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Second-harmonic-generation measurements on ZnSe under high pressure

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Abstract

Second-harmonic-generation (SHG) measurements on ZnSe at high pressure, up to 7 GPa, have been reported. The zinc-blende–rock-salt transition pressure has been determined at room temperature from the SHG in ZnSe using a femtosecond laser. The pressure required to induce transformation from a zinc-blende to a rock-salt structure decreases from 11.5 to 1.07 GPa in a femtosecond laser field. SHG can be used to monitor structural changes under pressure of some materials with nonlinear optical properties.

1. Introduction

The wide-gap II–VI semiconductors with the zinc-blende structure display large second-order nonlinear optics susceptibilities [1]. Wagner *et al* [2] measured the absolute values of the second-harmonic-generation (SHG) coefficient for the zinc-blende II–VI semiconductors ZnTe, ZnSe, and ZnS at room temperature in the fundamental wavelength region between 520 and 1321 nm using various laser sources. Here we report SHG measurements on ZnSe at high pressure, up to 7 GPa. Since the second-order susceptibility reflects the symmetry of the system, and structural change resulting from an intense laser pulse can change the crystal symmetry, SHG measurement may serve as a sensitive technique for signalling a change in chemical bonding of materials under high pressure.

2. Experiment

The experimental set-up consists of an exciting laser, a gasketed diamond anvil cell, and a detection system, as shown in figure 1. The powder sample of ZnSe with a purity of 99.99% was loaded into a gasketed diamond anvil cell, using 4:1 methanol–ethanol as the pressure-transmitting medium to generate pressure up to 7 GPa. The pressure measurements were made by the well-known ruby fluorescence technique. A 120 fs regenerative amplified Ti:sapphire

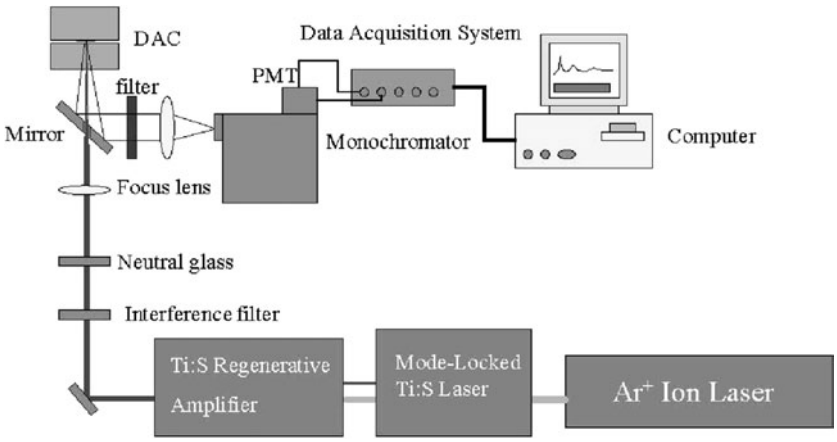

Figure 1. The experimental set-up.

laser, operating at a repetition rate of 250 kHz, was employed as the exciting light source. The maximum pulse energy was about 3 μJ at 800 nm and the spot on the sample had a diameter of about 50 μm, which resulted in a maximum peak intensity of 1 GW cm^{-2}. The SHG emission from the sample was measured by a 0.15 m monochromator with a 600 grooves mm^{-1} grating. A band-pass filter was used to prevent the laser light from entering the spectrometer. The electronic signal from the photomultiplier of the spectrometer was sent to the computer spectra acquisition system. Analysis of the second-harmonic emission intensity at 400 nm as a function of incident laser intensity shows the expected quadratic dependence of the SHG process.

SHG emission measurement allows one to monitor changes in the second-order optical response of the material [3]. In general, the optical response of a material is governed by the optical susceptibility χ. The linear response of a material to an optical field $\boldsymbol{E}(\omega)$, involving processes such as reflection, transmission, and absorption, is given by the linear electric polarization:

$$\boldsymbol{P}^{(1)}(\omega) = \chi^{(1)} \cdot \boldsymbol{E}(\omega).$$

Similarly, the second-order response of a material to $\boldsymbol{E}(\omega)$ is given by the second-order electric polarization:

$$\boldsymbol{P}^{(2)}(2\omega) = \boldsymbol{\chi}^{(2)}(2\omega) \cdot \boldsymbol{E}(\omega)\boldsymbol{E}(\omega).$$

The second-order electric polarization, which is produced by the electric field oscillating with frequency ω, acts as a source which drives an electric field with reduced 2ω. The reason for monitoring the second-order optical response in a structural change experiment is that the second-order susceptibility $\boldsymbol{\chi}^{(2)}$ reflects the symmetry of the system. For instance, in a material with inversion symmetry, $\boldsymbol{\chi}^{(2)}$ remains unchanged on application of an inversion operation. The vectors $\boldsymbol{P}^{(2)}(2\omega)$ and $\boldsymbol{E}(\omega)$, however, change sign under inversion:

$$-\boldsymbol{P}^{(2)}(2\omega) = \boldsymbol{\chi}^{(2)}(2\omega) \cdot [-\boldsymbol{E}(\omega)][-\boldsymbol{E}(\omega)],$$

implying that, for a material with inversion symmetry,

$$\boldsymbol{\chi}^{(2)}(2\omega) = -\boldsymbol{\chi}^{(2)}(2\omega) = 0.$$

In other words, no second-harmonic radiation can be produced in a material with inversion symmetry. However, structural change resulting from excitation by a pump pulse can change

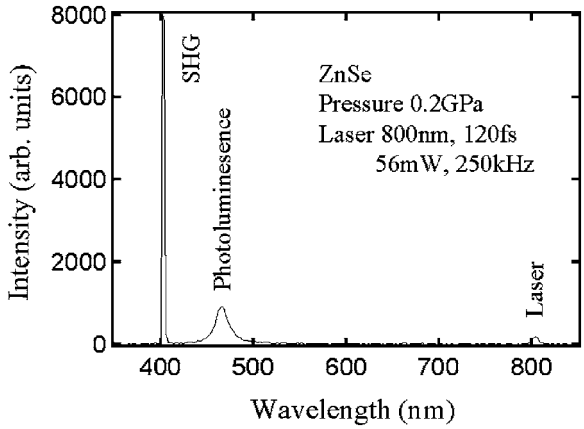

Figure 2. Second-harmonic emission spectra of ZnSe at room temperature.

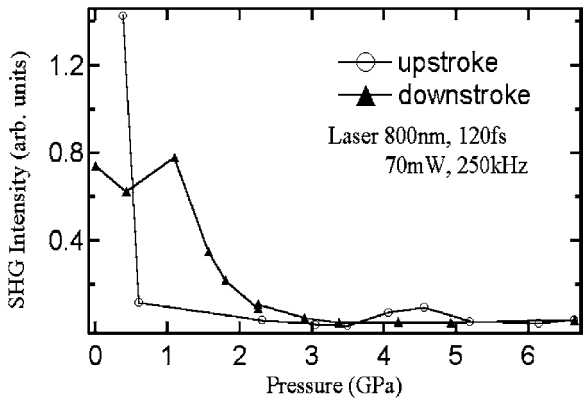

Figure 3. Hysteresis curves for the second-harmonic emission intensity of ZnSe.

the crystal symmetry in such a way that the material takes on inversion symmetry. Vanishing of the second-order susceptibility then serves to signal a change in the chemical bond structure.

3. Results

The time-integrated second-harmonic emission spectrum of ZnSe at room temperature is shown in figure 2. The two-photon-excited photoluminescence can easily be seen using our femtosecond pulse excitation, because the two-photon absorption coefficient in ZnSe is fairly large [4]. The intensity of the two-photon-excited photoluminescence decreases with increasing pressure. The emission peak of the two-photon-excited photoluminescence is at 467 nm. The two-photon-excited photoluminescence could not be observed during the pressure was released. In contrast, second-harmonic emission could be observed during the pressure release process.

Figure 3 gives the SHG intensity as a function of the applied pressures up to 6.7 GPa. Weill *et al* [5] had determined the behaviour of ZnSe by means of Raman spectra taken under pressure up to 15 GPa, and the zinc-blende–rock-salt transition at 11.5 ± 1 GPa was confirmed. This transition at 13 GPa has been established by means of electroresistance [6]. The SHG

intensity indicates the fraction of zinc-blende phase. The zinc-blende–rock-salt transition pressure is 1.07 GPa, which is given by the mid-point of the hysteresis curve (the average of upstroke and downstroke 50%-transformed pressures). The existence of a broad hysteresis curve indicates the presence of a significant barrier for phase transformation and thus suggests that the mid-point of the curve is the most appropriate point to be selected as the pressure of the phase transition [7]. The pressure required to induce transformation from a zinc-blende to a rock-salt structure decreases dramatically from 11.5 to 1 GPa under the femtosecond laser field.

It is possible to deposit the photon energy in ZnSe on a timescale which is short compared with the electron–lattice equilibration time of a few picoseconds using a 100 fs laser pulse. Furthermore, higher densities of excited electrons could be created because nonlinear absorption becomes important with the high peak intensities in the femtosecond laser pulse. If a sufficiently high fraction of the valence electrons are excited from bonding states to anti-bonding states, then the covalent bonds can no longer hold these atoms at the original positions and a structural transition occurs. Other recent experimental results have also shown that the response of a semiconductor to a femtosecond laser pulse is fundamentally different from its response to a picosecond or nanosecond laser pulse [8].

4. Conclusions

Our SHG results show, for the first time, that SHG can be used to monitor structural changes under pressure of some materials. This will provide new opportunities to study the nonlinear optical response of these materials, which may be important in many applications. For such studies, the use of a femtosecond laser is necessary, as a long pulse duration may cause other effects such as heating and cascade. During exposure to an ultrafast laser pulse, electron excitation is dominant. The huge electronic excitation may drive a structural change in a time period of 10^{-12} s. Furthermore, since the nonlinear response is of electronic origin, the electronic contribution can be isolated experimentally by using the ultrashort laser pulse. Therefore this technique may also be important for confirming the origin of certain nonlinearities exhibited by the materials.

Acknowledgments

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