Effect of Lutetium Co-Doping on the Main Dosimetric Peak of YAP:Mn²⁺ Thermoluminescent Detectors

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An effect of lutetium co-doping on photoluminescent and thermoluminescent properties of the Mn²⁺-doped (Lu-Y)AP crystals (with Lu content from 0 to 20% with respect to Y) grown by the Czochralski technique has been studied. It was found that the maximum of the thermoluminescent peak at 200 °C is shifted towards higher temperatures at Lu content more than 5%. At the same time the position of the second thermoluminescent peak near 350 °C remains unchanged. The observed changes in the thermoluminescent peak position are discussed in terms of the point defects of the material.

1. Introduction

Application potential of Mn²⁺-doped YAlO₃ (YAP) for thermoluminescent (TL) dosimetry of ionizing radiation has been shown previously (see [1] and references therein). For this purpose, one of the following two types of detectors can be used. The first type produces green emission near 530 nm (caused by Mn²⁺ ions) in the main TL peak at 200 °C, whereas the second type produces an orange emission around 640 nm in the TL peak near 350 °C. Detectors of the first type have a considerable daylight effect on fading (bleaching effect), and optical stimulation by blue-green light can be used for their readout [2, 3]. On the contrary, detectors of the second type with TL peak near 350 °C demonstrate no bleaching effect at daylight.

Main features of the YAP:Mn²⁺ detectors are as following: high thermochemical and time stability, high resistance to radiation damage, high sensitivity to ionizing radiation (up to 40 relative to TLD-100 for ^{60}Co), extremely wide range of linearity (from few μGy up to few kGy), high effective atomic number ($Z_{eff} = 31.4$) and consequently high energy response (about 40 for photon radiation of 55 keV/^{60}Co), low thermal fading of single crystalline detectors ($\leq 20\%$/year for 200 °C peak and $\leq 5\%$/year for 350 °C peak). In such a way the material is a good candidate for wide-range dose measurements, especially when tissue equivalence is not required, as well as for a purpose of the radiation quality determination if used alongside with other low-Z materials.

Partial substitution of yttrium with lutetium ($Y_{1-x}Lu_xAlO_3$) as well as complete substitution

with lutetium (LuAlO₃) allows to increase Z number of the material. The Lu³⁺ ion have smaller ionic radius than Y³⁺ that can effect on point defects responsible for the TL signal of the material. Besides, it is known that the energy band gap of LuAP is greater than for YAP (see e.g. [4, 5]) that can also affect the thermoluminescence of the material. As far as we know, up to now there are no reports on thermoluminescence properties of the Mn²⁺-doped (Lu-Y)AP crystals. Therefore, the aim of this work was to check an effect of lutetium co-doping (i.e. partial substitution of Y with Lu) on thermoluminescence of YAP:Mn²⁺ crystals.

2. Materials and methods

The Mn²⁺-doped (Lu-Y)AP single crystals with Lu content of 0, 5, 10, and 20% (with respect to Y) were grown by the Czochralski technique at the Institute of Physics of the Polish Academy of Sciences using the technological approaches described in [6]. Samples for studies were cut from one crystal boule into chips of dimensions $3 \times 3 \times 1$ mm³ (50 ±3 mg mass) as it is shown in Fig. 1. The relative sensitivity of the studied detectors (using the TL peak at 200 °C) to ^{60}Co radiation was up to 40 with respect to standard TLD-100 dosimeters.

Typically the studied detectors were stored and irradiated in darkness (wrapped in thin aluminum foil). Before each irradiation procedure the samples were annealed at 500 °C for 5 min to erase any possible TL signal due to previous irradiations.

A laboratory TL-reader with a Hamamatsu R928 photomultiplier was used for measuring of thermal glow at temperatures above room temperature. A blue-green bandpass filter (cutting off wavelengths >600 nm) or red edge filter (cutting off wavelengths <600 nm) were used for TL measurements.
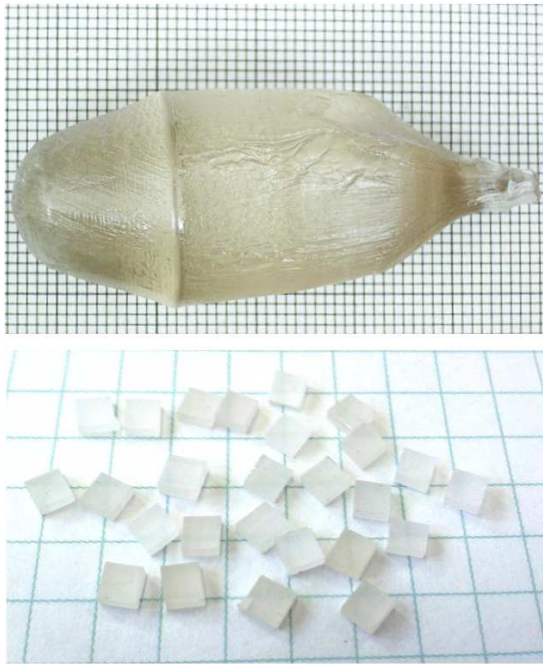
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Fig. 1. Typical view of the studied crystals grown by the Czochralski technique (a), and TL detectors made from the crystals (b).

Fig. 2. Room temperature PL (right) and PLE (left) spectra of Mn^{2+} ions in (Y-Lu)AlO_3 crystals.

The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the studied samples were measured at room temperature using a Horiba/Jobin-Yvon Fluorolog-3 and Edinburgh FS5-MCS spectrofluorometers.

3. Results and discussion

The PL and PLE spectra of Mn^{2+} ions in studied $YAlO_3$ and $Y_{0.8}Lu_{0.2}AlO_3$ crystals measured at room temperature are presented in Fig. 2. The PL spectrum of Mn^{2+} ions both in YAP and (Lu-Y)AP represents a broad emission band with maximum at 530 nm (transition $^4T_1$ (^4G) $\rightarrow$ $^6A_1$ (^6S) in Mn^{2+}). The energy of this transition being in the green spectral range testifies a low crystal field strength which the Mn^{2+} ions experience and is an evidence that Mn^{2+} ions occupy dodecahedral (Y^{3+} or Lu^{3+}) sites in the structure. It should be mentioned that the $YAlO_3 - -LuAlO_3$ system is a solid-solution system in the whole range of compositions with a linear decrease of the cell volume with increase of Lu content [7].

The thermal glow curves of the studied crystals registered in green spectral region that corresponds to a typical readout of the first type detectors are shown in Fig. 3. As is seen from the figure, the maximum of the main TL peak near 200 °C for the Lu-containing crystals is somewhat shifted towards higher temperatures. This shift reaches 20–40 °C depending on a heating rate used. The same shift of this TL peak is observed when registration
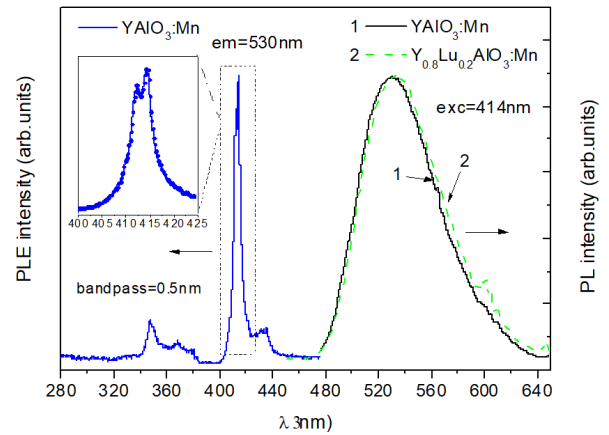
is in red spectral region (see Fig. 4b). The red TL emission, which is much less intensive than green TL emission for the studied crystals, is caused by residual Mn^{4+} ions (despite of co-doping with Hf^{4+} used for charge compensation of required Mn^{2+} ions) and Cr^{3+} ions present in the crystals as uncontrolled impurity (see [6, 8] for details). The multiplicity of TL curves in Fig. 4 show a repeatability of readouts from different detectors prepared from the same crystal. From the other hand, this testifies that the observed shift of the TL peak maximum is real feature of the crystal and it is not a particular case caused e.g. by bad thermal contact between sample and heater. The shift of the TL peak near 200 °C is visualized in Fig. 5. It looks like this shift is not monotonous with increase of Lu content. The TL peak shifts abruptly for the crystals with the Lu content more than 5%.

At the same time the position of the second TL peak near 350 °C that is observed mainly in red spectral region remains unchanged that is clearly seen from Fig. 4. This indicates that the traps responsible for this TL peak are not affected by Lu substituting Y ions.

Here it should be mentioned that maxima of the TL peaks observed before for YAP:Ce and LuAP:Ce crystals also do not coincide with each other (see e.g. [9]). Namely, for LuAP:Ce with respect to YAP:Ce crystals, the peak located near 200 °C was observed to be shifted towards higher temperatures about 30 °C at the heating rate of 1 °C/s. This allows us to say that for the studied crystals we are dealing with the same traps responsible for the TL peak near 200 °C. The fact that intensity of this TL peak increases substantially with increase of non-stoichiometry of the crystal (excess of Y over Al) (see [9] for details), clearly indicates that these traps are related to Y_{Al} antisites in $YAlO_3$ structure. It is assumed that the isolated Y_{Al}^{2+} electron centers are thermally destroyed at temperatures below room temperature [10]. However, in accordance with [11, 12], the EPR signal associated with Y_{Al}^{2+} electron centers stabilized by some defect at
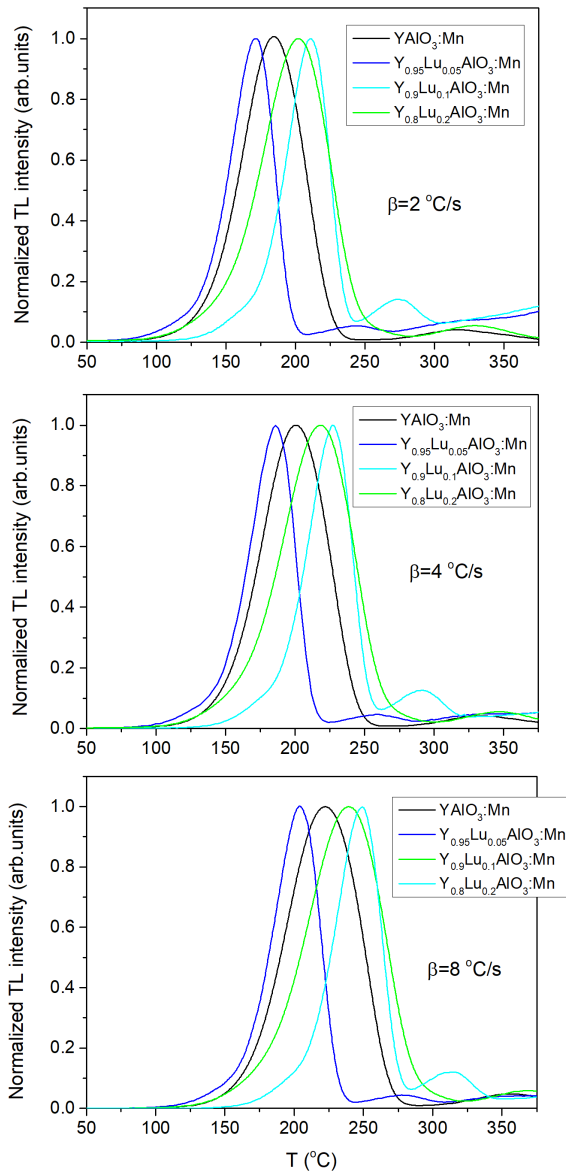
Fig. 3. Normalized thermal glow curves of the studied crystals measured in green spectral region at heating rates $\beta = 2$, 4, and 8 °C/s, after γ-irradiation at room temperature.

Fig. 4. Thermal glow curves of the studied crystals measured in green (a) and red (b) spectral regions after γ-irradiation at room temperature. The TL intensity is normalized to mass of the detectors.

neighboring Y site (which can be Mn_Y^{2+} in our case) remains stable at room and higher temperatures. To confirm existence of the Y_{Al}–Mn_Y^{2+} complexes in the studied materials, additional research is needed.

The observed shift of maximum of the TL peak near 200 °C as a result of substitution of Y by Lu can be explained by predominant formation of the Lu_{Al} antisites with somewhat different trap depth. The preferable formation of the Lu_{Al} antisites over Y_{Al} antisites due to smaller ionic radius of Lu^{3+} than Y^{3+} ions can explain the observed abrupt shift of the TL peak maximum with increase of the Lu content more than 5%. An alternative explanation of the observed shift of the TL peak maxi-
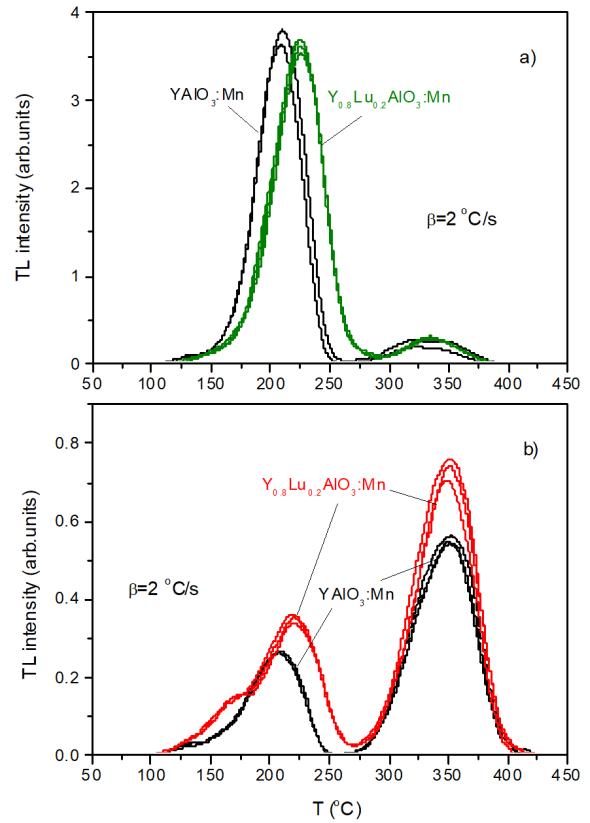
mum may be associated with a larger energy band gap for LuAP than for YAP that makes the energy levels of the antisites in the Lu-containing crystals deeper. Anyway the observed shift of the main TL peak position towards higher temperatures as a result of Lu co-doping can be used as a technological approach to decrease a thermal fading of the YAP:Mn^{2+} detectors by use of band-gap engineering. The band-gap engineering may be also a way for controlling effects related to other defects created in these materials by ionizing radiation [13, 14].

4. Conclusions

Comparative photoluminescence and thermoluminescence studies of the Mn^{2+}-doped (Lu-Y)AP crystals (with Lu content from 0 to 20% with respect to Y) grown by the Czochralski technique were performed. The studies reveal unchangeable emission band of Mn^{2+} ions with maximum at 530 nm. However the maximum of the TL peak at 200 °C was found to be shifted towards higher temperatures on 20–40 °C depending on a heating rate. Herewith this shift is not monotonous with increase of Lu content. The TL peak shifts abruptly for the crystals with the Lu content above 5%. At the same time the position of the second TL peak near 350 °C remains unchanged.
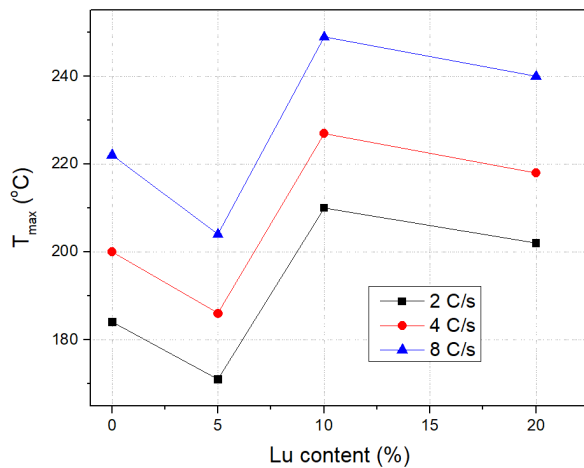
Fig. 5. A position of maximum of the TL peak near $200\,^{\circ}\mathrm{C}$ as a function of the Lu content in the studied crystals.

Acknowledgments

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