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Role of the Type of Impurity in Radiation Influence on Oxide Compounds

Susceptibility to radiation of rare-earth elements and transition metals in $Y_3Al_5O_{12}$, $YAlO_3$, $LiNbO_3$, $SrLaGa_3O_7$, $BaLaGa_3O_7$ and $SrGdGa_3O_7$ single crystals was investigated. Additional absorption bands after γ -irradiation with doses 10^3 - 10^7 Gy and protons with fluencies of 10^{13} - 10^{16} cm⁻² were found. A decrease in additional absorption with increasing Pr^{3+} , Dy^{3+} and Cu^{2+} and with decreasing Nd^{3+} and Fe^{3+} dopant concentration was observed. Dopants like Ce^{3+} and Cr^{3+} show a relatively complex behavior. This behavior strongly depend on the type of radiation and its dose.

Keywords: gamma and proton irradiations, additional absorption, thermal annealing, oxidizing atmosphere, reducing atmosphere

1. Introduction

The sources of color centers in oxide crystals are point defects as a result of nonstoichiometry and other defects forming during growth. The concentration and type of the color centers depends on the method of crystal growth and the quality of starting materials.

In YAG crystals introduction of Sm, Ho, Dy, Lu and Er does not influence their color after ionizing irradiation (MATKOVSKII et al. 1994). Contrary to this, Pr, Tb, Eu and Yb increase the susceptibility of the crystal to ionizing particles due to their tendency to change of the valency, and become shallow traps of electron excitations (BATYGOV et al. 1972). Low concentration of Ce (Ce < 0.1 at.%) in Nd:YAG crystals decreases their radiation susceptibility but at higher Ce concentration an opposite effect is observed (KOVALEVA et al. 1981).

The γ -irradiation causes clearing of YAG crystals near the fundamental absorption edge, which is associated with a valency change of Fe ions: Fe^{3+} near 253 nm and Fe^{2+} near 310 nm (MORI et al. 1977).

In YAG crystals additional absorption bands are observed for Mn (UV+VIS) and Cr ions (MATKOVSKII et al. 1994). In the latter case changes in the absorption spectrum after irradiation depend on the concentration of chromium ions. For Cr concentration greater than 0.38 at. %, the stable additional absorption bands arise at 380 and 480 nm giving defects that compete with other defects in the crystal in trapping of electron excitations (MATKOVSKII et al. 1994).

In the present paper we describe the influence of some dopants like V^{3+} , Mg^{2+} , Dy^{3+} , Ce^{3+} , Cr^{3+} , Nd^{3+} , Er^{3+} and Pr^{3+} on the susceptibility of $Y_3Al_5O_{12}$ (YAG), $YAlO_3$ (YAP), $SrLaGa_3O_7$ (SLGO), $BaLaGa_3O_7$ (BLGO), $SrGdGa_3O_7$ (SGGO) and $LiNbO_3$ (LN) single crystals to γ radiation. Changes in the additional absorption spectra after proton irradiation in YAG, Nd:

YAG, Ce: YAG, Ce,Nd : YAG, Er: YAP and Dy: SLGO single crystals have also been investigated and presented in comparison with gamma results.

2. Experimental

Gamma irradiation with the use of a ^{60}Co source with a 1.7 Gy/s efficiency and doses from 10^3 to 10^7 Gy was performed. Proton irradiation was done by means of a C-30 cyclotron, for energy of 21 MeV and fluencies from 10^{13} to 10^{16} cm^{-2} . All irradiations were performed on samples of 1 to 3 mm thick polished on both sides. The spectra were recorded using LAMBDA-2 Perkin-Elmer and FTIR spectrometers before and after radiation treatment. The additional absorption bands were obtained from the following relation:

$$\Delta K = \frac{1}{d} \ln \frac{T_1}{T_2}, \quad (1)$$

where K is absorption, ΔK is the additional absorption, d is the sample thickness, and T_1 and T_2 are the transmissions of a sample before and after the ionization treatment, respectively.

In all six oxides were investigated. Four of them, i.e. YAG, YAP, SLGO and LN grown in the Institute of Electronic Materials Technology (Warsaw) and two, i.e. SGGO and BLGO in Institute of Physics PAS (Warsaw). Concentrations of applied dopants are presented in table 1.

Do- pant	Ce ³⁺ at.%	V ³⁺ at.%	Cr ³⁺ Tm ³⁺ Ho ³⁺ at.%	Nd ³⁺ at.%	Pr ³⁺ at.%	Fe ³⁺ at.%	Dy ³⁺ at.%	Er ³⁺ at.%	Tb ³⁺ at.%	Mg ²⁺ at.%	Cu ²⁺ at.%	Cr ⁴⁺ at.%
YAG	0.05 0.1 0.2	0.1	5.7 0.36 1	1				33		0.6		0.1
YAP				1.2	0.05 3			50				
SLGO			0.1	5 10	0.5 1		0.5 1					
LN			0.3		1	0.1 0.3	0.3 1 1.7	0.01 0.03	1		0.03 0.06 0.1	
SGGO			0.05 0.1									
BLGO				6								

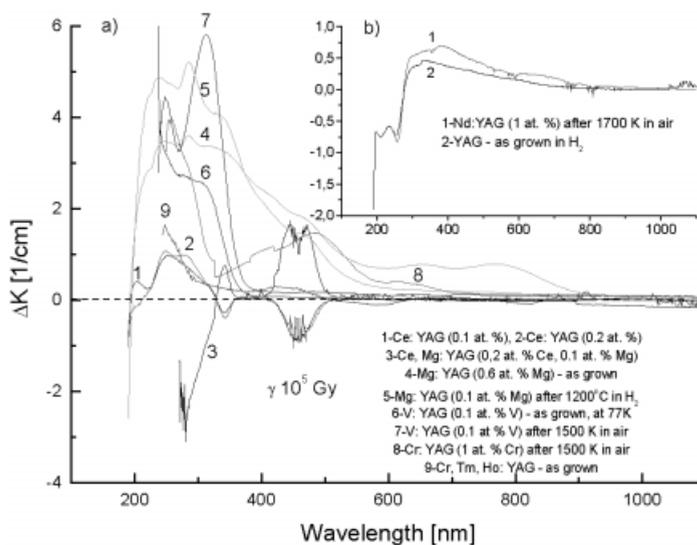
Table 1: Concentrations of dopants incorporated into: YAG, YAP, SLGO, SGGO, LN and BLGO crystals during growth

3. Results

Fig. 1 presents the results of γ -irradiation (10^5 Gy) on (a) pure YAG and Nd: YAG and (b) Ce, V, Cr, Tm, Ho and Mg doped YAG crystals. Intense bands in the UV and VIS regions of absorption spectra may be seen in the figure. The values and the shapes of additional absorption depend on crystal growth conditions and the radiation dose. Moreover, they depends on the type of the atmosphere used during thermal annealing before the irradiation (Fig. 1b, curves 1 and 2). For Nd: YAG crystal, annealing in air leads to the appearance an

additional color centers in a range of 380 nm (F-center and oxide vacancy as reported by AKHMADULIN et al. 1992) - curve 1. Contrary to previous, after annealing in N_2+H_2 mixture this color center is not observed (KACZMAREK₂ et al. 1998 a). Irradiation of Ce: YAG crystal (Fig. 1a, curves 1 and 2) leads to a change in Ce concentration (bands at 338 and 458 nm) due to recharging process of $Ce^{3+} \leftrightarrow Ce^{4+}$ type (KACZMAREK et al. 1996). In all additional absorption bands of the investigated crystals the presence of Fe ions is seen (bands centered at 253 and 275 nm - AKHMADULIN et al. 1992). Addition of Mg^{2+} dopant to Ce:YAG crystal leads to a shifting of fundamental absorption edge towards long-wave direction (from 190 to 270 nm) - curve 3. The lower absorption edge in the Mg-doped material is likely to be due to transitions from the filled acceptor-like states introduced by Mg (BARZOWSKA et al. 1998). As is seen from curve 3, change in Ce concentration for Mg codoped Ce: YAG crystals is opposite one with respect to that observed for Ce: YAG (curves 1 and 2).

Fig. 1: Additional absorption bands for (a) YAG's doped with Cr^{4+} ; Ce^{3+} ; Mg^{2+} ; Ce^{3+} and Mg^{2+} ; V^{3+} ; and Tm^{3+} , Ho^{3+} and Cr^{3+} and for (b) pure YAG and YAG doped with Nd after γ -irradiation with a dose of 10^5 Gy



The additional absorption values for V, Mg and Cr (Fig. 1a, curves 4-8) are greater than that for other impurities. Changes in the valency of V and Cr are clearly seen (change in intensity of V^{3+} transitions after irradiation) - curves 6 and 7. In the presence of Mg^{2+} ions strong defects arise in YAG crystals due to charge nonequilibrium. For the as grown crystals additional absorption bands in the VIS region of the absorption spectrum are seen - curve 4. These bands are removed by the annealing treatment performed at $1200^{\circ}C$ in N_2+H_2 atmosphere - curve 5. In the wide additional absorption band (curves 4 and 5), cerium bands are also seen at 338 and 458 nm.

Fig. 2 shows the results of (a) γ (10^5 Gy) and (b) gamma in comparison with proton irradiations (10^{16} cm^{-2}) on the shape and intensity of AA bands for YAP crystals. An increase in Pr^{3+} concentration leads to a decrease in additional absorption intensity and change in the shape of additional absorption band (Fig. 2a, curves 1 and 2). Moreover, changes in the absorption spectrum of Er: YAP crystal after γ (10^5 Gy) or proton (10^{16} cm^{-2}) radiation are almost the same except in the UV range - curves 1 and 2 in Fig. 2b. Additional absorption bands in the UV range arise in YAP crystals after annealing both in oxidizing and reducing atmospheres. Comparison of Figs. 1 and 2 reveals that YAP crystals are more susceptible to ionizing radiation than YAG crystals.

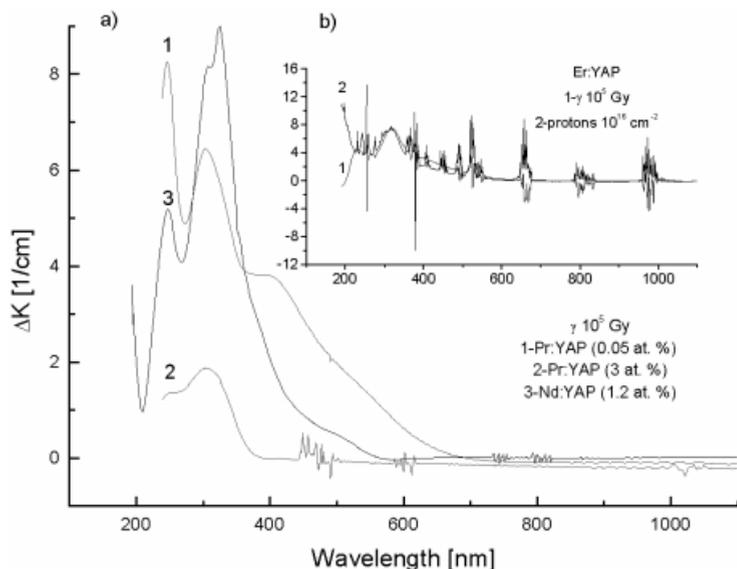


Fig. 2: Additional absorption bands for YAP's doped with (a) Nd and Pr after γ irradiation and (b) Er after γ and proton irradiation. The γ -dose was equal to 10^5 Gy while proton fluency was equal to 10^{16} cm $^{-2}$.

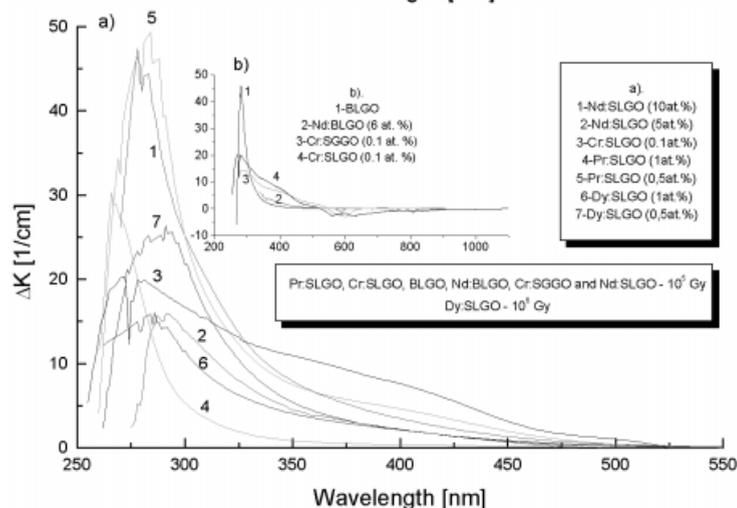


Fig. 3: Additional absorption bands for (a) SLGO's doped with Nd, Cr, Pr, Dy and (b) pure BLGO and doped with Nd and Cr doped SGGO and SLGO crystals after γ -irradiation with doses from 10^5 to 10^6 Gy

Fig. 3. presents the results of the effect of γ -radiation with doses from 10^5 to 10^6 Gy on (a) Dy, Pr and Nd doped SLGO crystals, (b) undoped and Nd-doped BLGO crystals, and Cr doped SGGO and SLGO crystals. At least two color centers can be distinguished in the additional absorption spectrum: at about 280 nm and 400 nm. The first is a G1-type paramagnetic defect while the second seems to be associated with an oxide vacancy (KACZMAREK et al. 1997). For Cr: SGGO, Cr: SLGO and Nd: BLGO changes in the valency of Cr and Nd ions are observed (see curve 3 in Fig. 3a and curves 1-4 in Fig. 3b).

As for Pr: YAP crystals (see Fig. 2), from Fig. 3 it follows that an increase in Pr $^{3+}$ concentration also leads to a decrease in the additional absorption intensity and a shift in the maximum of the band towards the short-wave range of absorption spectrum (see curves 4 and 5). Similarly an increase in Dy $^{3+}$ concentration gives the same effect (curves 6 and 7). In contrast to this, an increase in Nd $^{3+}$ concentration leads to an increase in the additional absorption intensity (curves 1 and 2).

Fig. 4. show the observations of additional absorption bands in LN crystals doped with Er, Dy, Tb, Pr, Cu and Fe after γ -irradiation with a dose of 10^5 Gy. As seen from Fig. 4a, relatively small values of additional absorption are observed for Er (curve 1), Dy (curve 2) and Tb (curve 3), as compared to e.g. Pr (curve 4). Increase in Cu^{2+} concentration leads to a decrease in the additional absorption intensity. Irradiation of the crystal at 77 K changes the shape and decreases the values of the additional absorption band (curves 5 and 6). Increase in Fe^{3+} concentration leads to an increase in the additional absorption intensity and change their shape (curves 7 and 8). As shown in Fig. 4b, the influence of an increase in Dy^{3+} concentration in LN crystal has rather complex nature. Moreover a change in the Dy ion valency is seen (the band near 900-1000 nm - see KACZMAREK, et al. 1998 b). This change is visible as increase in absorption value inside range of absorption spectrum characteristic for given type of dopant (e.g. Dy^{3+} - 900-1000 nm). It is possible that Dy^{2+} ions exists in the as grown Dy: LN crystals.

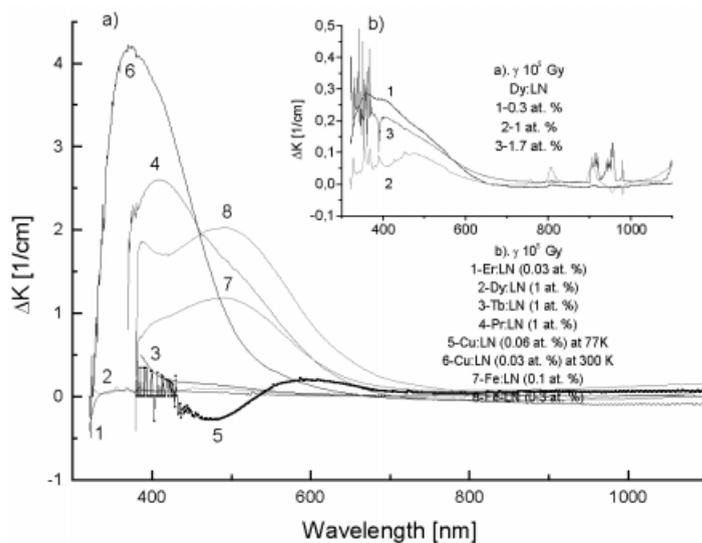


Fig. 4: Additional absorption bands in LiNbO_3 single crystals doped with (a) Cu, Fe, Pr, Tb, Dy and Er and (b) Dy after γ -irradiation with a dose of 10^5 Gy

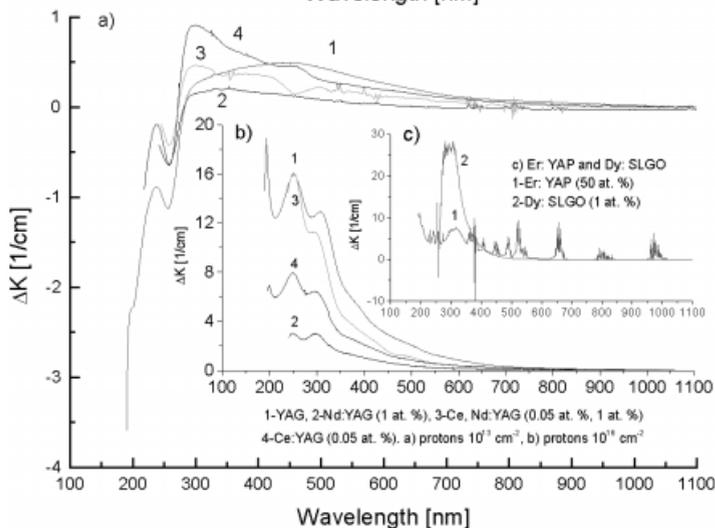


Fig. 5: Additional absorption bands in a pure and Ce, Nd and Ce,Nd doped YAG crystal after proton irradiation with a fluency of (a) 10^{13} and (b) 10^{16} cm $^{-2}$ and (c) in Er doped YAP and Dy doped SLGO crystals after proton irradiation with a fluency of 10^{16} cm $^{-2}$

Fig. 5 a and b presents the results of proton irradiations of pure YAG, Ce: YAG, Nd: YAG and Ce,Nd: YAG single crystals with fluencies of 10^{13} cm^{-2} (Fig. 5a) and 10^{16} cm^{-2} (Fig. 5b). Fig. 5c shows the same results as in Fig. 5b but for Er: YAP and Dy: SLGO single crystals. It may be seen from Fig. 5a that susceptibility of Nd:YAG crystals to proton irradiation is lower than that of γ -exposure. The properties of YAG crystals doped with Ce and double doped with Ce and Nd are more complex. More susceptible to proton irradiation is SLGO crystal (Fig. 5c, curve 2). For Er: YAP crystal a change in the valency of Er after proton irradiation is seen.

4. Summary

Oxide crystals doped with transition metals (e.g. V, Cr and Fe) are more susceptible to ionizing radiation than these doped with rare earth's. Ionizing radiations easily change the valency of these dopants. Also dopants with different valency from substituted ion (Mg^{2+} or Ca^{2+} substituting, e.g., Y^{3+}) strongly influence the absorption spectra of the investigated oxide compounds. Crystals containing Ce ions are high affected by irradiations but the mechanism of this phenomenon is more complicated.

Increase in Pr^{3+} concentration decreases the intensity and changes the shape of additional absorption bands in YAP and SLGO single crystals. Similarly, an increase in Dy^{3+} concentration affects SLGO and LN crystals. In contrast to the above mentioned dopants, increase in Nd^{3+} concentration in SLGO crystal and Fe^{3+} concentration in LN crystal leads to an increase in the intensity of additional absorption bands and changes their shape. Generally, doping with Nd of SLGO crystal gives a decrease in AA band maximum as compare to pure crystal.

After γ -radiation recharging process (change in valency) of the following dopants was observed: Er in YAP, Ce, V and Cr in YAG, Cr and Nd in SGGO, SLGO and BLGO, respectively, and Dy in LN crystals. Under proton radiation change in valency of Er in YAP and Ce in YAG crystals was stated.

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