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Infrared Lattice Vibrations of $PbGa_2S_4$

Infrared reflectivity spectra of $PbGa_2S_4$ single crystals are measured at room temperature in the wavenumber range from 30 to 4000 cm^{-1} for the polarization directions $E \parallel c$ and $E \parallel b$. The frequencies of 13 B_{1u} modes and 11 B_{2u} modes are derived from the spectra. The results are compared with previous studies and with lattice vibration data of ternary chalcopyrite and defect-chalcopyrite compounds.

Infrarotreflexionsspektren von $PbGa_2S_4$-Einkristallen wurden bei Raumtemperatur im Wellenzahlbereich von 30 bis 4000 cm^{-1} für die Polarisationsrichtungen $E \parallel c$ und $E \parallel b$ gemessen. Aus den Spektren wurden die Frequenzen von 13 B_{1u}-Moden und 11 B_{2u}-Moden ermittelt. Die Ergebnisse werden mit früheren Untersuchungen und mit Gitterschwingungsdaten für ternäre Chalkopyrit- und Defekt-Chalkopyrit-Verbindungen verglichen.

1. Introduction

In studying the near-edge optical properties of $PbGa_2S_4$ it has been established that this ternary compound is an indirect-gap semiconductor with a gap energy of 2.84 eV at room temperature (NEUMANN et al. 1988). However, even at low temperatures no phonon-induced structures on the absorption edge have been observed although they are expected to be present in an indirect semiconductor (JOHNSON). In discussing this result it has been argued, on the basis of existing at that time preliminary infrared reflectivity data of $PbGa_2S_4$ (GOLOVEI et al.), that the compound has a very rich phonon spectrum with modes at very low frequencies which prevents the resolution of phonon-induced structures in the near-edge optical absorption spectrum. Meanwhile, a rather comprehensive Raman scattering and infrared reflectivity study of $PbGa_2S_4$ has been reported (SYRBU et al. 1991) which qualitatively confirms this supposition. Especially in the Raman scattering spectra vibrational modes with frequencies down to 17 cm^{-1} have been detected. However, in the infrared reflectivity spectra reported by SYRBU et al. (1991) only polar modes with frequencies down to about 60 cm^{-1} have been observed, although it is evident from the frequencies of the Raman active modes that infrared active modes with frequencies below 60 cm^{-1} must exist, too. It was the aim of the present work to clarify this point by carefully measuring infrared reflectivity spectra of the compound up to frequencies as low as 30 cm^{-1}. Furthermore, a correct group theoretical analysis of the lattice vibrations of $PbGa_2S_4$ is given for the first time. Finally, the results obtained for $PbGa_2S_4$ are compared with lattice vibration data of other compounds containing Ga–S bonds.

2. Crystal structure and group theory

In several X-ray diffraction studies of the crystal structure of compounds with the composition $PbB^{III}_2C^{VI}_4$ (CHILOUET et al.; EHOLIE et al.; KLEE, SCHÄFER 1980; PETERS, BAGLIO) it has been established that, among others, $PbGa_2S_4$ crystallizes in an orthorhombic lattice

with space group D_{2h}^{24} and with 32 molecular units in the elementary cell. The positional coordinates of the atoms in $PbGa_2S_4$ have not been determined so far, but a complete analysis of the isostructural compound $PbGa_2Se_4$ has been given (KLEE, SCHÄFER 1980). Accordingly, there are three different sets of Pb atoms, 8 Pb(1) in sites 8a, 8 Pb(2) in sites 8b and 16 Pb(3) in sites 16e, two sets of 32 Ga(1) and 32 Ga(2) atoms both in sites 32 h, and finally four sets of 32 Se(i) atoms, $i = 1$ to 4, also all in sites 32 h. The primitive cell that has to be used in analysing the lattice vibration spectrum contains 8 molecular units which gives rise to a total number of 168 vibrational modes. With the site symmetries of the atoms known the group theoretical analysis is straightforward. For the irreducible representation of the phonon normal modes at the centre of the Brillouin zone we find

$$\Gamma_{ac} = 1\,B_{1u} + 1\,B_{2u} + 1\,B_{3u}$$

for the acoustic modes and

$$\Gamma_{opt} = 19\,A_g + 22\,B_{1g} + 22\,B_{2g} + 21\,B_{3g} + 19\,A_u + 21\,B_{1u} + 21\,B_{2u} + 20\,B_{3u}$$

for the optical modes. Of the optical modes the A_g, B_{1g}, B_{2g} and B_{3g} modes are Raman active, the B_{1u}, B_{2u} and B_{3u} modes are infrared active for the three possible polarization directions of incident radiation $\boldsymbol{E} \parallel \boldsymbol{c}$, $\boldsymbol{E} \parallel \boldsymbol{b}$ and $\boldsymbol{E} \parallel \boldsymbol{a}$, respectively, and the A_u modes are optically inactive. We note that this representation of the optical phonon normal modes differs from that of

$$\Gamma_{opt} = 24\,A_g + 24\,B_{1g} + 24\,B_{2g} + 24\,B_{3g} + 24\,A_u + 23\,B_{1u} + 23\,B_{2u} + 23\,B_{3u}$$

which has been tentatively proposed by SYRBU et al. (1991).

3. Experimental results

As in our presvious optical absorption study (NEUMANN et al. 1988) the samples used in the experiments were (100) oriented platelet-like single crystal specimens with thickness of about 0.4 mm cleaved from crystals having a thickness of about 1.5 mm. By the cleavage procedure we obtained samples with smooth and mirror-like surfaces which needed no further preparation for the optical measurements. With these samples we were able to measure reflectivity spectra for the polarizations $\boldsymbol{E} \parallel \boldsymbol{c}$ and $\boldsymbol{E} \parallel \boldsymbol{b}$. Attempts to prepare specimens with the surface planes (010) or (001) suitable for optical measurements with $\boldsymbol{E} \parallel \boldsymbol{a}$ were not successful. The infrared reflectivity spectra were recorded in the wavenumber range $\bar{\nu} = 30-4000\ \mathrm{cm}^{-1}$ with incident radiation polarized perpendicular to the plane of incidence in order to avoid mode leakage effects. All experiments were made at room temperature.

First let us consider the reflectivity spectra in the range of low frequencies which were of particular interest in order to complete the results of SYRBU et al. (1991) a far as the infrared active modes are concerned. In Figure 1 the result of our measurements is depicted for the frequency range $\bar{\nu} = 30-150\ \mathrm{cm}^{-1}$. The spectra exhibit 7 vibrational bands for the polarization $\boldsymbol{E} \parallel \boldsymbol{c}$ and 5 bands for $\mathbf{E} \parallel \boldsymbol{b}$. Furthermore, they reveal a distinct anisotropy of the vibrational properties of $PbGa_2S_4$ in this frequency range.

Comparing with the infrared reflectivity data of SYRBU et al. (1991) we find that in this frequency range only mode 5 for $\boldsymbol{E} \parallel \boldsymbol{c}$ and mode 4 for $\boldsymbol{E} \parallel \boldsymbol{b}$ have been unambiguously identified by these authors. In case of $\boldsymbol{E} \parallel \boldsymbol{c}$ SYRBU et al. (1991) observed a vibrational band