X-RAY LUMINESCENCE OF RARE-EARTH-ELEMENT IONS IN $\mathrm{Y_3Al_5O_{12}}$ CRYSTALS

PHYSICS

1969

SovietRxiv

Fig. 1. X-ray luminescence spectrum of YAG—Nd (0.16 wt.%) at 300°K

Figure 1: Fig. 1. X-ray luminescence spectrum of YAG—Nd (0.16 wt.%) at 300°K

Abstract

Full Text

UDC 535.37

PHYSICS

Yu. K. VORON' KO, B. I. DENKER, V. V. OSIKO,
Academician A. M. PROKHOROV, M. I. TIMOSHECHKIN

X-RAY LUMINESCENCE OF RARE-EARTH-ELEMENT IONS IN $Y_3Al_5O_{12}$ CRYSTALS

Crystals of $Y_3Al_5O_{12}$ (YAG) with an admixture of trivalent rare-earth ions (TR^{3+}) attract attention in connection with their use as active media in optical quantum generators (OQG) ([1,2]). In all previous works on the study of the spectroscopic and lasing properties of YAG, excitation of TR^{3+} was carried out optically, directly in the absorption bands corresponding to $f-f$ transitions of the rare-earth ions. In this case, all excitation and relaxation processes were localized in the optical centers without the participation of excitations of the host crystal itself. It is essential that the light sources usually used have low radiation intensity in the ultraviolet region of the spectrum, and the high-lying levels of TR^{3+} are therefore not excited. Certain features of x-ray excitation of TR^{3+} in fluorite-type crystals, as compared with optical excitation, were pointed out in Makovsky' s work ([3]). In Shand' s work ([4]), a high intensity of luminescence of rare-earth ions was noted at their very small concentrations in LaF_3 and $LiYF_4$.

Fig. 1. X-ray luminescence spectrum of YAG—Nd (0.16 wt.%) at 300°K

In the present work we investigate the emission of TR^{3+} in YAG crystals under steady excitation by x rays. A feature of this method of excitation is the participation of elementary excitations of the crystal (excitons, electrons, holes) in the excitation of TR^{3+}.

Crystals for the Studies and Experimental Procedure

YAG—TR^{3+} crystals were grown from the melt by the Czochralski method ([5,6]). TR^{3+} impurities were introduced at concentrations up to 0.5%. Samples with a polished end surface were prepared from the crystals. To excite the crystals, an X-ray tube (Mo anticathode) was used, with the power supply from a D-9-S

Fig. 2. Level scheme of a YAG—Nd crystal (0.16 wt.%)

Figure 2: Fig. 2. Level scheme of a YAG—Nd crystal (0.16 wt.%)

(Geigerflex) X-ray fluorescence analysis unit. The X-ray luminescence spectra were studied with an MDR-2 grating monochromator with a grating of 600 lines/mm and a dispersion of 40 Å/mm; at its exit, depending on the spectral region under study, either an FEU-22 photomultiplier cooled with liquid nitrogen or an FEU-18 was placed. The signal from the photomultiplier was fed to the DC amplifier of an EPS-157 unit and recorded with an EPP-09 M electronic potentiometer. To observe luminescence in the ultraviolet region, UFS-2 and SZS-8 filters were used, with the instrument grating operating in the second order. Absorption spectra were recorded on an SF-8 spectrophotometer.

Experimental Results

We observed intense X-ray luminescence of almost all rare-earth ions in YAG (Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Tu^{3+}, Yb^{3+}). As a rule, groups of lines in the X-ray luminescence spectra correspond to those observed under photoexcitation. However, in a number of cases (Nd^{3+}, Tu^{3+}) luminescence occurs from levels located in the region 35 000—40 000 cm^{-1}, which is absent under photoexcitation. This shows that, under the action of X-rays, excitation occurs up to the highest levels of the f-shell of TR^{3+}. Figures 1 and 2 give, as an example, the X-ray luminescence spectrum at 300° K and the level scheme of the YAG—Nd crystal (0.16 wt.%). As can be seen from the figures, along with the "usual" transitions ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$, transitions are observed from one of the levels S (7), located 37 500 cm^{-1} above the ground level. This means, first, that in YAG—Nd^{3+} crystals the level S is intensely populated and, second, that the probability of nonradiative transitions from this level is small. The latter is explained in part by the fact that the gap between level S and the next lower level ($R \sim 34\,000$ cm^{-1}) is large and amounts to 3500 cm^{-1}.

Fig. 2. Level scheme of a YAG—Nd crystal (0.16 wt.%)

One of the results of the present work is the possibility of determining small concentrations of TR^{3+} impurities in YAG crystals. Study of the X-ray luminescence spectra showed that the most favorable ions for carrying out the analysis are Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^3 and Yb^{3+}. These ions possess strong X-ray luminescence in the investigated spectral region (330—1000 mμ), and for each of these rare earths bands can be found that do not overlap with the X-ray luminescence bands of other ions.

To carry out experiments on determining the concentrations of rare-earth ions in YAG, YAG crystals were grown with a concentration

0.05% (Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Yb^{3+}) and 0.01 and 0.05% (Nd^{3+}, Dy^{3+}). A comparison of the luminescence of YAG—Dy^{3+} and YAG—Nd^{3+} crystals with different concentrations showed that the intensity of X-ray luminescence is proportional to the concentration of TR^{3+} ions. Estimates of the limiting concentration values that can be determined by the method under consideration were obtained by attenuating the X-ray luminescence of samples with the standard concentration (0.05%) by means of filters. The limiting impurity concentrations obtained by calculation are given in Table 1. In practice, however, such a limit for determining TR^{3+} concentrations in YAG is difficult to achieve. The most substantial obstacle is the intrinsic luminescence of the YAG lattice, which is especially strong in pure crystals.

Table 1

YAG–TR^{3+}	ν, cm^{-1}	Transition	Calculated sensitivity limit, %	Example of determination, %
Nd^{3+}	24 750	$S \to {}^4F_{5/2}\,{}^2H_{9/2}$	$5 \cdot 10^{-6}$	–
Nd^{3+}	11 350	${}^4F_{3/2} \to {}^4I_{9/2}$	$7 \cdot 10^{-5}$	$7 \cdot 10^{-5}$
Sm^{3+}	16 200	${}^4G_{5/2} \to {}^2H_{7/2}$	$2 \cdot 10^{-6}$	–
Eu^{3+}	16 700	${}^5D_0 \to {}^7F_0, {}^7F_1$	$2 \cdot 10^{-5}$	$1 \cdot 10^{-4}$
Eu^{3+}	14 100	${}^5D_0 \to {}^7F_4$	$4 \cdot 10^{-7}$	–
Gd^{3+}	31 800	${}^2P_{7/2} \to {}^8S$	$1 \cdot 10^{-6}$	–
Tb^{3+}	23 800	${}^5D_3 \to {}^7F_5$	$1 \cdot 10^{-5}$	–
Dy^{3+}	21 050	${}^4F_{9/2} \to {}^6H_{15/2}$	$1 \cdot 10^{-6}$	$1.5 \cdot 10^{-4}$
Yb^{3+}	10 300	${}^2F_{5/2} \to {}^2F_{7/2}$	$1 \cdot 10^{-5}$	$1 \cdot 10^{-5}$

The band of intrinsic luminescence is located in the ultraviolet region of the spectrum. Under limiting conditions (maximum voltage on the FEU, high tube power, wide monochromator slits), the "tail" of the band extends as far as 450 mμ, which at low TR^{3+} concentrations somewhat complicates the analysis of Dy^{3+}, Gd^{3+}, and Tb^{3+}. The intrinsic luminescence does not, however, hinder the determination of Nd^{3+} and Yb^{3+}. In a number of samples with low impurity concentration, luminescence of Cr^{3+} was observed (Fig. 1), which in some cases may interfere with analysis for the content of Eu^{3+} ions. In the last column of Table 1, as an example, are given the results of determining the concentrations of Nd^{3+}, Eu^{3+}, Dy^{3+}, and Yb^{3+} in arbitrarily selected YAG crystals.

P. N. Lebedev Physical Institute Academy of Sciences of the USSR Moscow

Received 24 VII 1969

CITED LITERATURE

1. A. A. Kaminskii, V. V. Osiko, *Neorg. materialy*, **1**, 2049 (1965).
2. A. A. Kaminskii, V. V. Osiko, ibid., **3**, 417 (1967).
3. J. Makovsky, W. Low, S. Yatsiv, *Phys. Lett.*, **2**, 186 (1962).
4. W. A. Shand, *J. Materials Sci.*, **3**, 344 (1968).
5. B. Cockayne, *J. Am. Ceram. Soc.*, **49**, 204 (1966).
6. W. Bardsley, B. Cockayne, *Crystal Growth*, Oxford, 1967.
7. G. H. Dieke, H. M. Crosswhite, *Appl. Optics*, **2**, 675 (1963).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.