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LASER SPECTROSCOPY OF $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ SINGLE CRYSTALS :
EMISSION MECHANISM AND SATURATION EFFECTS

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Résumé - Sous excitation laser de forte puissance, la bande large de fluorescence du germanate de bismuth présente des trous dont la formation est reliée à un processus d'absorption saturée des divers centres émetteurs qui contribuent à la fluorescence. On montre qu'une corrélation existe entre ce phénomène et les mécanismes de transfert d'excitation et un modèle est proposé pour expliquer les résultats expérimentaux.

Abstract - Under powerful laser excitation, the wide fluorescence band of bismuth germanate shows holes the formation of which is related to a saturated absorption process of various emitting centers which contribute to the overall fluorescence. It is shown that a correlation exists between this phenomenon and the excitation transfer mechanism and a model is proposed to interpret the experimental results.

In a recent paper, we have presented numerous new results concerning the optical properties of bismuth germanate crystals by using laser-excited techniques (ROGEMOND, PEDRINI, MOINE and BOULON, to be published). The absorption was shown to occur in bismuth and germanate centers while both intrinsic and perturbed Bi^{3+} ions together with some impurities contribute to the overall fluorescence. We have reported for the first time formation of deep holes in the wide emission band. This phenomenon was found to be strongly temperature and laser excitation pump power dependent and was attributed to a saturated absorption process of various centers, leading as a result, to a slowing down of the growing of their own emission intensities as the pump energy increases. The saturation effects were studied by exciting more especially in the low energy side of the so-called A excitation peak, and were found to be very strong at room temperature for all the emitting centers while at very low temperature, only the red emission, assigned to impurity centers, was affected by the phenomenon. Thermally-activated energy migration, which was found to occur in this material /1/, probably promotes the saturation process. In order to establish a correlation between energy transfer and saturation effect, new experiments were performed and it is the purpose of this paper to report new results and to discuss possible models explaining the absorption and emission mechanisms occurring at low and room temperature.

Under strong laser excitation in the A peak ($\lambda = 2775 \text{ \AA}$ or 36036 cm^{-1}), a saturation effect on the fluorescence at low temperature is clearly observed as indicated in Fig. 1. For weak laser pulses (0.09 mJ), the emission band has its usual shape and is represented by curve 1. Curves 2, 3, 4, obtained by exciting with laser pulses of higher energy, are represented as if they were obtained under the same low excitation energy (0.09 mJ) which gives curve 1 and by supposing that their intensities vary linearly with this energy. Such a representation permits to compare the profiles of saturated emission bands with that of non-saturated one. One observes a strong variation of the emission band profiles with formation of holes. As already seen in our previous work by exciting with photons of lower energy, the relative decrease of the fluorescence is more pronounced in the lower energy part of the wide fluorescence band. The real variation of the emission intensity versus laser pulse energy is represented in the insert of Fig. 1. Curve 1 shows a linear dependence of the part of the fluorescence taken in the high energy wing of the band, indicating

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that no saturation occurs in this region. On the other hand, the intensity of the fluorescence corresponding to the maximum of the emission band (curve 2) presents first a linear dependence for weak excitation energy less than around $100 \mu\text{J}$, and then a strong slowing down of the increase of the signal which becomes almost constant for energy more than $500 \mu\text{J}$. Fig. 2 shows the temperature dependence of the saturation effects. Curves 2 to 7 were obtained with constant laser excitation energy (0.9 mJ) and compared in the same way than in Fig. 1 to the non-saturated band 1 weakly excited (0.13 mJ) at very low temperature ($T = 4.4 \text{ K}$). A weak increase of the temperature induces a strong increase of saturation. Since for $T < 100 \text{ K}$, no temperature dependence of the integrated fluorescence was detected previously under lamp excitation /2,3/, it therefore exists a phenomenon responsible of the saturation promotion and occurring with a very weak activation energy.

Laser excitation in the C peak region ($\lambda = 2257 \text{ \AA}$ or 44307 cm^{-1}) leads to different results. Saturation effects are not observed at very low temperature but begin to occur really at temperature greater than few tens K (see Fig. 3). The thermal activation energy of the process promoting the saturation is therefore larger than in the previous case.

We have shown in the earlier paper previously mentioned that several emitting centers contribute to the overall fluorescence appearing as a very wide band : intrinsic bismuth centers, perturbed bismuth centers so-called traps, and impurity centers, the most important of which giving rise to a strong red contribution at low temperature. If saturated absorption process occurs for one or some of these centers, formation of holes in the emission band is expected and indeed observed. The emission of traps and impurity centers which are present in weak concentration in the material can be saturated even at low temperature if they are directly excited in their absorption bands. Most of them probably are present in the absorption tail below the band-edge energy but some may also lie at higher energy close to the B and C bands. However the most efficient way to excite these centers is indirect excitation in bismuth and germanium intrinsic absorbing centers, which are in larger concentration, followed by a multistep energy migration process. Then thermally-activated exciton migration can occur explaining the temperature dependence of saturation effects. In order to interpret the experimental results and to describe the fluorescence dynamics, we use the model represented in Fig. 4. The diffusion of excitation is supposed to occur along two channels : exciton band $(\text{GeO}_4)^{4-}$ (peak A) and exciton band $(\text{BiO}_6)^{9-}$ (peaks B and C), with an interaction between them. Because the weak activation energy ΔE_1 of the self-trapped exciton, excitation in the peak A is followed, even at low temperature, by a fast diffusion among GeO_4 tetrahedrons and therefore induces an efficient indirect excitation of traps and impurities leading to saturation effects. The same kind of excitonic process occurs among BiO_6 octahedrons. However owing to saturation effects are much less efficient and begin to occur at higher temperature when bismuth germanate is excited in the C band, the phenomenon involves a weaker excitation transfer probability and a larger thermal absorption energy ΔE_2 of the self-trapped exciton. Saturated absorption process in intrinsic Bi^{3+} centers is much more difficult to obtain since they are present in large concentration in the crystal. Such a phenomenon is not observed in our experiments since no decrease or quenching of the overall fluorescence occurs. Instead, under strong excitation, the intensity of the fluorescence at the center of the band continues to slightly increase with laser power as shown by curve 2 of insert of Fig. 1. These experimental data are interpreted as a result of a balance between linear increase of intrinsic bismuth center emission and strong decrease of fluorescences due to traps and impurities.

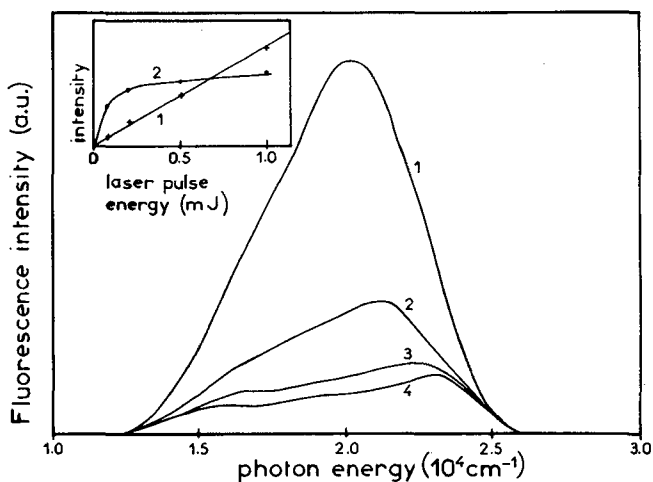


Fig. 1 - Laser intensity dependence of the fluorescence excited in the A excitation peak ($\lambda = 2775 \text{ \AA}$ or 36036 cm^{-1}) at $T = 12.5 \text{ K}$. Laser pulse energy : (1) 0.09 mJ ; (2) 0.225 mJ ; (3) 0.550 mJ ; (4) 1.1 mJ.
 Insert : variation of the fluorescence intensity versus laser pulse energy : (1) in the high energy side of emission band (23810 cm^{-1}) ; (2) at the maximum of the emission band (20000 cm^{-1}).

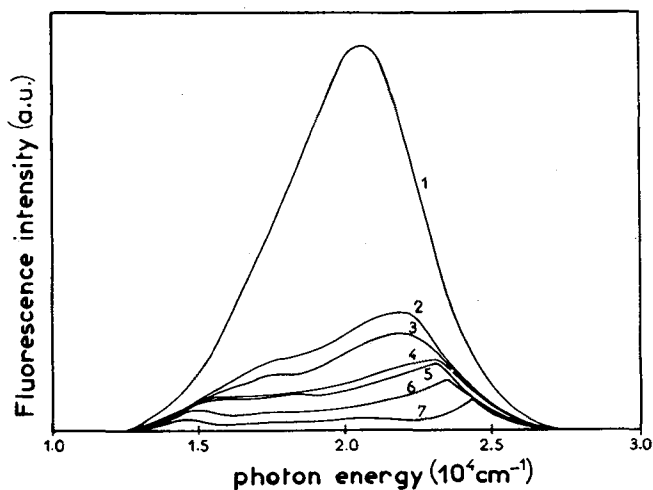


Fig. 2 - Temperature dependence of the fluorescence excited in the A excitation peak ($\lambda = 2775 \text{ \AA}$ or 36036 cm^{-1}) and obtained (1) with weak laser pulse energy (0.13 mJ) at $T = 4.4 \text{ K}$ and with strong laser pulse energy (0.9 mJ) at (2) $T = 4.4 \text{ K}$; (3) $T = 10 \text{ K}$; (4) $T = 12.5 \text{ K}$; (5) $T = 15 \text{ K}$; (6) $T = 20 \text{ K}$; (7) $T = 25 \text{ K}$.

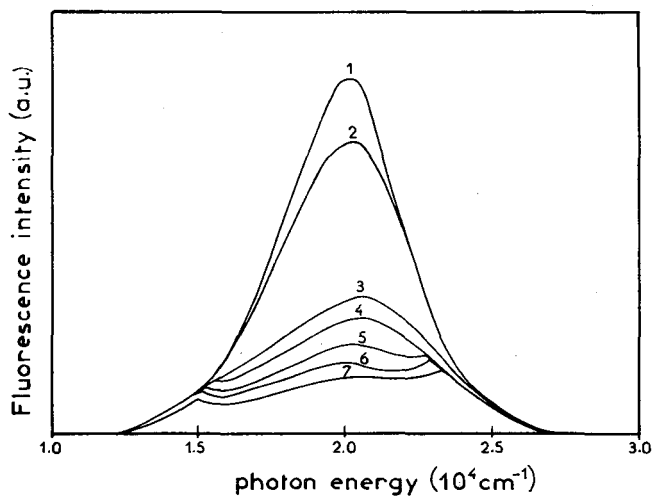


Fig. 3 - Temperature dependence of the fluorescence excited in the C excitation peak ($\lambda = 2257 \text{ \AA}$ or 44307 cm^{-1}) obtained with strong laser pulse energy (0.6 mJ) at : (1) $T = 4.4 \text{ K}$; (2) $T = 20 \text{ K}$; (3) $T = 50 \text{ K}$; (4) $T = 80 \text{ K}$; (5) $T = 120 \text{ K}$; (6) $T = 160 \text{ K}$; (7) $T = 200 \text{ K}$.

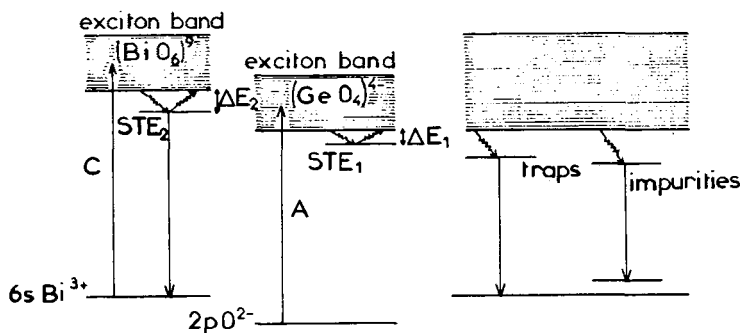


Fig. 4 - Simple model explaining fluorescence dynamics.

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