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Terahertz optical properties of nonlinear optical CdSe crystals

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ABSTRACT

We investigate the optical properties of cadmium selenide (CdSe) crystals in a wide terahertz (THz) range from 0.2 to 6 THz by THz time-domain spectroscopy (THz-TDS) and Fourier transform infrared spectroscopy (FTIR). The refractive index, absorption coefficient and transmittance are measured and analyzed. The properties are characterized by several absorption peaks which represent the relevant phonon vibrations modes. The experimental results are in agreement with the theoretical results. The dispersion and absorption properties of CdSe crystal are analyzed in THz range. These properties indicate a good potential for THz sources and THz modulated devices.

1. Introduction

Terahertz (THz) sources based on nonlinear optical frequency conversion technologies have attracted much attention for its potential applications in spectrum analysis, biological detection, and imaging systems. As the key elements in optical terahertz sources, several nonlinear optical crystals have been explored as the high-efficient media for THz generation, such as GaP [1], GaSe [2], $ZnGeP_2$ [3], GaAs [4] and DAST [5]. However, the limited transparency range and small crystal size will restrict practical applications in frequency conversion and the function devices.

Cadmium selenide (CdSe) is a positive uniaxial wurtzite crystal with hexagonal structure of 6*mm* point group and a band gap $E_g = 1.73$ eV at T = 300 K [6]. CdSe crystal is one of the promising crystals in mid-infrared region because it has wide transparency range (0.75–25 μm) and small birefringent walk-off angle [7]. In 2013, Gabriel Mennerat used CdSe crystal in difference frequency generation (DFG) to generate the mid-infrared wave with a continuously tunable wavelength from 10 to 22 μm [8]. Furthermore, large size of CdSe crystal can be readily grown with very stable characteristic due to covalent bonding. In 2017, J. H. Yuan et al. obtained average power of 170 mW output at 12.07 μm in CdSe crystal based on optical parametric oscillator (OPO) [9]. Optical characteristics of CdSe crystal from near-to mid-infrared range have been studied extensively [8,10]. These properties show the potential applications in tunable long-wave coherent light generation in the mid- and far-infrared range.

In this research, we make the first investigation about the optical properties of CdSe crystal in THz range. The crystals are grown by high pressure vertical gradient freeze (HPVGF) technique. The intrinsic vibration of CdSe crystals is theoretically analyzed based on the density functional perturbation theory (DFPT). The refractive index, absorption coefficient and transmittance of CdSe crystal have been measured in the frequency range of 0.2–6 THz by THz time-domain spectroscopy (THz-TDS) and Fourier transform

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infrared spectroscopy (FTIR) system. The experimental results are in agreement with the theoretical results. The results show that CdSe crystal has the potential of application in THz generation and other THz function devices.

2. Theoretical calculation

The phonon dispersion of the nonlinear optical crystals is one of the main influencing factors in the interaction between the THz wave and the crystal lattice. We calculated the phonon dispersion spectra and projected phonon density of states of CdSe crystal based on the density functional perturbation theory. The first-principle calculations are carried out by the plane-wave pseudo-potential method implemented in the CASTEP package [11,12]. The generalized gradient approximation with the Perdew-Burke-Ernzerhof [13] is used to describe the exchange-correlation (XC) functions, and the ion-electron interactions are modeled through the optimized norm-conserving pseudopotentials [14]. We set the kinetic energy cutoffs of 1000 eV and Monkhorst-Pack k-point meshes with a span of less than 0.07/Å^3 in the Brillouin zone. The lattice constants and atom sites of CdSe crystal are fully fixed within experimental values. The linear response method is employed to obtain the phonon dispersion [15].

The calculated phonon dispersion spectra and projected phonon density of states of CdSe crystal are plotted in Fig. 1. Wurtzite CdSe belongs to $P6_3mc$ space group (C_{6v}^4 point group), so the 8 normal modes at the Brillouin zone center are distributed among the various irreducible representations as follows: $\Gamma = 2E1+2E2+2A1+2B2$, where A1 and E1 are polar Raman active modes having transverse optical (TO) and longitudinal optical (LO) modes, E2 is nonpolar Raman active modes, and B2 is an optically inactive mode. The main groups of states near 30, 120, 180 and 210 cm^{-1} can be assigned into the E2, B2, E2, B2 vibrational mode, respectively [16]. In particular, the atomic illumination of 30 cm^{-1} (0.9 THz) and 182 cm^{-1} (5.8 THz) are illustrated in Fig. 2. Both of them belong to Raman active E2 mode and can interact with external electromagnetic field. The atomic illumination of 120 cm^{-1} (3.7 THz) is also shown in Fig. 2. This belongs to optically inactive B2 mode. Accordingly, the absorption peaks at 0.8 THz and 1.45 THz can be attributed to single-phonon and two-phonon absorption of vibrational mode at 30 cm^{-1}, respectively. Meanwhile, the absorption peak at 5.0 THz can be assigned to the two phonons coupling between 30 cm^{-1} and 120 cm^{-1} modes. Notably, there is an optical forbidden gap ranged from 130 to 160 cm^{-1}, which make the crucial contribution to the high transparency from 4.0 to 4.75 THz.

3. Sample details and the experimental schemes

The CdSe crystals were prepared based on the HPVGF technique using [001]-oriented seed. After putting a high quality cylindrical CdSe single crystal with [001] orientation into a PBN crucible as seed, the CdSe with high purity (6 N, CNBM Optoelectronics Materials Co., Ltd.) was adopted as raw materials and settled in the PBN crucible in vertical induction furnace. Ar gas with high purity (99.999%) was introduced into the chamber during the heating process. The growth surface was controlled to be a stable state with a temperature gradient. After 7–10 days, the PBN crucible was cooled slowly to the indoor temperature. Finally, a crack-free CdSe single crystal was obtained.

After the [110] crystal orientation of CdSe single crystal was determined by an X-ray diffractometer, three crystals were cut into 15 mm × 15 mm or 10 mm × 10 mm square slices with 0.65 mm, 1.0 mm and 1.36 mm thickness and polished both sides as shown in Fig. 3.

The THz uniformity of the CdSe crystal is verified based on our home-made THz imaging system [17,18]. The transmittance of the CdSe crystal with thickness of 0.65 mm is about 15% under the frequency of 2.52 THz, as shown in Fig. 4.

THz-TDS experiments were performed on the standard four parabolic mirror THz-TDS system with the THz range of 0.2–2 THz [19]. THz pulses are generated from a photoconductive antenna. The excitation source is from a Ti:sapphire laser with 75 fs duration of 80 MHz repetition rate working at 800 nm. A ZnTe crystal is used for detection. All the experiments were carried out at 300 K with the humidity of less than 5%.

A roof-mirror FTIR (SPS-300, Sciencetech Inc) working in Michelson interferometer mode was used in our experiment to extend the measured frequency to 6 THz, and the detailed schematic diagram of the system is introduced in our previous work

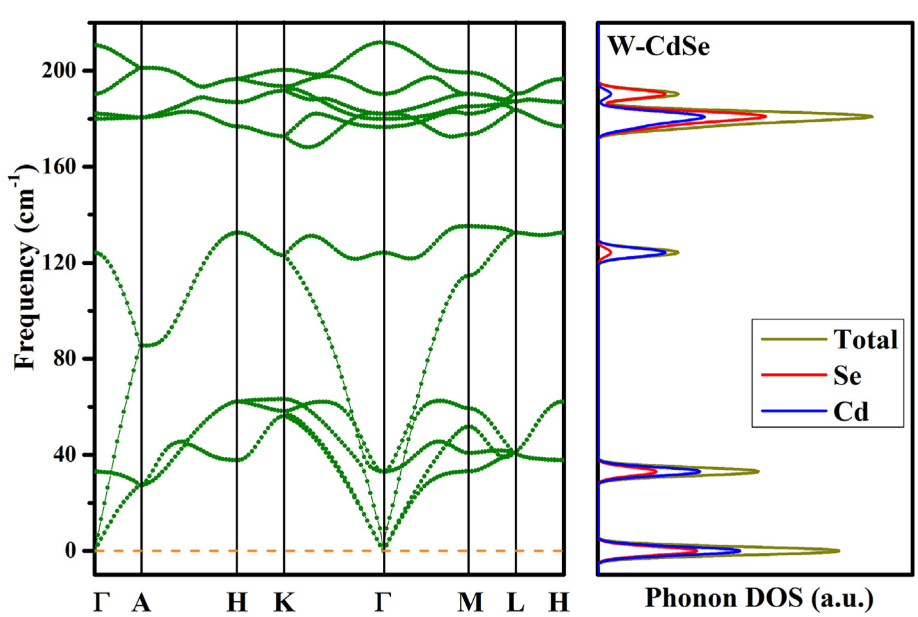

Fig. 1. Calculated phonon dispersion (left) and phonon density of states (right) for CdSe.