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Neutron irradiation effects in magnesium-aluminate spinel doped with transition metals

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Abstract

We present data on optical properties for stoichiometric ($MgO \cdot Al_2O_3$) and non-stoichiometric ($MgO \cdot 2Al_2O_3$) spinel crystals: (1) nominally pure; (2) doped with transition metals Mn, Cr, and Fe to a concentration of 0.01 wt%; (3) irradiated with neutrons to a fluence of 1.8×10^{21} m^{-2}; (4) post-annealed at 650 K. The temperature during neutron irradiation was 350 K. Optical absorption and thermoluminescence measurements were performed on irradiated and annealed samples at room temperature. Results of absorption measurements show spectra with the following features: (1) a prominent band at 2.33 eV (for stoichiometric spinel); (2) overlapping bands attributed to hole centers (3.17 eV); (3) optical centers on antisite defects (3.78 and 4.14 eV); (4) F^+- and F-centers (4.75 and 5.3 eV); (5) bands related to defect complexes. For nominally pure samples, the efficiency of optical center formation in stoichiometric spinel is half that in non-stoichiometric spinel. Doped crystals exhibit high efficiencies for defect creation, independent of spinel composition. All dopants enhance the efficiency of defect creation in spinel. Doping with Mn has the least effect on increasing the number of radiation-induced stable defects. Apparently, impurities in spinel serve as centers for stabilization of irradiation-induced interstitials or vacancies.

1. Introduction

Optical properties of nominally pure spinel crystals, irradiated with UV, γ-rays, X-rays, and electrons, have been the subject of several previous investigations [1–3]. Under these ionizing irradiation conditions, it is not possible to produce new lattice defects. Therefore, such investigations provide information about optical centers formed after the capture of charge carriers at growth defects and impurity ions. Neutron irradiation leads to creation of additional defects that interact with impurity ions (primarily transition metal ions, with concentrations of the order of 10 ppm in real spinel crystals). Impurity ions with ionic radii different from Mg and Al, create centers of distortion in the spinel lattice. These distortions serve as centers of attraction or repulsion for different radiation-induced point defects (Frenkel pairs). If impurities interact preferentially with vacancies (compared to interstitials, or vice versa), the efficiency of interstitial–vacancy recombination will be lower and the fraction of surviving defects will be higher. Previous investigations of the influence of neutron irradiation on the optical properties of nominally pure spinel crystals, showed the complex nature of the interaction between irradiation-induced defects and impurity ions [4,5]. After neutron irradiation in the fluence range $3 \times 10^{19} - 3 \times 10^{21}$ m^{-2}, some optical bands were identified with optical transitions at transition-metal impurity ions, perturbed by neighboring F-centers [6]. Neutron irradiation to high fluences ($(5.3–24.9) \times 10^{26}$ m^{-2}) at different temperatures, produces very complicated absorption spectra in spinel, indicating the nucleation and growth of defect clusters [7,8]. A high degree of the cation disorder is observed in $MgAl_2O_4$. This is caused by mixing of Mg^{2+} and Al^{3+} ions between the tetra- and octahedral sites. This creates additional irregularities in the crystal lattice, which can serve as the centers for the localization or stabilization of radiation-induced defects. $MgO \cdot nAl_2O_3$

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spinel samples with $n > 1$ are distinguished by their large concentrations of charge compensating cation vacancies [9]. In this study we examine the interrelationship between metal dopants (Cr, Mn, and Fe) and composition (n), and their effects on optical properties in spinel crystals subjected to neutron irradiation.

2. Experimental details

Spinel single crystals of two compositions: stoichiometric ($MgO \cdot Al_2O_3$) and non-stoichiometric ($MgO \cdot 2Al_2O_3$) were grown from the same starting materials by the Verneuil method. The crystals grown were: (1) nominally pure; and (2) doped with Cr, Mn, and Fe metals to concentration 0.01 wt%. The concentration of dopant ions in the as-grown crystals was not measured. Therefore, it is quite possible that the content of metal ions in the stoichiometric and non-stoichiometric crystals may be slightly different. Samples measuring $12 \times 12\ mm^2$, and 0.5–1.0 mm in thickness, were irradiated in the mixed gamma-neutron field of a fission reactor at a temperature of 350 K. The dose of gamma irradiation was 2.3×10^8 R. The fluence of thermal neutrons was $2.7 \times 10^{22}\ m^{-2}$ and fast neutrons $1.8 \times 10^{21}\ m^{-2}$. Absorption spectra of as-grown, irradiated, and annealed samples, were measured with a single beam spectrophotometer in the photon energy range 6.5–1.2 eV at room temperature. Samples were annealed during measurement of thermoluminescence (TL) at a heating rate of 0.21 K/s in air in the temperature range 300–650 K. The emitted light was measured with a photomultiplier in the spectral range 200–800 nm.

3. Results and discussion

3.1. Nominally pure spinel crystals

Fig. 1 shows absorption spectra obtained from the following nominally pure, stoichiometric spinel crystals: (1) as-grown; (2) neutron-irradiated; and (3) post-annealed to 650 K. The absorption spectrum from the neutron-irradiated crystal shows a prominent band at 2.33 eV and featureless, strong absorption in the high energy range. The difference between the irradiated and annealed crystals is also shown in this plot. It represents the absorption of the optical centers that were destroyed by heating of the irradiated samples in the temperature range 350 K (irradiation temperature) to 650 K (the highest temperature of annealing). It can be seen that a large portion of the absorption in the low photon energy range in the irradiated crystals was annealed at this temperature. Fitting of this difference spectrum with Gaussian curves gives several strong bands with maxima at 2.33, 3.17, 3.78, 4.14, and near 6 eV. For the annealed samples, the absorption spectrum consists of two main bands with maxima at 4.75 and 5.3 eV, and a high energy band with maximum position outside the measured photon range. The bands at 4.75 and 5.3 eV were previously identified with F^+- and F-centers (anion vacancies with one or two captured electrons, respectively) [4].

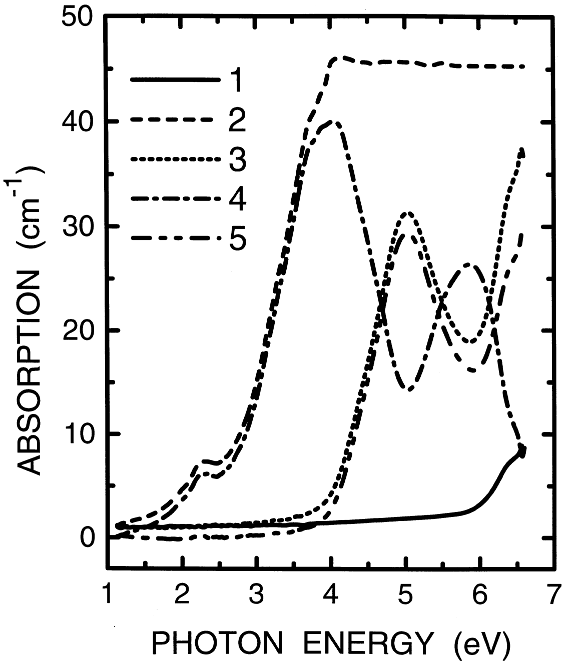

Fig. 1. Optical absorption spectra obtained from nominally pure $MgO \cdot Al_2O_3$ spinel crystals: (1) unirradiated; (2) irradiated with neutrons; (3) irradiated with neutrons and annealed by heating to 650 K; (4) difference between the absorption of irradiated and annealed samples; (5) difference between the absorption of annealed and non-irradiated samples.

The band at 3.17 eV is ascribed to V-centers [1,4]. The position of the maximum of this band varies over a wide range of photon energies [10], depending on the type and temperature of irradiation, as well as the composition of the crystals. The position depends on the relative contribution from different types of hole centers, including: (1) V_t^--, V_t^0-centers (holes stabilized by cation vacancies with tetrahedral symmetry); (2) $V_o^=$-, V_o^--centers (holes stabilized by cation vacancies with octahedral symmetry); and (3) V_{OH}^--, V_{OH}^o-centers (hole centers containing hydrogen for partial charge compensation).

High intensity, radiation-induced bands at 3.78 and 4.14 eV belong (most probably) to optical centers on intrinsic defects related to the spinel structure. Gritsyna et al. [11] studied optical absorption and luminescence in spinel crystals of different compositions irradiated with UV-light, X-rays, and electrons. They concluded that these bands are due to optical transitions at centers formed on antisite defects [11]. Neutron irradiation leads to mixing of cations among polyhedra. The Al^{3+} ion at a tetrahedral site forms a $(Al^{3+}_{tet})^{+}$-defect with excess positive charge; the Mg^{2+} ion at an octahedral site forms $(Mg^{2+}_{oct})^{-}$-defect with excess negative charge. It was shown previously that neutron irradiation leads to an increase in Mg^{2+} on octahedral sites and Al^{3+} on tetrahedral sites [12]. The $(Al^{3+}_{tet})^{+}$-defect can capture an electron and form an optical $(Al^{3+}_{tet})^{0}$-center that produces absorption at 4.14 eV. The $(Mg^{2+}_{oct})^{-}$-defect, with a captured hole, forms an optical $(Mg^{2+}_{oct})^{0}$-center that results in absorption at 3.78 eV.

3.2. *Crystals doped with transition metals*

In Figs. 2–4 we present optical absorption results for neutron-irradiated spinel crystals doped with Cr, Mn, and Fe, to concentration 0.01 wt%. The main features of the absorption spectra obtained from doped crystals, are the same as for the nominally pure spinel. However, the intensity of absorption in the high energy region is two times higher. Moreover, the relative intensities of different bands are different. Iron is the most common, uncontrolled impurity in spinel crystals, and sometimes its concentration reaches as much as 100 ppm. Our results show that doping with transition ions to the similar concentrations leads to dramatic changes in the response of a crystal to neutron irradiation.

Absorption spectra from doped crystals following annealing (Figs. 2–4, spectra 4), can be fitted with the same set of bands. The strongest bands have maxima at 2.33, 3.35, 3.78, and 4.25 eV. The positions and intensities of the absorption bands in the UV region, depend on the doping ion species. The lack of dependence of the intensity of the 3.33 eV band on the dopant species,

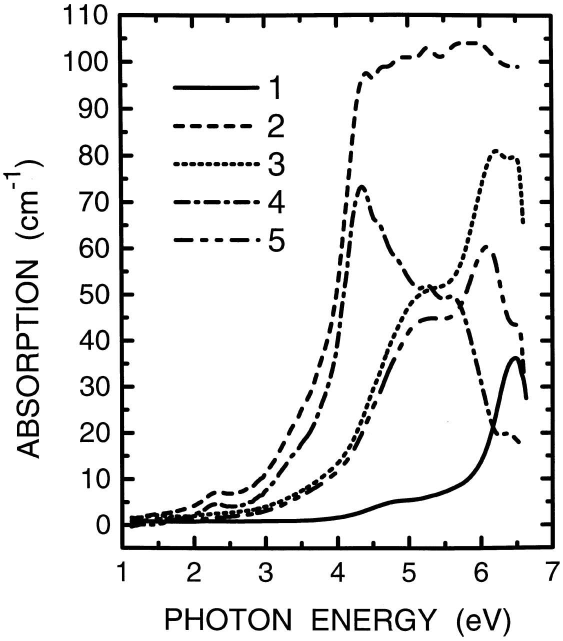

Fig. 2. The same as Fig. 1, but for $MgO \cdot Al_2O_3$:Fe crystals.

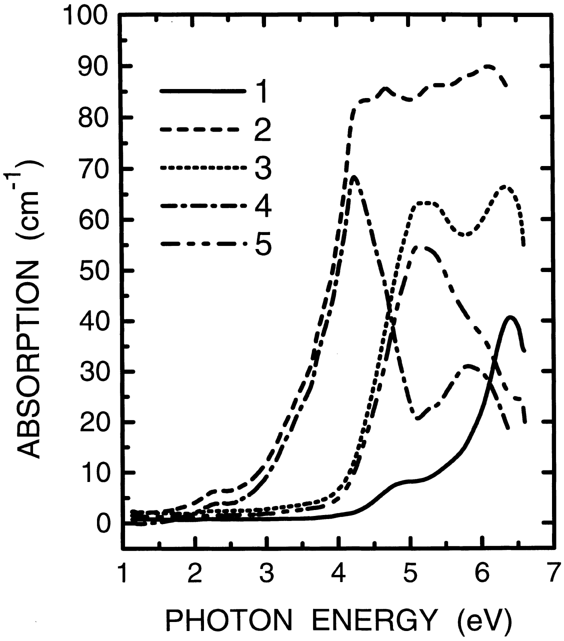

Fig. 3. The same as Fig. 1, but for $MgO \cdot Al_2O_3$:Cr crystals.

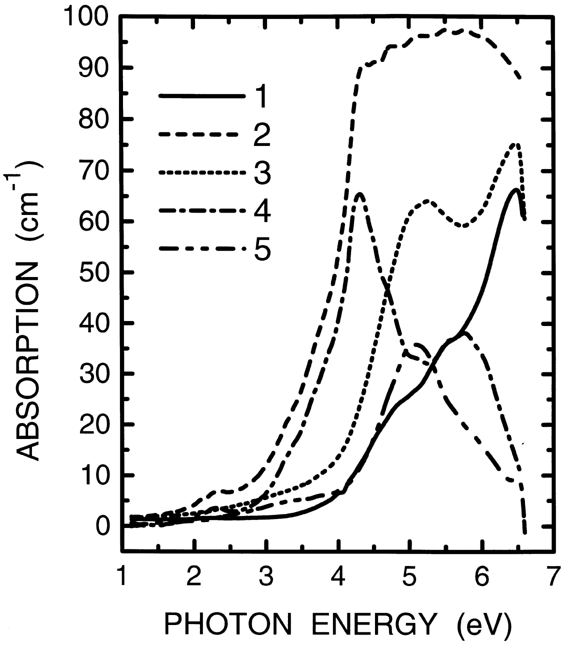

Fig. 4. The same as Fig. 1, but for $MgO \cdot Al_2O_3$:Mn crystals.

indicates that this band is not related to any of the dopant ions studied here. The shift in position of the main bands to higher photon energies (compared to nominally pure crystals), is due to the influence of the transition metals ions. The 3.35 eV band can be related to V-type centers. Its intensity is approximately the same as in the nominally pure crystals. In doped crystals, the intensity of the 3.78 eV band is lower and the intensity of the 4.25 eV band higher, compared to the nominally pure spinel samples. Both the shift in energy and the increase in intensity of the 4.25 eV band (4.14 eV for nominally pure crystals), indicates the influence of dopant ions on the probability for creation of $(Al^{3+}_{tet})^0$-optical centers.

Absorption spectra obtained from irradiated and post-annealed spinel crystals doped with metals, contain the same two prominent bands at 4.75 and 5.3 eV, as in nominally pure crystals. For the doped spinel samples, there is an additional band near 3.6 eV. The position and intensity of this band depends on the type of dopant. At high photon energy, there are several bands that vary with dopant. The intensity of these bands is much higher than in nominally pure spinel crystals. This suggests that these bands are due to complex defect centers, such as transition metal ion in association with radiation-induced defects.

Glow curves from neutron-irradiated crystals in the temperature range 350–650 K are shown in Fig. 5. The glow peaks are located at 440, 490 and 630 K. The latter peak is the most prominent following neutron irradiation. On the contrary, after UV-and X-ray irradiation, the first two peaks were observed to be strongest [2]. The high temperature peak at 630 K has not been reported before. According to our measurements, the maximum contribution to the emitted light, is due to the UV-light. Therefore, it is reasonable to assume that the thermoluminescence is caused by electron-hole recombination [13] along with thermal annealing of centers on antisite defects. In $MgAl_2O_4$:Fe crystals, thermoluminescence intensity seems to increase with increasing absorption at 4.25 eV.

3.3. Comparison with non-stoichiometric crystals

Fig. 6 shows difference absorption spectra obtained from the following spinel crystals: (1) neutron-irradiated nominally pure; and (2) neutron-irradiated doped with transition metals. These spectra were obtained by subtracting the absorption of non-stoichiometric crystals from the absorption of stoichiometric ones. The absorption associated with nominally pure, neutron-irradiated $MgO \cdot 2Al_2O_3$ crystals in UV-region, is twice as large as the absorption of stoichiometric crystals. These results are in agreement with the lower radiation resistance of non-stoichiometric spinel under ion irradiation [14]. However, in visible region, absorption is lower for

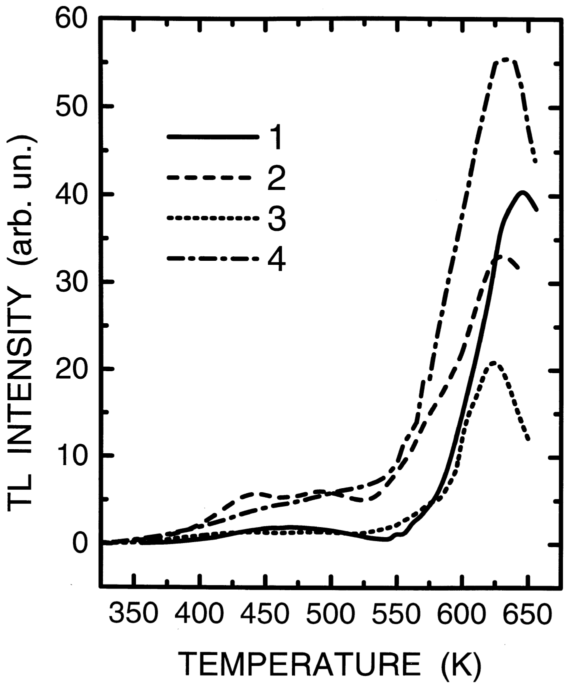

Fig. 5. Glow curves obtained from neutron-irradiated $MgO \cdot Al_2O_3$:Me spinel crystals, doped with different ions: (1) nominally pure; (2) Cr; (3) Mn; (4) Fe.

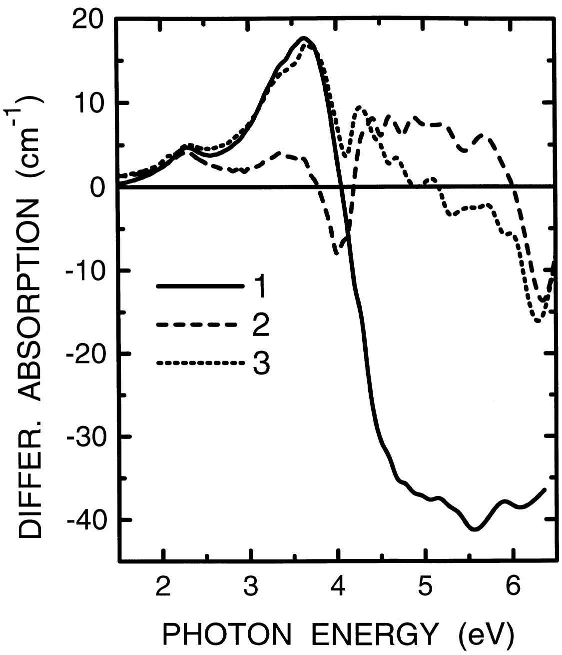

Fig. 6. Differential optical absorption spectra obtained from neutron-irradiated spinel crystals. The plots indicate the difference in absorption between $MgO \cdot Al_2O_3$ and $MgO \cdot 2Al_2O_3$ samples: (1) nominally pure; (2) doped with Fe; (3) doped with Mn.

non-stoichiometric crystals. The 2.33 eV band is absent in these crystals, independent on the dopant ion. In the difference absorption spectra, two bands are present at 3.35 and 3.7 eV (in addition to the band at 2.33 eV). These observations suggest that in stoichiometric spinel crystals, V-type centers (hole centers) are formed more readily than in non-stoichiometric crystals. The efficiency of electron center formation in doped spinel crystals is nearly independent of composition.

The correlation between the behavior of V-type absorption (holes stabilized by cation vacancies) and the 2.33 eV band, suggests that this band be assigned to transitions at cation vacancy complexes. One of the reasons for the low efficiency of cation vacancy creation in non-stoichiometric spinel, is the existence of a high concentration of octahedral cation vacancies in as-grown crystals. These vacancies are the result of the deviation of composition from stoichiometry. Because the irradiation was performed at elevated temperature (350 K), the mobility of radiation-induced defects was higher in the highly defective spinel lattice. This leads to the enhancement of recombination of radiation-induced cation Frenkel pairs. In addition, at this temperature, electronic processes are enhanced. This leads to the release of holes from V-type centers. The concentration of cation vacancies remains unchanged.

4. Conclusions

Neutron irradiation of spinel crystals leads to formation of optical centers that exhibit absorption primarily in the UV-region. This is where optical absorption bands related to electrons captured by anion vacancies (F-type centers) are usually observed. Doping of stoichiometric spinel crystals with Cr, Mn, and Fe, to a concentration of 0.01 wt%, leads to enhancement of this type of center. This may be due to increased stabilization of radiation defects by impurity ions. It is evident that cationic disorder (concentration of antisite defects) is also increased. In neutron-irradiated, non-stoichiometric spinel crystals, absorption in the UV-region is approximately the same as in doped, stoichiometric crystals. This is true regardless of whether or not the crystals are nominally pure or doped with transition metals. Thus, many cationic vacancies of non-stoichiometric origin in $MgO \cdot 2Al_2O_3$ crystals, serve as centers for radiation defects stabilization.

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