Effect of Manganese Concentration on Thermoluminescent Properties of YAlO$_3$:Mn Crystals

YA. ZHYDACHEVSKII$^{a,*}$, A. SUCHOCKI$^{b,c}$, M. BERKOWSKI$^b$ AND S. WARCHOL$^d$

$^a$Lviv Polytechnic National University, 12 Bandera, 79646 Lviv, Ukraine
$^b$Institute of Physics, Polish Academy of Sciences, al. Lotników 32/46, 02-668 Warsaw, Poland
$^c$Institute of Physics, Kazimierz Wielki University, Weyssenhoffa 11, 85-072 Bydgoszcz, Poland
$^d$Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland

This work is devoted to experimental study of the effect of manganese concentration on thermoluminescent properties of YAlO$_3$:Mn crystals grown by the Czochralski method. A new type of emitting centers beside of Mn$^{2+}$ and Mn$^{4+}$ ions was revealed at low concentration of manganese ions in the crystal. These centers are responsible for the high-temperature thermoluminescent peak at 570 K. A potential of this thermoluminescent peak for thermoluminescence dosimetry application is discussed.

PACS numbers: 78.60.Kn, 61.80.Ed, 61.72.Ji

1. Introduction

Yttrium orthoaluminate (YAlO$_3$), called also yttrium aluminum perovskite (YAP), when doped with rare earth elements is known mainly as active media for solid-state lasers alternative to the most widely used lasers on the basis of yttrium aluminum garnet (Y$_3$Al$_5$O$_{12}$). Manganese-doped YAlO$_3$ crystals became of particular interest after it was shown their application potential for holographic recording and optical data storage [1–3] as well as for thermoluminescent (TL) dosimetry of ionizing radiation [4, 5].

Manganese ions in YAlO$_3$:Mn crystals as a rule are present in the form of Mn$^{4+}$ ions in octahedral coordination (Al$^{3+}$ positions) and Mn$^{2+}$ ions in strongly distorted dodecahedral coordination (Y$^{3+}$ positions) [1, 6–9]. The crystals being exposed to blue-green laser light show an intensive bluish-gray coloration caused by Mn$^{2+}$ ions created as a result of the Mn$^{4+}$ → Mn$^{5+}$ + e$^-$ photoionization process [1, 2, 6]. In such a way the Mn$^{4+}$ ions demonstrate sensitivity to the visible light exposure.

The Mn$^{2+}$ ions are sensitive to the ionizing radiation such as X- or γ-rays as well as UV radiation [4]. Such type of irradiation of YAlO$_3$:Mn crystals besides ionization of Mn$^{4+}$ ions causes also recharging of Mn$^{2+}$ ions (most likely the Mn$^{2+}$ → Mn$^{3+}$ + e$^-$ ionization) [10]. The electrons released by ionization of both Mn$^{2+}$ and Mn$^{4+}$ ions are captured on deep traps available in the host. During warming up of the irradiated crystals from room temperature to about 650 K, the electrons are released from the traps and recombine on Mn ions. This process is accompanied by the red and yellow-green TL emissions that correspond to the luminescence of the Mn$^{4+}$ ($^2E$ → $^4A_2$ transitions) and Mn$^{2+}$ ($^4T_2$ → $^6A_1$ transitions) ions, respectively. The yellow-green TL emission with a maximum near 530 nm originating from Mn$^{2+}$ ions can be used as a TL signal for detecting of ionizing radiation [4]. For this purpose the crystal must have an efficient yellow-green TL emission and the red TL emission, that is parasitic in this case, should be as small as possible. Though the red TL emission can be cut off by optical system, evidently it is desirable to have YAlO$_3$:Mn crystals with the yellow-green TL emission solely or at least with very low red TL emission. The technological methods allowing increasing the thermoluminescence efficiency of Mn$^{2+}$ ions and decreasing as much as possible the efficiency of Mn$^{4+}$ ions (such as form of manganese doping (MnO$_2$ or MnO), crystal stoichiometry (Y$_2$O$_3$–Al$_2$O$_3$ ratio) and influence of after-growth high-temperature thermal treatments of the crystals in oxidizing and reducing atmosphere) were studied by us previously [11].

The present work is aimed to study an effect of manganese concentration on the thermoluminescent properties of YAlO$_3$:Mn crystals grown by the Czochralski method in order to find out an optimal concentration providing the highest TL efficiency of the crystals.

2. Experimental procedures

In the present work the following Mn-doped YAlO$_3$ single crystals, grown by the Czochralski method in the Institute of Physics of the Polish Academy of Sciences, were studied:

(i) YAP:Mn(0.1%),Si(0.2%);
(ii) YAP:Mn(0.05%),Si(0.2%);
(iii) YAP:Mn(0.035%),Si(0.2%) and
(iv) YAP:Mn(0.02%),Si(0.2%). All of them were grown
in the same technological conditions from the yttrium-rich melt (containing 2 mol.% more \( \text{Y}_2\text{O}_3 + \text{MnO} \) than \( \text{Al}_2\text{O}_3 + \text{SiO}_2 \)). The dopants’ concentration used in the crystal designation corresponds to a nominal concentration in the melt with respect to yttrium or aluminum.

The thermoluminescence measurements of the crystals were performed using a setup equipped with a compact furnace with programmable heating and a Triax 320 (Jobin Yvon-Spex) monochromator with a CCD camera. Application of the monochromator with CCD camera allowed to separate TL emission in a desired spectral region as well as to obtain spectra of TL emission during the TL experiments. The multimeter (thermocouple) and the monochromator with CCD camera were interfaced by IEEE 488 (GPIB) to a computer where the experimental data were processed and stored.

Irradiation of the crystals with \( \gamma \)-rays was performed using a \(^{60}\text{Co} \) source with 1.6 kGy/h dose rate.

3. Experimental results and discussion

The thermoluminescence glow curves of the studied crystals after \( \gamma \)-irradiation registered separately in the yellow-green (at 530 nm) and red (at 710 nm) spectral regions are presented in Fig. 1. The glow curves consist of two main TL peaks at 400 K and 450 K that agrees with our previously reported results [4, 5, 10–12]. At that, the red TL emission from Mn\(^{4+}\) ions is observed mainly at 400 K, whereas the yellow-green TL emission from Mn\(^{2+}\) ions is observed mainly at 450 K (see also Fig. 2). As it is seen from Fig. 1, the highest efficiency of TL emission from Mn\(^{2+}\) ions is demonstrated by YAP:Mn(0.05%), Si(0.2%) and YAP:Mn(0.035%), Si(0.2%) crystals.

As regards the third main TL peak at 570 K, it was revealed to grow up drastically with decrease of the manganese content. Thus, the highest intensity of this TL peak relative to other two peaks is observed for the YAP:Mn(0.02%), Si(0.2%) crystal with lowest content of manganese ions. Spectrum of emission in this TL peak (curves 3 in Fig. 2) represents a broad band stretching from 550 nm to 800 nm. It should be noted that up to here we have not observed such TL emission spectrum for other previously studied YAP:Mn crystals [4, 10, 11], which contain manganese in the amount larger than 0.05 at.%. Similar photoluminescence spectrum stretching from 550 nm to 900 nm was observed for the strongly reduced YAP:Mn(0.2%) crystal, which was not completely annealed after \( \gamma \)-irradiation [12], and was attributed to Mn\(^{3+}\) ions created in place of Mn\(^{4+}\) ions. Note that the crystals studied in [12] demonstrate negligible intensity of the TL peak at 570 K in comparison with ones at 400 K and 450 K. Here we can only suppose that the observed TL emission in the peak 570 K is caused by Mn\(^{3+}\) ions. If it is really caused by Mn\(^{3+}\) ions, it remains questionable why this TL emission is observed only for the crystals with low concentration of manganese. In order to estimate origin of this TL emission additional studies are needed that are away from the present work.

It is known that TL peaks at 400 K and 450 K are very sensitive to visible light exposure [5]. Such exposure, due to optical stimulation, diminishes TL emission in these peaks, whereas the TL peak at 570 K caused by the broad emission at 550–800 nm is insensitive to visible light exposure. As it is seen from Fig. 3, the day-light exposure during 2 hours of the \( \gamma \)-irradiated crystal almost completely removes both the TL peaks at 400 K and 450 K, whereas the peak at 570 K remains practically unchanged. Actually, some decrease of the peak at 570 K is observed after exposure to day-light. However, our measurements of TL emission spectra show that this decrease is caused only by lessening of the TL signal originating from Mn\(^{4+}\). Figure 4 demonstrates the TL emission spectrum recorded at 570 K just after \( \gamma \)-irradiation.
Fig. 2. Spectra of TL emission of the studied crystals recorded at 400 K (1), 450 K (2) and 570 K (3). (curve 1) and the differential spectrum (curve 2) on which this TL signal diminishes as a result of following exposure to day-light. One can see that this differential spectrum belongs to Mn$^{4+}$ ions. In other words, the exposure to visible light following by the high-energy irradiation can completely remove the TL signal from both Mn$^{2+}$ and Mn$^{4+}$ ions. In this case, the TL signal from the newly revealed centers remain as a single TL peak at 570 K.

The TL signal from newly revealed centers can be produced only by high-energy irradiation, e.g., γ-irradiation. Visible light illumination (we used 0.5 W Ar-laser at 514.5 nm) does not produce TL signal from these centers. As it is seen from Fig. 5, such laser illumination produces only red TL emission originating from Mn$^{4+}$ ions.

In such a way, the TL signal from the newly revealed centers, that occurs in one TL peak at 570 K, looks very attractive for TL dosimetry application. First of all, it is well separated from other low-temperature peaks. Secondly, its high-temperature position can possibly avoid...
fading of the TL signal even at elevated temperatures. Besides, appropriate level of doping can provide high intensity of this TL peak, even higher than peaks at 400 K and 450 K, ensuring high sensitivity of the phosphor. Last, this TL signal is insensitive to visible light exposure. Additional studies of dosimetric properties of this TL peak should be done in order to reveal its nature.

4. Conclusions

It was revealed that at low concentration of manganese ions (≤ 0.05 at.%) a new type of emitting centers beside Mn$^{4+}$ and Mn$^{2+}$ ions becomes apparent in thermoluminescence of the γ-irradiated YAP:Mn crystals. TL emission of these centers as a broad band stretching from 550 nm to 800 nm occurs in one TL peak at 570 K.

This TL emission occurs only after high-energy irradiation (we used γ-irradiation) and is insensitive to visible light. Illumination with visible laser does not produce this TL emission. Exposure to visible light following by the high-energy irradiation does not cause fading of the TL signal as well.

Acknowledgments

The work was partially supported by the Ukrainian Ministry of Education and Science (project DB/Tern and the research grant of Lviv Polytechnic National University) and by the research grant of the Polish Ministry of Science and Higher Education for years 2006–2009.

References