

Investigation of the spatial distributions of Fe^{3+} ions in the TGS crystals using luminescence and absorption*

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In the paper the results of examinations of luminescence and absorption attributed to Fe^{3+} ion complexes in TGS crystals are reported. The luminescence method may be exploited to examine the heterogeneous distribution of doping in TGS crystals. In the luminescence excitation spectrum the presence of spectrum of a complex structure has been stated as well as the existence of a narrow band with maximum at 385 nm connected with the transition of d-d type to the ${}^4E_g({}^4D)$.

1. Introduction

In order to modify the properties of the TGS crystals, the latter are activated by transition metal ions [1-4], in particular by Fe^{3+} ions [5, 6]. These ions may penetrate into crystal as the material imperfections. The Fe^{3+} ions create an octahedric complex with two glycine molecules G II and G III and with two SO_4^{2-} groups. Four oxygen and two nitrogen ions pay here the part of ligands. In addition to properties of modifying the dielectric permittivity of the crystal the complexes of Fe^{3+} ions have also their characteristic optical properties, among others absorption bands connected with the transitions of d-d type. These bands are of very low intensity and occur mainly within the visible light range. Between the self-absorption edge of TGS crystal and the visible range there exists a very intensive charge-transition band with maximum at 280 nm. For high concentration of Fe^{3+} ions the long-wavelength wing of this band may (partly) overlap the visible region. The luminescence of Fe^{3+} ion complexes occurs at excitation in the charge-transition bands as well as in the bands of d-d transitions [8, 9].

The aim of this work is to examine the luminescence and absorption properties of the TGS crystals. To our best knowledge no works devoted to luminescence of Fe^{3+} as well as to other activators in this crystals have been carried out so far.

2. The measurements method

Plates of TGS crystals of different thicknesses were cut off in the XY plane. The TGS crystal under test was grown from the ferroelectric phase of the water solution of 0.1% TGS with the addition of 0.5% $\text{Fe}_2(\text{SO}_4)_3$ by the method of isothermal evaporation of the solution.

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The transmittivity of the plates was measured within the range from 200 to 700 nm with the Specord UV VIS spectrophotometer of Zeiss make provided with additional diaphragms to restrict the area of measurement. The spectral distributions of luminescence were recorded in a setup (fig. 1a) composed of a UM-2 monochromator, M12FC51

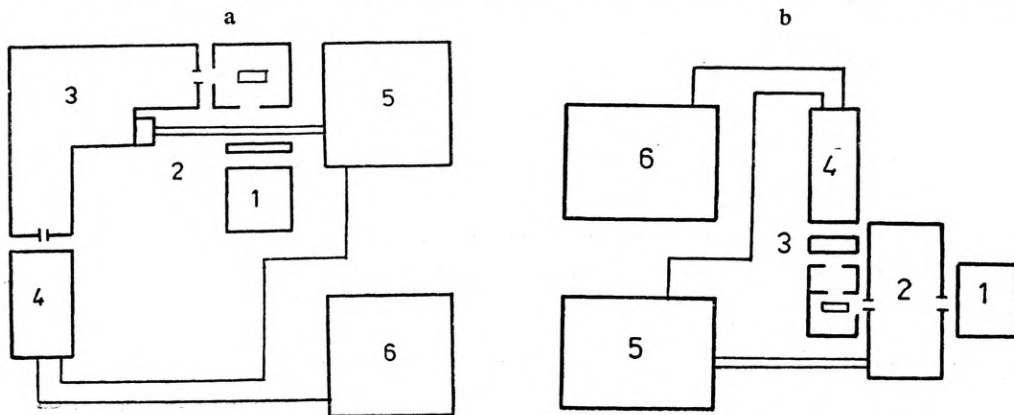


Fig. 1. a. Block scheme of the setup used to measure the spectral distribution of luminescence:

1 – HBO-50 lamp, 2 – UG1 filter, 3 – UM-2 monochromator, 4 – M12FC51 photomultiplier, 5 – recorder, 6 – ZWN-2.5 amplifier.

b. Block scheme of the setup used to the measurement of excitation spectra:

1 – deuterium lamp, 2 – SPM2 monochromator, 3 – filters, 4 – M12FC51 photomultiplier, 5 – G1B1 recorder, 6 – ZWN-41 amplifier

photomultiplier and a G1B1 recorder. The luminescence was excited via a UG1 filter by irradiating with the HBO-50 lamp. The TGS luminescence spectra were calculated with respect to the standard luminescence spectrum of quinone sulphate. On the other hand, the luminescence excitation spectra were recorded for excitation realized with the deuter lamp via the SPM2 monochromator, the latter being equipped with a quartz prism (fig. 1b). The type of photomultiplier used was the same as that applied to examination of luminescence spectrum distribution. The spectra were recorded on a B1G1 recorder. To transilluminate the plate with UV-radiation a xenon lamp with exchangeable filter was exploited. The plate of TGS crystal was placed in front of the filter but close to it. The exposure time for the film was selected with a photographic camera shutter. A HBO-200 and XB101 lamps with filters of UG1 type were used, in turn, both to observe and take pictures of spatial distributions of luminescence in the TGS crystal plates. An interference filter IF-475 was put on the camera lens.

3. Results of measurements

The effect of transillumination of the whole TGS crystal plate at the presence of the UG1 filter ($\lambda_{\max} = 365$ nm) is shown in fig. 2. The plate thickness was 3.5 mm. The darker part of the photography of this plate corresponds to greater concentration of the Fe^{3+} ions. For the regions of extreme shining intensity the measurements of transmittivity were made. The results were presented in fig. 3. The curve 1 corresponds to lens concentration of Fe^{3+} ions (bright part of the plate). The curve 2 corresponds to high concentration of Fe^{3+} ions

(darker part of the plate). A weak absorption band observed in the curve 2 is attributed to the transition of the ${}^4\text{E}_g({}^4\text{G})$ and $\text{A}_g({}^4\text{G})$ [5, 6].

In figure 4 the same plate of TGS crystal is shown as photographed in luminescence light through an interference filter ($\lambda = 475 \text{ nm}$). Greater numbers of Fe^{3+} ions correspond to the darker places. The luminescence intensity depends upon the pyramid of crystal growth and depends on the concentration of Fe^{3+} ions [7]. The spectral distribution of luminescence is presented in fig. 5. The curve 1 refers to the part of the plate of small

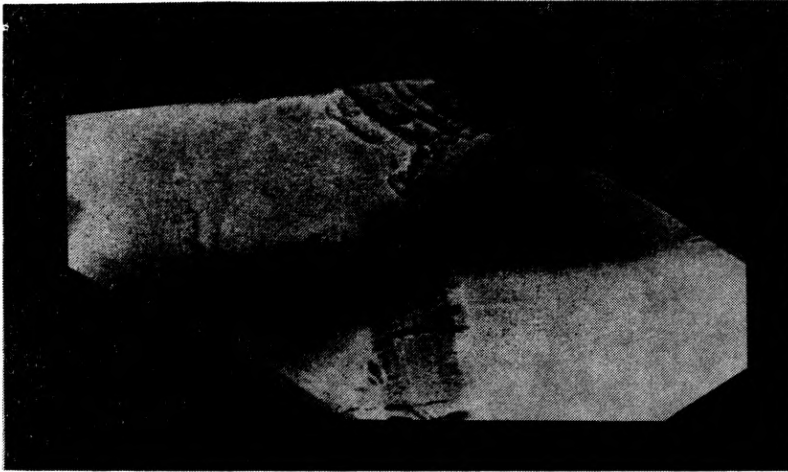


Fig. 2. A photograph of the transilluminated TGS crystal plate through the UG1 filter

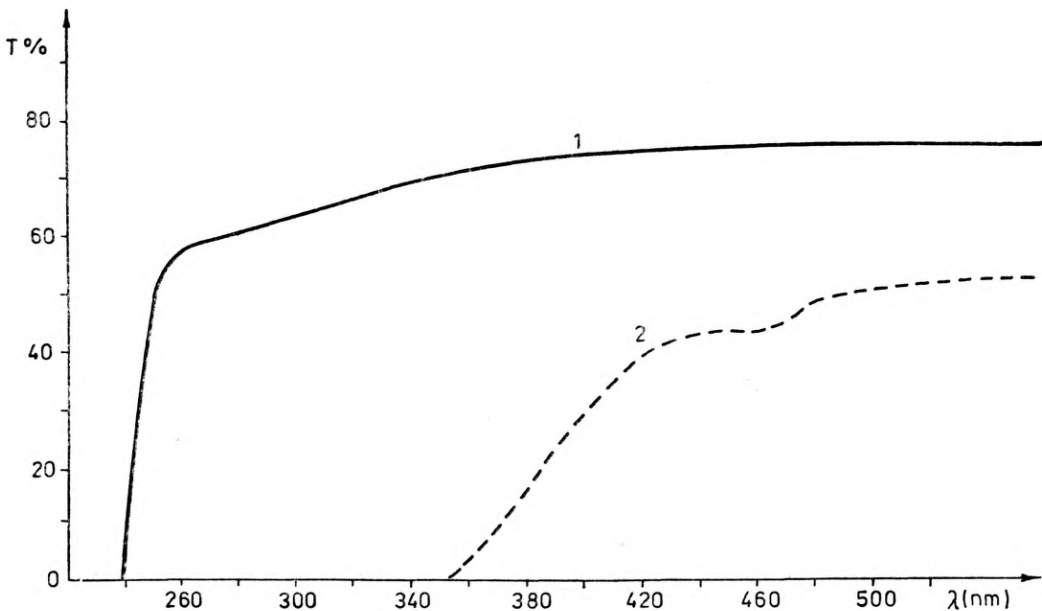


Fig. 3. Dependence of the transmission in the plate of TGS crystal upon the light wavelength:

1 - bright regions, 2 - dark regions

concentration of Fe^{3+} ions, while the curve 2 represents that part of the plate where high concentration of these ions occurs. An example of the luminescence excitation spectrum which was recorded through the VG9 filter within the interval 500–600 nm in the bright part of the plate is shown in fig. 6. The luminescence was excited with a deuterium lamp through the SPM-2 monochromator at constant slit width. The curve presented is created for fixed spectral width. On this curve a group of bands positioned side by side in the region of spectral absorption may be seen, accompanied by a very strong narrow band with maximum at 385 nm.

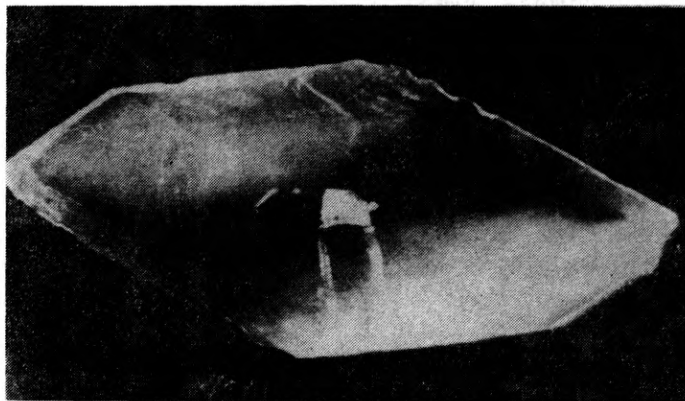


Fig. 4. Photography presenting a luminescence intensity distribution in the TGS crystal plate

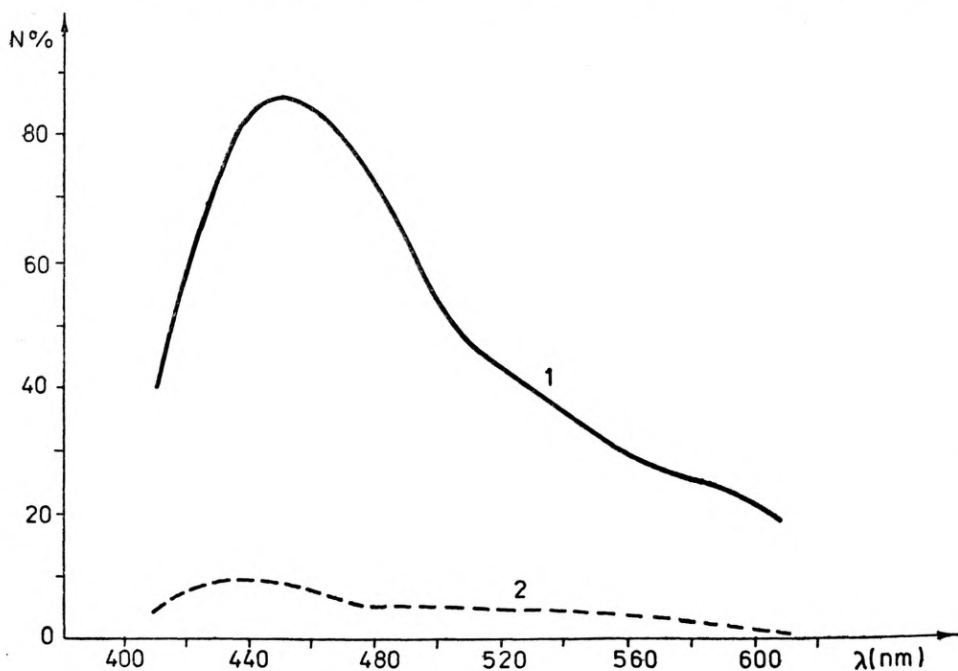


Fig. 5. Spectral distribution of luminescence in the TGS plate:

1 — region of low concentration of Fe^{3+} ions, 2 — region of high concentration of Fe^{3+} ions

In figure 7 the curves of the excitation spectra of luminescence measured in the region of its main band between 400 and 500 nm are presented. The curves 1 and 2 correspond to the measurements at the regions of small and large concentration of Fe^{3+} ions, respectively. Within the region of charge transition a complex structure of these band may be observed on these curves.

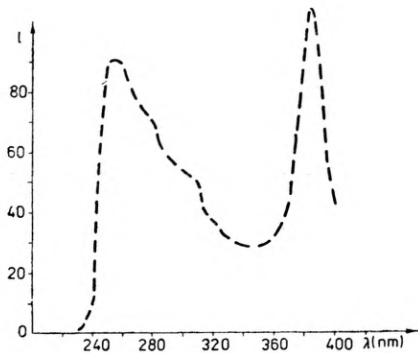


Fig. 6. The excitation spectrum of luminescence measured through the VG9 filter in the TGS plate at the region of low concentration of Fe^{3+} ions. (Intensity of luminescence in relative units)

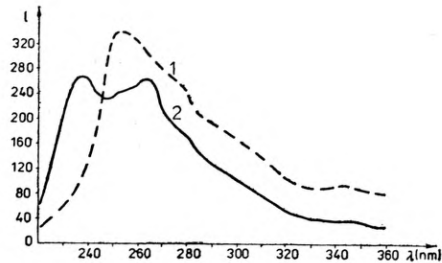


Fig. 7. The excitation spectrum of luminescence measured in the interval 400–500 nm:

1 — region of low concentration of Fe^{3+} ions, 2 — region of high concentration of Fe^{3+} ions. (Intensity of luminescence in relative units)

4. Discussion of results

Narrow luminescence band with maximum at 385 nm should be attributed to the ${}^4E_g({}^4D)$ level belonging to d-d transitions. This would be the second band of this group. The band ${}^4E_g({}^4G)$ is observed for $\lambda = 460$ nm on the transmission curve (fig. 3). This fact would allow to determine the electric field parameters for Fe^{3+} complexes in TGS crystal. The bands of charge transitions in the luminescence excitation spectrum indicate that a more complex model should be assumed for interpretation.

An essential point in this work is that it shows an easy way of examination of the non-homogeneous spatial doping distribution in the TGS crystals exhibiting both absorption and luminescence bands.

References

- [1] STANKOWSKI J., *Acta Phys. Polon.* **33** (1968), 387–400.
- [2] STANKOWSKI J., *Fizyka Dielektryków i Radiospektroskopia V* (1972), 295–316.
- [3] STANKOWSKI J., WAPLAK S., *Fizyka Dielektryków i Radiospektroskopia V* (1972), 317–321.
- [4] WINDSCH W., VÖLKELE G., *Ferroelectric* **17** (1978), 187–195, 491–499.
- [5] POLOVINKO J., STANKOWSKA J., STANKOWSKI J., *Ferroelectrics* **25** (1980), 523–525.
- [6] STANKOWSKA J., POLOVINKO J., ROMANYUK N., *Acta Phys. Polon.* **A55** (1979), 803–809.

- [7] MRÓZ J., GĘBALA S., (in preparation for publication).
[8] HUMMEL F. A., SARVER J., *J. of the Electrochem. Soc.* **111**, (1964), 252–253.
[9] GĘBALA S., *XXVI Polish Physical Society Meeting*, 1979. Vol. I, p. 47 (in Polish).

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Использование люминесценции и абсорбции для исследований пространственных распределений ионов Fe^{3+} в кристаллах TGS

Представлены результаты люминесценции и абсорбции комплексов ионов Fe^{3+} в кристаллах TGS. Люминесцентный метод может использоваться для исследования неоднородного распределения примесей в кристаллах TGS. В спектре люминесцентного возбуждения выявлено в области переноса заряда наличие сложной структуры спектра и узкой полосы с максимумом при 385 нм, связанной с переходом типа d-d на уровне ${}^4E_g({}^4D)$.