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THE LUMINESCENCE OF $Bi_{12}GeO_{20}$ DOPED WITH Dy, Ho AND Er

By T. Łukasiewicz, J. Żmija

Institute of Technical Physics, Military Technical Academy, Warsaw*

and J. Mochniak

Institute of Physics, Pedagogical Academy, Opole**

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Excitation spectra and emission spectra of $Bi_{12}GeO_{20}$ doped with erbium, holmium and dysprosium were studied. The measurements were done at 78 K. An analysis of the spectra obtained is presented. The luminescence results from transitions taking place on the isolated rare earth ions whose energy states have been distorted by the crystallic field of their neighbours (discrete characteristic of the spectrum), or from recombinations created by the defects in the crystals where a continuous character of the spectrum is expected in the yellow-red range. The results are consistent with those published concerning the energy structure of rare earth ions and other luminescence materials. The excitation spectra of these materials showed independently on the atomic number, at least for Er, Ho and Dy, the maximum luminescence efficiency when a 3.35 eV electromagnetic wave was used as the excitation agent. This is because for this energy the band to band transfer takes place with the transfer of excitation energy to the activator's ion.

1. Introduction

In recent years there has been an increasing interest in crystals with elasto-optical, electro-optical and photoconducting properties because of their usefulness as phase converters, light modulators or memory elements. This group of crystals includes bismuth–germanium oxide ($Bi_{12}GeO_{20}$) and bismuth–silicon oxide ($Bi_{12}SiO_{20}$). Interesting optical properties observed in these crystals when electric field or electromagnetic wave stimulates them, for example, the relation between the electro-optical effect and natural activity are still controversial [1, 3].

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* Address: Instytut Fizyki Technicznej, Wojskowa Akademia Techniczna, Lazurowa 21, 00-908 Warszawa, Poland.

** Address: Instytut Fizyki, Wyższa Szkoła Pedagogiczna, Oleska 48, 45-052 Opole, Poland.

Studies on the luminescence of these crystals activated with rare earth ions (Nd, Eu, Sm) are aimed toward their applications as lasering materials [4–6]. Practical reasons led others to study various germanium–bismuth types of crystals, e.g. $Bi_4Ge_3O_{12}$, their absorption spectra, reflection spectra and emission and excitation of the luminescence. Various models of the luminescence centres have been proposed for these compounds [7, 8] suggesting that the coupling ions BiO_6^{9-}, GeO_4^{4-} and Bi^{3+} ions have an important function.

The radial transitions between the energy levels of these centres in the field of the lattice of $Bi_4Ge_3O_{12}$ have been proposed [7].

Some of the results of luminescence studies, mainly emission and excitation spectra, for $Bi_{12}GeO_{20}$ crystals activated with rare earths ions, Er^{3+}, Dy^{3+}, Ho^{3+}, are given here.

2. *Experiments and results*

In early experiments it was found that $Bi_{12}GeO_{20}$ pure crystals at liquid nitrogen temperature had a very weak orange–red photoluminescence excited by a 365 nm mercury line. The spectrum of this emission is continuous and its broadened maximum appears around 1.7 eV. The thermoluminescence is also very weak, and the curve of the temperature glow has a maximum at about 133 K which corresponds to the trap level of activation thermal energy, $E_T = 0.12$ eV.

Activated with Dy, Er, and Ho, single crystals of $Bi_{12}GeO_{20}$ were grown from the liquid phase by the Czochralski method. The concentration of the rare earth ions was 10^{-3}%. For ground material Bi_2O_3, GeO_2, and the rare earth oxides were used. The photoluminescence emission spectra were done at 78 K when a 365 nm wave was used as the exciting factor. The apparatus consisted of a double monochromator DMR-4, photomultiplier EMI-9558, and a K-100 recorder. The accuracy of the measurements in the visible range

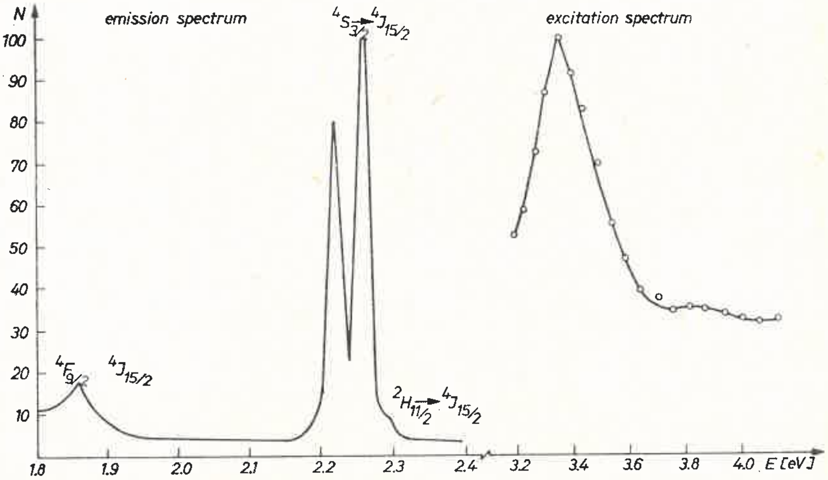

Fig. 1. The photoluminescence spectrum and excitation spectrum, standarized to a common maximum, for $Bi_{12}GeO_{20}$: Er

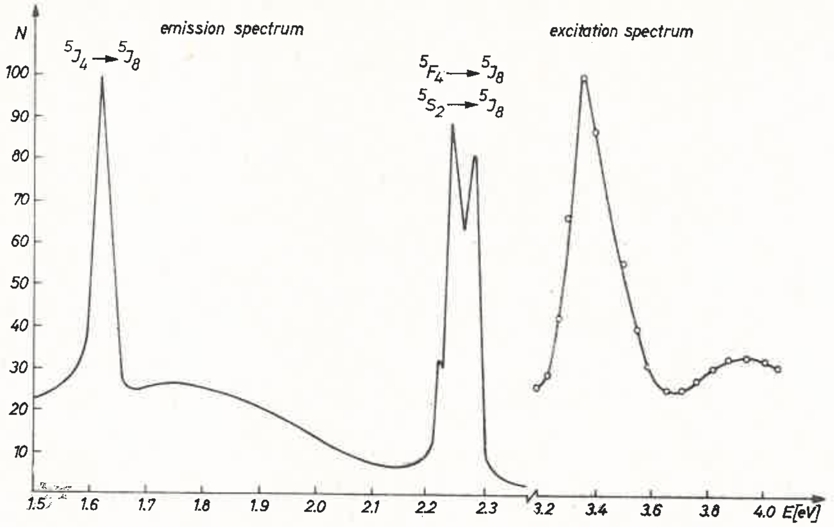

Fig. 2. The photoluminescence and exitation spectrum (standarized) for $Bi_{12}GeO_{20}$: Ho

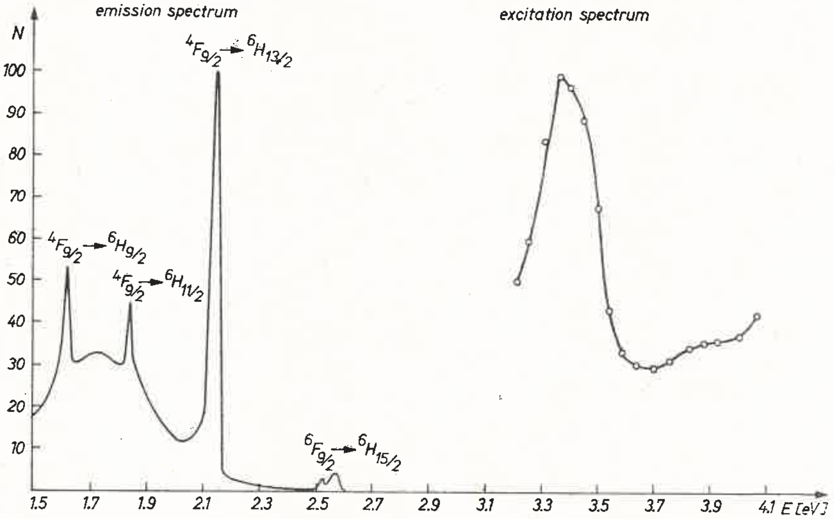

Fig. 3. Photoluminescence and excitation spectrum (standarized) for $Bi_{12}GeO_{20}$: Dy

of the electromagnetic wave was 0.01 eV. The excitation spectra at liquid nitrogen temperature were measured using a xenon burner XBO-450, a quartz-prism monochromator ZMR-3, photomultiplier PEU-79, filters, and a G1B1 recorder. Measurements of the optical transmission at room temperature were done within the range of 350 nm to 2500 nm using a "Specord" UV VIS and NIR spectrometer. Measurements of the optical transmittance of $Bi_{12}GeO_{20}$, Er, Dy and Ho crystals at room temperature have shown that in the range of 500–2500 nm they are practically independent of the type of rare earth ions. The optical absorption spectrum of samples 120 μm thick were used to estimate the energy gap. The value of 3.20 eV is in good agreement with those reported previously [17, 18]. In Figs 1–3 (right side) excitation spectra of the single crystals doped with the rare earth elements are shown. On the left side, the emission spectra are shown.

3. *Discussion*

An intensive photoluminescence at liquid nitrogen temperatures was observed in $Bi_{12}GeO_{20}$ single crystals doped with rare earth elements which form characteristic emission centres in the lattice of that compound. It is known [9, 10] that nearly the whole group of rare earth elements have an identical structure in the outer electron shell made of two 6*s* electrons. The rare earth elements enter into the crystallic lattice of various compounds as trivalent ions (eight $5s^2p^6$ electrons in the outer shell). The results from studies of a similar material, $Bi_4Ge_3O_{12}$, activated by the rare earth elements, Nd, Er and Yb show that the impurity atoms replace bismuth [11] in the crystal lattice. The high similarity of both

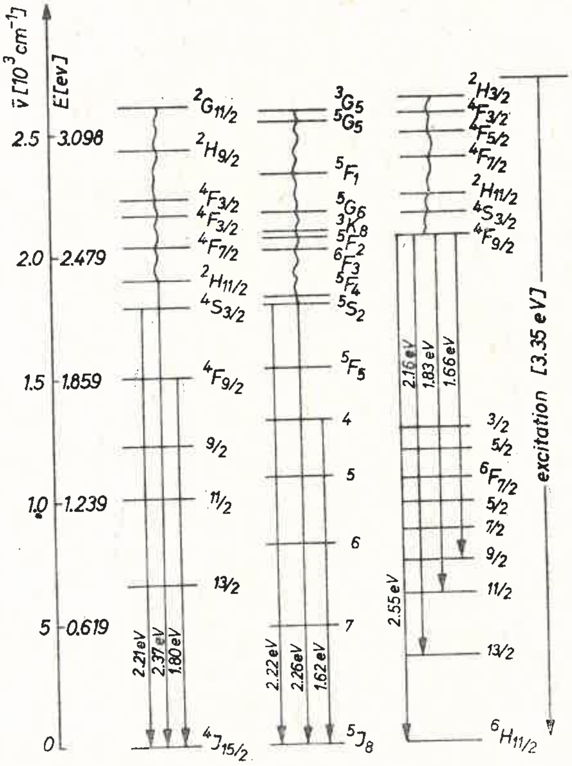

Fig. 4. Structure of energy levels in the trivalent rare earth ions (Er^{3+}, Ho^{3+} and Dy^{3+}) [9, 10]

compounds permits one to assume that in $Bi_{12}GeO_{20}$ single crystals the situation is the same. Despite a very similar configuration of the outer electrons, the trivalent rare earth ions show very distinct differences in the structure of the $4f$ shell which is screened by the $5s$ and $5p$ shell. The electric dipole transitions in rare earth ions obey the selection rule of Laporte which results from the parity of the wave function and from the conservation of the angular momentum. One can assume that the lattice field influencing the configuration of $4f$ electrons in the rare earth ions adds to the existing configurations the excited states having opposite parities. The electric dipole radiator can appear, only between the states of different parity.

In the emission spectra of compounds containing rare earth elements one can distinguish sharp and narrow bands or lines and relatively wide bands.

Lines and narrow emission bands, particularly typical at low temperatures, characterize the transitions between the terms in the $4f$ shell, while the wide bands manifest the creation of complexes of these ions with ions having a crystalline lattice.

Fig. 4 shows the structure of energy levels of the undisturbed trivalent Er^{3+}, Ho^{3+} and Dy^{3+} ions [9, 10]. In Fig. 4 are marked the radial transitions observed in the photoluminescence spectra. The characteristic feature of the excitation spectra is their high luminescence efficiency which is independent of the type of impurity and corresponds to 3.35 eV of the exciting electromagnetic radiation. Similar forms of excitation spectra, independent of the type of impurity, suggest that the excitation of rare earth ions in $Bi_{12}GeO_{20}$ takes place by way of transfer of the excitation energy from the basic lattice through one of the sub-lattices or BiO_6 or GeO_4 onto the activator's ion with the participation of phonons. The value of the excitation quantum is comparable with the value of the energy gap in $Bi_{12}GeO_{20}$ (3.40 eV in 4.2 K [18]), and the rare earth ions create in the forbidden area the energy levels responsible for the luminescence of these crystals.

The photoluminescence spectrum of $Bi_{12}GeO_{20}$, that is Er single crystals (Fig. 1) is composed of the two main groups of emission lines which clearly dominate the background of the continuous spectrum of the non-doped single crystals of $Bi_{12}GeO_{20}$. There is a very intensive group of lines in the energy range of 2.2–2.3 eV. For these lines in Er^{3+} ions one can assign the transitions between the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ levels. In the red region one can see the transition from the level: $^4F_{9/2} \rightarrow {}^4I_{15/2}$, where the quantum energy has a value in the range of 1.84 to 1.86 eV.

In the emission spectrum of crystals of $Bi_{12}GeO_{20}$, Ho (Fig. 2) there are also two groups of emission lines originating from the Ho^{3+} ions observed on the background of the continuous spectrum of the photoluminescence of $Bi_{12}GeO_{20}$. One is located in the range of 2.22–2.28 eV. In accordance with the structure of the energy levels of Ho^{3+} one can assign to these lines the transition from the $^5F_4$ and $^5S_2$ levels to the $^5I_8$ level. The second group of lines corresponds to the $^5I_4 \rightarrow {}^5I_8$ transitions with a quantum energy of approximately 1.62 eV. The emission spectrum curve for the $Bi_{12}GeO_{20}$, Dy (Fig. 3) has four characteristic groups of emission lines corresponding to transitions from the $^4F_{9/2}$ level the $^6H_{15/2}$, $^6H_{13/2}$, $^6H_{11/2}$, $^6H_{9/2}$ levels with quantum energies of 2.55, 2.16, 1.83 and 1.66 eV, respectively. These lines were also observed on the background of the continuous spectrum from the undoped single crystals of $Bi_{12}GeO_{20}$.

4. Conclusions

From the studies of certain properties associated with the luminescence of $Bi_{12}GeO_{20}$ single crystals activated with Er, Ho, and Dy, one can conclude that the luminescence in these compounds takes place as a result of radial transitions in isolated rare earth ions which energy states were distorted by the field of the lattice and which are responsible for the narrow-band character of the spectrum. Secondly, they may occur as a result of the recombination transition in the luminescence centres formed by structural defects in $Bi_{12}GeO_{20}$. These defects may be responsible for the continuous character of the spectrum in the yellow–red region.

The location of the spectral lines and narrow emission bands are in fairly good agreement with the results of other works concerning the energy structure of rare earth ions in other luminescent materials [12–16]. The symmetry of the crystallic field of the base, by deforming the energy structure of the rare earth ions, is observed as a line shift or as a broadening of the energy levels. The radial transitions, however, take place in the $4f \rightarrow 4f$ shell. From the short-wave side, the luminescence energy of these crystals as well as for the ions Er^{3+}, Ho^{3+} and Dy^{3+} is limited by the value of the energy gap of the oxide which at room temperature is 3.20 to 3.16 eV.

The excitation spectra of $Bi_{12}GeO_{20}$ activated with rare earth elements show independently the atomic number of the admixture, at least for Er, Ho and Dy the highest luminescence efficiency when excited by the electromagnetic wave of 3.35 eV.

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