# Defects and Surface-Induced Effects in Advanced Perovskites

edited by

Gunnar Borstel
Department of Physics,
University of Osnabrück, Germany

Andris Krumins
Institute of Solid State Physics,
University of Latvia,
Riga, Latvia

and

Donats Millers
Institute of Solid State Physics,
University of Latvia,
Riga, Latvia

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# RADIATION INDUCED DEFECTS IN YTTRIUM ALUMINIUM PEROVSKITE

V. SKVORTSOVA[1], N. MIRONOVA-ULMANE[1], A. MATKOVSKI[2], S. UBIZSKII[2]
[1] *Institute of Solid State Physics, University of Latvia, 8 Kengaraga St., LV-1063, Riga, Latvia*
[2] *State University "Lvivska Politechnika", 12 Bandera St., Lviv, 290646, Ukraine*

## 1. Introduction

The yttrium aluminium perovskite single crystals $YAlO_3$ (YAP) doped with rare -earth ions belong to the most prospective materials of solid-state laser engineering. Laser based of $YAlO_3$ crystals have the advantage in comparison with yttrium aluminium garnet (YAG). The main of them consists in anisotropy of optical properties [1], which are stipulated by the low symmetry of orthoaluminate crystals. Continuos wave (CW ) laser action at 549.6 nm was achieved in 1% Er:YAP crystal at below 77 K [2]. The YAP:Nd allows to obtain a CW generation at 1079 nm, 1340 nm and 1440 nm [3, 4]. It is known, that the color center can completely suppress laser generation in the crystal.

Results of investigation of defects induced by γ-, electron and fast neutron irradiation in neodymium and erbium doped yttrium aluminium perovskite are presented hereafter.

## 2. Experiment

The investigated samples were cut from single crystals grown by the Czochralski technique. The sample thickness was in the range of 0.5–2 mm. Neodymium content in YAP:Nd crystal was about 1 at.%. YAP:Er crystal had the composition $Y_{0.5}Er_{0.5}AlO_3$.

Irradiation by electrons with energy of 3.5 MeV of integral fluence up to $10^{16}$ $cm^{-2}$, that corresponds to absorbed dose of about $2 \cdot 10^6$ Gy was carried out in accelerator ELU (Salaspils, Latvia).

The neutron and γ- quanta irradiation up to $8 \cdot 10^5$ Gy absorbed dose was made in Latvian 5 MW research reactor. The neutron irradiation was performed in the VEK-8 vertical channel. The fluence of fast neutrons with energy > 0.1 MeV was in the range $10^{14} - 5 \cdot 10^{18}$ $cm^{-2}$. Accompanied γ-irradiation with average energy 1.1 MeV gave an absorbed dose 0.33 Gy. The sample temperature did not exceed 60°C during the γ– and electron irradiations and was below 40°C during the neutron irradiation. The thermal behavior of the absorption bands was observed by isochronic annealing for 10 min at each temperature.



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The common technique used to measure absorption spectra was based on a "Specord M-40" (Karl Zeiss Jena) double-beam spectrophotometer operating in the wavelength region of 50000–11000 $cm^{-1}$ (200–900 nm). Optical measurements before and after irradiation were made at room temperature.

## 3. Results and discussion

The absorption spectra of $YAlO_3$ doped with Nd consist of a number of fine lines in ultraviolet, visible and infrared regions corresponding to the f-f transition of $Nd^{3+}$ ions from the ground state. Absorption spectra of erbium doped $YAlO_3$ also consist of a number of fine lines. Since the erbium concentration is sufficiently large the intensities of these lines are very high.

After irradiation by γ-quanta, electrons and fast neutrons additional absorption (AA) were observed (Fig. 1). The bands with maxima at 45000, 42000, 35000, 33000, 26000, 23000 and 20000 $cm^{-1}$ are distinguished in the AA spectra . It should be noted that the intensity of the additional absorption induced by neutron irradiation in this range is somewhat lower than the AA level after irradiation by γ–quanta or electrons.

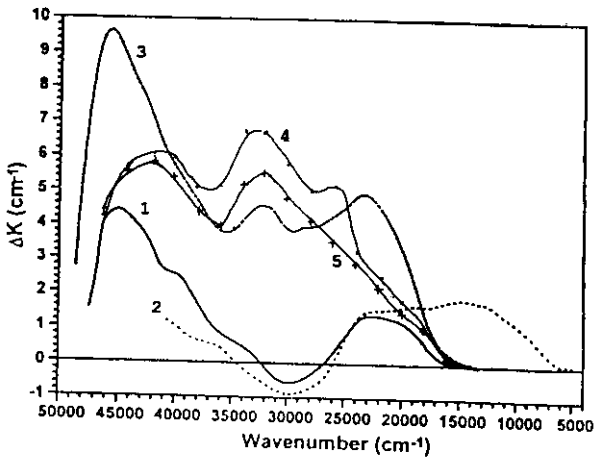


*Figure 1.* Additional absorption spectra of $YAlO_3$:Nd crystal irradiated by: 1. UV Ar-ion laser at 300 K [5]; 2. UV Ar-ion laser at 40 K [5]; 3. the γ-quanta (dose$10^5$ Gy at 300 K); 4. electrons, fluence $10^{16}$ $cm^{-2}$; 5. fast neutrons, fluence $10^{15}$ $cm^{-2}$.

A similar disposition of the AA bands maxima and their independence upon irradiation kind suggest that these bands and corresponding color centers induced by different irradiation have a similar nature and are caused by recharging genetic defects. Figs. 2 and 3 show dependence of the AA band intensities on fast neutron fluence in $YAlO_3$:Nd and $YAlO_3$:Er crystal respectively. The process of defects accumulation is roughly divided into four stages.

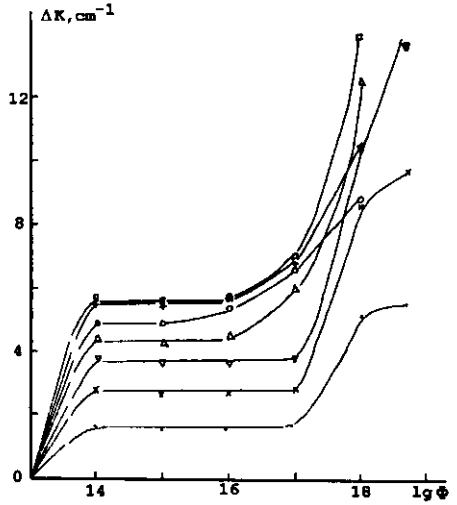


*Figure 2.* Additional absorption bands depending on fast neutrons fluence in $YAlO_3$:Nd : o - 45000 $cm^{-1}$; + -42000 $cm^{-1}$; Δ - 35000 $cm^{-1}$; □ - 32000 $cm^{-1}$; ∇ - 26000 $cm^{-1}$; × - 23000 $cm^{-1}$; • - 20000 $cm^{-1}$.

The first stage occurs at fluence < $10^{14}$ $cm^{-2}$ and consists of a rapid rise of the AA intensity. The second stage takes place at fluence from $10^{14}$ to $10^{16}$ $cm^{-2}$ when the additional absorption bands do not depend on neutron fluence. During the third stage at fluence > $10^{16}$ $cm^{-2}$ the AA intensity increases again. Intensities of the 23000 and 20000 $cm^{-1}$ AA bands saturate in the fourth stage at fluence > $5 \cdot 10^{18}$ $cm^{-2}$. Since the intensities of additional absorption bands in the $YAlO_3$:Er crystal to fluence < $10^{17}$ $cm^{-2}$ are less compared to $YAlO_3$:Nd crystal, the concentration of genetic defects in erbium doped crystal is likely smaller than in the Nd-doped crystal.

AA bands have a different thermal stability. Intensities of several bands' as functions of annealing temperature in $YAlO_3$:Nd crystals are shown in Fig. 4. The intensity of band 42000 $cm^{-1}$ decreases rather quickly in the range from 470 to 670 K and does not change further. The 35000 $cm^{-1}$ band intensity decreases slowly in the whole temperature region. As it is seen in Fig. 4, intensities of the 32000 and 23000 $cm^{-1}$ bands increase and reach their maxima at 823 and 673 K, respectively. They disappear at temperature over 900 K.

Iron ions known to be the most common impurity in YAP crystals exist in the valence states $Fe^{2+}$ and $Fe^{3+}$ [6]. The $Fe^{3+}$ ions in $YAlO_3$ crystals mainly enter in octahedral configuration with isomorphous substitution of the $Al^{3+}$ ions. The $Fe^{2+}$ ions primarily occupy $Y^{3+}$ sites. They are considered to be responsible for the intense absorption at 45000 $cm^{-1}$ and the weak band at 32000 $cm^{-1}$. During the irradiation reactions $O^{2-} + h\nu \rightarrow O^- + e^-$ and $Fe3^+ + e^+ \rightarrow Fe^{2+}$ take place resulting in appearance of AA maxima at 42000 and 32000 $cm^{-1}$ [6, 7]. AA bands at 23000 and 20000 $cm^{-1}$ are assumed to be associated with the hole center $O^-$ located close to cation vacancy and F-type centers [8, 9].

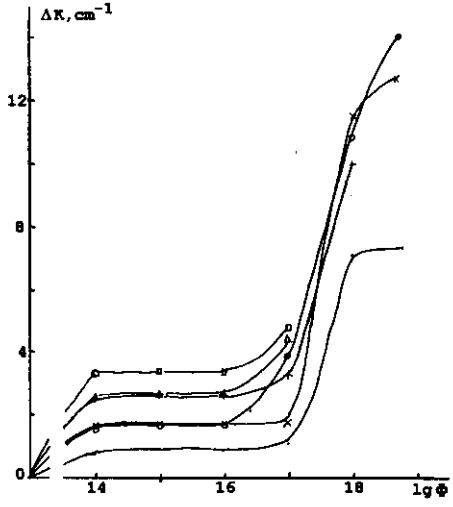


*Figure 3.* Additional absorption band intensity in $YAlO_3$:Er as function of fast neutrons fluence : o - 45000 $cm^{-1}$; + -42000 $cm^{-1}$; Δ - 35000 $cm^{-1}$; □ - 32000 $cm^{-1}$; × - 23000 $cm^{-1}$; • - 20000 $cm^{-1}$.

The decay of hole centers may occur either as a result of holes being released and re-trapped at other centers or recombined with electrons, or as a result of electrons being released from electron centers and recombining with holes at hole centers. There are two non-equivalent positions of oxygen ions in YAP structure [9] and, consequently, two types of F- and $O^-$ centers of non-equivalent energy' can be formed. The F-centers with absorption band in the range of 20000–24000 $cm^{-1}$ have been observed in other irradiated garnet and perovskite crystals [10, 11]. Thus, annealing leads to decay of complex centers and restoring of the initial absorption spectra.

The AA intensity grows rapidly and the short-wave absorption edge broadens at neutron fluence of $10^{18}$ $cm^{-2}$ indicating to appearance of new radiation defects in irradiated crystals. The concentration of the displacement defects at $10^{18}$ $cm^{-2}$ neutron fluence is about $2 \cdot 10^{19}$ $cm^{-3}$ the oxygen vacancies forming the main part of them. So, the radiation displacement defects (RDDs) in oxygen sublattice should be responsible for the revealed additional absorption growth. The simulation of atom-atom collision cascades taking account of the role of atoms of different kind in the displacement formation in each sublattice of a complex compound (see details in [12]) was used to calculate the concentration of RDD created by impacts under irradiation. The obtained results are presented in the Table 1. The threshold energy values $T_d$ for atoms of rare-earth perovskite were assumed to be equal to those estimated for the $Gd_3Ga_5O_{12}$ crystal [13]. The deceleration of the additional absorption rise slows down at neutron fluence $\sim 5 \cdot 10^{18}$ $cm^{-2}$ indicating the saturation of the RDD formation. Due to high optical density of the studied samples we could not separate maxima in the AA spectra. Upon irradiation with the $10^{14}$ $cm^{-2}$ neutron fluence the AA intensity is higher in YAP:Nd crystals compared to YAP:Er crystals, but the reverse is observed at fluence $10^{18}$ $cm^{-2}$

when the RDDs are formed. It testifies that dopant presence can play an important role in formation of the color centers since the RDDs concentration is about the same in both the studied YAP crystals.

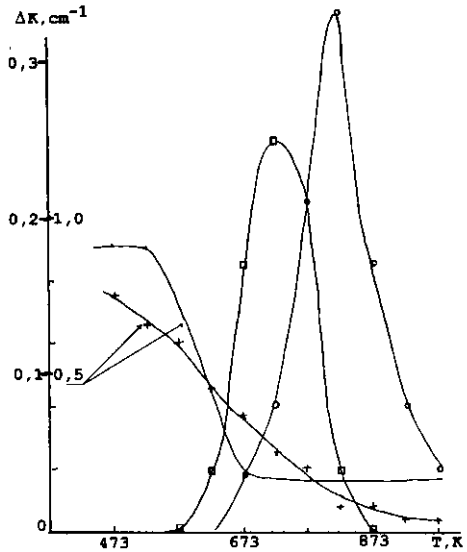


*Figure 4.* Additional absorption band intensities of $YAlO_3$:Nd as functions of annealing temperature: •- 42000 $cm^{-1}$; o- 32000 $cm^{-1}$; □- 23000 $cm^{-1}$; + - 35000 $cm^{-1}$.

TABLE 1. Displacement defect concentration per unit fluence of irradiation particles ($n_d/\Phi$, $cm^{-1}$) in sublattices of perovskite crystals.

| Crystal | Atom | Electrons (3.5 MeV) | Fast reactor neutrons |
|---|---|---|---|
| $YAlO_3$ | Y | 0.578 | 2.39 |
| | Al | 0.356 | 2.08 |
| | O | 1.580 | 17.27 |
| $Y_{0.5}Er_{0.5}AlO_3$ | Y | 0.291 | 1.19 |
| | Er | 0.326 | 0.91 |
| | Al | 0.353 | 2.02 |
| | O | 1.574 | 16.85 |

## 4. Conclusions

The electron centers, hole centers and impurity ions take part in the creation and destruction of additional absorption bands in irradiated $YAlO_3$:Nd and $YAlO_3$:Er crystals. They have different thermal stability. The calculated radiation defect concentration suggests that formation of the induced color center is a secondary process in which displacement defects created by irradiation participate together with the intrinsic growth defects of the crystal.

## 5. Acknowledgments

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