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Technological approaches for improving thermoluminescent properties of the Czochralski-grown $YAlO_3$:Mn crystals

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ABSTRACT

This work is devoted to experimental study of a few technological approaches allowing improving thermoluminescence efficiency of Mn^{2+} ions in the Czochralski-grown $YAlO_3$:Mn crystals applicable for thermoluminescent (TL) dosimetry of ionizing radiation. These approaches include changes of the crystal stoichiometry (Y_2O_3–Al_2O_3 ratio), the form of manganese doping (MnO_2 or MnO) and the after-growth high-temperature thermal treatments of the crystals in oxidizing and reducing atmosphere. It is shown that these measures allow to increase the TL efficiency of Mn^{2+} ions in the $YAlO_3$:Mn crystals several tens of times.

1. Introduction

Yttrium orthoaluminate crystals ($YAlO_3$) when doped with rare-earth elements are known mainly as active media for solid-state lasers alternative to the most widely used lasers on the basis of yttrium aluminum garnet ($Y_3Al_5O_{12}$). Manganese-doped $YAlO_3$ crystals became of particular interest after their high application potential for holographic recording and optical data storage were shown [1–3], as well as for thermoluminescent (TL) dosimetry of ionizing radiation [4].

Manganese ions in $YAlO_3$:Mn crystals can be 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) [1,5–8]. The crystals being exposed to blue-green laser light show an intensive bluish-gray coloration caused by Mn^{5+} ions created as a result of the $Mn^{4+} \rightarrow Mn^{5+}+e^-$ photoionization process [1,2,5]. In such a way the Mn^{4+} ions demonstrate sensitivity to the visible light exposure.

On the other hand, 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 also causes recharging of Mn^{2+} ions (most likely the $Mn^{2+} \rightarrow Mn^{3+}+e^-$ ionization) [9]. The electrons released at 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+} ($^2E \rightarrow {}^4A_2$ transitions) and Mn^{2+} ($^4T_1 \rightarrow {}^6A_1$ transtions) 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 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

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should be as small as possible. Though the red TL emission can be cut off by optical systems, 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. In such a way to optimize $YAlO_3$:Mn crystals for TL dosimetry of ionizing radiation, it is very important to study the technological methods allowing increasing the thermoluminescence efficiency of Mn^{2+} ions and decreasing as much as possible the efficiency of Mn^{4+} ions in the crystal. As it was shown previously [9], the same traps of the host act both in the yellow-green and red TL emission. So, it is required to study the technological approaches allowing doping of the crystal mainly with Mn^{2+} ions and increasing of their TL efficiency.

The present work is devoted to study the technological approaches such as the form of manganese doping (MnO_2 or MnO) and the crystal stoichiometry (Y_2O_3–Al_2O_3 ratio) on the thermoluminescence properties of $YAlO_3$:Mn crystals grown by the Czochralski method. Besides, the influence of after-growth high-temperature thermal treatments of the crystals in oxidizing and reducing atmosphere on the TL performance of the crystals has been studied.

2. Experimental procedures

2.1. Crystals growth

Manganese-doped $YAlO_3$ single crystals studied in the present work were grown by the Czochralski method in the Institute of Physics of the Polish Academy of Sciences. Two types of crystals were grown: the first one with a stoichiometric composition (equal amount of Y_2O_3 and Al_2O_3 starting oxides) and the second one—with yttrium-rich composition (containing 4 mol% more Y_2O_3 than Al_2O_3), hereafter named as non-stoichiometric composition. Manganese dopant was introduced in the melt in the form of MnO_2 or MnO oxides as seen from Table 1. In the case of MnO_2 doping, a co-doping with silicon (SiO_2) was used. The idea of Si^{4+} co-doping was exploited by us previously [10] as one of the possible ways to reduce concentration of Mn^{4+} ions in the crystals. The dopant concentration used in the crystal designation (see Table 1) corresponds to a nominal concentration in the melt with respect to yttrium or aluminum.

The growth processes were carried out in an iridium crucible of 40 mm in diameter at the pulling rate of 1–1.5 mm/h and a rotation rate of 20 rpm in pure nitrogen atmosphere. Good-quality single crystals of 19 mm in diameter were grown using seed oriented along ⟨0 0 1⟩ crystallographic direction in Pbnm setting.

In such a way, four different crystals were studied in this work. The pairs of crystals (Nos. 1 and 2) and (Nos. 3 and 4) have the same nominal content of dopants and differ one from another only by the Y_2O_3–Al_2O_3 ratio. On the other hand, the pairs of crystals (Nos. 1 and 3) and (Nos. 2 and 4) have the same Y_2O_3–Al_2O_3 ratio and differ one from another by the dopants content. Comparative analysis of their optical and luminescence properties that is given below allows studying the effect of these technological approaches on the properties of the crystals.

Beside the as-grown crystals, samples of the non-stoichiometric $YAlO_3$:Mn(0.1%) crystal annealed in air ($T = 1500$ K during 1 h) or in hydrogen ($T = 1300$ K during 1 h) were also studied.

The manganese and/or silicon concentration in the crystals was not measured directly. However, as shown previously, the distribution coefficient of manganese in $YAlO_3$ is essentially smaller than unity, namely <0.1 when comparing the manganese concentration in the crystal and in the melt, or 0.55 when comparing the concentration in the top and bottom parts of the crystal [1]. According to our previous studies of the silicon co-doped crystal (crystal No. 2 in the present work) in comparison with crystals doped only with MnO_2 [10], the silicon co-doping of the crystals practically does not change an amount of Mn^{2+} ions and reduces the amount of Mn^{4+} ions. Owing to small ionic radius of Si^{4+} ions it was assumed that they occupy Al positions in the host and so prevent Mn^{4+} ions entering these positions.

2.2. Spectroscopic methods and experimental setups

Optical absorption of the crystals was measured using a Cary 5000 UV–vis–NIR spectrophotometer.

The thermoluminescence measurements were performed using a home-made setup equipped with a compact furnace and a Triax 320 (Jobin Yvon-Spex) monochromator with a CCD camera. A linear heating from room temperature to 650 K with the 0.4 K/s rate was used. Application of the monochromator with CCD camera allowed to separate the red and yellow-green TL emissions as well as to obtain spectra of TL emission during the TL experiments. The multimeter and the monochromator with CCD camera were interfaced by IEEE 488 (GPIB) to a computer where the experimental data were processed and stored.

The emission spectra at X-ray excitation were registered through a monochromator by a photomultiplier. The excitation was performed by a microfocus X-ray tube operated under a voltage of 45 kV with a current of 0.3 mA. The emission spectra were corrected for the dispersion of monochromator and spectral response of the photomultiplier.

Irradiation with γ-rays was performed using a ^{60}Co source with a 1.6 kGy/h dose rate.

3. Experimental results and discussion

3.1. Influence of MnO or MnO_2 doping on the manganese incorporation into $YAlO_3$:Mn crystals

The optical absorption spectra of the MnO_2-doped crystals are presented in Fig. 1. As seen from the figure, spectra of the stoichiometric and non-stoichiometric crystals are practically identical. The spectra confirm presence of Mn^{4+} ions (the band centered at about 21,000 cm^{-1} caused $^4A_2 \rightarrow {}^4T_2$ transition [7]) and Mn^{5+} ions (bands near 12,000, 15,000, 18,000 and ~26,000 cm^{-1} caused by the transitions $^3T_1(^3F) \rightarrow {}^3T_2(^3F)$, $^3T_1(^3F) \rightarrow {}^3T_1(^3P)$ and $^3T_1(^3F) \rightarrow {}^3A_2(^3F)$ [11]) in the as-grown crystals. A spectrum of the photocolored sample with the increased absorption of Mn^{5+} ions is also present in the figure for clarity.

Table 1
List of the samples studied in the present work

No.	Crystal designation	Doping used	Y_2O_3–Al_2O_3 ratio
1	$YAlO_3$:Mn (0.2%), Si(0.2%), stoichiometric	MnO_2 and SiO_2 addition to the stoichiometric $YAlO_3$ composition	Stoichiometric ratio
2	$YAlO_3$:Mn (0.2%), Si(0.2%), non-stoichiometric	MnO_2 and SiO_2 at the expense of Al_2O_3	4 mol% more Y_2O_3 than Al_2O_3
3	$YAlO_3$:Mn (0.1%), stoichiometric	MnO addition to the stoichiometric $YAlO_3$ mixture	Stoichiometric ratio
4	$YAlO_3$:Mn (0.1%), non-stoichiometric	MnO addition at the expense of Y_2O_3	4 mol% more Y_2O_3 than Al_2O_3