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Growth and characterization of large size lead germanate single crystals

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Abstract

Ferroelectric lead germanate crystal ($Pb_5Ge_3O_{11}$, PGO) has been grown by the vertical Bridgman method. Compositional deviation and cracking were the main problems often encountered during the growth. The polycrystalline PGO powder was pre-synthesized by sintering the PbO and GeO_2 mixture with slight GeO_2 excess. An in situ annealing process was employed to prevent PGO crystals from cracking during cooling. PGO single crystals up to 55 mm in diameter and 35 mm in length were obtained. Dielectric properties of the grown PGO crystal were measured.

Keywords: B. X-ray methods; B. Defects; C. Dielectric properties; Lead germanate

1. Introduction

Ferroelectricity in lead germanate ($Pb_5Ge_3O_{11}$) was first observed by Iwasaki et al. and independently by Nanamatsu et al. [1,2]. Because of the pyroelectric effect, reversible optical activity and lasing characteristic, ferroelectric lead germanate has attracted considerable interest around researchers. Its dielectric and optical properties have been extensively studied: the spontaneous polarization is unidirectional (parallel to the crystallographic *c*-axis) and the crystal undergoes enantiomorphic transformation with electric field reversal and with the sign of optical rotatory power also reversed. Spontaneous polarization observed at room temperature is 4.8 $\mu C/cm^2$ and the ferroelectric phase transition temperature is 177 °C [1–4].

Intensive efforts have been made on the growth of PGO crystals. Initially, PGO crystals were grown from the melt by the Czochralski method [1]. However, it has been found difficult to obtain large size PGO crystals. Recently, the vertical Bridgman method was applied to grow PGO crystals [5]. Up to now, the largest size of PGO crystal is about 25 mm in diameter and 60 mm in length. Compositional deviation and cracking are the main problems often occurring during Bridgman growth of PGO crystals [5]. The aim of this work is to solve these problems and develop large PGO crystals.

2. Experimental procedure

High purity PbO and GeO_2 raw materials were weighted with an accuracy of 1 mg and mixed thoroughly using an agate mortar and pestle. The mixture was sintered in a platinum container at about 650 °C for 12 h. XRD patterns demonstrate that polycrystalline PGO was synthesized, as shown in Fig. 1. A platinum crucible Ø55 mm × 150 mm with a seed well Ø25 mm × 70 mm was used. ⟨1 0 0⟩-oriented PGO crystals obtained from a previous growth were processed into a cylinder of Ø25 mm × 35–55 mm as seeds. The polycrystalline PGO powders were loaded into the platinum crucible when the PGO seed was inserted into the seed well at the bottom of the crucible. In order to prevent evaporation of PbO, the crucible was sealed and then moved to a refractory tube. Al_2O_3 powder was filled into the tube to support the crucible as well as to isolate it from external temperature fluctuations. A pair of Pt-Pt/Rh thermocouples was installed in the tube to measure the temperature near the

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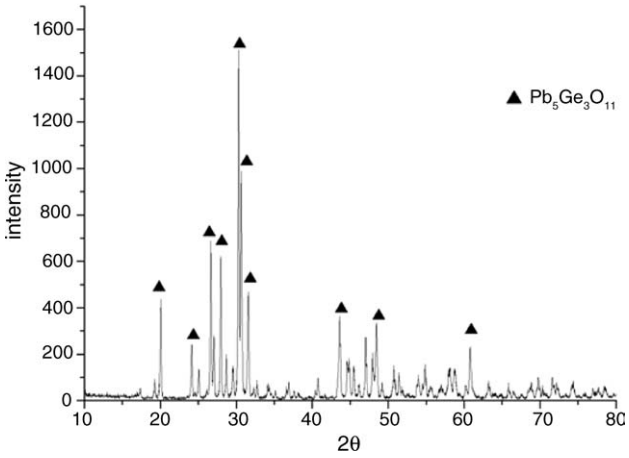

Fig. 1. X-Ray powder diffraction diagram of PGO polycrystalline.

melt and the top of the seed. Seeded growth was carried out in a homemade vertical Bridgman furnace. The furnace temperature was set to about 830 °C. The crucible was initially positioned at the bottom of the furnace in a lower temperature zone and then slowly moved up to the high temperature zone. The charge melted gradually from the top to the bottom and a stable equilibrium was established at the upper part of the seed. The seeding temperature was controlled as 740–750 °C, which was about 10 °C higher than that of the melting point (738 °C). After the charge was soaked at 750 °C for 12 h, the crucible was lowered at a rate of 0.1–0.3 mm/h. The furnace was cooled to room temperature at a rate of 30 °C/h when the whole melt crystallized calculated from the batch and the growth rate.

As-grown PGO crystal was oriented and cut into several slices perpendicular to ⟨0 0 1⟩. These slices were polished to a size of 10 mm × 10 mm × 1.5 mm. The PGO slice was immersed into 10% acetic acid at room temperature for 15 min and the dislocations were observed by optical microscopy. Pt electrodes were applied on the surfaces of the PGO slice and the temperature dependence of dielectric constant was studied using a HP4192A impedance analyzer.

3. Results and discussion

The PbO–GeO_2 phase diagram showed that the congruent melting PGO was composed of PbO and GeO_2 with the molar ratio of 5:3 or with 21.95 wt% GeO_2 in PGO crystal [6]. However, small quantities of black slag were observed on a certain side of as-grown boule when PGO was grown from a stoichiometric mixture of PbO and GeO_2. The compositional analysis showed that the compositions of the black slag deviated seriously from the stoichiometric ratio and that the GeO_2 content was less than for the nominal composition [5]. It was suggested that PGO crystal should be grown from GeO_2-rich starting melt. In our experiments, PGO crystals were grown from the starting materials with excess of 0.25, 0.5 and 1% GeO_2, respectively. Only small amount of slag occurred when growing from 0.25% GeO_2-rich melt, while the crystal ceased growing when five 6th melt crystallized from the starting melt of 1% GeO_2-rich. It was found that the slag disappeared and only small amount of the residual was observed when growing PGO crystals from 0.5% GeO_2-rich starting melt. The melting points of PbO and GeO_2 are 886 and 1115 °C, respectively. When the mixture of PbO and GeO_2 was sintered at 650 °C for 12 h, a solid-state reaction took place and PGO crystalline powder was synthesized. However, the reaction proceeded incompletely due to the difference of the melting points. The increase of the sintering temperature caused the powder adhering to the Pt crucible. Therefore, GeO_2-rich starting materials were adopted to solve the compositional deviations and growth results showed that 0.5% GeO_2-rich starting materials were suitable.

Cracking is another troubling problem for Bridgman growth of PGO crystals. Sometimes, the seed broke to pieces when the crystal was taken out from the crucible. Nevertheless, the cracking was not so serious for the body of the crystal. It was found that cracking usually occurred along the (1 0 0) plane with a rough surface. This meant that (1 0 0) was an incomplete cleavage plane. The crystal structure of PGO was deduced to be interleaving segments of the apatite and nasonite structures in layers perpendicular to *c*-axis [7]. The stacking faults between the layers played an important role in reducing the strains accumulated in the structure [8]. Thus, cracking rarely occurred on (0 0 1) plane although a layer structure was constructed along *c*-axis. Additionally, due to its ferroelectric and pyroelectric characteristics, a large amount of charges accumulated when as-grown PGO crystal cooled down, which resulted in cracking along the domain boundary. Based on the above considerations, a small temperature gradient of less than 25 °C/cm and a slow cooling rate of 30 °C/h were adopted for the Bridgman growth of PGO crystals. Furthermore, an in situ annealing process was applied to reduce the thermal stress in as-grown crystals. When the growth finished, the furnace temperature decreased slowly to 550 °C. The grown crystal was moved up to the high temperature zone and held at 550 °C for 12 h.

Fig. 2. PGO crystal grown by the vertical Bridgman method.

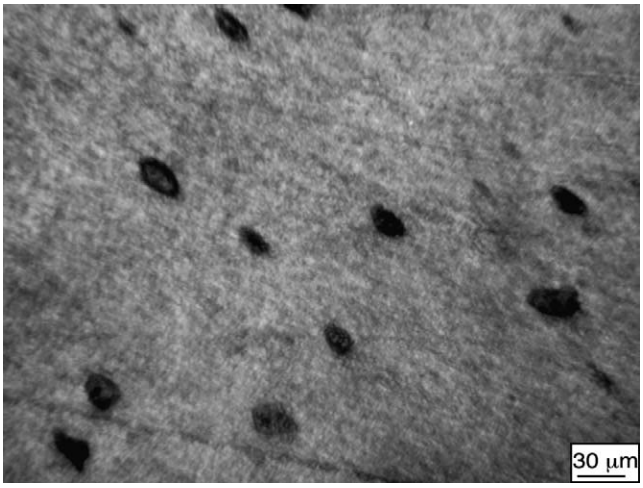

Fig. 3. Etch dots of grown PGO crystal revealed by chemical etching.

Through optimizing the growth condition, a PGO crystal up to 55 mm in diameter and 35 mm in length was obtained, as shown in Fig. 2. Fig. 3 shows the etch dots in the grown PGO crystal. The dislocation density was about 10^4 cm^{-2}.

Fig. 4 shows the temperature dependence of dielectric constants at the frequencies of 1, 10, 100 and 1000 kHz during heating process of an unpoled ⟨0 0 1⟩ PGO sample. At room temperature, the dielectric constant ε_{33} was about 30. An anomaly was observed at 174 °C, corresponding to the phase transition from the trigonal ferroelectric to the hexagonal paraelectric phase.

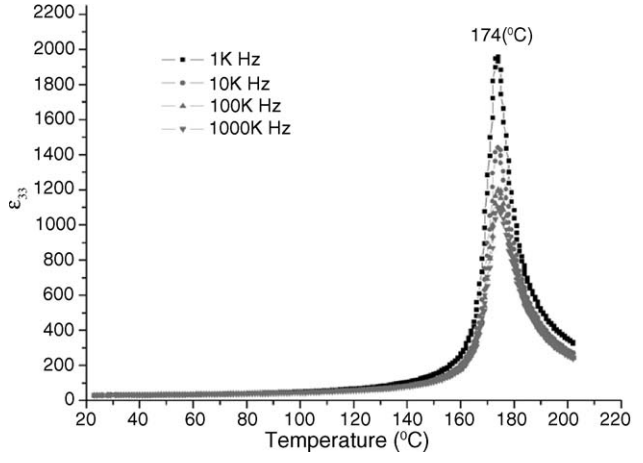

Fig. 4. Temperature dependences of the dielectric constant of the unpoled PGO sample.

4. Conclusions

PGO crystals of Ø55 mm × 35 mm in size have been grown by the vertical Bridgman method. The polycrystalline PGO powder was pre-synthesized by sintering a mixture of PbO and GeO_2. The compositional deviation was solved by growing PGO from 0.5% GeO_2-rich melt. An in situ annealing process was used to reduce the thermal stress in as-grown PGO crystals. The temperature versus dielectric constant relationship showed the Curie temperature of PGO crystal to be 174 °C and the dielectric constant ε_{33} to be 30 at room temperature.

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