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Spectroscopy of color centers in yttrium–aluminium perovskite crystals

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Abstract

The color centers, which are generated in yttrium–aluminium perovskite YAP:Nd(1 at.%) and YAP:Er(50 at.%) crystals under the influence of ultraviolet and γ-irradiation, have been studied by absorption spectroscopy. Both stable and transient at room temperature color centers are generated. It is shown that the transient color centers are mainly responsible for the decrease of laser generation efficiency of Nd:YAP and YAP:Er irradiated crystals, although physical mechanisms leading to efficiency decrease are different in these materials. © 1998 Elsevier Science S.A.

Keywords: Defects in laser materials; YAP; Color centers; Er^{3+}; Nd^{3+}

1. Introduction

The yttrium–aluminium perovskite single crystals $YAlO_3$ (YAP), doped with rare-earth ions (Nd, Er), are very often used for solid-state laser active elements [1,2]. The YAP:Nd crystals generate laser radiation at 1.079, 1.34 and 1.44 μm, the YAP:Er can lase in the range of 1.6–3 μm depending on the erbium content. Color centers (CC) created during the growth procedure, post-growth thermal treatment or under the influence of ionizing radiation, including the ultraviolet part of the flash lamp radiation [3,4], strongly influence the performance of the YAP crystals in laser systems. For example, the CC arising during the growth process in the gas atmosphere can completely suppress laser generation in the crystals. The generation efficiency of laser crystals can be restored by after-growth annealing of the crystals in a reducing atmosphere or in vacuum [5].

It is known that YAP crystals are prone to creation of color centers. Their nature is not well known. Among other sources of creation of color centers the ionizing radiation is one of the most important since laser crystals are very often exposed to the ultraviolet part of the pumping lamps spectrum. Knowledge of the influence of the ionizing radiation on the optical properties of the YAP crystals still remains limited despite some studies performed in the past [6–9]. This work presents the influence of ultraviolet light and γ-quanta irradiation on the optical and lasing characteristics of YAP:Nd and YAP:Er crystals.

2. Experiment

The YAP:Nd crystals were grown by the Czochralski method in the *b* crystallographic direction in iridium crucibles under an atmosphere of 98% Ar and 2% O. The Nd content in the crystal did not exceed 1 at.% (in relation to the amount of Y^{3+} ions).

Plane-parallel polished samples, cut perpendicular to the *b* direction, with a thickness of 0.5–2 mm were used for the investigation of the optical properties. For studying the laser generation characteristics, crystal rods with diameter of 8 mm and length of 100 mm were prepared from the crystal parts which did not contain twins, strains and inclusions. The laser rods were coated with antireflection layers (R=0.3%).

The YAP:Er single crystals were obtained by the Czochralski technique in a N_2 atmosphere. In fact, they were mixed as $Y_{0.5}Er_{0.5}AlO_3$ perovskite crystals but we decided to keep the same convenient notation as in the case of much less doped YAP:Nd crystals. Flat-parallel plates samples of 1–3 mm thickness that were cut off perpen-

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dicularly to the growth axis were examined (axis *b* in *Pbnm* system). Laser rods were cut off along the *b* axis from crystals that were annealed in the reducing atmosphere. Cylindrical rods of 4 mm in diameter and 51 mm long were studied. The experimental details of the laser generation set-up have been described elsewhere [10].

The crystals were irradiated by ultraviolet Ar^+ laser radiation (351 nm) and by γ-quanta with a dose of 10^5 Gy for the creation of the CC. The creation of stable and transient CC have been detected. The stable CC were studied by means of a Hitachi-Perkin Elmer spectrophotometer (model 340) in the region 52 000–4000 cm^{-1} wavenumbers. A differential absorption (DA) coefficient, ΔK, induced by the ultraviolet or γ-quanta was determined as:

$$\Delta K = 1/d \cdot \ln(T_1/T_2) \quad (1)$$

where d is the sample thickness, T_1 and T_2 are the sample transmissions before and after irradiation, respectively.

The samples were illuminated by ultraviolet (UV) light pulses of duration of about 2 ms for studying the transient CC. The changes of sample absorption were estimated from the changes of the probe light intensity, measured in a typical set-up with a GDM 1000 monochromator and a photomultiplier with an S 20 type cathode. The DA decay kinetics were stored in a SR430 multichannel scaler. For low temperature measurements the crystals were mounted in a continuous-flow cryostat.

3. Results and discussion

The DA related to the creation of CC in the YAP:Nd crystals is shown in Fig. 1. The DA bands with maxima at 45 000 cm^{-1}, 41 500 cm^{-1}, 32 000 cm^{-1}, 23 000 cm^{-1} and 20 000 cm^{-1} arise in YAP:Nd crystals after illumination with ultraviolet light at room temperature. A weak bleaching of the crystal occurs in the region between 32 000 cm^{-1} and 27 000 cm^{-1}. Very similar absorption spectra but with a much higher intensity are also induced by γ-irradiation. When UV illumination is performed at low temperatures (40 K) the DA appears in the region of 17 000–7000 cm^{-1}. The absorption of CC, transient at room temperature with a lifetime of about 6 ms, occurs in the same spectral region. Therefore we associate the stable DA at low temperatures and the transient DA in this spectral region with the same type of CC in the YAP crystals.

The influence of CC on lasing properties of the YAP crystals has been directly studied in the laser cavity pumped by a flash lamp. The threshold energy for laser generation in the YAP:Nd non-irradiated crystal at the 1.079 mm wavelength was about 5 J. The efficiency reached a maximum value of 2.3% at a pumping energy of 11.8 J. After γ-irradiation up to an absorbed dose of 10^5 Gy at the first 10 pulses of a pumping flash lamp, the laser generation was not observed. The laser generation was again restored after more than 10 pulses of flash pumping lamp. After 1000–10 000 lamp flashes full initial efficiency was recovered. This means that some color centers created under the influence of γ-irradiation were destroyed by the flash lamp illumination.

Laser rod irradiation with γ-quanta leads to a decrease of YAP:Er laser output energy. Before γ-irradiation the laser output energy at a wavelength of 2.9 μm was equal to about 8 mJ at a pumping energy of 115 J. After irradiation the output energy decreased down to 3 mJ.

The absorption bands of color centers in the YAP:Er crystal that are formed under the influence of ultraviolet light and gamma irradiation, are very similar to the absorption of color centers in the YAP:Nd crystal. They are presented in Fig. 2. This suggests that the examined CC

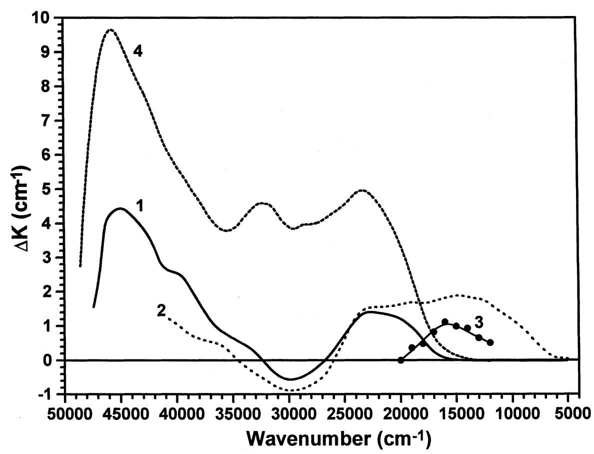

Fig. 1. The differential absorption spectra of stable color centers in YAP:Nd crystal generated by: – the γ-irradiation (dose 10^5 Gy at 300 K), curve 4; – UV Ar-ion laser irradiation at 300 K, curve 1; – UV Ar-ion laser irradiation at 40 K, curve 2. The differential transient absorption spectra generated by UV argon-ion laser irradiation at 300 K-full points, curve 3.

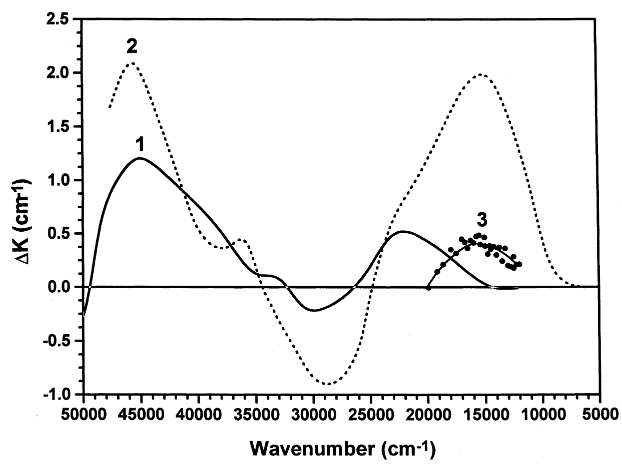

Fig. 2. The differential absorption spectra of stable color centers in YAP:Er crystal generated by: – the UV Ar-ion laser irradiation at 300 K, curve 1, – UV Ar-ion laser irradiation at 40 K, curve 2. The differential transient absorption spectra generated by UV argon-ion laser irradiation at 300 K – full points, curve 3.

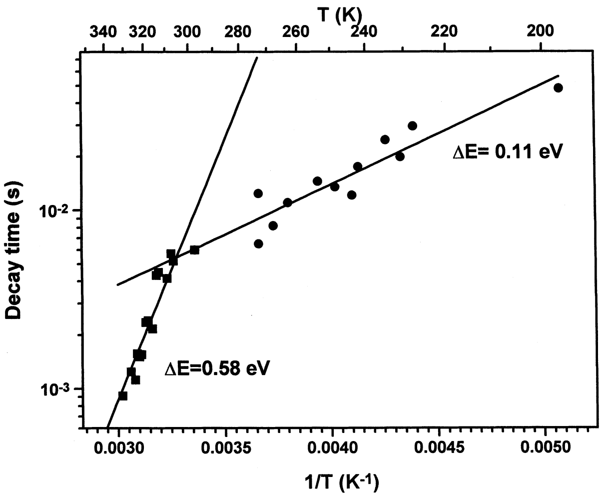

Fig. 3. The temperature dependence of the decay times of the transient color centers in YAP:Nd crystal, induced by the UV argon-ion laser illumination. The activation energies are marked on the graph.

created in YAP crystals are associated with the crystal host and their nature does not depend strongly on the type of dopant, even for high levels of dopant concentration.

The decay kinetics of the DA of a transient color center induced by UV argon-ion laser illumination have been measured at 14 000 cm^{-1} in both types of crystals as a function of temperature. Most of the decay kinetics is well described by a single-exponential dependence. The decay times, τ, depend on the temperature and have an exponential activation character, described by the formula:

$$\tau = \tau_0 \exp(\Delta E / k_B T)$$

where ΔE is the activation energy and k_B is the Boltzmann constant.

The results of measurements are presented in Figs. 3 and 4. Two activation energies of the DA decay kinetics, that are equal to 0.11 eV and 0.58 eV below and above 300 K, respectively, have been detected in the case of YAP:Nd crystals.

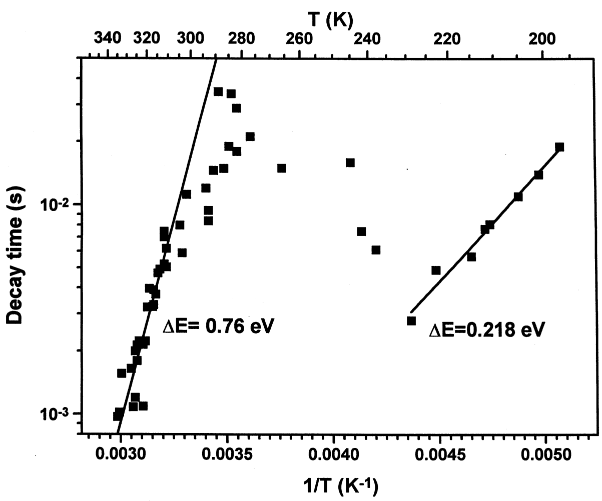

Fig. 4. The temperature dependence of the decay times of the transient color centers in YAP:Er crystal, induced by the UV argon-ion laser illumination. The activation energies are marked on the graph.

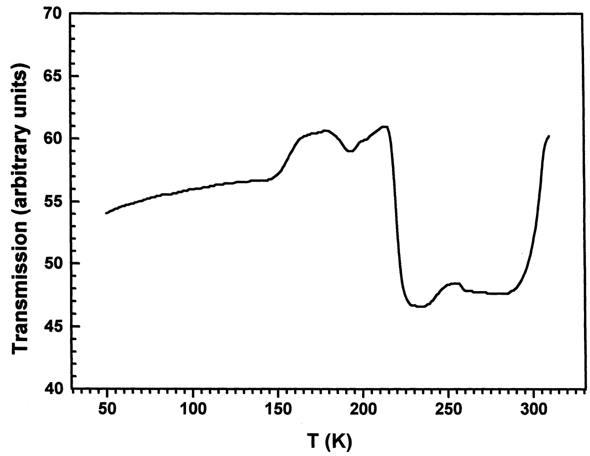

Fig. 5. The temperature dependence of the transparency of the UV irradiated YAP:Er (50 at. %) single crystal at temperature $T = 40$ K.

A more complicated situation occurs in the YAP:Er crystal (see Fig. 4). In the temperature region between 310 K and 340 K the activation energy of the temperature dependence of the transient CC decay kinetics is equal to 0.76 eV. The activation energy between 190 K and 230 K is equal to 0.22 eV. These two temperature regions are separated by the region where the measurements were less reliable. Additionally the decay times at $T_1 = 310$ K are longer than at temperature $T_2 = 230$ K and equal to about 10 ms and 3 ms, respectively. The decay kinetics could not be described by a single exponential dependence at temperatures between 230 and 310 K. Simultaneously, in the same temperature region the transparency of the YAP crystal diminishes apparently which reduces signal intensity. Therefore we were not able to distinguish the type of the time dependence of the decay kinetics in this temperature region. The temperature dependence of the YAP:Er crystal transparency is presented in Fig. 5. Similar (although not identical) results are also observed for YAP:Nd crystals. The nature of the process responsible for the transparency reduction in this temperature region is not known. Some kind of phase transition or creation of additional CC could be responsible for this phenomenon. Similar phenomena have been also observed by Akkerman et al. in the same temperature region in [9]. The two distinct activation energies of the DA decay kinetics suggest that two types of CC are associated with this DA band.

4. Conclusions

The CC created in the YAP:Nd and YAP:Er crystals by the UV illumination and by the γ-irradiation have the same nature. The changes of a charge state of the point defects created during the crystal growth are most probably responsible for the creation of the CC in the YAP crystals. The charge carriers, generated by the radiation are re-trapped by the various color centers. The oxygen vacancies, the Y^{3+} ions in the crystallographic positions of the Al ions, as well as other uncontrollable impurity (most probably Fe and Cr ions [11]) can constitute such growth defects. Additional studies are necessary to explain the detailed nature of the CC in the YAP crystals.

Both stable and transient at room temperature CC arise in the YAP:Nd and YAP:Er crystals upon irradiation by the ionizing radiation. According to our knowledge the creation of transient color centers in YAP crystals has not been yet reported in the literature.

The irradiation induced CC worsen lasing efficiency of the YAP crystals. The transient CC mostly affect the lasing efficiency of the YAP:Nd since their absorption is coincident with the lasing wavelength. On the other hand there is no CC absorption at lasing wavelength of the YAP:Er crystals. The decrease of the lasing efficiency of these crystals is related to the decrease of the pumping effectiveness since part of the pumping lamp energy is absorbed by the CC.

A part of the stable CC in YAP crystals can be destroyed by illumination by pumping flash lamps, that self-improves the laser performance of the irradiated YAP crystals.

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