Short communication

Second-Harmonic Generation in Thermally/Electrically Poled Transparent BaTiO₃ Thin Films Prepared by Dip-Coating Method

Iwao SAKAIHARA*, Katsuhisa TANAKA**, Takashi WAKASUGI**, Rikuo OTA**,
Yoshinori YONESAKI*** and Kazuyuki HIRAO***

*Department of Chemistry and Materials Technology, Graduate School of Industrial Arts and Science, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

**Department of Chemistry and Materials Technology, Faculty of Engineering and Design, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

***Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Yoshidahonmachi, Sakyo-ku, Kyoto 606-8501, Japan

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1. INTRODUCTION

When a large electric field like that of a laser is applied to a dielectric material, the polarization is given by

$$\mathbf{P} = \epsilon_0 (\chi^{(1)} \mathbf{E} + \chi^{(2)} \mathbf{E}^2 + \chi^{(3)} \mathbf{E}^3 + \cdots), \quad (1)$$

where $\mathbf{E}$ is the electric field, $\chi^{(1)}$ is the electric susceptibility, and $\chi^{(2)}$ and $\chi^{(3)}$ are nonlinear susceptibilities [1]. The generation of light with a wavelength which is half that of incident light is known as second-harmonic generation (SHG). This phenomenon arises from the second term in Eq.(1). A substance which exhibits large SHG is expected to be applied in optoelectronic devices such as a frequency converter of a laser in an optical fiber.

A number of substances exhibit large SHG. For inorganic compounds, poled glasses as well as transparent single crystals which do not have inversion symmetry have been studied extensively from both fundamental and practical viewpoints.

The purpose of this study is to fabricate transparent BaTiO₃ thin films with second-order nonlinearity, by the dip-coating technique using sol solution. In this note, we report that the resultant BaTiO₃ thin film shows SHG only after thermal/electrical poling.

2. EXPERIMENTAL PROCEDURE

BaTiO₃ thin films were prepared by a dip-coating technique using sol solutions. The molar ratio of the starting chemicals was Ti[OCH(CH₃)₂]₄:Ba(CH₃COO)₂:CH₃COOH:H₂O:(CH₃)₂CHOH = 1 : 1 : 9.08 : 20 : 20 [2]. The mixture of these chemicals was put into a beaker. The beaker was sealed, and the solution was stirred for 1 - 2 h. BaTiO₃ thin film was deposited on a Corning 7059 glass substrate by a dip-coating method. The thickness of the Corning 7059 glass plate was 1 mm. The rate of pulling of the substrate was 3 cm/min. The

resultant specimen was dried at 50 °C for 1 - 2 h and then was subjected to heat treatment at 700 °C for 10 min with a heating and cooling rate of 1 °C/min. This procedure was repeated four times.

Thermal/electrical poling was carried out at 180 °C, which is about 50 °C higher than the Curie temperature of BaTiO₃, for 15 min with an applied voltage of 2 kV. Stainless steel electrodes were used.

Second-harmonic intensities of BaTiO₃ thin films before and after thermal/electrical poling were measured. α -Quartz of 1.046 mm thickness was used as a reference material.

3. RESULTS AND DISCUSSION

For a gel film prepared by a single dip-coating, heat treatments were performed at various temperatures. It was found that the gel film was transparent when it was heat-treated at 700 °C, but became opaque at higher temperatures.

It was clarified by scanning electron microscope (SEM) observation that the thickness of BaTiO₃ thin films dip-coated four times is about 0.6 μ m.

Figure 1 shows the dependence of second-harmonic intensity on the angle of incidence after thermal/electrical poling for BaTiO₃ thin film dip-coated four times. The second-harmonic intensity is about half that for α -quartz. Moreover, the specimen maintained the same intensity even after one month. It should be noted that no SHG was observed in the specimen before poling.

Figure 2 shows the X-ray diffraction (XRD) patterns for BaTiO₃ thin films and commercially available BaTiO₃ powder. The XRD patterns of BaTiO₃ thin films do not show the splitting of (002) and (200) reflections, whereas XRD patterns of commercially available BaTiO₃ powder do. XRD patterns also show no difference before and after thermal/electrical poling. The crystallite size estimated from the (111) width using

Fig. 1. Variation of the second-harmonic intensity with angle of incidence, i.e. Maker fringe pattern for BaTiO₃ thin film dip-coated four times and poled at 180 °C with an applied voltage of 2 kV.

Scherrer's equation was approximately 20 nm for BaTiO₃ thin films.

It was reported that the Curie temperature is lower in BaTiO₃ ceramics consisting of grains of submicron size, and that eventually, the ferroelectricity ceases with decreasing grain size, resulting in the stabilization of the pseudocubic phase even below the Curie temperature, i.e., 130 °C [3]. According to that report, the pseudocubic phase may be stable in BaTiO₃ thin films because the crystallite size of these specimens is smaller than submicron order.

The orientation of the crystalline phase in BaTiO₃ thin films was also investigated using XRD patterns. However, no difference was detected before poling, on the anode side after poling, or on the cathode side after poling. Therefore, thermal/electrical poling has no influence on the orientation of crystallites in the present BaTiO₃ thin films.

Nevertheless, the SHG was observed only for the specimen after poling. We speculate that the direction of the BaTiO₃ microcrystals is random, but the polarization is in the direction of the external electric field upon thermal/electrical poling. This orientation of polarization brings about C_{ov} symmetry in the thin film, leading to the SHG, as shown in Fig. 1.

4. CONCLUSIONS

Transparent BaTiO₃ thin films were prepared by a dip-coating method. Thermally/electrically poled BaTiO₃ thin films exhibited second-harmonic generation

Fig. 2. XRD patterns before and after poling for BaTiO₃ thin film dip-coated four times and commercially available BaTiO₃ powder. (a) and (c) are (002) and (200) peak positions of tetragonal BaTiO₃ after JCPDS card No. 05-0626, respectively, and (b) is (200) peak position of cubic BaTiO₃ after JCPDS card No. 31-0174.

although the SHG was barely observed for BaTiO₃ film before poling.

XRD patterns of BaTiO₃ thin films revealed no splitting of the (002) or (200) reflection. Also, XRD patterns verified that there is no difference in the crystal structure or orientation of the crystalline phase before and after thermal/electrical poling. These results suggest that the SHG of BaTiO₃ thin films prepared in this work is attributable to an induced macroscopic orientation of the polarization of each BaTiO₃ microcrystal precipitated in the film.

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