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Frequency dependent optical and dielectric properties of zinc sulfide in Terahertz regime

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HIGHLIGHTS

- Comparison of various grades of ZnS samples using terahertz time-domain and millimeter wave spectroscopy systems.
- Good agreement of vibrational modes exhibited by ZnS samples at 0.78 THz and 2.20 THz with literature.
- Comparison of frequency dependent dielectric properties of the ZnS samples using both techniques.
- Comparison of frequency dependent refractive index of the ZnS samples using undamped harmonic oscillator model.

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ABSTRACT

Frequency dependent optical and dielectric properties for several grades of chemical vapor deposited (CVD) zinc sulfide (standard, elemental, and multi-spectral) was performed using a terahertz time-domain spectroscopy (THz-TDS) system in the frequency range from 0.15 THz to 2.5 THz. Zinc sulfide exhibits low frequency vibrational modes characterized by the THz-TDS. Two low-frequency phonon resonance lines were revealed at 0.78 THz and 2.20 THz. These samples were also characterized in the GHz range using a backward wave oscillator (BWO) source quasi-optical spectrometer, and the data obtained by both approaches were compared. Experimental data were also compared with an undamped harmonic oscillator model. These results compare well with the literature values obtained using other methods.

1. Introduction

Zinc sulfide (ZnS) is a II–VI semiconductor with bandgap energy of 3.8 eV and is widely used as an infrared window in engineering applications due to excellent combined optical, mechanical, and thermal properties. As a doped semiconductor, it is also used in cathodo- and electro-luminescent devices, and undoped as an optical thin film material for filters and antireflection coatings. ZnS is an extremely important material for missile domes and some space-borne systems that require long-wave infrared transmissivity [1,2].

Many solids, liquids, and gases exhibit unique spectroscopic "fingerprints" at THz frequencies, which are used for identification of chemicals and substances. THz time-domain spectroscopy (THz-TDS) is highly sensitive in detecting the fundamental phonon modes of these dielectric materials, which occur at low frequencies [3–8]. At room-temperature, ZnS is crystalline solid with the cubic zinc-blende (sphalerite) or hexagonal wurtzite structure, and exhibits characteristic absorptions due to single and multiphonon processes arising from the critical points in the Brillouin zone. These phonon bands may be classified as sum or difference of longitudinal optical (LO), transverse optical (TO), longitudinal acoustic (LA) and transverse acoustic (TA) phonons at the zone boundary [9]. Acoustic phonon absorption peaks in ZnS have been observed at 73 cm^{-1} (2.20 THz) corresponding to TA(L) phonons and at 93 cm^{-1} (2.80 THz) corresponding to TA(X) phonons. These values were obtained from infrared absorption, spectral emittance, X-ray scattering, and neutron scattering [10]. Raman spectra of wurtzite type ZnS crystal exhibited a phonon peak at 72 cm^{-1} (2.20 THz) [11]. Nilsen [12] performed an extensive study on cubic ZnS using Raman spectroscopy and predicted phonon resonances for TA at 88 cm^{-1} (2.64 THz), LA at 110 cm^{-1} (3.30 THz), and superposition of two difference phonons (LO-TO) and (LA-TA) at 27 cm^{-1} (0.78 THz). Advancing the fundamental understanding of the dielectric properties of ZnS depends on characterization of the fundamental phonon resonances, and thus requires characterization in the broad frequency range that extends to the THz regime.

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This paper reports THz-TDS measurements of ZnS in this important frequency range.

2. Experimental procedure

2.1. ZnS samples

In this paper, results are reported on three different samples of ZnS measured in the GHz–THz range using both quasi-optical millimeter wave (MMW) spectrometry and THz-time domain spectroscopy (THz-TDS) approaches. Samples were obtained from Raytheon Co, USA, including standard chemical vapor deposited (CVD) ZnS made from hydrogen sulfide gas and zinc vapor, legacy elemental ZnS (eZnS®) made by CVD from hydrogen gas, sulfur, and zinc vapor [1], and multi-spectral ZnS made from CVD ZnS subsequently hot-isostatic pressed (HIP) in the presence of platinum metal. Standard and elemental CVD ZnS are yellowish and opaque to slightly scattering in the visible, while multi-spectral ZnS is colorless and transparent. The microstructures of all CVD materials without subsequent processing (i.e., before HIP) are similar, with elongated grains along the deposition axis [13,14], 5–10 μm in diameter by 50–100 μm long. Multi-spectral ZnS material has larger grains, typically 40–100 μm, which are relatively uniform.

2.2. MMW and THz characterization

For MMW measurements, a free-space quasi-optical MMW T-scan 260 spectrometer (Microtech Instruments, USA), equipped with a set of high-power back wave oscillators (BWOs) for transmittance measurements in the frequency range 180–260 GHz, was used to obtain low frequency dielectric data. A commercially available TPS Spectra 3000 (Teraview, UK) was used to measure material properties using short pulses of THz radiation. A typical THz-TDS system consists of a femtosecond laser, a computer controlled optical delay line, THz source, detector, optics for collimating and focusing the THz beam, a current preamplifier, and a digital signal processor controlled by a computer [15]. The generation and detection of a THz pulse starts with a femtosecond laser, which produces an optical pulse train. A mode-locked Ti:Sapphire laser with a center wavelength approximately 800 nm, repetition rate of 80 MHz, and pulse width of 100 fs is used. Each pulse is separated into synchronized pump and probe beams. The pump beam is used to generate the THz beam and the probe beam to detect it. THz-TDS utilizes the generation and detection of a broadband, sub-picosecond THz pulse that is generated and detected in the time-domain. As a result, Fourier transforms of THz time-domain pulses retain both the spectral amplitude and phase data allowing for the calculation of optical parameters. Fig. 1 shows the typical THz-TDS (a) and MMW (b) spectrometer set-ups.

3. Results and discussion

The frequency-dependent coefficient of power absorption, dielectric constant, loss tangent, and refractive index for these samples at room temperature are reported below. Data from MMW-BWO and THz-TDS approaches are compared. Two low-frequency phonon resonance lines are seen at 0.78, and 2.20 THz. Refractive index data at room temperature is compared with the undamped harmonic oscillator model using coefficients reported by Hattori et al. [16].

3.1. Dielectric characterization of ZnS samples using THz-TDS at room temperature

A characteristic measurement consists of the THz pulse being reflected at the sample surface or transmitted through the sample. This propagating pulse is compared to the reference pulse being captured without the sample being present. The quantities that are generally used for analysis are amplitude, time delay, and Fourier transform of the time-domain pulse. Two obvious differences between the reference pulse and sample pulse will be the reduction in the signal strength when the pulse hits the sample due to the absorption and shifting (delay) of the sample pulse due to the refractive index of the sample. Since the time-domain technique yields both amplitude and phase information, it allows one to obtain refractive index and absorption coefficient without the need to perform any complicated calculations. The measurements were made using THz-TDS at room temperature in a nitrogen purged chamber as reference to remove any atmospheric water vapor. Fig. 2(a) depicts the initial analysis of the time-domain plots of the reference, standard, elemental and multispectral ZnS samples. It can be seen from the time-domain plots that the ZnS samples show decreased THz electric field amplitude as compared to the reference. The decrease in amplitude of the time-domain pulse from the samples compared to the reference is due to the absorption and the reflection at the surface of the samples. Due to large thickness, standard (6.32 mm thick) and multispectral ZnS (6.30 mm thick) are delayed further in time and exhibit reduced signal strength compared to elemental ZnS (4.58 mm thick). Fig. 2(b) shows the frequency domain plot which indicates that the collected signal for ZnS samples extends to ~2.5 THz,

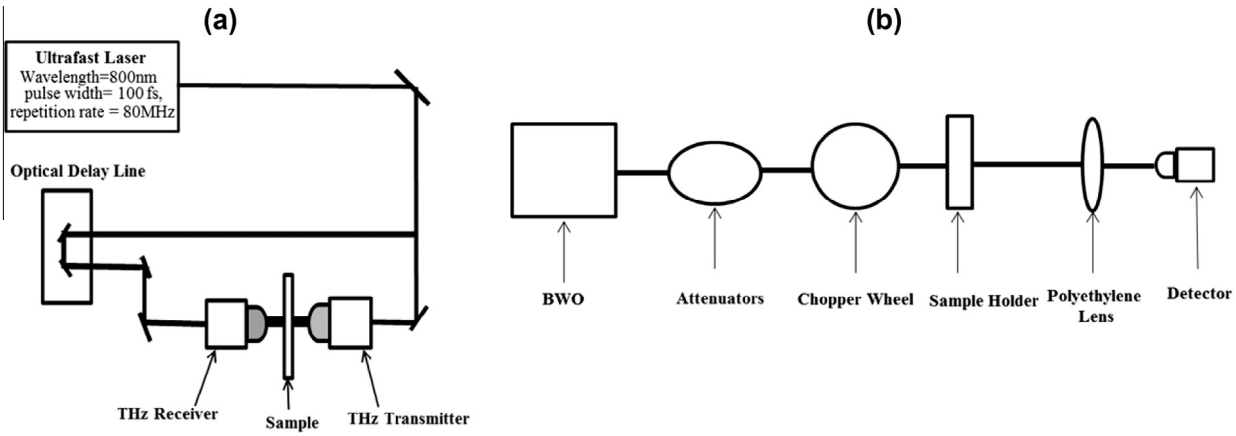

Fig. 1. A typical (a) THz-TDS system set-up, (b) MMW spectrometer set-up.