crystal $SrTiO_3$ show Pr=25 μC/cm^2 [9]. In the case of PZT films, anyhow, though the physical properties depend on the texture, crystallinity, crystal axis, etc., the remanent polarization are usually attained two-digits μC/cm^2. For the reason of the low remanent polarization observed on our 1-3 composite film, it is believed that the PZT grains do not normally function as the piezoelectric component. That is to say, this is because the electrical contacts with PZT grains are still incomplete. If thin layer of polyimide resin obstructs the electrical contact, the fabrication process is to be further improved.

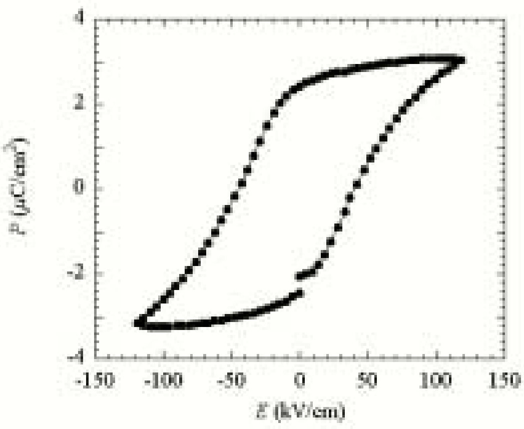

Fig. 5 DE loop of 1-3 composite sheet.

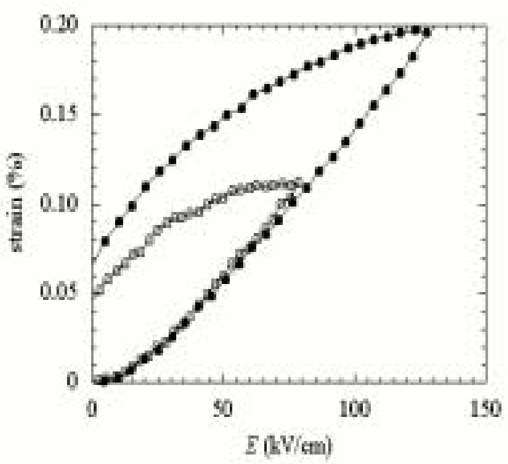

Fig. 6 Plots of electric field-induced strain vs. applied electric field for the 1-3 composite sheet.

Figure 6 shows plots of electric field-induced strains against the applied electric field, measured by a unipolar method. The strain curves are hysteretic, and the strains go up to about 0.11% and 0.2%, under the electric fields of 80 and 125kV/cm, respectively. These values are comparable to those in the usual PZT ceramics. It is evident that the 1-3 composite sheet has a certain piezoelectric function. Though it was first anxious in this sample that the strain is low followed by the low P_r, the strains observed are not lower than the prediction. This is considered to be associated with the fact that the PZT grains are of a rhombohedral structure and highly oriented to [100]. It is well-known in the rhombohedral piezoelectric crystal that the field-induced strain is markedly enhanced by polarization along the [100] direction. This operation is so-called engineered domain method [1-3]. The appearance of a meaningful strain in our 1-3 composite sheet is considered to be due to the same phenomenon. That is, this is resulted from the application of high voltage along the [100] direction. However, we cannot believe that such the strain behavior are directly came from the PZT single crystal grains, as described above about the result of the remanent polarization. Further interesting piezoelectric behavior should be anticipated, if the electrical contacts with PZT grains are improved.

4. Conclusion

PZT single crystals with PZ/PT=55/45 composition were grown by a PbO flux method. The crystals obtained were cube-shaped with a relatively uniform size distribution around 80μm. Composite sheets of 1-3 type were fabricated by rolling the mixture of the PZT grains obtained and liquid polyimide resin in thickness same as the size of PZT grains on a glass plate. This rolling process resulted in a high orientation of PZT grains, as the {100} are parallel to the substrate plane. The degree of grain orientation attained about 90%. The 1-3 composites sheet fabricated showed well-defined DE hysteresis loop, but the remanent polarization was too low, 2.4μC/cm^2, in the cycle between -100 and 100kV/cm. This was considered to be because the electrical contacts with PZT grains are not sufficiently gained. The longitudinal field-induced strain is 0.2% under 120kV/cm, which is also lower than expected. In this 1-3 composite sheet, therefore, it is very difficult to say that the PZT grains well-exhibit their own ability as single crystals. A more interesting ferroelectric and piezoelectric behaviors should appear, if the fabrication process is further improved to gain the electrical contacts between PZT grains and electrodes.

References

[1] S-E. Park and T. Shrout, *J. Appl. Phys*., **82**(1997), 1804.

[2] Y-M. Chang, G. W. Farrey and A. N. Soukhojak, *Appl. Phys. Lett*., **73**(1998), 3683.

[3] S. Wada, S. Suzuki, T. Noma, T. Suzuki, M. Osada, M. Kakihana, S-E. Park, L. E. Cross and T. Shrout, *Jpn. J. Appl. Phys*., **38**(1999), 5550.

[4] R. E. Newnham, D. P. Skinner and L. E. Cross, *Mat. Res. Bull*., **13**(1978), 525.

[5] X. Geng and Q. M. Zhang, *J. Appl. Phys.*, **85** (1999), 1342-1350.

[6] R. J. Meyer Jr., S. Yoshikawa and T. Shrout, *Mat. Res. Innovat*., **3**(2000). 324-331.

[7] F. K. Lotgering, *J. Inorg. Nucl. Chem*., **9**(1959), 113.

[8] I. R. Abothu, Y. Ito, P. Poosanaas, S. Kalpat, S. Komarneni and K. Uchion, *Ferroelectrics*, **232**(1999), 191.

[9] V. Nagarajan, A. Roytburd, A, Stanishev, S. Prasertchoung, T. Zhao, L. Chen, J. Malngailis, O. Aucliello and R. Ramesh, *nature materials*, **2**(2003), 43.