Paper

Dielectric Properties of $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ Thick-Films Prepared by Rapid-Quenching

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超急冷法によるゲルマン酸鉛厚膜の作製とその誘電性

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Thick-films of $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ with full density and thickness of $60\ \mu\text{m}$ were prepared by rapid-quenching. A pyroelectric detectivity of $10^7\ (\text{cm}\cdot\text{Hz}^{1/2}/\text{W})$ was obtained, equivalent to that of a commercial infrared detector. Polarization reversal by applied voltage was very slow, indicative of a relaxation phenomenon. [Received March 13, 1990; Accepted May 24, 1990]

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1. Introduction

Lead germanate $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ (PGO) with Curie temperature of 177°C is well-known as a ferroelectric material at room temperature.^{1,2)} It is of much interest as an infrared detector³⁾ because of its large pyroelectric coefficient and relatively small dielectric constant. There have been a few reports referring to preparation of thick-films by rapid-quenching for developing a pyroelectric detector.^{4,5)}

Shimanuki reported that highly-oriented thick-films of PGO were prepared by the technique⁶⁾: however, no information of dielectric and pyroelectric properties were described.

We prepared thick-films of PGO by rapid-quenching, characterized them by X-ray diffraction (XRD) and scanning electron microscopy (SEM), and further, measured its ferro- and pyroelectric properties to find potentiality as a pyroelectric detector.

2. Experimental

The compositions of the samples in the system $\text{PbO}-\text{GeO}_2$ where $x\ (\text{mol}\%) = 100\ \text{PbO}/(\text{PbO} + \text{GeO}_2)$ were settled as $x = 62.0, 62.5, 62.75$ and 63.5 . PGO powder was obtained by a solid phase reaction in such a way that both 4NPbO and 6NGeO_2 powders were mixed and fired twice at a firing temperature of 600°C for 2h. Using a $50\ \text{mm}\phi$ soft-twin roller,⁴⁾ PGO thick-films were prepared: after the PGO powder (10-20 mg) was put into a platinum nozzle ($5\ \text{mm}\phi$) and melted at $750^\circ\text{--}850^\circ\text{C}$ for about 1 min, the melt was blown by air onto the rollers rotating at 1000-2000 rpm. For X-ray analysis as well as the measurements of electrical properties, the as-quenched films were heat-treated at 680° or 700°C to be crystallized.

Crystallization process of the samples was traced with a Philips X-ray diffractometer and a scanning electron microscope.

The degree of preferred orientation of $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ crystallites in lead germanate ceramics in the form of film was evaluated by XRD. The diffraction patterns were compared with those of

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$\text{Pb}_5\text{Ge}_3\text{O}_{11}$ powder to measure the degree of c - and a -plane orientation (F_c and F_a respectively), which were calculated by the use of Lotgering's equation.⁷⁾ DE-hysteresis loops were observed with Sawyer-Tower circuit (Suzuki Seisakusho Co., Model DE-612), resulting in obtaining spontaneous or remanent polarization P_s or P_r and coercive field E_c . Prior to the measurements of pyroelectric sensitivities, a DC bias of 400 V (about 44 kV/cm) was applied for 1h between the Ag surface electrodes of the films, and further, black paint was put on the electrodes to make the sample absorb the laser beam efficiently. Both responsivity R_v and detectivity D^* were obtained with a synchrotrack lock-in amplifier (NF Electronic Instruments Co., Model LI-575) and a 2.68 mW He-Ne laser.

3. Results and discussions

3.1 Preparation and characterization

Firstly powder of PbO - GeO_2 system including

(a) Surface

5 μm

(b) Section

10 μm

Fig. 1. SEM photos of the thick-film of PbO - GeO_2 system (PbO : 62.0 mol%) annealed at 680°C for 1h. (a) surface, (b) section.

$\text{Pb}_5\text{Ge}_3\text{O}_{11}$ and Pb_3GeO_5 crystals was obtained by a solid phase reaction between PbO and GeO_2 . Using the soft-roller, films with nearly-full density was prepared in the form of 60-100 μm thick $\times$ 10-15 mm wide $\times$ 30-60 mm long. The powder of the as-quenched film was detected to be amorphous by XRD, since its pattern had a broad peak near $2\theta = 29^\circ$ for $\text{Cu K}\alpha$. After annealing the as-quenched film ($x = 62.0$) at 680°C for 1h, SEM photos (Fig. 1) were taken; Fig. 1(a) for the surface and (b) for the section. Both long crystallite (3 μm long $\times$ 2 wide) and a few pores were observed on the surface, while there were no open pores in the interior. This suggests the film has nearly-full density.

No peaks except for $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ were found on the film surface by XRD. Crystallite orientations (F_c and F_a) of the films ($x = 62.0$ and 62.5) annealed at 680°C are shown in Fig. 2. It is noted that the longer the annealing time, the larger the c -plane orientation (c -axis perpendicular to the surface), while the a -planes decreased.⁶⁾ This means planes with higher surface free energy (ex. a -plane) transforms into ones with lower energy (ex. c -plane) during the annealing process.

3.2 Dielectric and ferroelectric properties

In the measurement of spontaneous polarization (P_s), "aging phenomenon" was observed. The value of apparent P_s increased with aging time as shown in Fig. 3, where the curve is almost saturated after about 1h, so that more than 1h is required for poling in the measurements of pyroelectric properties. As illustrated in Fig. 4, the values of P_s and P_r increased with an increase in applied voltage and then became saturated over 1h. Therefore, the P_s -values measured after that period were regarded as true ones. As far as the absolute values of P_s and coercive field E_c are concerned, P_s (0.4 $\mu\text{C}/\text{cm}^2$) for the PGO thick-

Fig. 2. Annealing time dependence of F_a and F_c for the PbO - GeO_2 system (the samples with PbO : 62.0 and 62.5 mol%; annealed at 680°C).

Fig. 3. Aging process of apparent spontaneous polarization P_s ($\mu\text{C}/\text{cm}^2$). The sample: PbO : 62.5 mol%, film annealed at 700°C for 1h.

Fig. 4. Electric field E (kV/cm) dependence of apparent spontaneous and remanent polarization P_s , P_r ($\mu\text{C}/\text{cm}^2$). The sample with PbO : 62.0 mol% : film annealed at 680°C for 10h.

film in this study is one tenth as large as that of the one ($5 \mu\text{m}/\text{cm}^2$) for its single crystal, while E_c (66 kV/cm) for the thick-film in this study is one order of magnitude as large as that (5 kV/cm) for its single crystal.

Judging from these data, two mechanisms for such an aging phenomenon might be considered. One is insufficient application of an electric field to the bulk in the film because of existence of paraelectric phase in the surface and the other is an intensive clamping effect caused by the strain between the crystallites.

In the case of amorphous-ceramic KNbO_3 film^{4),8)} prepared by rapid-quenching, a paraelectric layer with a low permittivity might appear in the surface due to weak chemical durability of the crystal, so that the layer might reduce the field

applied to the bulk. But chemical durability of PGO is large enough against humidity.

Kokubo et al.⁹⁾ have reported on crystallization of $\text{BaTiO}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ system glass, resulting in the phases of barium titanate, BaTiO_3 and hexacelsian, $\text{BaAl}_2\text{Si}_2\text{O}_8$. A thin glass-ceramic had a low permittivity; those with thickness smaller than $200 \mu\text{m}$ are half as large as those larger than the value. This is thought to be due to a low-permittivity hexacelsian with high concentration in the surface layer.

As far as the dielectric permittivity (ϵ) of PGO at room temperature is concerned, the value ($\epsilon = 26\text{-}35$) for the amorphous-ceramic by rapid-quenching is almost the same as that ($\epsilon = 30$)¹⁰⁾ for the sintered body. Formation of a paraelectric layer with a low permittivity might have a small possibility in the surface of the amorphous-ceramics. So far, this mechanism is thought to rule out as an origin of the aging phenomenon.

Let us consider the latter mechanism. In the crystal structure¹¹⁾ of lead germanate $\text{Pb}_5\text{Ge}_3\text{O}_{11}$, only 180° domains are allowed. In the high temperature phase ($P3/m$), a mirror exists in the a - b plane, so that the sites of lead (Pb) and oxygen (O) ions are symmetrical, no spontaneous polarization occurs. On the other hand, in the low temperature phase below 177°C , the sites of these ions become non-symmetrical and therefore, P_s takes place, parallel to the c -axis.

When an electrical voltage is applied to the crystal parallel to the c -axis, a shift in the Pb position along c -axis would impart a clockwise twist to germanium tetrahedra. In order to cause a polarization reversal, these ions must pass over a high potential barrier. In case a crystallite is

Fig. 5. Annealing time dependence of apparent spontaneous and remanent polarization P_s , P_r ($\mu\text{C}/\text{cm}^2$). The samples with PbO : 62.0 mol% : film annealed at 680°C .

Fig. 6. Frequency f (Hz) dependence of pyroelectric responsivity R_v (V/W) and detectivity D^* ($\text{cm} \cdot \text{Hz}^{1/2} / \text{W}$). The samples: films annealed at 680°C for 10h for $\text{PbO} : 62.0 \text{ mol } \%$ and for 1h for 62.75 .

subjected to a stress by surrounding crystallites, it is natural that the shifts of ions are retarded, so that a polarization reversal becomes difficult: that is, a clamping effect. We consider that the aging phenomenon in the application of electric voltage might be caused by this mechanism.

For the samples with $x=62.0$ annealed at 680°C , Fig. 5 shows annealing time dependence of P_s and P_r , the two values increase with an increase in time. This phenomenon accords with the increase of c -planes with increasing annealing time as shown in Fig. 2.

For the film samples ($x=62.0$ annealed at 680°C for 10h and $x=62.75$ at 680°C for 1h), both responsivity R_v (V/W) and detectivity D^* were measured as a function of chopping frequency f (Hz) as shown in Fig. 6. $\log R_v$ decreased linearly with an increase in $\log f$, while D^* decreased gradually with increasing frequency. It is noted that the value of $D^* \sim 10^7$ ($\text{cm} \cdot \text{Hz}^{1/2} / \text{W}$) at 5–50 Hz range is equivalent to that for one of the commercial pyroelectric detectors. This means that the film prepared by rapid-quenching is quite hopeful for a commercial detector.

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