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Radiation displacement defect formation in some complex oxide crystals

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Abstract

The work is devoted to an analysis of the formation processes of radiation displacement defects (RDDs) and color centers (CCs) under irradiation of complex oxide crystals. The results of the displacement process simulation as well as the analysis of the RDDs and CCs accumulation kinetics in some complex oxide crystals are presented. New experimental results on additional absorption spectra induced by neutron irradiation of $LiNbO_3$ (LNO) crystals doped with Fe and Cr and $YAlO_3$ (YAP) crystals doped with Nd and Er as well are presented. Dose dependencies are compared and their peculiarities are discussed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is known that color centers (CCs) formed under various kinds of irradiation (UV-light, γ-quanta, electrons, fast neutrons) have an essential influence on optical and output characteristics of complex oxide laser and nonlinear crystals (for example $YAlO_3$ (YAP), $Y_3Al_5O_{12}$ (YAG), $Gd_3Ga_5O_{12}$ (GGG), $LiNbO_3$ (LNO)) [1–4]. Unfortunately, the formation of displacement defects in complex oxide crystals is studied insufficiently. This work is devoted to the investigation of the radiation displacement defects (RDD) formation processes in YAP and LNO crystals.

2. Experimental details

The samples under investigation were cut from single crystals grown by the Czochralski technique in the form of flat plates with thicknesses of

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0.5–2 mm. The LNO:Cr crystal contained less than 0.02 wt.% of chromium and the LNO:Fe crystal contained 0.08 wt.% of iron. The neodymium content in YAP:Nd crystal was about 1 at%. The YAP:Er crystal had the nominal composition $Y_{0.5}Er_{0.5}AlO_3$.

The irradiation by electrons with an energy of 3.5 MeV was carried out in a linear accelerator with an integral fluence of the pulsed beam up to 10^{16} cm^{-2} (about 2×10^6 Gy absorbed dose). The neutron and γ-quanta irradiations were done in the IRT–5000 research nuclear reactor. The reactor γ-contour was a source of γ-quanta with an energy of 1.1 MeV and absorbed doses up to 8×10^5 Gy. The fast neutron irradiation was performed with fluences in the range of 10^{14}–5×10^{18} cm^{-2}. The temperature of the samples did not exceed 60°C during irradiation.

The absorption spectra were registered by the spectrophotometer ‘Specord M-40’. The reflection losses were not taken into account. The induced absorption was determined as the difference between the absorption coefficients after and before irradiation.

3. Results and discussion

The recharging of growth defects with increasing irradiation dose is limited by their quantity. An insignificant part of the radiation energy is lost in elastic collisions of radiation particles or secondary ones with crystal atoms. If the energy transmitted to an atom during the elastic scattering exceeds some value T_d, it is displaced. This model is known as the impact mechanism of the RDD formation and the energy T_d is named as threshold displacement energy. RDDs as well as growth defects may be recharged under the ionizing influence of radiation that leads to the creation of new defect centers. Unlike to the recharging of growth defects this process is not limited by the quantity of the defects because it increases with dose. Nevertheless, the accumulation of radiation defects and CCs on them may be limited by the annihilation of the components of Frenkel pairs. The general equations describing the dependencies of the concentration of RDDs $n_d(\Phi)$ and CCs $n(\Phi)$ on particle fluence Φ may be obtained as follows:

$$n_d(\Phi) = n_0 e^{-n_a \sigma_d v_r \Phi} + \left(1 - e^{-n_a \sigma_d v_r \Phi}\right)/v_r, \tag{1}$$

$$n(\Phi) = \frac{1}{v_r}\left(\left(1 - e^{-\sigma_I \Phi}\right) + \frac{\sigma_I (n_0 v_r - 1)}{\sigma_I - n_a \sigma_d v_r}\left(e^{-n_a \sigma_d v_r \Phi} - e^{-\sigma_I \Phi}\right)\right), \tag{2}$$

where n_a is the concentration of atoms, n_0 is the concentration of growth defects, σ_I and σ_d are the cross-sections for the ionization and the displacement processes, respectively, and v_r is the volume of the unstable zone. The corresponding dependencies are presented in the Fig. 1 together with some particular cases that explain the role of various factors in the type of the dose dependence. Because usually $\sigma_d \ll \sigma_I$, the CCs are formed by recharging of the growth defects mainly in the fluence range of $\Phi \ll 1/\sigma_I$ (curve 4 coincides with curve 5) and they are formed by recharging of RDDs when $\Phi \gg 1/\sigma_I$ (curve 4 coincides with curve 1).

To estimate the concentration of RDDs the simulation of the atom–atom collision cascades was used. The procedure taking into account the role of atoms of different kinds in the formation of displacements in each sublattice of the complex

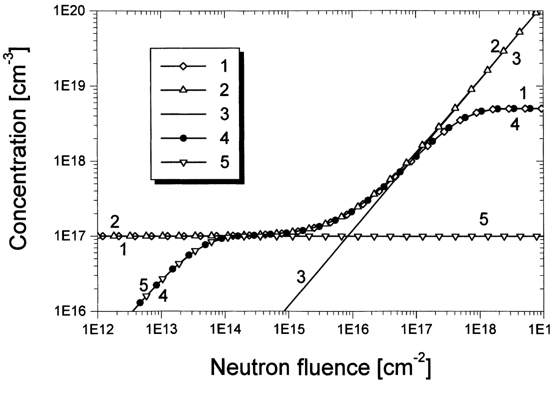

Fig. 1. Accumulation kinetics of radiation defects (1–3) and CCs (4 and 5). Curves 1 and 4 correspond to general case (Eqs. (1) and (2)). Other curves conform to particular cases: 2 – without anihilation ($v_r \to 0$); 3 – the same for $n_0 = 0$; 5 – the absence of RDD formation ($\sigma_d = 0, v_r \to 0$).

compound was described earlier in detail [5]. The T_d values taken for the calculation are listed in the Table 1. For Y, Al and Er they were assumed to be equal to those estimated for the GGG crystal [3]. The T_d value for oxygen in LNO was taken from [4] and the values for Li and Nb ions were varied in a wide range with maintaining its ratio equal to the valence ratio for these ions in the LNO crystal. As a result the accumulation rate was obtained for some crystals with garnet and perovskite-like structure presented in Table 1 confirming that the main part of RDDs are oxygen defects. The value $n_d/\Phi = n_a\sigma_d$ may be an estimation of the accumulation rate of CCs in the frame of the linear accumulation model (curve 3 in Fig. 1). As one can see from the table the uncertainty of the T_d value of the cations has a weak influence on the estimated concentration of the oxygen RDD.

Lithium niobate. The irradiation of LNO:Cr and LNO:Fe crystals with fast reactor neutrons leads to the induced absorption in the visible range of the spectrum (see Fig. 2) that looks like additional absorption (AA) induced by γ-quanta and electrons presented in Fig. 2 (see also [4,6]). The similar absorption structure testifies the identical nature of the CCs induced by radiation of various kind. But the absorption intensity after the neutron irradiation reaches much higher values.

There are some distinctions in the change of the induced absorption with increasing neutron fluence for LNO:Cr and LNO:Fe crystals. The dose dependencies of the induced absorption for wavelength of 475 nm (21050 cm^{-1}) are presented in Fig. 3. The induced absorption in the LNO:Cr crystal reaches the value of about 1.5 cm^{-1} already at a fluence of 10^{14} cm^{-2}, and remains nearly constant in the fluence range of 10^{14}–10^{16} cm^{-2}. In the case of the LNO:Fe crystal the induced absorption is practically unmeasurable at fluences less than 10^{16} cm^{-2}.

The level of AA induced by γ-quanta and electrons presented in Fig. 2 conforms approximately to the saturation of the ionizing recharging process [3]. The formation process of the RDDs becomes significant at increased doses of the high energy irradiation and causes the AA rise at much higher fluences of the irradiation [4,6]. The ionizing processes at the neutron irradiation take place due to the energy loss of charged secondary particles and accompanied γ-radiation. Thus, the

Table 1
The displacement defect concentration per unit fluence of irradiation particles in sublattices of some complex oxide crystals

Crystal	Atom	T_d (eV)	Electrons (3.5 MeV) n_d/Φ (cm^{-1})	Fast reactor neutrons n_d/Φ (cm^{-1})
$Gd_3Ga_5O_{12}$	Gd	66	0.413	1.92
	Ga	56	0.641	2.70
	O	40	1.285	19.45
$Y_3Al_5O_{12}$	Y	66	0.411	1.58
	Al	56	0.416	2.10
	O	40	1.526	14.62
$YAlO_3$	Y	66	0.578	2.39
	Al	56	0.356	2.08
	O	40	1.580	17.27
$Y_{0.5}Er_{0.5}AlO_3$	Y	66	0.291	1.19
	Er	66	0.326	0.91
	Al	56	0.353	2.02
	O	40	1.574	16.85
$LiNbO_3$	Li	5–25	0.28–1.26	2.97–7.09
	Nb	25–125	0.17–0.82	0.68–1.47
	O	53	0.99–1.04	11.5–12.0

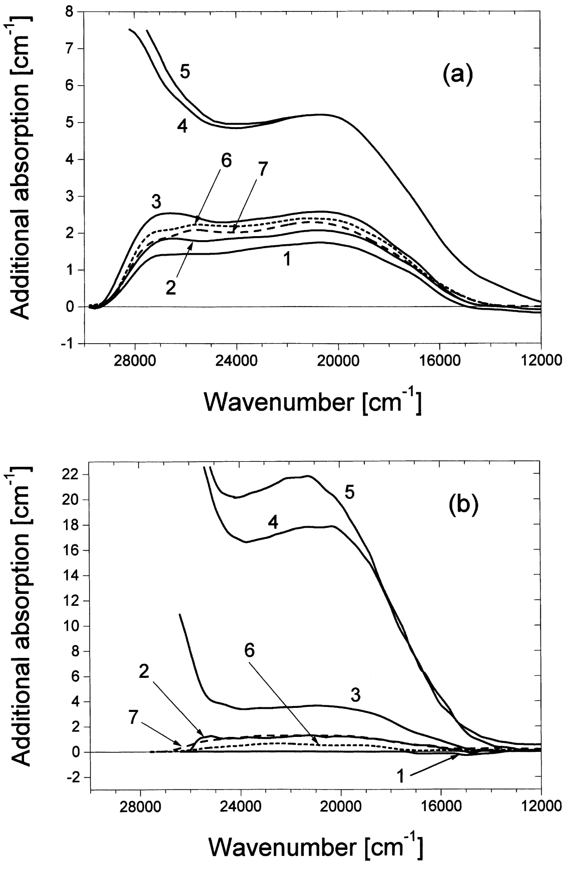

Fig. 2. The AA spectra of LNO : Cr (a) and LNO:Fe (b) crystals irradiated by fast reactor neutrons with fluences 10^{14} (1), 10^{16} (2), 10^{17} (3), 10^{18} (4) and 5×10^{18} cm^{-2} (5), γ-quanta (6) and by electrons (7).

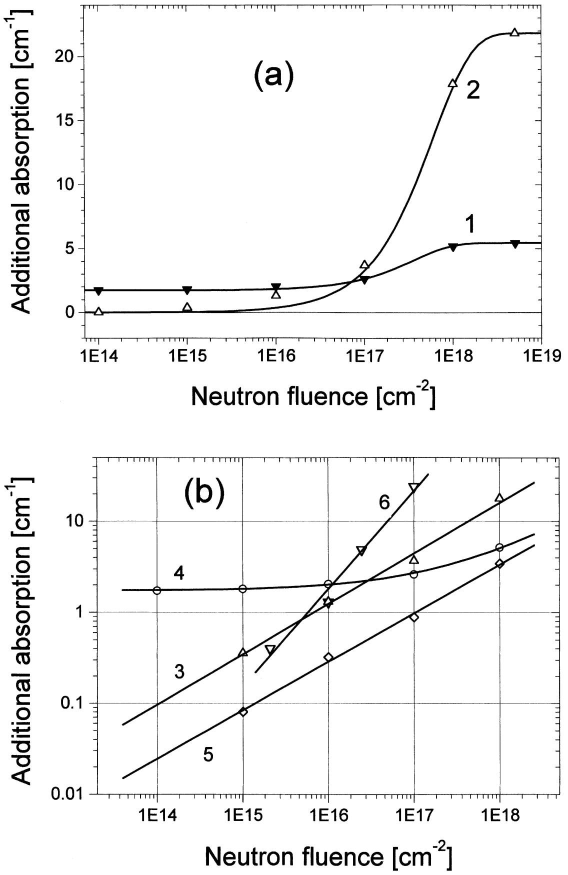

Fig. 3. The dose dependencies of AA in neutron irradiated crystals in semi-logarithmic (a) and double logarithmic (b) scales. The dose dependence of AA induced by irradiation at wavelength 475 nm in LNO : Cr (1,4,5) (5 is the absorption above the level at fluence 10^{14} cm^{-2}) and LNO : Fe (2,3) single crystals and at 300 nm in GGG (6).

presence of induced absorption in the LNO:Cr crystal already at a fluence of 10^{14} cm^{-2} should obviously be connected with an ionization of growth defects because, according to our calculations, the RDDs concentration at such fluence is too small ($\sim 10^{15}$ cm^{-3}). At that the value of this absorption is approximately equal to the AA saturation level at the ionizing recharging after γ- and electron irradiation. The RDDs concentration at neutron fluences of 10^{16}–10^{18} cm^{-2} reaches an essential value and the RDDs formation is responsible for the AA rise. In the case of the LNO:Fe crystal the AA is not observed at neutron fluences up to 10^{15} cm^{-2}. The induced absorption in this crystal after the 'soft' irradiation is considerably lower than in the LNO:Cr crystal at the same irradiation dose. Thus, the dose dependencies for both crystals coincide well with the CCs accumulation model (Eq. (2) and curve 4 in Fig. 1).

As it is seen from Fig. 3(a) the induced absorption has a saturation tendency at $\Phi > 10^{18}$ cm^{-2} in both crystals. This may be explained by the annihilation of the defects when their concentration reaches a considerable value. The approximation of the dose dependence of AA ($\Delta\alpha(\Phi)$) by the corresponding equation mentioned above allows to estimate the size of zones of instability of radiation defects in LNO crystals. The obtained volumes of these zones are 1.42×10^{-19} cm^3 for LNO:Fe and 2.35×10^{-19} cm^3 for LNO:Cr crystals. The dose dependencies in the double logarithmic scale at $\Phi < 10^{18}$ cm^{-2} are presented in Fig. 3(b). The lines 3 and 5 are linear approximations of the dose dependencies. As one can see the dose dependencies for LNO:Fe and LNO:Cr crystals differ from each other only by a parallel shift.

The RDDs formation rate at $\Phi < 10^{18}$ cm^{-2} may be considered as a constant one. It is defined by the concentration of the crystal atoms and the total cross-section for the displacement of the atoms of each sublattice. The latter one is defined by the T_d energy, the differential cross-section for the energy transfer and the cascade function which conforms to the number of RDDs per one neutron (see [5]). All mentioned parameters are determined by the main content of the crystal and cannot depend significantly on the presence of dopands. Both RDDs or CCs formed with RDDs participation due to recharging or the complex formation may reveal themselves in the optical absorption spectra. In the first case the concentrations of active optical centers must be equal for both LNO crystals. That is why we conclude that the CCs, responsible for the absorption induced by neutron irradiation, were formed during the secondary processes with the participation of RDDs. The same conclusion was made in [6] studying the destroying of radiation defects and induced CCs during annealing. The concentration of CCs formed during each particular process depends on its probability i.e. on its cross-section. The intensity of the induced absorption in the maximum of the band is proportional to the concentration of the corresponding CCs and to the oscillator strength of the optical transition. If we assume that the absorption at 475 nm is caused by CCs of the same type then the difference in the dose dependencies for the crystals investigated may be explained by different cross-sections of the same formation process of CCs or different oscillator strengths caused by the presence of dopands. An alternative explanation may be based on the assumption that different CCs in the same spectral region are formed in LNO crystals with different dopands.

The slope of the dose dependency in the double logarithmic scale (Fig. 3(b)) is one more peculiarity of the induced absorption in LNO crystals. The change of the scale factor of the variables when taking the logarithm of the $\Delta\alpha(\Phi)$ dependence leads only to a parallel shift of the curves. Its slope gives an information about the type of CCs accumulation kinetics. The formation process of the CCs may be considered as a quasi-chemical reaction. To find the reaction order we have used a linear approximation of the dependence $\lg(\Delta\alpha)$ vs $\lg(\Phi)$ at low fluences ($\Phi \leqslant 10^{18}$ cm^{-2}). It can be shown that the quasi-chemical reaction order is connected with the slope coefficient $A = \lg(\Delta\alpha)/\lg(\Phi)$ by the simple relation: $N = 1 - 1/A$. Then the kinetics of the change of the CC concentration is described in the form of $\mathrm{d}n_c/\mathrm{d}\Phi \sim n_c^N$. The estimation shows that the reaction orders for both LNO crystals are practically the same ($N \approx -0.8$), that indicates the similarity of the CC formation processes for the crystals under investigation. The dose dependence of the induced absorption risen in the GGG crystal at wavelength of 300 nm ($\sim$33300 cm^{-1}) after neutron irradiation as a result of the formation of RDDs [3] is presented in Fig. 3(b) (curve 6) for comparison. The reaction order for the GGG crystal is very near to zero, that corresponds to a reaction with constant velocity. Analogous observations were made in [7] with the irradiation of corundum crystals. In the case of the formation of CCs such kinetics can describe the accumulation of CCs directly on single RDDs that are created with constant rate (see curve 5 in Fig. 1). Another situation is observed in the LNO:Fe and LNO:Cr crystals in which the rate of the change of the concentration of the CCs decreases with increasing concentration by the law $\mathrm{d}n_c/\mathrm{d}\Phi \sim 1/n_c^{0.8}$. The last dependence indicates the decrease of the cross-section for the formation of the CCs with increasing CC concentration. The investigations carried out do not allow us to give the reason of such a behavior of the dose dependencies of AA in LNO crystals. Nevertheless, one can assume that such behavior is a result of the Debye–Hückel screening effect [8] during the interaction of the charged defects, that leads to a decrease of its ionization cross-section with increasing defect concentration.

Yttrium aluminium perovskite. The irradiation of YAP:Nd and YAP:Er crystals by fast neutrons leads to the induced absorption (Fig. 4) with maxima at 42000 cm^{-1}, 33000 cm^{-1}, 23000 cm^{-1} and 20000 cm^{-1}. AA spectra of YAP crystals of the same structure and intensity are observed after γ- and electron irradiation. The AA intensity depends weakly on the neutron fluence in the range of 10^{14}–10^{17} cm^{-2}. The similar structure of the AA indicates the same nature of CCs created in YAP crystals under irradiation of various kinds (γ-quanta, electrons and neutrons) with doses mentioned above.

The AA intensity grows rapidly and the broadening of the shortwave absorption edge takes place at neutron irradiation with a fluence of about 10^{18} cm^{-2}. It indicates the appearance of new radiation defects in the irradiated crystals. The concentration of the displacement defects at a neutron fluence of 10^{18} cm^{-2} is about 2×10^{19} cm^{-3} (see Table 1) and the main part of them are oxygen vacancies. So, the RDDs in the oxygen sublattice should be responsible for the revealed AA growth.

The deceleration of the AA rise is found at a neutron fluence of $\sim 5 \times 10^{18}$ cm^{-2} that indicates the saturation of the RDD formation process as it was observed also in LNO crystals. Due to the high optical density of irradiated samples we could not obtain the dose dependencies in the maxima of the AA bands.

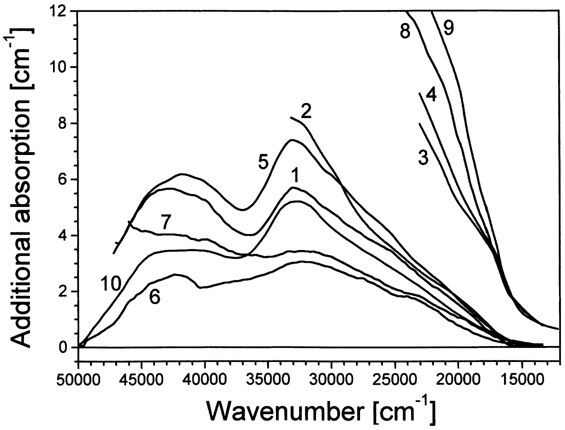

Fig. 4. The AA spectrum of YAP : Nd (1–5) and YAP:Er (6–10) crystals irradiated by fast reactor neutrons with fluence 10^{15} (1,6), 10^{17} (2,7), 10^{18} (3,8) and 5×10^{18} cm^{-2} (4,9) and by electrons with energy $E_e = 3.5$ MeV and fluence 10^{16} cm^{-2} (5,10).

It should be emphasized that the AA intensity is higher in YAP:Nd crystals after irradiation with a neutron fluence of 10^{14} cm^{-2} than in YAP:Er crystals, but the reverse behavior is observed at a fluence of 10^{18} cm^{-2} when the RDDs are formed. Like in LNO crystals it testifies that the impurity presence can play an important role in the CC formation because the concentration of RDDs is nearly the same in both YAP crystals studied.

4. Conclusions

The calculated concentrations of the RDDs in crystals of complex oxides show that they are formed most effectively in the oxygen sublattice (Table 1). The formation of the single displacement defects in LNO and YAP crystals saturates at a neutron fluence higher than 10^{18} cm^{-2}. The analysis of accumulation kinetics of CCs formed on growth and radiation defects shows that in the general case there are two regions of saturation. The first of them takes place at lower fluences and corresponds to saturation of the recharging process of the growth defects. The second one occurs at higher fluences and conforms to the equilibrium between the formation of the RDD and the annihilation of their components. The expressions obtained from the analysis allow to describe satisfactorily the dose dependencies obtained experimentally for LNO crystals and to get an estimation of the dimension of the instability zone for RDD.

The created RDDs participate in the formation of optically active CCs as well as the growth defects and impurities. The comparison of absorption induced by neutron irradiation in the LNO and YAP crystals with the AA induced by γ-irradiation or electrons confirm that practically the same CCs are formed in both cases. On the other hand the comparison of the behavior of crystals with different impurity contents shows that the AA caused by the formation of RDDs can differ significantly in its intensity while the structure of the spectrum remains generally the same. This fact can be explained by the suggestion that the CC formation proceeds in secondary processes that are significantly affected by the presence of impurities. The difference in the dimensions of the annihilation zone of the Frenkel pairs in the LNO:Cr and LNO:Fe crystals confirms this suggestion too.

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