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Ceramic Films of $Pb_{4.95}Ba_{0.05}Ge_3O_{11}$ by Printing Technique and Their Pyroelectric Characteristics

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Printing technique was applied to preparing pyroelectric elements of infrared detectors. Completely sintered ceramic films were obtainable using only pastes that were made from raw powders as fine as 1.0 μm. The films indicated ferroelectricity. The measured pyroelectric coefficient, resistivity and relative permitivity were nearly same as those obtainable on the bulk ceramics formed by conventional sintering technique.

§1. Introduction

Pyroelectric infrared detector elements are obtained from pyroelectric single crystals or ceramics through various processings, such as cutting, grinding, etc. Trials were made in this paper on the new method that such processings were not required for obtaining ceramic films. The technique comprises printing of $Pb_5Ge_3O_{11}$(PGO) paste, peeling and sintering the green films. Described in this paper are electrical properties of thus formed ceramic films centering its pyroelectric characteristics.

Shown in Fig. 1 are the temperature dependence of pyroelectric coefficients of PGO and its isomorphs. These data* were obtained from PGO single crystal and PGO, $Pb_{4.95}Ba_{0.05}Ge_3O_{11}$(PBGO) and $Pb_{4.95}Sr_{0.05}Ge_3O_{11}$ ceramics obtained by conventional technique. Although pyroelectric coefficient of single crystal PGO was obtained at more than 10×10^{-9} C/cm^2·K under lower than the room temperature, it was decreased along with the temperature increase. The reason for such tendency has not been cleared yet. On the other hand, pyroelectric coefficients of ceramic materials were obtained at rather constant within the temperature range of 0-80°C, although their absolute values were not so high. From this view points, it is concidered that ceramic materials are more suitable than single crystal of PGO as the practical materials. Several advantageous points would be added, furthermore, by applying printing technique to the manufacturing of PGO ceramics: *i*) They can be sintered under ambient conditions since their sintering temperature is low (about 720°C) and evaporation of Pb can be neglected., *ii*) Thickness and shape of pyroelectric films can be decided arbitrarily since printing technique is applicable to them., *iii*) No work strain is observed on the films formed by the printing technique., *iv*) Material waste can be kept at minimum.

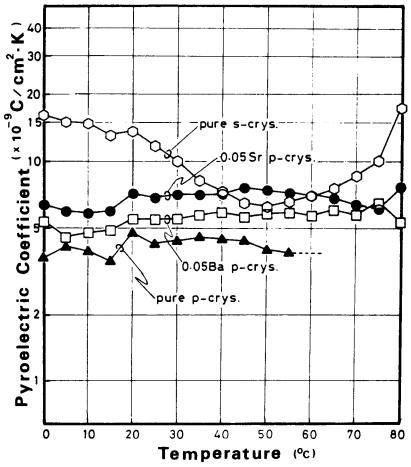

Fig. 1. Pyroelectric coefficients of $Pb_5Ge_3O_{11}$ and its isomorphs.

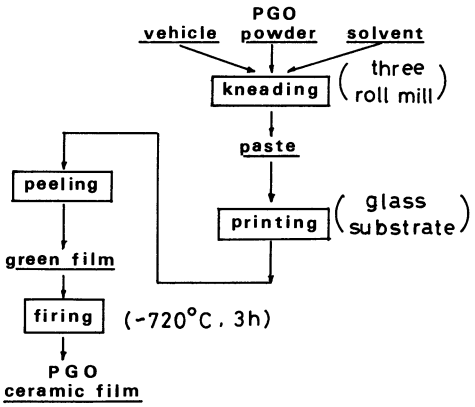

Fig. 2. Manufacturing procedure of PGO ceramic films.

§2. Preparation of samples

Resistivity ρ of PGO ceramics is 1.8×10^{11} Ω·cm at 25°C. Dielectric breakdown may occur when it is poled under such resistivity, Therefore, it was decided to use $Pb_{4.95}Ba_{0.05}Ge_3O_{11}$, in which a part of Pb site was replaced with Ba to increase the value of ρ, was used as the paste material. Raw material powders were obtained by applying following processes on the blend of chemicals of special grade: Prefiring at 650°C for 3 hours.→Melting at 850°C.→Quenching and Crushing by putting it in ion exchanged water.→Calcining for recrystallization at 650°C for 3 hours.→Pulverization. Shown in Fig. 2 is the manufacturing procedure of PBGO ceramic films applying printing technique. The vehicle was mainly consisted of Ethylcellulose, and Terpineol was used as solvent. Screen printing was carried out on the surface of a ground pyrex glass plate which was prepared as sabstrate.

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The printed films were dried at the temperature of 120°C, peeled off from the substrate, and fired at the temperature of about 720°C for 3 hours under the atomospheric conditions. Although the thickness of ceramic films can be adjusted by changing the printing frequency, at least the thickness of 60 μm of sintered film was required for obtaining complete films which were free from pin holes.

§3. Results

3.1 *The texture of the ceramic films*

Since ceramic films obtained according to paste printing technique are usually incorporated with large amount of binders such as vehicles, etc., it was hard to sinter them completely and the formed films tended to leave pores in them. On the other hand, complete sintering was possible on PBGO films as far as attentions were paid on the particle size of the raw powders. Shown in Fig. 3 are particle size distributions after pulverizing powders obtained after calcining for recrystallization by means of a jet mill (TURBO KOGYO Co., Ltd. TJ-120) and by means of an agate mortar. The particle size of the jet mill-powder was as fine as 1.0 μm and its distribution range was very narrow. On the other hand, the mortar-powder was not only coarser, but distributed over wider range (0.5–20 μm) than the jet mill-powder. Shown Fig. 4 are the sintered results of the printed films formed by using pastes of these two kinds of raw powders. As can be seen in A of Fig. 4, grain growth was so remarkable to indicate the particle size of several 10 μm that one of the particles penetrated the film toward the thickness direction. Degrees of grain- orientation (f factor) were obtained according to the method[1] proposed by Lotgerling by carrying out X-ray diffraction on the natural surface of sintered films. Obtained results were: −0.09 average for *a*-plane and 0.04 for *c*-plane. Taking these results into concideration, it is assumed that there should be no grain-orientation on a specific plane. In the case of B of Fig. 4, however, grain size was still observed very small despite of nearly completion of sintering and pores are observed at a part of the film.

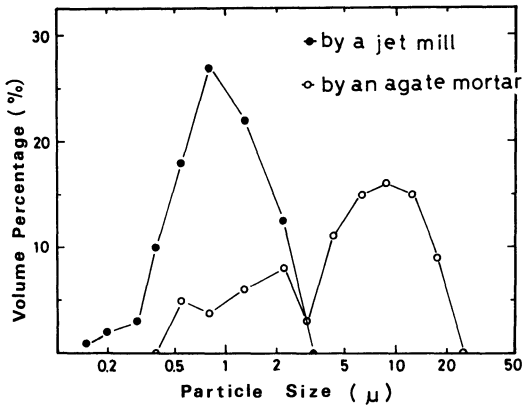

Fig. 3. Particle size distributions of PBGO powders.

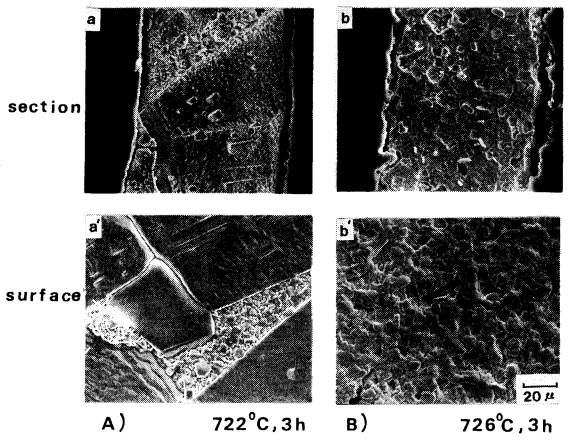

Fig. 4. SEM micrographs of sections (a), (b) and natural surfaces (a'), (b') of the ceramic films. Sample A and B were made from powders pulverized by a jet mill and by an agate mortar respectively.

3.2 *D-E hysteresis*

Shown in Fig. 5 are *D-E* hysterisis loops of PBGO ceramic films and the relation between applied electric field and remanent polarization P_r. They were measured using Sawyer and Tower Circuit modified by Diamant, *et al.*[2] AC electric fields of 50 Hz was applied at 25°C to the sample in the measurement. (Electrodes of 5.7 mm^2 were formed evaporating Au on both surfaces of the film.) From the loops, it can be understood that PBGO ceramic films formed using printing technique indicates ferroelectricity. Although P_r reaches to saturation at nearly 50 kV/cm, it continues to indicates slight increase even above 50 kV/cm. It was, however, impossible to measure P_r at above 80 kV/cm because of the occurrence of dielectric breakdown.

3.3 *Pyroelectric coefficient*

Pyroelectric coefficients of PBGO ceramic films were measured by direct method.[3] In advance of the measurement, DC pulse was impressed to the samples for poling. This was because of the danger of the occurrence of dielectric breakdown by applying DC electric field of about 100 kV/cm which was assumed to be the required electric field to saturate completely the polarization of the sample, as can be understood from the results shown in Fig. 5. It is considered that the possible cause of the breakdown should be due to heat generation of the sample. Applied pulse was of 0.01 sec length and of 1: 4 duty

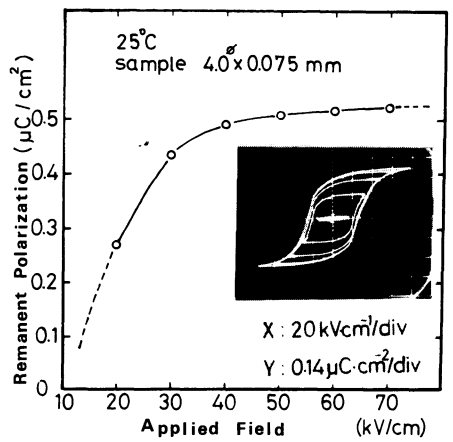

Fig. 5. D-E hysterisis loops, and relation between applied field and remanent polarization for PBGO ceramic film.

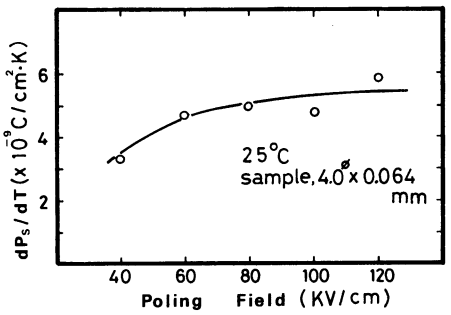

Fig. 6. Relation between pyroelectric coefficients and poling fields.

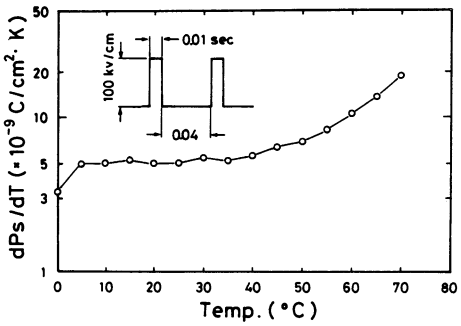

Fig. 7. Typical temperature dependence of pyroelectric coefficient of the ceramic film at 25°C.

ratio. (Impression for 75 minutes, Aging at 120°C for 3 hours) Shown in Fig. 6 is the relation between the poling field and the pyroelectric coefficient of PBGO ceramic film at 25°C. As can be seen in the figure, pyroelectric coefficient reaches to nearly saturation under the field of about 80 kV/cm which almost agrees to the behavior of P_r shown in Fig. 5. Shown in Fig. 7 are typical temperature dependence of the pyroelectric coefficient of the ceramic film. Comparing these results with data obtained on the bulk ceramics shown in Fig. 1, it can be understood that both of these data are nearly same. Pyroelectric coefficient of 5.1×10^{-9} C/cm²·K was obtained on PBGO ceramic film at 25°C.

3.4 *Resistivity and relative permittivity*

Shown in Fig. 8 are the temperature dependences of resistivities of PBGO bulk ceramics formed by conventional technique and ceramic films formed by printing method. Measurements were made by impressing DC 1 V. It can be said that the change of ρ according to the

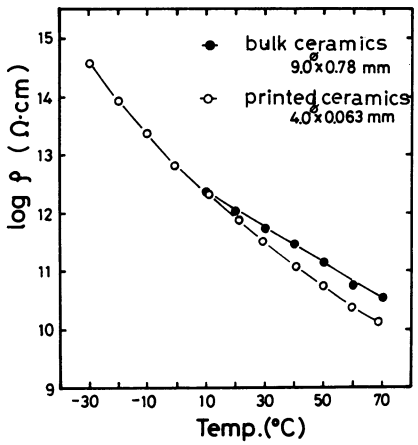

Fig. 8. Temperature dependence of resistivities of PBGO ceramics that were made by conventional technique and printing technique.

change of the temperature on both of the ceramic samples were nearly same. ε_r and $\tan\delta$ was obtained at 32 and 0.005 (1 kHz, 25°C) on both of the samples respectively.

§4. Summary

Completely sintered PBGO ceramic films were obtainable by applying printing technique using pastes that consisted of fine raw powder. The ceramic films indicated ferroelectricity as well as bulk ceramics. The measured pyroelectric coefficient, resistivity and relative permittivity of thus formed ceramic film were nearly same as those obtainable on bulk ceramics formed by conventional technique. Pyroelectric coefficient of PBGO ceramic film was obtained at 5.1×10^{-9} C/cm²·K at 25°C.

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