

RADIATIVE RECOMBINATION CENTERS in GaTe

Hüsnü Salih Güder, Bahattin Abay, Hasan Efeoğlu and Yahya Kemâl Yoğurtçu

Atatürk University, Faculty of Science&Arts, Department of Physics,
25240 Erzurum-TURKEY

ABSTRACT. - Radiative recombination mechanisms in GaTe have been investigated by low temperature and temperature dependent photoluminescence (PL) measurements. Three emission bands have been observed located at 1.781 (A-band), 1.735 (B-band) and 1.575 eV (C-band) in the 1.5-1.8 eV energy region at 10 K. A- and B-bands have been found to be strongly dependent on temperature while C-band has been weakly dependent. The radiative recombination mechanisms of the A-, B- and C-bands have been associated with the direct free exciton, band-acceptor and donor-acceptor pair (DAP) transitions from the temperature dependences of the PL intensities and peak energies of the bands.

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1. INTRODUCTION

III-VI layered semiconductor compounds (GaS, GaSe, GaTe and InSe) are of special interest as they have potential applications for photon detectors and other optoelectronic devices. Some of their physical properties are highly anisotropic, and they exhibit strong exciton spectra [1].

GaTe has a monoclinic structure with $C2/m$ space group. Its crystallographic unit cell contains 12 molecules with 108 valence electrons as proposed by Pearson [2]. Because of the low symmetry and complex unit cells no band structure calculation is currently available yet. It has Ga-Te-Te-Ga fourfold packaged layers and the chemical bonding is mainly strength covalent in the intralayer and is of weak Van der Waals type in the interlayer as in other layered III-VI semiconductors [3].

Although the structural, electrical, optical absorption, Raman scattering and infrared absorption properties have been widely investigated, there has been only a few studies on the photoluminescence (PL) properties of GaTe.

In this paper, we present the results of low temperature (10 K) and temperature dependent PL measurements of GaTe in the energy region of 1.5-1.8 eV in order to determine the radiative recombination mechanisms. We discuss the recombination mechanisms of the emission bands with the temperature variation of the peak energies and PL intensities of the bands.

2. EXPERIMENTAL PROCEDURE

Single crystals of GaTe were grown by the Bridgman-Stockbarger method, from a stoichiometric melt of starting materials sealed in an evacuated and carbon coated quartz ampoules with a tip at the bottom, in our crystal growth laboratory. Details of the experimental procedure for crystal growth are reported elsewhere [4].

The samples (with about 3×3 mm² area and 100-300 μ m thickness) were easily cleaved along the plane perpendicular to the *c*-axis from the grown ingot with a razor blade

and no further polishing or cleaning treatments were required because of the natural mirror-like cleavage faces. Hall effect and thermal electromagnetic force (emf) methods showed them to be p-type [4] as to be for all the samples reported in literature grown by different techniques.

Measurements were made using a cw Ar-ion laser (514.5 nm) as excitation source. The excitation spot of laser and the excitation intensity I_{ex} were about 800 μm in diameter and 1 Wcm^{-2} , respectively. Laser light was filtered by a 514.5 nm band-pass filter and chopped at 1200 Hz with a HMS 221 model light beam chopper. The collected emission of the excitation spot was directed through a 650 nm long-pass filter, dispersed by a 0.5 m Thermo Jarrel Ash monochromator, detected by a Hamamatsu R955HA model photomultiplier tube, and measured synchronously by a Stanford SR850 model digital lock-in amplifier operating with a reference signal supplied by the optical chopper. Sample temperature was cooled down to 10 K using a Leybold-Heraeus closed-cycle helium cryostat and controlled within an accuracy of ± 0.2 K by a Leybold-Heraeus HR1 model modified temperature controller. All the parts of the system were automatically controlled by a computer.

3. RESULTS and DISCUSSION

Figure 1 shows the PL spectra of GaTe single crystals measured at 10 K in the wavelength region 1.5-1.8 eV. Three emission bands are observed in the figure: there is a strong, well resolved band centered at 1.781 eV (A-band), a broad band, about two times stronger than the A-band, extending from 1.670 to 1.770 eV and centered at 1.735 eV (B-band), and a third relatively weak, slightly asymmetric Gaussian-shape band centered at 1.575 eV (C-band), respectively.

In order to determine the radiative recombination mechanisms of these peaks, temperature dependent PL measurements were done in the range of 10-140 K. A- and B-bands were quenched quickly with temperature and disappeared at about 80 K while the C-band was slowly dependent on temperature and disappeared at a relatively high temperature 140 K. The variation of the peak energy positions for A-, B- and C- bands vs. temperature is given in Figure 2. Peak energies of the emission bands were shifted to the lower energies with temperature. The variation rate of B-band peak energy was comparable with the A-band peak energy below 50 K and greater than above this temperature while the variation rate of the C-band was almost the same as that of the A-band peak energy.

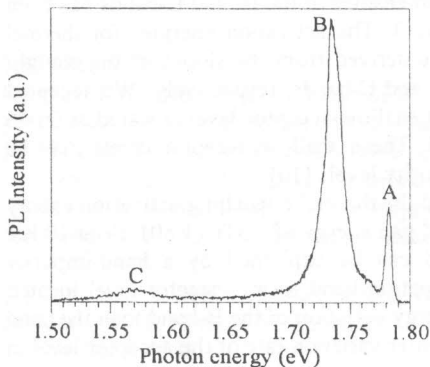


Figure 1. Photoluminescence (PL) spectra of GaTe at 10 K.

In order to interpret the peak energy variations of the emission bands with temperature, we combined the results of the optical absorption measurements with our PL results. Peak energy position values for the $n=1$ exciton peak was obtained from the absorption data in the 10-280 K temperature range. The band gap values of GaTe as a function of temperature were also calculated from both PL and absorption spectra using $n=1$ exciton peak energy values added with the value of 20 meV for the Rydberg energy [4]. The peak energy values obtained for both $n=1$ exciton peak and the band gap of GaTe are also shown in Figure 2. The fact that the

variation of the energy position of the A-band is consistent with that of the values obtained for $n=1$ exciton peak from the absorption data can be clearly shown from the figure.

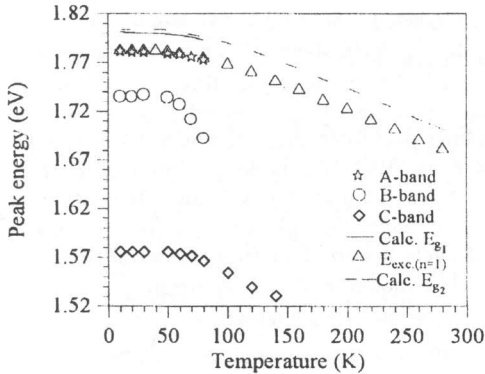


Figure 2. Peak energy variations of the A-, B- and C-bands. Δ indicates the peak energy values of the $n=1$ exciton obtained from absorption. The solid and dashed lines indicate the variation of the band gap of GaTe calculated from PL and absorption data.

since they are located on the lower energy side of the free and bound-exciton emissions region. The main luminescence mechanisms related to impurities in semiconductors are the band-impurity or the donor-acceptor pair (DAP) recombinations. That the peak energy position decreases with the same band gap energy as temperature increases has been observed for the band-impurity transition [8]. Similar behaviour has also been observed for the DAP transition and explained by the transition involving a substitutional acceptor and interstitial deep donor levels [9]. Considering the Figure 2, the peak energy variation of the B- and C-bands with temperature satisfies the expected variation for both band-impurity and DAP recombinations.

In a further attempt, integrated PL intensities of the B- and C-bands were measured as a function of temperature. Semilog plots of the PL intensities of the B- and C-bands has been shown against the reciprocal temperature in Figure 3. The activation energies for thermal quenching of about 0.046 ± 1 and 0.056 ± 1 eV were derived from the slopes of the straight lines using a nonlinear least-squares fit for the B- and C-bands, respectively. We accepted these two bands as the bands related with different shallow acceptor levels located at 0.046 and 0.056 eV above the top of the valence band. These shallow acceptor levels may be associated with the presence of the defects and impurity levels [10].

The sum of the emission energy 1.735 eV and the thermal quenching activation energy 0.046 eV of the B-band almost agrees with the band gap energy of GaTe (1.801 eV at 10 K). Therefore, the radiative transition of the B-band can be explained by a band-impurity recombination considering a transition from conduction band to an acceptor level located 0.046 meV above valence band. A greater peak energy variation of the B-band than the band gap energy above 50 K can be explained by the greater variation rate of the acceptor level in the B-band with temperature.

In the PL measurements carried out at 4 K and pumped liquid helium temperature [5,6], the observed emission bands at 1.778 and 1.780 eV were reported as the recombination of direct free excitons. A sharp and very strong ($\Gamma = 2.5$ meV, $\alpha = 16000$ cm⁻¹) absorption peak observed at 1779.5 ± 1.5 meV, recorded under high resolution and 1.6 K [7], was also identified as the absorption of the $n=1$ exciton peak. From these results, the A emission band can be attributed to the recombination of direct free excitons.

Concerning with the B- and C-bands, they are probably related to the impurity levels (such as residual impurity, defects or defect complexes) localized in the forbidden energy gap

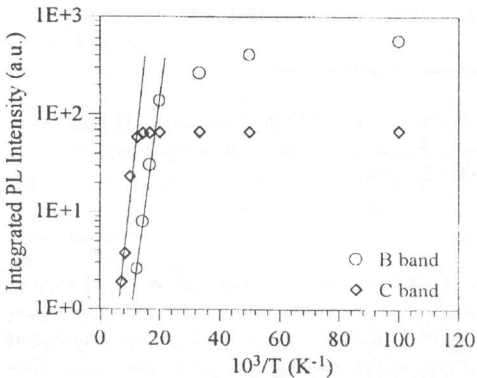


Figure 3. Variation of PL intensities with reciprocal temperature for the B- and C-bands.

explained to be a DAP transition from the donor level at 0.056 eV considering the agreement between the temperature variations of the C-band and band gap energy.

4. CONCLUSIONS

Low temperature and temperature dependent PL measurements were carried out for GaTe single crystals. Three emission bands were observed located at 1.781 (A-band), 1.735 (B-band) and 1.575 eV (C-band) in the 1.5-1.8 eV energy region at 10 K. A- and B-bands were found to be strongly dependent on temperature while C-band was weakly dependent. The radiative recombination mechanisms of the A-, B- and C-bands were associated with the direct free exciton, band-acceptor and DAP transitions from the temperature dependences of the PL intensities and peak energies of the bands, respectively.

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REFERENCES

- [1] Wan, J. Z., Brebner, J. L., Leonelli R. and Graham, J. T., *Phys. Rev. B* **46**, 1468, 1992.
- [2] Pearson, W. B., *Acta Cryst.*, **17**, 1, 1964.
- [3] Fielding, P., Fischer, G. and Mooser, E., *J. Phys. Chem. Solids*, **8**, 434, 1959.
- [4] Güder, H. S., Ph. D. Thesis, Erzurum-Turkey, 1999 (Unpublished).
- [5] Taylor, R. A. and Ryan, J. F., *J. Phys. C: Sol. State Phys.*, **20**, 6175, 1987.
- [6] Meneses, E. A., Jannuzzi, N., Freitas, J. R. and Gouskov, A., *Phys. Stat. Sol. (b)*, **78**, K35, 1976.
- [7] Camassel, J., Merle, P. and Mathieu, H., *Physica B* **99**, 309, 1980.
- [8] Giles, N. C., Hwang, S., Schetzina, J. F., McDevitt, S. and Johnson, J. C., *J. Appl. Phys.*, **64**, 2656, 1988.
- [9] Yu, P. W. and Park, Y. S., *J. Appl. Phys.*, **48**, 2434, 1977.
- [10] Capozzi, V., *Phys. Rev. B* **28**, 4620, 1983.