Second Harmonic Generation of BaTiO₃ under High Pressure

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Second harmonic generation (SHG) of BaTiO₃ has been measured as a function of pressure with use of diamond anvil cell(DAC). The power of the SHG tensor component d_{31} is one order of magnitude larger than that of d_{33} and its pressure dependence is compared with the spontaneous polarization to ensure the Jerphagnon's empirical relation.

[second harmonic generation, BaTiO₃, phase diagram]

1. Introduction

Second order nonlinear optical properties have been extensively studied in the last two decades for a variety of solids, mainly through the SHG coefficient from both experimental and theoretical points of view. One of the major reasons is that the SHG coefficient provides a useful information about acentric charge distribution of bonding electrons for studying the structure of solid. Further, the SHG measurement is useful in study of the structural phase transition from a centro-symmetric phase to a non-centro-symmetric one such as NH₄Cl, BaTiO₃, etc. Therefore it will be worth extending a similar SHG measurement to solid substance under high pressure.

One of the purposes of the present work is to investigate the feasibility of SHG measurement of a crystal sample placed in a high pressure cell such as diamond anvil cell, where a small and thin sample is inevitably required. And the other is to determine the pressure dependence of the SHG coefficient in BaTiO₃ and to examine the Jerphagnon's relation. Special care was taken to inquire whether any experimental difficulties such as caused by the used diamond anvil was encountered to determine the value of SHG coefficient or not, inasmuch as the SHG measurement under high pressure does not seem to have been reported till now.

2. Experiments and Results

The SHG measurement is usually performed by observing the Maker fringe pattern. There are two methods to observe the Maker fringe pattern: one is the rotating method of a plane-parallel sample and the other the sliding method of a wedge-shaped sample. In the case of high pressure experiment, the wedge technique can be adequately employed. The analysis of the wedge technique has been given independently by Chemla *et al.*[1] and Boyd *et al.*[2]. If the absorption effect is neglected, from their analysis the SHG power P_2 is given in MKS units as follows,

$$P_2 = 4 T_1^2 T_2 K P_1^2 l_c^2 S / (\pi w)^2, \quad (1)$$

$$K = 2 \omega_1^2 d^2 / (\pi n_1^2 n_2 \epsilon_0 c^3), \quad (2)$$

$$S = [1 - F + 2F \sin^2(\pi l / 2 l_c)] / 2, \quad (3)$$

$$l_c = \lambda / 4(n_2 - n_1), \quad (4)$$

$$F = \exp [-(\pi w \tan \theta / 4 l_c)^2] \\ = (S_{\max} - S_{\min}) / (S_{\max} + S_{\min}), \quad (5)$$

where the subscripts 1 and 2 denote the fundamental and harmonic frequencies, respectively; ω_1 and λ are the fundamental frequency and wavelength; n_i and T_i ($i=1,2$) are the refractive index and the power transmission coefficient; w , θ and l are the Gaussian beam radius of the fundamental beam, the wedge angle and the sample thickness, respectively; and d and l_c denote the SHG coefficient and the coherence length. Further, ϵ_0 is dielectric permeability in vacuum, c is light velocity and F is the fringe visibility.

BaTiO₃ belongs to the point group 4mm for which SHG tensor is given as follows,

$$\begin{vmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{vmatrix}. \quad (6)$$

The detailed SHG measurement of BaTiO₃ at ambient pressure was performed by Miller [3]. The SHG coefficients d_{31} and d_{33} have the same negative sign. For $\lambda = 1.058 \mu\text{m}$, the values of the coherence lengths l_{31} and l_{33} are 2.90 and 2.03 μm , respectively.

A wedge shaped BaTiO₃ sample with a thickness of 0 to 30 μm was prepared to have the wedge angle of about 4 degrees from a single crystal grown by a flux method, which is of the transition temperature 117 °C.

Fig. 1. Schematic diagram of the experimental setup for SHG measurement(F, filter; BS, beam splitter; P, polarizer; L, lens; S, sample; LF, liquid filter of CuSO_4 aqueous solution; A, analyzer; PM, photomultiplier; PD, photo-diode).

The crystallographic c-axis is in plane of the sample. The single-domain crystal was obtained by applying a stress along a fixed direction at polishing process and electric poling. The crystal was cut in size of $0.45 \times 0.45 \text{ mm}^2$ and placed in a diamond anvil cell(DAC) of which the anvil-face diameter was $1.2 \text{ mm } \phi$ and the diameter of gasket hole was $0.8 \text{ mm } \phi$. Since in SHG measurement, the light polarization is especially important, one pair of diamond with so good optical quality that exhibits clear extinction under cross Nicols was selected from a number of diamonds. The experimental setup for SHG measurements is shown in Fig.1. A Q-switched YAG laser ($\lambda = 1.06 \mu\text{m}$ and a peak power = 10 kW) with a repetition rate of 400 pps, and a peak-to-peak stability of about 20 % was used as the fundamental light source. The properly polarized beam was focused with a lens ($f = 10 \text{ cm}$) in the wedge-shaped sample in DAC set on a micrometer-stage, that it could move along the direction perpendicular to the beam path. The generated second harmonic radiation was detected by a photomultiplier after passing through the analyzer, a liquid filter of CuSO_4 aqueous solution, and a monochromator. The detected signal was fed to the channel(A) of a boxcar integrator through a delay line. On the other hand, the second harmonics from a reference quartz crystal, generated by another beam split by a beam splitter was used to compensate the influence of the fluctuation of fundamental power. The reference signal was fed to another channel(B) of the boxcar integrator through a delay line. The ratio of the integrated signal(A) to the reference(B) was recorded as the boxcar output.

The pressure dependence of the SHG power is shown in Fig. 2. Since the SHG power is stronger

Fig. 2. The SHG power vs. Pressure. Solid lines are guide to eyes and the broken line shows the square of the spontaneous polarization measured by Samara[6].

one order of magnitude than that due to d_{33} , we could not independently observe the d_{33} component in the pressure

range higher than 1 GPa, where an optical distortion of the diamond anvil caused a mixing of d_{31} component. Since the observed fringe visibility was smaller than 0.5, the average of the spectral maximum $S_{\max}$ and the minimum $S_{\min}$ was taken as the SHG power.

The vector part of the SHG coefficients reduced to the Miller's Δ [4], that is, $(2\Delta_{31} + \Delta_{33})$ is related to the spontaneous polarization (P_s) through the Jerphagnon's relation [5]. Since the SHG power is proportional to the square of the relevant SHG component, the square of P_s is also shown in Fig. 2 for comparison. The pressure dependence of the SHG power due to d_{31} alone is similar to that of the square of the spontaneous polarization measured by Samara [6]. This result shows that the Jerphagnon's relation holds in BaTiO_3 under high pressure since the SHG power due to d_{31} is one order of magnitude larger than that of d_{33} and each coherence length is the same order.

It is possible to measure continuously the temperature dependence of SHG at constant pressure by focusing to illuminate the rather larger area of the wedge-shaped sample, that is, by measuring directly the average power of the fringe spectrum. This technique should be useful for the determination of the phase diagram of various materials. The DAC was placed in an electric furnace and the temperature was measured by a thermocouple attached directly to the anvil. The temperature dependence of SHG power of BaTiO_3 under pressures 0.4 and 1.53 GPa is shown in Fig. 3.

Fig. 3. The temperature dependence of SHG power of BaTiO_3 under pressures 0.4 and 1.53 GPa. The respective transition temperatures are 92 and 33 °C.

Fig. 4. The phase diagram of BaTiO_3 determined by SHG measurement.

The phase line of BaTiO_3 determined by SHG measurement is almost linear as shown in Fig. 4. This is in agreement with the result of Samara [6]. The detailed study of the phase diagram of BaTiO_3 has been recently performed by Ishidate *et al* [7].

3. Summary

The second harmonic generation (SHG) of BaTiO_3 was measured as a function of pressure. It has turned out that the Jerphagnon's relation holds in BaTiO_3 under high pressure.

References

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