

Non-Linear Raman Scattering in II-III₂-VI₄ Compounds

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The paper presents an experimental substantiation of the theory (based on the optical vibration anharmonism) of non-linear Raman scattering (RS) in defective II-III₂-VI₄ compounds. In the transparency region of those compounds the anharmonicity assures processes of direct photon-phonon interaction resulting in the independence of RS characteristics upon the free carrier concentration. When the laser quantum energy approaches the band gap E_g an effective thermalization of the absorbed radiation takes place which in one's turn gives rise to the anharmonic generation of two or more phonons by a laser photon. These phenomena are shown to result in a non-linear dependence of the RS intensity upon the laser beam power.

KEYWORDS: Raman scattering, II-III₂-VI₄ compounds, phonon, photon, anharmonicity, non-linear dependence

1. Introduction

Most of II-III₂-VI₄ compounds belongs to the class of defect diamond-like semiconductors containing ordered stoichiometric vacancies and crystallizing in the tetragonal lattice with S₄ space group.¹⁾ The interest to such compounds is caused by their high photosensitivity and intensive photoluminescence as well as by unique non-linear characteristics.^{2,3)} Last decade the non-resonant Raman scattering has been widely used for the purpose of identifying the optical phonon spectrum in different II-III₂-VI₄ compounds. Some regularities were established such as the predominance of a peculiar mode (so-called "breathing" one) in the non-polarized RS spectra and the relative smearing of the RS spectra in II-III₂-VI₄ compounds containing isoperiodical II- and III-group cations.³⁻⁶⁾ The latter feature was connected with antistructural disorder inherent to the compounds with isoperiodical cations.^{5,6)} That kind of disorder proved to result in the polarization independence of RS spectra, which impeded the assignment of the vibrational modes in the compounds involved.

The resonant RS has been employed to investigate the behaviour of the Raman cross-section for different vibrational modes in CdGa₂Se₄ when the exciting quantum energy $\hbar\omega_L$ tends to E_g .⁷⁾ A strong resonance of the highest frequency LO-modes and a saturation of the "breathing" one have been revealed.

The aim of the present work is to study the peculiarities of RS in II-III₂-VI₄ compounds as a function of both the $\hbar\omega_L$ and the laser beam power density. The main effect observed is the non-linear dependence of the RS intensity upon the exciting beam power when real electron states are involved in the RS process. This phenomenon is explained by an idea based on the anharmonism of optical vibrations.

In this paper the experimental results concerning ZnGa₂Se₄ and CdGa₂Se₄ single crystals are presented. The reasons for such a choice are the following. Firstly, both materials are direct-gap ones with close values of the band gap energy E_g (2.58 eV for ZnGa₂Se₄ and 2.57 eV for CdGa₂Se₄ at 300 K⁸⁾). Secondly, the considered com-

pounds give the possibility for a comparative study of RS in materials characterized by quite different degrees of intrinsic disorder.²⁾ At the same time it is to be noted that other compounds (such as ZnGa₂S₄, CdGa₂S₄, CdAl₂S₄) have been investigated as well. Therefore the paper includes some comments concerning the peculiarities of RS in those wide-band-gap-compounds ($E_g \approx 4$ eV⁹⁻¹¹⁾).

2. Experimental

The ternary compound single crystals studied have been prepared by the iodine transport technique. The excitation quantum energy $\hbar\omega_L$ was changed from the transparency region of ZnGa₂Se₄ and CdGa₂Se₄ to near the band gap, E_g , using He-Ne (632.8 nm), solid-state (532 nm, second harmonic) and Ar (514.5; 488.0 nm) laser lines. The peculiarities of Stokes component RS were studied as a function of the laser beam power up to 150 mW (the diameter of the focused laser beam in the crystal was about 100 μ m). The non-polarised RS spectra have been measured in 90°-geometry in the temperature range from 300 to 570 K by an automatic set-up based on a double DFS-52 spectrometer with the spectral resolution ranging from 0.5 to 2 cm⁻¹. A FEU-79 photodetector was used in the quantum counter regime.

3. Results

Figure 1 presents the normalized spectra of RS in ZnGa₂Se₄ and CdGa₂Se₄ at 300 and 570 K for $\lambda_{exc} = 632.8$ nm. As it has been expected, at a fixed temperature the RS spectrum of intrinsically disordered ZnGa₂Se₄ is more smeared than that of CdGa₂Se₄. With temperature rise the RS bands broaden and shift to the long-wavelength side in the both compounds.

At the center of Brillouin zone the vibrational spectrum in the defective II-III₂-VI₄ compounds is described by RS active 3A + 5B + 5E optical modes.⁴⁾ Non-polar A-modes are caused by oscillations of anion atoms, the lowest-energy A-mode (the "breathing" one) being connected to the symmetric oscillations of anions surrounding a stoichiometric vacancy.¹²⁾ In CdGa₂Se₄ all the A-symmetry modes (141, 188 and 210 cm⁻¹) have been identified, while in ZnGa₂Se₄ only the "breathing" one