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Infrared absorbance in CaS as a function of pressure

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Abstract. The infrared absorbance of CaS (the *B1* structure) in the 150–500 cm⁻¹ wavenumber range is studied up to 17.0 GPa. The microscopic Grüneisen parameter at constant temperature $T = 298$ K, correlating the pressure dependence of the absorbance band with the pressure dependence of the unit cell volume, is in the range 1.42–1.62. There is no indication for pressure-induced opaqueness for the sample or loss of infrared intensity in the entire pressure range studied here.

Calcium sulphide, CaS, is a closed-shell ionic compound with the NaCl (*B1*) structure at atmospheric pressure. Upon compression, it reversibly transforms from the *B1* to *B2* (CsCl) structures at about 40 GPa [1, 2]. The equation of state and *B1* and *B2* bulk moduli of this compound were previously investigated using both the energy-dispersive x-ray diffraction technique [1, 2] and different theoretical electron-gas models [2]. The general systematics of *B1*–*B2* transition pressures and isothermal bulk moduli at zero pressure in the entire family of the MeX alkaline earth metal chalcogenides (Me: Mg, Ca, Sr, Ba; X: S, Se, Te) were thoroughly discussed in [2]. However, there are no experimental data available on the pressure dependence of optical phonon frequencies in this group of compounds. Such results could provide a rigorous test for accuracy of several theoretical models applied to investigations of structures and electronic properties of related oxide and non-oxide systems under pressure. It is particularly crucial for the compounds with a large polarizability of the anionic species. In this paper, the infrared absorbance in CaS in the 150–500 cm⁻¹ range is investigated at high pressure and room temperature in a diamond anvil cell. The microscopic Grüneisen parameter (γ) inferred from the infrared data at $T = 298$ K is compared with the reported γ values for other compounds with the *B1* structure.

Absorbance spectra of CaS in the 100–500 cm⁻¹ range were collected on a Bruker 113v instrument equipped with a Mylar beamsplitter (6 μ m), Si bolometer detector and ceramic global source. The run conditions were: 256 scans with spectral resolution 4 cm⁻¹ and a spectral aperture open to 1 cm. Pressures were determined from the shift of the ν_3 internal asymmetric stretching mode in MgCO₃, using the scale previously established [3], similar to the one based on the pressure shift of the ν_3 asymmetric stretching oscillations of planar nitrite and nitrate ions in dilute solid solutions of these ions in sodium bromide [4]. The powdered CaS

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sample (Alfa) and CsI pressure medium (Aldrich), along with a trace of MgCO_3 (Aldrich), were loaded into a Mao–Bell-type cell with type II-a diamonds, brilliant cut with $600\ \mu\text{m}$ culets, and a sample chamber diameter of $250\ \mu\text{m}$. The weak external bands of MgCO_3 below $500\ \text{cm}^{-1}$ were obscured by the strong absorption band of the chalcogenide. The infrared absorbance spectra in the $500\text{--}1800\ \text{cm}^{-1}$ range for the ν_3 pressure measurements were performed on the same instrument using a Ge coated KBr beamsplitter, deuterated triglycine sulphide detector with a KBr window and ceramic globalar source. The run conditions were: 1024 scans with spectral resolution $4\ \text{cm}^{-1}$ and a spectral aperture open to 1 cm. The estimated error in the pressure determinations did not exceed 6% relative of the measured value. Reference spectra in the two separate wavenumber regions were collected through a gasketed diamond cell loaded only with CsI and ruby chips.

Only one triply degenerate infrared active vibration is predicted in the $B1$ structure (F_{1u}), while the first order Raman spectrum is not allowed [5]. In the infrared reflection spectrum of a single $B1$ crystal, a broad region of nearly total reflectivity occurs between the lower limit corresponding to the transverse optic mode (TO) and the higher limit corresponding to the longitudinal optic mode (LO). These two modes are separated due to long range coulombic interactions. Weak second order resonances could also be found involving transverse and longitudinal modes of the optical and acoustic oscillations. Infrared transmission spectra of the powder or polycrystalline samples are dominated by an intense band, related to the transverse optic mode, at a wavenumber that in fact lies between the TO and LO limits because of non-zero dampings of these modes. A much weaker band, corresponding to the LO mode, could also be present due to the incorporation of surface mode features and oblique incidence of the light passing through the sample.

There are no single crystal reflectivity data available on the transverse optic (TO) and longitudinal optic (LO) modes in calcium sulphide and other MeX chalcogenide compounds with the $B1$ structure (Me: Mg, Ca, Sr, Ba; X: S, Se, Te). The infrared absorption maximum, related to the TO mode, occurs at $244\ \text{cm}^{-1}$ in our spectrum of CaS measured at ambient conditions (figure 1). Upon compression to about 12 GPa, all the spectra contain interference fringes from multiple infrared beam reflection between the culets of the diamonds. The curvature in the pressure dependence of the absorbance band at near ambient conditions could be explained by an initial compaction of the powder CaS sample and CsI solid solvent (figure 2). On the other hand, such curvature could also result from a mixed TO/LO character of the observed absorbance band due to a relatively small TO–LO splitting, and sizable TO and LO dampings at ambient and near ambient pressures. Dampings of the TO and LO modes could change in different ways upon compression. As a result, the character of the absorbance band would tend to correspond more closely to the TO mode at increased pressures, becoming more symmetric at the same time (figure 1). Thus, it would suggest that polarizability would significantly change with pressure. Increase in the band width and integral intensity, and decrease in the absolute intensity, would point towards the increasing oscillator strength of the TO mode with pressure, despite the possible band broadening effects due to the non-hydrostacity of the CsI pressure medium. Optical observation of the sample under the microscope did not reveal any pressure-induced opaqueness that would be related to the changes of the electronic structure of CaS on compression. Another confirmation for this is that there is no dramatic intensity loss and no background rise in the absorption spectra collected up to 17.0 GPa. The steep increase in absorbance below $200\ \text{cm}^{-1}$ in the experiments above 10 GPa is due to the absorption band of the CsI pressure medium moving into the spectrum [5].

The pressure dependence of the infrared absorbance band (figure 2) can be correlated with the pressure dependence of the unit cell volume through a microscopic Grüneisen parameter (γ)

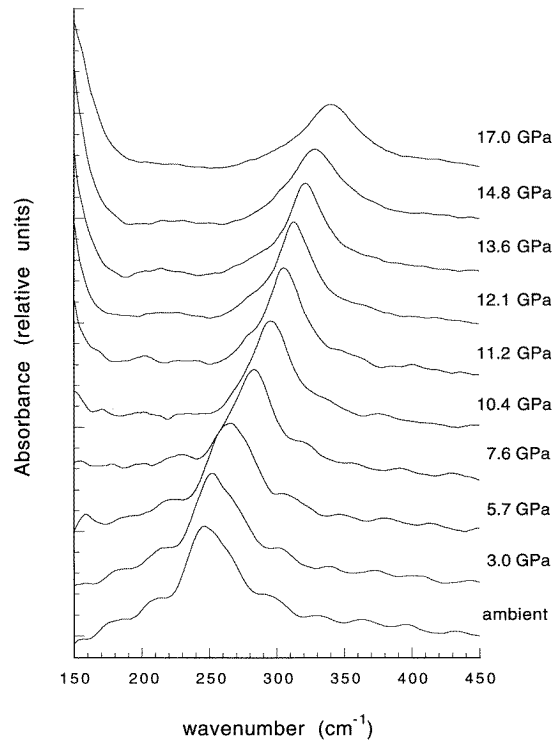


Figure 1. Absorbance spectra of CaS as a function of pressure. The spectra are vertically offset for clarity.

at constant temperature ($T = 298$ K), $\gamma = (\partial \ln \nu / \partial \ln V)_T = (K_0 / \nu_0)(\partial \nu / \partial P)_T$ where ν_0 is the wavenumber of the vibrational mode at ambient conditions (cm^{-1}), ν is the wavenumber of the vibrational mode (cm^{-1}), V is the corresponding unit cell volume (\AA^3), P is the corresponding pressure (GPa) and K_0 is the isothermal bulk modulus at zero pressure (GPa). The resulting value of the $(\partial \nu / \partial P)_T$ parameter is 6.18 (0.14) ($\text{cm}^{-1} \text{GPa}^{-1}$) with the fitted ν_0 value equal to 235 (2) cm^{-1} . There are two reports on the isothermal bulk modulus of CaS [1, 2]. The values of this parameter differ between those two studies, because in one of them there was no pressure medium used [1], and in the other one argon was used both as a pressure medium and as a pressure calibrant [2]. The value of K_0 also varies depending on the equation of state (EoS) used to extract it from the *pressure–volume* data [2]. If $K_0 = 64$ GPa from the third-order Birch–Murnaghan EoS [1] and measured $\nu_0 = 244$ cm^{-1} are substituted in the above equation, the γ parameter is equal to 1.62 . When $\nu_0 = 244$ cm^{-1} and the numbers by Ekbundit *et al* [2] are utilized (52.6 GPa, 56.3 GPa and 52.4 GPa from the third-order Birch–Murnaghan, second-order Birch–Murnaghan and universal EoS equations, respectively), the resulting value of γ varies from 1.33 to 1.42 , with the average $\gamma = 1.36$. On the other hand, the average value of the microscopic Grüneisen parameter is 1.42 ($\nu_0 = 244$ cm^{-1}), assuming that the average K_0 of all the four numbers is 56.4 GPa. The use of CsI as a pressure medium, which is less hydrostatic than argon, would imply that the γ parameter obtained with the data shown in figure 2 is in the range 1.42 – 1.62 . If the fitted $\nu_0 = 235$ cm^{-1} is used, the following γ parameters are obtained, with the corresponding bulk moduli given in brackets [1, 2]: 1.38 (52.4 GPa), 1.38 (52.6 GPa), 1.48 (56.3 GPa) and 1.68 (64 GPa).

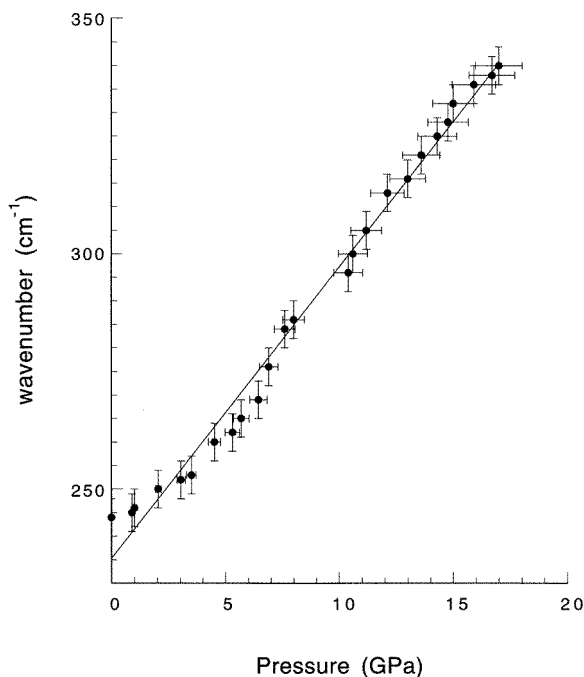


Figure 2. Pressure shift of the absorbance band in CaS.

Our results could be correlated with the available data on the other compounds with the *B1* structure. Grüneisen parameters for the absorbance bands in alkali halides are close to 2, with no clear tendency for them to change in passage from lighter to heavier anions or cations [6]. On the other hand, the respective γ parameter for MgO is equal to 1.56 [7]. This would suggest that the microscopic Grüneisen parameters for the MeX compounds, including oxides (Me: Mg, Ca, Sr, Ba; X: O, S, Se, Te), have similar values approximately equal to 1.4–1.6. These numbers, lower than the ones for alkali halides [6], could be explained taking into account the differences in bonding between halides and chalcogenides within the same *B1* structural type [1, 2, 6]. The changes in the absorbance band shape in CaS would further imply the changes of ionic polarizabilities at high pressures. Such an effect could be quite different in various *B1* compounds, despite their similar Grüneisen parameters [7].

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