

Luminescence as an indicator of spatial distribution of Mn^{2+} ions in TGS crystals

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In this paper photos of spatial distribution of luminescence in TGS crystal doped with manganese are presented. The observations were carried out in the XZ-plane. A strongly polarized luminescence of blue colour in the growth pyramid (001) as well as a green luminescence in the (203) pyramid without any oriented centres were detected. Spectral distributions and luminescence excitation spectra are shown. In these spectra some differentiation in the charge transition spectral region and an appearance of bands connected with d-d transitions are stated.

1. Introduction

An introduction of transition metal ions to the crystal lattice causes some deformation changing physical properties of the latter. These admixtures perturb the wide-range interaction, impede the polarization process and influence both the size and quantity of domains [1, 2]. Examinations of coordination of complexes Cu^{2+} , Cr^{3+} , Mn^{2+} , made by Stankowski and co-workers by using the methods of electron microscopy, indicated some differentiation among the doped octahedric ion complexes with glycine ions [3-6].

The following specific optical properties are connected with ion complexes of $3d^n$ electron configuration: absorption bands of d-d type, charge transition bands and luminescence. While the d-d bands are very weak and positioned within the visual band range, charge transition bands are intense being located in far ultraviolet. The long-wave wing of this band reaches usually the visual range which makes the discovery of d-d band more difficult. The changes in both coordination and its symmetry result in changes of absorption and luminescence of the crystal. The absorption properties of the doped ion complexes in TGS crystals were hardly investigated because of high measuring difficulties. No works concerning the doped Mn^{2+} ion luminescence in TGS crys-

tals are known to the authors. The earlier examinations of Fe^{3+} ion luminescence in TGS crystals carried out by the authors gave interesting results [7-8]. For these reasons the continuation of these investigations for other admixtures, like Mn^{2+} ions, seemed to be reasonable.

2. Method of examinations

The TGS crystals were grown from the water solution containing 1% $\text{Mn}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$. The crystal growth was carried out in the ferroelectric phase at 316 K temperature by using an isothermic method of solution evaporation. The samples were cut out perpendicularly to the ferroelectric axis *b* in the XZ-plane. The samples were ground down to the thickness of 2-3 mm. The following method of examination was used: The spatial distribution of luminescence in TGS plates was photographed while exciting the lattices with a HBO-200 lamp via an UG1 filter ($\lambda_{\text{max}} = 365 \text{ nm}$). A 450 edge filter and a polaroid M from a Zeiss set were deposited on the photo camera objective. This allowed to take pictures of luminescence above 450 nm. The polaroid was positioned visually to achieve the maximum and minimum of the luminescence intensity in the (001) growth pyramid. The direction of electric vector was read out from the angular scale coupled with the polaroid. The measurements of spectral distributions and luminescence excitation spectra were carried out in a setup presented in the paper [7]. All the measurements were performed at the room temperature.

The estimation of Mn content in a particular growth cones was made at the Institute of Inorganic Chemistry and the Rare Earth Metallurgy, Technical University of Wrocław, Poland, with the help of the absorption method of atomic spectroscopy, using a graphite cuvette.

3. Results of measurements

The spatial distribution of luminescence in a TGS:Mn crystal plate for different positions of the electric vector is presented in photos (Figs. 1a,b). The luminescence observed in the (001) growth pyramid is of blue colour, being simultaneously highly polarized in the XZ-plane. The luminescence in (203) pyramid is green and shows no changes while rotating the polaroid. The traces of growing edges in

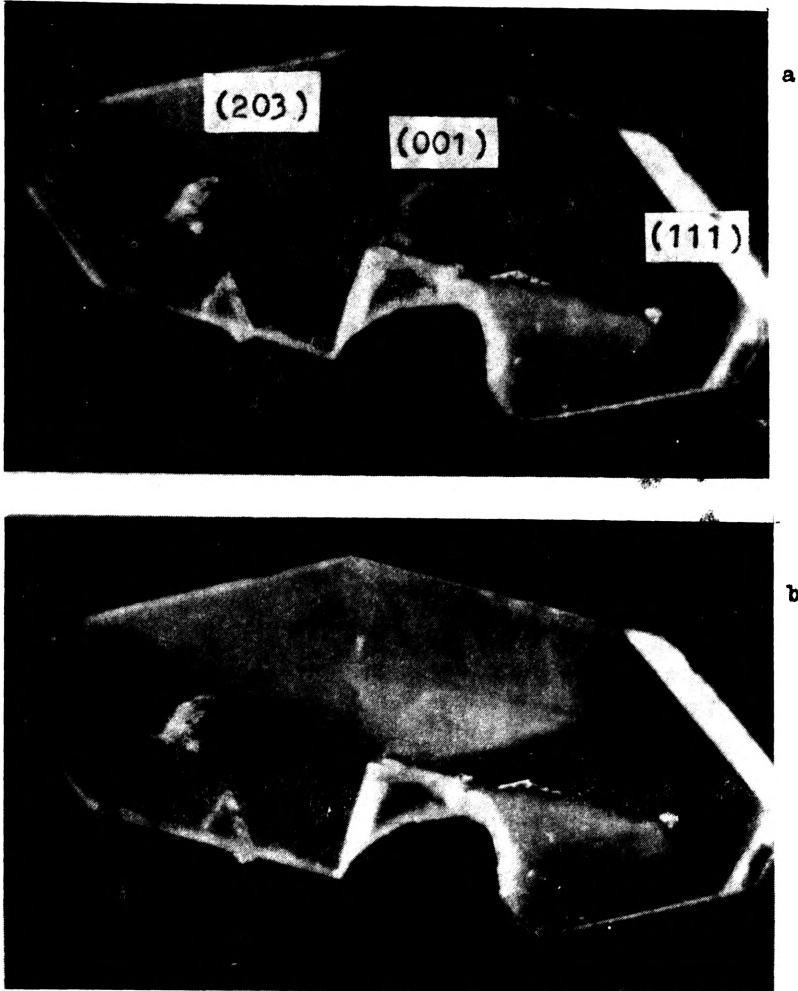


Fig. 1. Photography of the spatial distribution of luminescence in the TGS crystal plate polarized in the XZ-plane. a. $\vec{E} \parallel X$, b. $\vec{E} \parallel Z$

grown crystals may be observed in the spatial distribution of luminescence in the TGS crystal plate.

The content of Mn in particular cones of growth was determined by the ASA method. The following results were obtained: in the (203) growth pyramid - $0.85 \cdot 10^{-5}$ per cent by weight, in the (001) growth pyramid - $7.0 \cdot 10^{-5}$ per cent by weight, in (111) growth pyramid - $22.3 \cdot 10^{-5}$ per cent by weight.

In the Figure 2 the spectral luminescence distributions measured in different growth pyramids are shown. The spectral distributions are corrected to meet the photomultiplier sensitivity. From the curve 2

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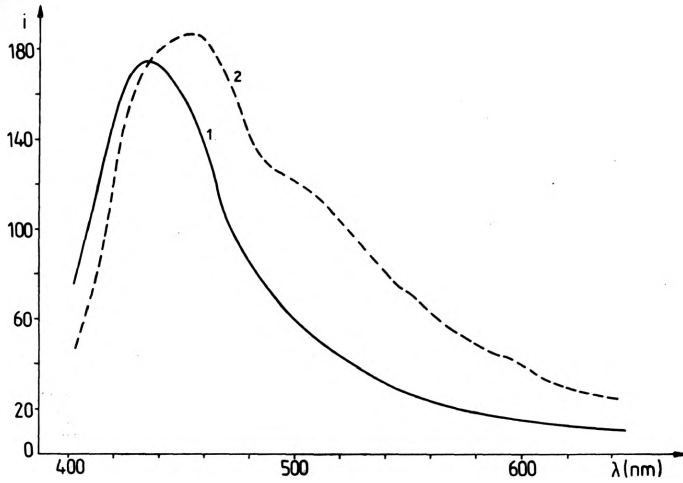


Fig. 2. The spectral distribution luminescence measured in the region of (001) growth pyramid - 1, and (203) growth pyramid - 2.
 $\lambda = 365 \text{ nm}$

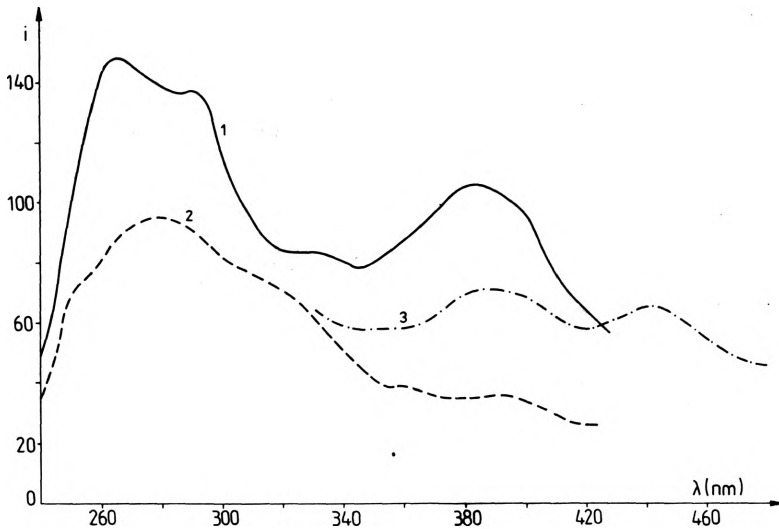


Fig. 3. The spectrum luminescence excitation measured via the VG-9 filter (λ - for 490 to 570 nm) in the (001) growth pyramid - 1, and (203) growth pyramid - 2, and measured via OG5 filter ($\lambda > 580 \text{ nm}$) in the (001) growth pyramid - 3

it may be noted that the luminescence in (203) pyramid has a second band with a maximum close to 500 nm.

In the Figure 3 luminescence excitation spectra are shown for (001) and (203) growth pyramids. It may be assumed that, similarly as it is the case for Mn^{2+} complexes in other crystals [9, 10], the excitation spectra located below 300 nm are connected with the charge transition

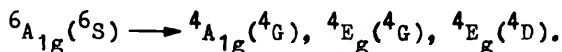
mechanism, while those positioned above 300 nm are attributed to d-d transitions. The excitation spectra show not only some differentiation between the growth pyramids but also indicate a complex structure within the same pyramids. The curve 3 shows the luminescence excitation bands measured via OG5 filter ($\lambda > 580$ nm) for the (001) growth pyramid. In the excitation spectrum there are bands connected with d-d transition close to 330 nm, 380-400 nm and 420-460 nm.

4. Discussion of results

The shown spatial variety of luminescence effects, so far as both colour and polarization are concerned, presents a convenient material to observation of structure differentiation in Mn^{2+} activated TGS crystals. This method being nondestructive is worth noticing.

The number of problems which are connected directly or indirectly with this work is considerable. Among others the differentiation of charge transition spectrum and d-d bands (Fig. 3) should be noticed. We will consider the latter because it seems that they have been for the first time presented for the Mn^{2+} complexes in TGS crystals.

These bands are observed for very low concentration of Mn^{2+} ions and may be detected by the luminescence method. Let us assume that Mn^{2+} creates complexes of cubic symmetry in TGS crystals in accordance with the results of the electron resonance measurements reported in [6]. The Tanabe-Sugano-diagram, i.e., the dependence of energy bands on the crystal field force Dq , is applied to the description of d-d transitions similarly as to the octahedric complexes. The absorption bands are connected with the transitions from the lowest term ${}^6A_{1g}({}^6S)$ to the higher terms ${}^4T_{1g}({}^4G)$, ${}^4T_{2g}({}^4G)$, ${}^4A_{1g}({}^4G)$, ${}^4E_g({}^4G)$, ${}^4T_{2g}({}^4D)$, ${}^4E_g({}^4D)$. These transitions are forbidden and the corresponding absorption bands are very weak. In the crystals of octahedric symmetry for Mn^{2+} , the narrowest and most intensive bands corresponding to the transitions



The other bands are much broadened. For the complexes of cubic symmetry for Mn^{2+} in the crystals KCl and BaF_2 all the bands are broadened, being located above 500 nm [9, 10]. The bands shown in Fig. 3 and ascribed to the d-d transitions in Mn^{2+} of cubic symmetry, seem to be the most similar to the bands in the mentioned crystals of the

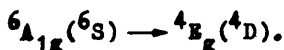
same symmetry. The luminescence is connected mainly with the transition from ${}^4T_{1g}({}^4G)$ -level to ${}^6A_{1g}({}^6S)$ -level. The colour luminescence depends upon the coordination of the Mn^{2+} complex and thus in the case of coordination number four the luminescence of green colour will appear, while for the coordination number six - that of orange-red colour should be expected [9, 10]. The application on Mn^{2+} luminescence to examination of the d-d bands structure has been initiated by one of the authors in [11] for the case of low concentration. This method is successful also, for the case of TGS crystal, and allows to detect the d-d bands for low concentrations of Mn^{2+} , which is not possible for absorption measurements. The measurements were carried out at the room temperature and, therefore, it may be approximately assumed that the band 420-460 nm corresponds to the transition



the band 390 nm - to the transition



and the band 330 nm - to the transition



The broadening band may be connected with the dynamic Jan-Teller effect. This, however, should be examined more carefully.

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ИСПОЛЬЗОВАНИЕ ЛУМИНЕСЦЕНЦИИ ДЛЯ ИССЛЕДОВАНИЯ ПРОСТРАНСТВЕННЫХ РАСПРЕДЕЛЕНИЙ ИОНОВ Mn^{+2} В КРИСТАЛЛАХ TGS

Представлены снимки пространственных распределений люминесценции в кристаллах TGS с примесью марганца. Наблюдения проводились в плоскости XZ. Было выявлено наличие сильно поляризованной люминесценции голубого цвета в пирамиде роста (001), а также люминесценции зеленого цвета в пирамиде (203) без направленности центров. Представлены спектральные распределения и спектры возбуждения люминесценции. В этих спектрах выявлена дифференциация в спектральной области переноса заряда, а также наличие полос, связанных с переходами d-d.