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DEFECTS FORMATION IN SPINEL CRYSTALS UNDER ELECTRON AND GAMMA BEAM IRRADIATION

S.P. Gokov*, V.T. Gritsyna, S.S. Kochetov*, V.I. Kasilov*, Yu.G. Kazarinov

V.N. Karazin Kharkov National University, Kharkov, Ukraine;

****National Scientific Center "Kharkov Institute of Physics and Technology", Kharkov, Ukraine***

There were investigated the optical absorption centers formation in magnesium aluminate spinel crystals at the action of high energy gamma or electron beams. It was revealed that at gamma irradiation the most probably the hole centers are formed to compare with that in electron irradiation. At electron beam irradiation the temperature of sample was raised which leads to thermal annealing of unstable radiation-induced centers.

INTRODUCTION

The study of the radiation effects in oxide ceramics of potential use in nuclear industries appears to be a major challenge in the next decades [1]. In the long list of recommended oxides magnesium aluminates spinel ($MgAl_2O_4$ or $MgO{\cdot}Al_2O_3$) possesses especial position because of high resistance to displacive irradiation [2]. Despite of many publications devoted to radiation effects in spinel crystals the effect of composition of spinel crystals on sensitivity to ionizing irradiation practically has not been investigated. The specific feature of this compound consist in possibility to form spinel structure in the wide range of constituent oxides MgO and Al_2O_3 that can be written as $MgO{\cdot}nAl_2O_3$ where n=1…7. In spinel with n>1.0 (non-stoichiometric composition) the additional cationic vacancies are formed predominantly in octahedral sites for charge compensation. Therefore, non-stoichiometric spinel is more defective material to compare with stoichiometric one.

Under high energy ionizing irradiation such as gamma-rays or fast electrons the process of optical center formation goes through creation of free charge carriers with subsequent trapping by defects and impurity ions.

The aim on this research is to reveal the influence of type of irradiation on the formation of defects in anion or cation sub-lattices of spinel crystals of different composition through the measurements the optical absorption spectra of irradiated spinel crystals of different compositions.

Spinel crystals were grown by Verneuil or Czochralski methods from nominally pure initial materials of different composition $MgO{\cdot}nAl_2O_3$ with n=1.0, 1.5, 2.0, 2.5. Previous investigations of radiation induced optical centers gave a possibility to identify the absorption bands with corresponding lattice defects. Absorption band at 5.3 eV is related to F-centers, i.e. anion vacancies captured two electrons [3]; absorption band 4.75 eV is related to F^+-centers, also anion vacancies but captured one electron [4]; 4.2 eV absorption band was tentatively identified with electron centers formed at positively charged anti-site defects.

Absorption of spectra at photon energy lower 4 eV contains many overlapping bands which were identified with different types of hole centers, i.e. cationic vacancies and negatively charged anti-site defects captured one or more holes. Mostly comprehensive investigations of V-type centers were provided by Ibarra et al. [5,6]. Partial annealing and optical bleaching of spinel samples allow them to distinguish the existence of specific bands in this spectral range: 2.7, 3.4, and 3.8 eV. Earlier some indication was obtained on the existence of the slightly different energy of absorption bands: 2.8, 3.1, 3.6, and 3.9 eV [7]. Finally, absorption at high photon energy (E_{ph}<6 eV) most probably caused by transitions in impurities ions [8].

In this paper we present results of comparative investigations of optical center formation under influence of high energy gamma or electron beam in magnesium aluminate spinel crystals of compositions $MgO{\cdot}nAl_2O_3$ with n=1.0, 1.5, 2.0, 2.5.

EXPERIMENTAL PROCEDURE

Irradiation of spinel samples with electron beam was provided at linear accelerator LUE-300 with nominal electron energy of 30 MeV. There was used deflected output which allows to decrease the energy spread of electron beam and contribution of bremsstrahlung gamma-rays at irradiation. The energy of electron was 16 MeV, the beam current about 10 $\mu A/cm^2$ and fluence $3{\cdot}10^{16}$ $electrons/cm^2$.

The irradiation with gamma beam was provided at strait output to increase the irradiation dose. Gamma-rays were generated by conversion of electrons with energy of 7 MeV in tantalum target with thickness of 2.0 mm. Using deflecting magnet the gamma component was separated from electrons. Gamma-beam was formed using collimator and was directed to targets. Electron fluence on conversion target was $3.4{\cdot}10^{17}$ electrons, which corresponds to 10^{16} gamma $quant/cm^2$ on samples under investigation.

RESULTS AND DISCUSSION

The absorption spectra of pristine crystals have no definite bands indicating the absence of large amount of impurities. In the gamma-ray-irradiated samples the absorption spectra contains several overlapping bands which form maxima at approximately 3.1 and 5.0 eV (Fig. 1). Therefore we conclude that under gamma irradiation both types of the hole and electron centers formed but different intensity. The absolute value of absorption due to hole centers (E_{ph}<4 eV) practically the same in spinels of different composition, also absorption due to electron centers very different.

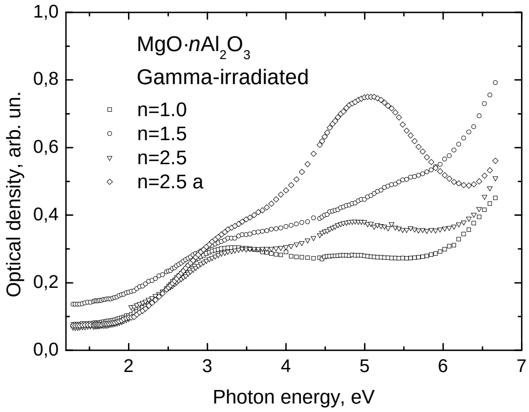

Fig. 1. Absorption spectra of spinel crystals of different compositions irradiated with gamma-rays

To derive the contribution of initial absorption to that of irradiated samples we present the differential spectra (Fig.2). Each spectrum represents the difference of absorption of irradiated and non-irradiated crystals for every composition of crystal. These spectra were separated into Gaussians and absorption bands at 3.1, 3.8 and 4.75 eV were found which were identified with centers at cationic vacancies (3.1 eV), positively charged anti-site defects (3.8 eV) and F^+-centers [9]. The positive difference of absorption indicates that intensity of the given absorption band at irradiation increases. Therefore it is clearly seen, that contribution of hole centers is overwhelming and stable for each crystal. At the same time absorption in the vicinity of photons energy corresponding to F-centers and impurities becomes negative. It means that main contribution of absorption in this spectral region is originated from the charge change of uncontrolled impurity ions.

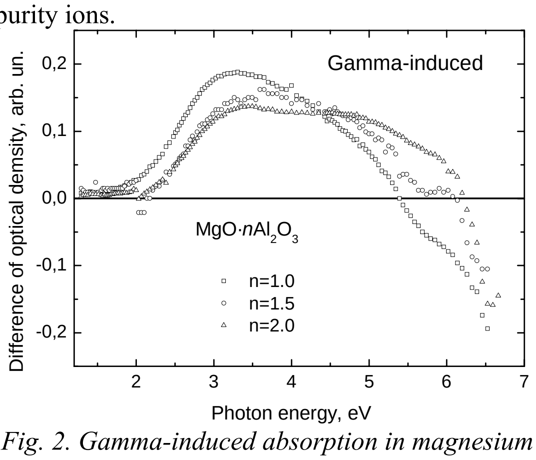

Fig. 2. Gamma-induced absorption in magnesium aluminate spinel of different compositions

The irradiation with electrons was provided at density current about 10 μA/cm^2 which causes raising temperature of samples up to 200 °C. Therefore, during irradiation only that centers and defects survive which are stable at the temperature below 200 °C. According to previous investigation [10] the stability of hole centers is lower to compare with that of electron ones. From Fig.3 one can see very low absorption in the spectral range of lower 4.0 eV confirming the thermally stimulated destruction of hole centers during high energy electron irradiation.

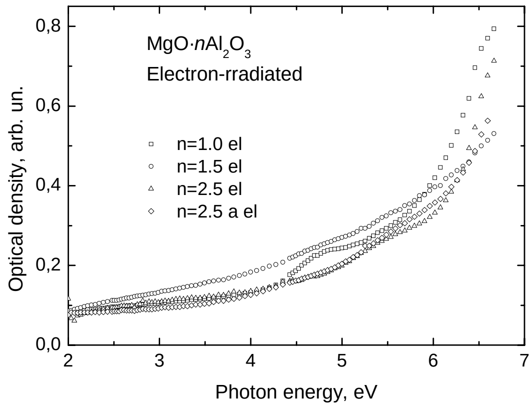

Fig. 3. Absorption spectra of electron irradiated spinel samples of different compositions

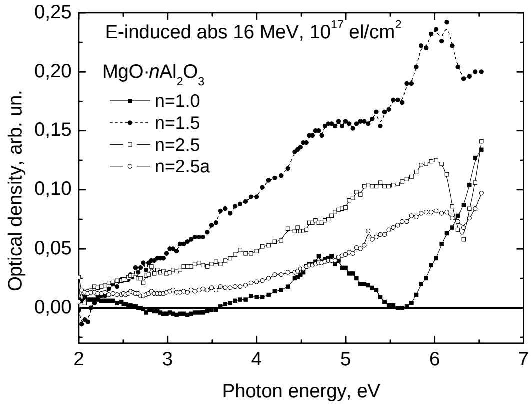

Fig.4. Electron-induced absorption spectra in magnesium aluminate spinel crystals of different compositions

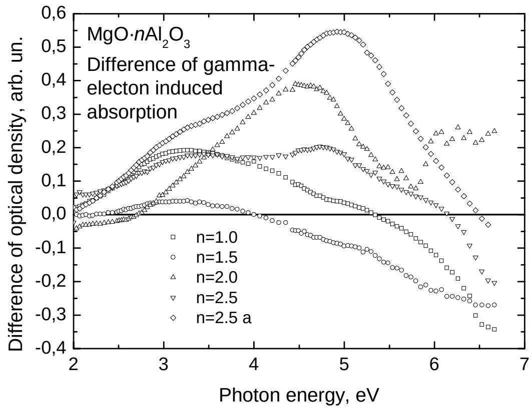

Fig. 5. Differential absorption spectra of gamma-induced and electron-induced absorption spectrum in spinel crystals of different composition

The net electron-induced absorption spectra in magnesium aluminate spinel crystals are presented in Fig. 4. Each spectrum represents the difference of absorption of irradiated and non-irradiated crystals for every composition of crystal. In stoichiometric spinel crystals (*n*=1.0) we observed three absorption bands at 4.0, 4.75, and 5.3 eV, which were identified with electron centers at positively charged anti-site defects, the F^+- and *F*-centers, respectively. In non-stoichiometric spinel crystals (n=1.5, 2.0, and 2.5) the electron irradiation-induced absorption spectra are more complicated, but again, most prominent bands are situated in UV-region (E_{ph}>6.0 eV) where absorption due to transitions in impurity ions is predominate.

The differential gamma-induced and electron-induced absorption spectra are presented in Fig.5. The difference includes the influence on the formation of optical centers as type of irradiation also the different temperature of samples under irradiation. Still we should note:

1. In stoichiometric or close to stoichiometric spinel crystals (n=1.0 and 1.5) formation of defects at the action of gamma and electron beams is not very different.

2. In spinel crystals of high excess of alumina (n=2.0 and 2.5) the efficiency of defect formation under influence of gamma rays much higher to compare with that of electron beam. Also, because under electron beam the temperature of samples was much higher, it could be effects of lower thermal stability of radiation-induced defects (optical centers) in crystals of these compositions.

CONCLUSIONS

There were provided the detailed investigations of absorption spectra in magnesium aluminate spinel crystals subjected to gamma or electron beam irradiation. From changes of absorption spectra in dependences on the type of irradiation it was revealed the more efficient formation of the hole centers under gamma beam. The irradiation with electron beam leads to elevated temperature of samples and as consequently to annealing of hole centers, the thermal stability of which is lower to compare with that of electron centers. Also there was registered the influence of different types of irradiation on spinel crystals of different compositions $MgO \cdot nAl_2O_3$ in the range of n=1.0, 1.5, 2.0, 2.5. The efficiency of defects formation in spinel crystals with large excess of aluminum oxide is higher to compare with that of composition close to stoichiometric one.

Acknowledgments

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ФОРМИРОВАНИЕ ДЕФЕКТОВ В КРИСТАЛЛАХ ШПИНЕЛИ ПОД ДЕЙСТВИЕМ ЭЛЕКТРОННОГО И ГАММА-ОБЛУЧЕНИЯ

С.П. Гоков, В.Т. Грицына, С.С. Кочетов, В.И. Касилов, Ю.Г. Казаринов

Проведены исследования образования оптических центров поглощения в монокристаллах магний-алюминиевой шпинели при воздействии высокоэнергетических гамма- или электронных пучков. Установлено, что гамма-облучение приводит преимущественно к образованию дырочных центров. При электронном облучении происходит повышение температуры образца, что приводит к термическому отжигу нестабильных радиационно-наведенных центров.

ФОРМУВАННЯ ДЕФЕКТІВ У КРИСТАЛАХ ШПІНЕЛІ ПІД ДІЄЮ ЕЛЕКТРОННОГО ТА ГАММА-ОПРОМІНЕННЯ

С.П. Гоков, В.Т. Грицина, С.С. Кочетов, В.І. Касілов, Ю.Г. Казарінов

Проведено дослідження утворення оптичних центрів поглинання в монокристалах магнійалюмінієвої шпінелі під дією високоенергетичних гама- або електронних пучків. Установлено, що гама-опромінення призводить переважно до утворення діркових центрів. При електронному опроміненні настає підвищення температури зразка, що призводить до термічного відпалу нестабільних радіаційно-наведених центрів.