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Controlling of the charge states in laser crystals

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ABSTRACT

In this paper changes in active and lattice ions valence were investigated in some laser materials such as: Cr: Y₃Al₅O₁₂, Cr:LiNbO₃ and Cr:Li₂B₄O₇ glass, Ti:Al₂O₃ and Ti:LaGaO₃, Co:SrLaGa₃O₇ and Co:Li₂B₄O₇ glass, Eu, Dy: Li₂B₄O₇ glass, Ho:LiTaO₃, Nd:YVO₄, Nd: SrLaGa₃O₇ and Pr: SrLaGa₃O₇ after annealing in oxidizing and reducing atmospheres, ionizing with gamma, electrons and protons. After γ -irradiation 446 nm emission is observed for Ti:LaGaO₃ single crystal due to ${}^2E \rightarrow {}^2T_2$ transition of Ti³⁺.

Keywords: laser crystals, γ -irradiation, Cr doped crystals

1. INTRODUCTION

In the past decade, the renewal in the search of new laser materials covering wide spectrum from ultraviolet to infrared has been very strong and the demand of various applications in many areas is increased. In many lasing materials there arise, however, not only intentional active dopant but also dopants with other valence states. As an example one can take into account Cr doped crystals. In some of them there may exist chromium in: 2+, 3+, 4+, 5+ and 6+ states. The last state is very unstable and exist in oxide complexes only, e.g. Cr⁶⁺O₄ (e.g. in Li₂B₄O₇ glasses), while other are stable and influence laser characteristics of different materials¹⁻².

Generally annealing in the air (in normal pressure) leads to the increase in valence of uncontrolled or active impurity (Cr³⁺:Y₃Al₅O₁₂, Nd³⁺:Y₃Al₅O₁₂), while gamma, electron and proton irradiation (or annealing in reducing atmosphere), due to ion recombination with secondary or primary electrons (or reduction), leads to the decrease in valence (Cr⁴⁺:Y₃Al₅O₁₂)³. There are some ions, although which are ionized by gamma, electrons and protons (Co²⁺:SrLaGa₃O₇, Cr³⁺:Y₃Al₅O₁₂). It depends on a previous treatment (starting defect structure), local symmetry of an ion and crystal field.

In this paper we show changes in optical properties of some laser materials observed after ionizing radiation or annealing treatment and their possible influence on performance of opto-electronic devices.

2. EXPERIMENTAL

The following crystals were investigated: Y₃Al₅O₁₂ (YAG), SrLaGa₃O₇ (SLGO), LiNbO₃ (LN), LiTaO₃ (LT), LaGaO₃, Al₂O₃ and Li₂B₄O₇ (LBO) glass. They were obtained in the Institute of Electronic Materials Technology, Institute of Physics of the Polish Academy of Sciences and Institute of Physics Military University of Technology in Warsaw. The as grown crystals and glasses were cut and polished into samples with approximate dimensions: about 10 mm in length and 1 mm thick.

Using various ⁶⁰Co sources the samples were irradiated by γ -rays in the Institute of Chemistry and Nuclear Technology (ICNT) in Warsaw, Poland. For the electron irradiation a 300 keV or 1 MeV beams from the Van de Graaf accelerator of the ICNT were used, while for irradiation with 21 MeV protons a beam from compact isochronous proton cyclotron installed in the Soltan Institute of Nuclear Studies, Świerk, was applied.

The dose of γ -irradiation was varied from 10² to 10⁷ Gy, fluency of electrons was varied from 10¹⁴ to 5*10¹⁶ particles/cm², and protons fluencies from 5*10¹² to 10¹⁶ particles/cm² were applied.

Annealing was performed in three regimes: (i) thermal relaxation by annealing in the air at 400°C for YAG and at 800°C for LN and LT, for 3 hours in order to remove radiation defects, (ii) annealing in the range 1100-1400°C for 3 h in air (an oxidizing atmosphere) in order to change the defect structure of a crystal, and (iii) annealing in a mixture of hydrogen and nitrogen (a reducing atmosphere) at 1200°C for 0.5-2 h.

Optical transmission spectra were recorded before and after each irradiation or thermal treatment of the samples using LAMBDA-900 PERKIN-ELMER, and FTIR 1725 PERKIN-ELMER spectrophotometers. The induced additional absorption (AA) was calculated from the formula:

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

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where K is the absorption, d is the sample thickness, and T_1 and T_2 are the optical transmissions of a sample before and after irradiation or annealing treatment, respectively.

Photoluminescence was recorded using PERKIN-ELMER spectrofluorimeter. Radioluminescence spectra were measured in the range 200-850 nm using excitation with X-rays (DRON, 35 kV / 25 mA) and Spectrograph: ARC SpectraPro-500i (Hol-UV 1200 gr/mm grating, 0.5 mm slits), PMT: Hamamatsu R928 (1000 V).

The dimensions of samples for ESR investigation were the following 3.5x3.5x2 mm. They were investigated in the Bruker ESP300 ESR spectrometer (X-band). The spectrometer was equipped with helium flow cryostat type ESR900 Oxford Instruments. The ESR investigations were performed in the temperature range from 4 to 35 K and microwave power from 0.002 to 200 mW.

3. RESULTS

Fig. 1 shows the absorption (K) – curves 1 and 3 and changes in the absorption (ΔK) (curve 2) for Cr^{4+} (Cr^{4+} : YAG crystal, curve 1) and Cr^{3+} doped YAG crystals (curve 3 - after annealing of Cr^{4+} : YAG crystal in reducing atmosphere). The "as-grown" Cr^{4+} : YAG crystal was black in color, while the Cr^{3+} : YAG one was green. As it is seen from absorption curves both crystals contain a dopant of second type (Cr^{4+} : YAG crystal contains also Cr^{3+} and Cr^{3+} : YAG crystal contains also Cr^{4+}). The dashed lines mark the positions of absorption bands characteristic for a given type of the active dopant.

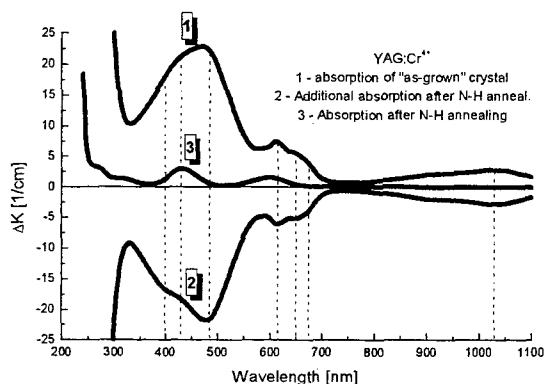


Fig. 1. Absorption coefficient of YAG single crystal doped with chromium 4+ and 3+

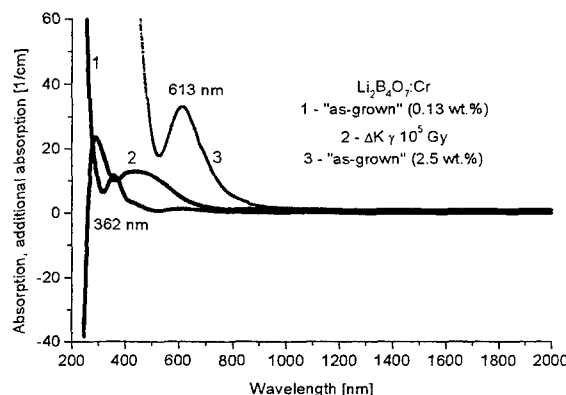


Fig. 2. Absorption (1, 3) and additional absorption (2) of Cr doped (0.15wt.% - 3+ and 6+ - and 2.5wt.% - 3+) $\text{Li}_2\text{B}_4\text{O}_7$ glass

Thus, annealing of the crystal in reducing atmosphere (curve 3), leads to a decrease in concentration of Cr^{4+} ions, due to reduction ($\text{Cr}^{4+} \rightarrow \text{Cr}^{3+}$).

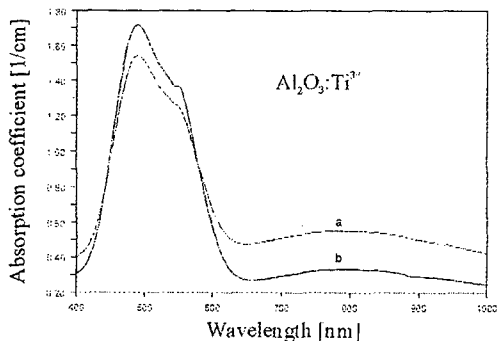


Fig. 3. Absorption coefficient of $\text{Al}_2\text{O}_3:\text{Ti}$ (3+, 4+)

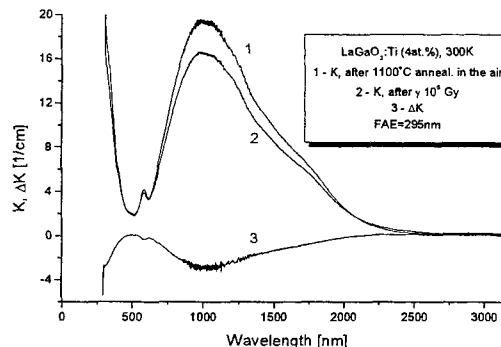
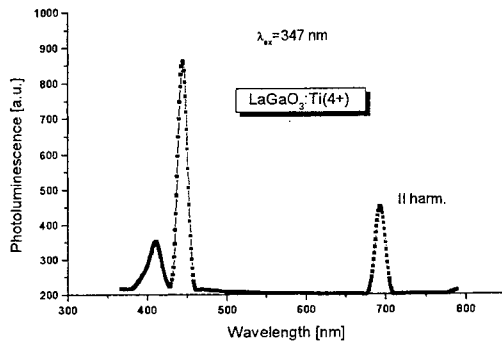


Fig. 4. Absorption coefficient of $\text{LaGaO}_3:\text{Ti}$ (3+, 4+) before (1) and after (2) γ -irradiation with a dose of 10^5 Gy and additional absorption (3)

In the 0.15wt% chromium doped LBO glass (Fig. 2, curve 1) we observe Cr^{3+} and Cr^{6+} ions spectra⁴. Fundamental absorption edge of the glass is equal to 245 nm and lattice absorption origin at 2700 nm. The Cr^{3+} ion has two absorption bands centered at about 430 and 614 nm due to d-d transition: the former was attributed to the spin-allowed but parity forbidden ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ transition and the latter to the spin-allowed but parity-forbidden ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ transition. The Cr^{6+} ion has strong absorption band centered at 358 nm and a weak one at 318 nm. It seems that these bands refer to Cr^{6+}O_4 complex of 3d^0 configuration rather than to Cr^{6+} ion². Curve 2 shows additional absorption of the glass after 10^5 Gy γ -rays. There are seen at least two bands in the additional absorption centered at about 297 and 450 nm. Curve 3 shows the absorption of highly doped with Cr (2.5wt.%) $\text{Li}_2\text{B}_4\text{O}_7$ glass. One can see that in case of high doping only 614 nm band due to ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ transition in Cr^{3+} ions is present.

a).



b).

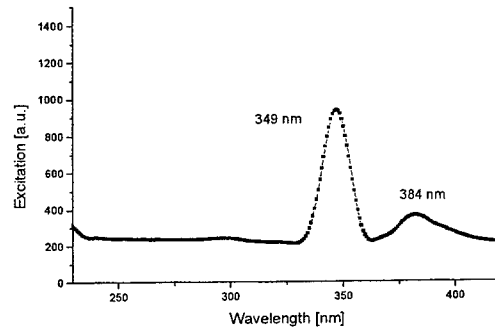


Fig. 5. Photoluminescence (a) of $\text{LaGaO}_3:\text{Ti}(3+,4+)$ single crystal after gamma irradiation with a dose of 10^5 Gy, $\lambda_{\text{ex}} = 347$ nm, and excitation spectrum (b) of 446 nm emission.

Fig. 3 present results of absorption measurements for $\text{Ti}:\text{Al}_2\text{O}_3$ single crystal before (a) and after (b) annealing in reducing atmosphere. As one can see figure of merit (FOM) is two times greater for the annealed crystal than for "as-grown"⁵. It means that annealing in reducing atmosphere leads simply to change in titanium valence $\text{Ti}^{4+} \rightarrow \text{Ti}^{3+}$ without other changes characteristic for the ions diffusion. In Fig. 4 one can see absorption of mainly Ti^{4+} doped LaGaO_3 single crystal (curve 1). In this case annealing in oxidizing atmosphere also leads to valence change of titanium ions. It is seen especially in the change of crystal coloration (from light green to almost transparent). Irradiation with gamma quanta changes amount of Ti^{4+} ions as can be seen in curves 2 and 3. But not only. As is seen from Fig. 4 some lightening of the crystal in the UV range is observed.

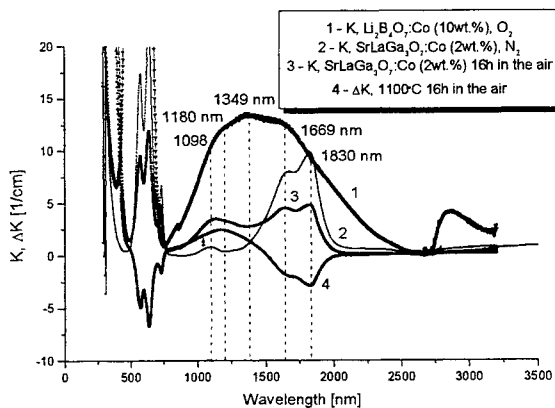


Fig. 6. Absorption coefficient of LBO glass and $\text{SrLaGa}_3\text{O}_7$ single crystal doped with cobalt 2+ and 3+

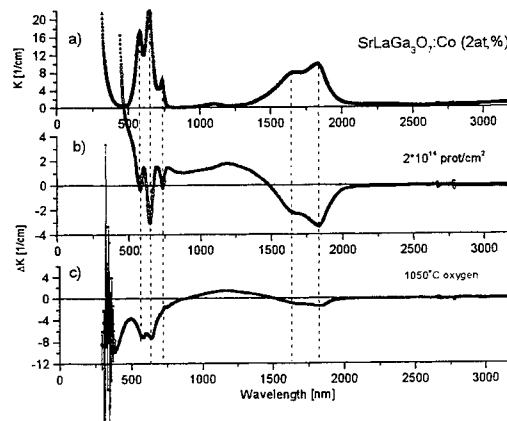


Fig. 7. Absorption (a) and additional absorption of $\text{SrLaGa}_3\text{O}_7:\text{Co}$ single crystal after $2 \cdot 10^{14}$ protons/cm² (b) and subsequent annealing at 1050°C in the oxygen (c)

This lightening leads to arising of some emission in the visible range of emission spectrum (382, 414 and 446 nm bands excited with bands peaked at 304, 339, 374 nm, respectively, Fig. 5). The emission is probably due to ${}^2E \rightarrow {}^2T_2$ transition of Ti^{3+} ions ⁶.

In Fig. 6 absorption of LBO glass doped with cobalt in oxidizing atmosphere (1) as compare to Co:SLGO obtained in reducing atmosphere (2) is shown. In the first case Co^{2+} and Co^{3+} ions are seen in the absorption spectrum. In second one Co^{3+} ions arise only after annealing of the crystal in the oxygen (3). Additional absorption curve (4) indicate probable absorption peak of ${}^5T_2 \rightarrow {}^5E$ transition inside Co^{3+} ion of octahedral coordination. In this case ⁷ change in a valence takes place due to ionization $Co^{2+} \rightarrow Co^{3+}$. This fact is confirmed by Fig. 6, where absorption (a), additional absorption after proton irradiation (b) and subsequent additional absorption after annealing in the oxygen are presented.

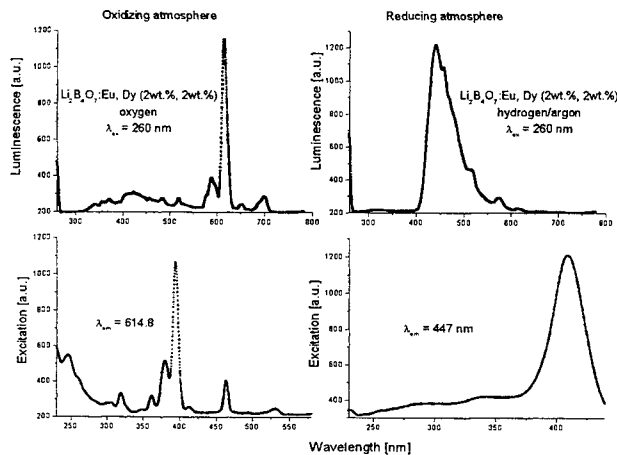


Fig. 8. Photoluminescence and excitation of LBO glass obtained at different growth atmospheres

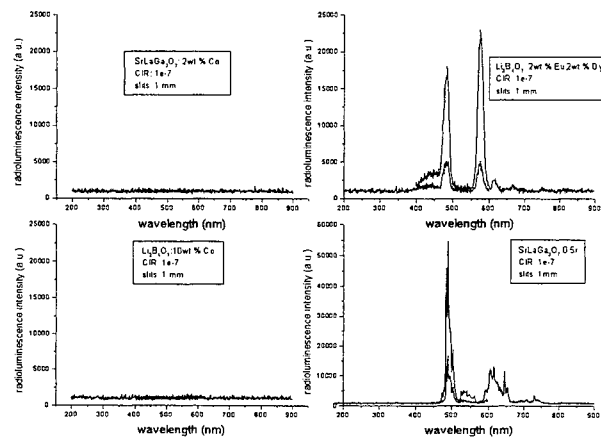


Fig. 9. Radioluminescence of LBO glass and $SrLaGa_3O_7$ single crystal doped with Co, Eu, Dy and Pr

Fig. 8 shows results of excitation-emission measurements for Eu and Dy doped LBO glass in two cases: oxidizing and reducing growth atmosphere. As one can see dependently on the type of atmosphere Eu^{2+} or Eu^{3+} doping takes place. Fig. 9 presents radioluminescence measurements for LBO glass doped with Co and Eu, Dy (reducing atmosphere) and SLGO single crystal doped with Co and Pr. As one can see Co ions does not give any emission in the range up to 900 nm for both cases, moreover, emission of Eu, Dy: LBO glass has other shape than photoluminescence for the glass seen in Fig. 7. It means that not only active dopant concentration has influence on sample emission. Very important factor is also effectivity of energy transfer from lattice to active dopant ion. In the case of Pr: SLGO single crystal the latter is very high.

In Fig. 10 one can see ESR spectra of Cr, Mn: LN single crystal also influenced by gamma and electron irradiation. As is seen only electron irradiation changes Mn valence ionizing it to Mn^{3+} state. Mn was uncontrolled dopant in the crystal. In Fig. 11 radiation defect seen as additional ESR spectrum is presented. As it was shown elsewhere ⁸ this defect is connected with $Ga^{3+} \rightarrow Ga^{2+}$ transition of lattice ion.

Fig. 12 shows absorption (1) and additional absorption (2-4) for Ho: LT single crystal after γ -irradiation (2), subsequent annealing at 800°C (3) and annealing in reducing atmosphere (4) at 1200°C. As is seen, some part (about 10%) of Ho ions changes valence under γ -irradiation⁹. This change is reversible after annealing in the air. Annealing in hydrogen does not give univocal changes.

Fig. 13 presents result of the annealing of Nd:YVO₄ single crystal in reducing H₂ atmosphere. As one can see structural transition take place to Nd:YVO₃ crystal where vanadium is of 3+ valence as compare to previous 5+, according to ref [10]. This is one more case (see Fig. 11), where lattice ion changed your valence. Similar situation took place also for LN single crystal underwent to gamma or proton irradiation when Nb^{4+} ion pairs are observed¹¹.

4. DISCUSSION

Chromium and magnesium doped YAG crystal (Fig. 1) reveals the simultaneous presence of 3+ and 4+ chromium ions the amount of which may be changed by proper annealing process.

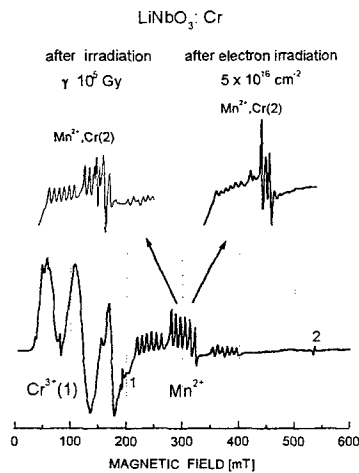


Fig. 10. ESR spectra of LiNbO_3 single crystal doped Cr^{3+} and Mn^{2+} before and after gamma (10^5 Gy) and electron ($5 \times 10^{16} \text{cm}^{-2}$) irradiation

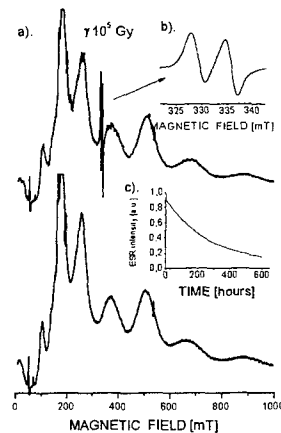


Fig. 11. ESR spectra of $\text{SrLaGa}_3\text{O}_7:\text{Nd}$ single crystal before and after γ -irradiation (a), additional ESR line (b) and time quenching (c)

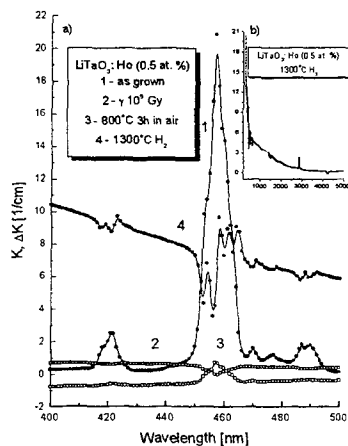


Fig. 12. Absorption (1a) and additional absorption after gamma irradiation (2a), subsequent annealing at 800°C in the air (3a) and annealing in hydrogen at 1300°C (4a and b) of LiTaO_3 single crystal doped with Ho (0.5at.%)

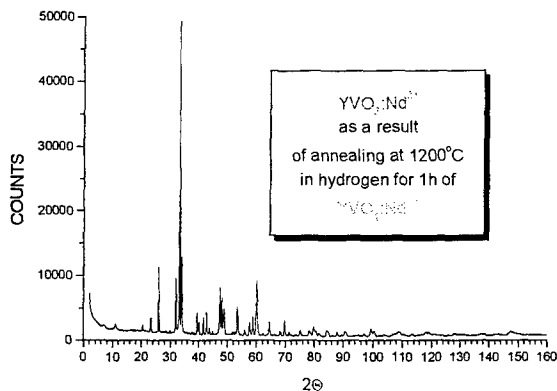


Fig. 13. Structural transition in $\text{YVO}_4:\text{Nd}^{3+}$ single crystal under H_2 annealing

Chromium doped lithium tetraborate glass (Fig. 2) (low doping) shows classical 3+ absorption and, for 362 nm absorption of Cr^{6+}O_4 complex. After gamma irradiation this complex disintegrates for Cr^{3+} and Cr^{4+} . The same glass highly doped with chromium reveal only 613 nm absorption. Analyzing low and high doping in case of $\text{Li}_2\text{B}_4\text{O}_7$ glass one can state that there exists compositional dependence of the valence states of Cr ions in the glasses. In ² it was stated that the contents of Cr^{3+} and Cr^{6+} vary systematically with basicity in the silicate and borate glasses.

Titanium doping of the both crystals (Fig. 3-5) simultaneously shows the presence of 3+ and 4+ ions the relevant amount of which may be changed by proper annealing procedure. Gamma irradiation may lead to significant change of emission properties of $\text{LaGaO}_3:\text{Ti}$ single crystal.

SLGO:Co "as-grown" single crystal (Fig. 6-7) seems to be doped with 2+ cobalt only but it is possible to change a half of these ions to 3+ state by ionizing with gamma, electrons, protons or annealing in oxidizing atmosphere. Opposite to

it wide absorption bands seen in the visible as well as IR parts of the absorption spectrum of LBO:Co glass suggest the presence of both Co^{2+} and Co^{3+} ions simultaneously.

Luminescence and radioluminescence spectra of LBO:Eu glass (Fig. 8-9) confirm dependence of europium valence on the atmosphere of growth. Moreover, radioluminescence spectra indicate high efficiency of energy transfer from lattice ions to active dopants in case of Eu, Dy: LBO glass and Pr: SLGO single crystal and low one in the case of Co: LBO glass and Co: SLGO single crystal.

Different type of radiation in other way acts on the investigated crystals leading to recombination and/or ionization phenomena or Frenkel defects. Especially change in a valence of uncontrolled but optically active dopant (Mn) takes place (Fig. 10) and sometimes change in a valence of lattice ion (Ga) (Fig. 11).

Simple recombination with Compton electrons was observed for Ho: LT irradiated with gamma quanta (Fig. 12) giving increase in amount of Ho^{2+} ions. The change of valence was confirmed by annealing treatment. In case of YVO_4 crystal doped with Nd (Fig. 13) annealing in reducing atmosphere leads to a structural transition observed in raw powder diffraction pattern.

5. CONCLUSIONS

Generally, annealing in the air leads to an increase in valence of uncontrolled or active impurity (Cr^{3+} :YAG), while γ , electron or proton irradiation (or annealing in reducing atmosphere) (Cr^{4+} :YAG), due to ion recombination with secondary Compton or delta electrons (or reduction), leads to a decrease in valence (Fig. 1). However there are some ions, which are ionized by gamma quanta (Cr^{3+} :YAG, Co^{2+} :SLGO) due to the Compton interaction. In particular case recharging depends on a previous treatment, local symmetry of ion, and crystal field. Protons can also interact similarly as gamma rays. The only difference in the mechanisms of their interaction with oxide crystals is the source of secondary electrons or, ionization mechanism.

Different treatments (annealing in reducing or oxidizing atmospheres, irradiation) produce different characteristic defects. They may be CC's, such as F, F^+ , F^- , F^{2+} , F^{2-} , polarons, trapped holes, AA bands attributed to recharged active dopants (Co^{2+} , Pr^{3+} , Ho^{3+} , Cr^{3+} , Eu^{2+} , Ti^{3+}), uncontrolled ions (Mn^{2+} , Fe^{3+} , Fe^{2+}) or lattice ions (Ga^{2+} , Nb^{4+} , V^{3+}).

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