UDC 535.3

RADIATION INDUCED OPTICAL CENTERS IN MAGNESIUM ALUMINATE SPINEL CERAMICS

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There were investigated the optical absorption centers formation in magnesium aluminate spinel ceramics under irradiation with UV-light, X-, and gamma-rays. The lithium fluoride doped ceramics were produced by using hot-pressing technology. It was revealed that generation by irradiation changes in optical absorption spectra can be used for detection of invisible point defects in prepared ceramics, their distribution through the bulk of spinel disk, and predict the behavior of ceramics in different radiation fields.

INTRODUCTION

Ceramic materials have important properties which make them suitable for a number of applications in fission and fusion reactors. Magnesium aluminate spinel ($MgAl_2O_4$ or $MgO{\cdot}Al_2O_3$) in particular has been shown to be very resistant to radiation damage. Considerable attention has been, therefore, directed to spinel, such as for a host of inert matrix fuels in light water nuclear reactors, and a transmutation target for minor actinides and long life fission products. Under environment of such nuclear applications $MgAl_2O_4$ will be exposed to electronic excitation for a wide range of intensity with electrons, gamma rays, ions and other fission products. Therefore, investigation of nature and concentration of defects and optical centers formed under ionizing irradiation is issue of the present time.

The spinel crystal lattice has fcc structure of oxygen ions with a lattice parameters of 0.808 nm. There are eight molecules in its unit cell forming the 64 tetrahedral symmetry sites and 32 octahedral ones. In natural spinel crystals magnesium ions (Mg^{2+}) occupy 8 tetrahedral positions and aluminum ions (Al^{3+}) occupy 16 octahedral sites. At non-equilibrium growth conditions, for example, in ceramic technology at high temperature and high pressure, there was observed the partial cationic disordering, i.e. part of Al^{3+} ions occupy tetrahedral position and equal part of Mg^{2+} ions occupy octahedral sites, forming so called anti-site defects. As a result, at the high concentration of different types of point defects in crystal there are appeared complexes of defects and it lost optical transparency. Also anti-site defects play important role in radiation resistance of this material because oppositely charged anti-site defects form charge compensated clusters which serve as recombination centers of radiation induced Frenkel pairs [1, 2]. The main task of this research is to investigate the spatial distribution of intrinsic defects in spinel ceramics by using radiation induced processes of formation and evolution of optically active centers.

In numerous papers there were investigated radiation induced processes in nominally pure magnesium aluminate spinel crystals and ceramics of different origin and compositions [3-5].

EXPERIMENTAL DETAILS

In this paper we report the results of investigations of optical center formation in spinel ceramics fabricated by hot-pressing technique of spinel powder synthesized with adding up to 1.0 wt. % LiF at Colorado School of Mines, USA [6]. A uniaxial die pressure of 35 MPa was applied at about 1550 °C to fabricate block of transparent ceramics. Therefore, the non-equilibrium conditions of spinel structure formation could lead to different types of defects and their concentration to compare with that in single crystals. Moreover, the variation of technological parameters inside of spinel disk (temperature, pressure, composition and so on) causes the change of ceramic structure on microscopic level [7]. Back scattered electron images of magnesium aluminate spinel ceramics ($MgAl_2O_4$) disc obtained by vacuum hot- pressing technique indicates that there exists the variation of structure in cross-sections through the ceramics plate surface area [8]. The difference in structure on the microscopic level may indicate also variation of point defects and atomic structure.

Samples for optical investigation were cut into slices of 0.7 mm thickness across the disk of ceramics and polished to optical finish. The optical absorption spectra were measured in the wavelengths range of 185…1000 nm (6.7…1.2 eV) by using single beam spectrophotometer SF-46. Irradiation with UV-light was provided by using mercury lamp of quartz balloon, X-ray irradiation by using X-ray tube of Cu-anode at voltage of 35 keV, and current of 0.4 mA. Also ceramics were irradiated with bremsstranglung gamma-rays from energetic electrons of 7 MeV at linear accelerator. The time for irradiation was chosen to reach the saturation in the value of absorption density.

RESULTS AND DISCUSSION

At first we investigated the uniformity of optical absorption through the disk of spinels prepared by hot-pressing. The absorption spectra measured in pristine samples cut from different places of disk demonstrate no definite bands; also there is difference in absolute values of optical density of samples. After subtraction of absorption spectra of different samples we found the additional information on the optical centers.

It turned out that in pristine samples cut from different sites of disk in the difference spectra there exist several absorption bands the main of which have maxima at 2.8, 4.2 4.75, and 5.3 eV (Fig. 1). The intensity of these bands varies from place to place through plates indicating the variation of hot-pressing parameters during preparation (temperature and pressure) and/or composition [8]. As a matter of fact this optical data can be used for determination of optimal conditions for preparation of optical ceramics of the homogenous properties.

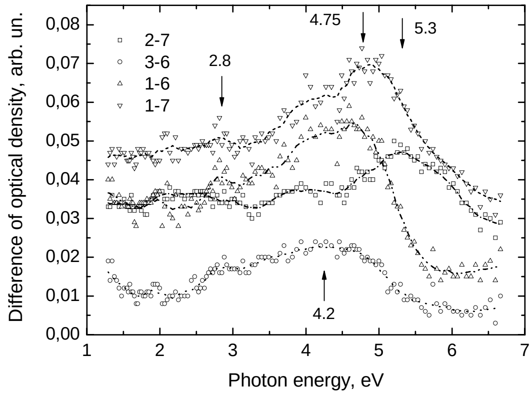

Fig. 1. Examples of variation of optical absorption spectra of samples cut in cross-sections through the ceramics plate surface area (difference of absorption in different samples)

The origin of initial absorption in pristine ceramics samples could be explained by non-equilibrium process of ceramics production. During the hot-pressing process at elevated temperature (1550 °C) the formation of lattice defects could be possible. At the high temperature these charged defects can capture the charge carriers of opposite signs forming residual optical centers.

CENTERS IN UV-IRRADIATED CERAMICS

To activate the optical absorption in the samples were irradiated with UV-light, X- and gamma-rays. The UV-induced optical absorption spectra of three samples cut from the different part of ceramic disc are shown in Fig. 2. These spectra were obtained by subtraction of initial spectra of pristine samples from that of the UV-irradiated samples. The decomposition of these spectra in elementary absorption bands gives several bands related to different centers some of which was found in irradiated single crystals with exception of band at 5.65 eV [5].

The UV-induced absorption bands are situated at 3.1 eV related to hole centers at cationic vacancies, 3.8 eV hole ascribed to centers at anti-site defects, and band at 4.75 eV are related to F^+-centers. Finally the intensive absorption band at 5.65 eV was observed in irradiated ceramics which is absent in spinel crystals. The formation of optical absorption centers under UV-irradiation could be explained in the next manner. Because of UV-photons energy (E_{ph}<6.7 eV) less than energy gap of spinel (E_g~7.8 eV) the generation of free charge carriers is unlikely. Therefore, under UV-irradiation the charge carrier transfer happened between near neighbor defects. From Fig. 2 one can see that simultaneously formation of electron and hole centers were happened, i.e. the direct transfer of electron from one defect to another take place near neighbor defect. Also, the change of charge states of already existing optical centers also possible.

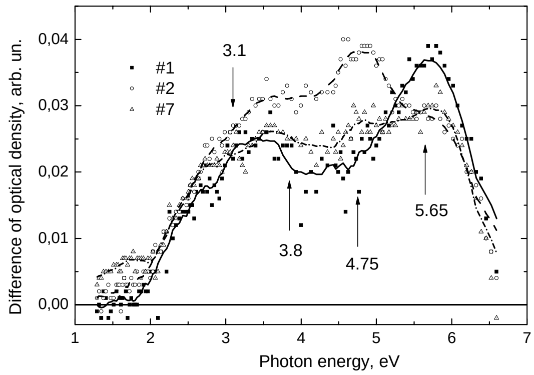

Fig. 2. UV-irradiation induced optical absorption spectra of samples cut from different parts of spinel disc

Fig. 3 demonstrates the transformation of F-centers in initial crystals (anion vacancy captured two electrons) into F^+-centers (anion vacancy captured one electron) by taking off one electron under UV-irradiation.

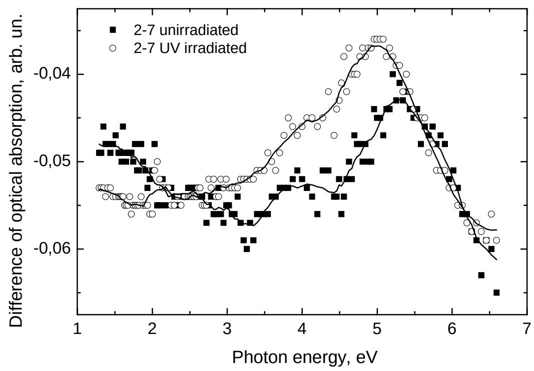

Fig. 3. Difference of absorption spectra in two pristine and UV-irradiated spinel samples

CENTERS IN X-IRRADIATED CERAMICS

Because the energy of X-rays much higher to compare with energy gap of spinel we may expect during the X-irradiation the generation of free charge carriers in crystals which can be captured by the existing lattice defects and impurities. Therefore, the absolute value of X-ray induced optical absorption is much higher to compare with UV-irradiation. Fig. 4 shows the difference in absorption spectra of two samples cut from different parts of ceramic disc before and after X-ray irradiation.

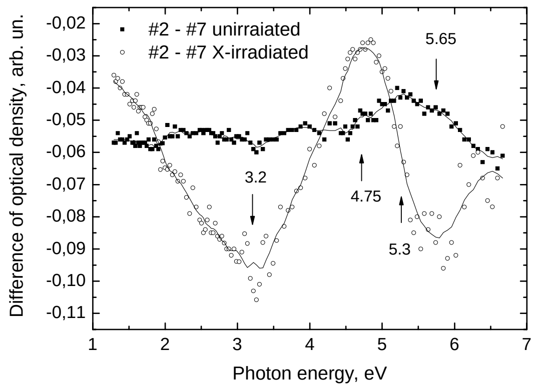

Fig. 4. Difference of absorption spectra in two pristine and X-irradiated spinel samples

These spectra we can compare with that after UV-irradiation shown in Fig. 3. Despite of very low net difference in absorption of two pristine samples (low intensity 5.3 and 5.65 eV bands) the net difference for X-ray irradiated samples drastically changed. Therefore, the existing defects in pristine samples captured electron and holes under irradiation forming in one sample (#2) larger concentration of F^+-centers, in another (#7) – V-type centers and unknown centers (5.65 eV).

From these data we conclude that in some samples there exists large concentration of anionic vacancies which can not be seen in pristine samples but under X-irradiation the F^+-centers can be formed leading to absorption band at 4.75 eV. Analysis of reaction between $MgAl_2O_4$ and LiF leads to conclusion on the formation of oxygen vacancies due to the incorporation of both Li and F ions into crystal lattice [9]:

$$3LiF \xrightarrow{MgAl_2O_4} Li_{Mg}^{-} + 2Li_{Al}^{2-} + 3F_{O}^{+} + V_{O}^{2+}.$$

The residual oxygen vacancies (V_O^{2+}) under X-irradiation can capture one or two electrons forming F^+- or F-centers and corresponding absorption bands. Other product of this reaction the fluorine ions in oxygen site (F_O^+) serve also as electron traps forming electron centers, transition in which may lead to absorption band at 5.65 eV. Moreover, other products of this reaction Li ion in Mg (Li_{Mg}^{-}) or in Al sites (Li_{Al}^{2-}) could lead to creation of optically active hole centers. The spectral position of absorption band near 3 eV changes from sample to sample in dependence on contribution of V-type centers at isolated cationic vacancies or Li-containing hole centers having slightly different spectral position of individual absorption bands.

This is very striking example for demonstration of possibility optical measurements of irradiated with ionizing radiation ceramics (without formation of additional lattice defects) for determination the nature and concentration defects in ceramics prepared at different technological conditions.

CENTERS IN GAMMA-IRRADIATED CERAMICS

Irradiation with high energy gamma-rays causes the strong change of initial absorption in spinel ceramics leading to the optical absorption spectra containing many overlapping bands (Fig. 5). The irradiation with gammas of 7 MeV leads to generation of secondary electrons (photo- or Compton-electrons) which may create the free charge carriers and also lattice defects and may form additional optical centers. Also, the analysis of gamma induced spectra shows the existence of already discussed bands of different intensity.

After irradiation with high energy gamma-rays the intensity of absorption bands which related to hole centers (bands at 3.2 and 3.8 eV) increases, but intensity of bands ascribe to electron centers at anion vacancies decreases, i.e. the radiation-induced absorption in gamma-irradiated ceramics become negative.

The negative value of the 4.75 eV band along with (specific for ceramics) band at 5.65 eV means that this band could be related also to electron centers.

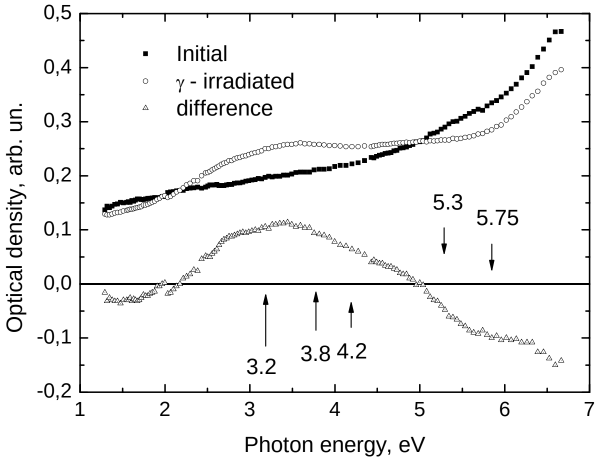

Fig. 5. Absorption spectra of initial ceramic sample, after gamma-irradiation and difference spectra of irradiated and initial sample

To define the nature of optical centers formed by gamma-irradiation we provided measurements of absorption spectra after the subsequent UV- and gamma irradiation of these samples (Fig. 6).

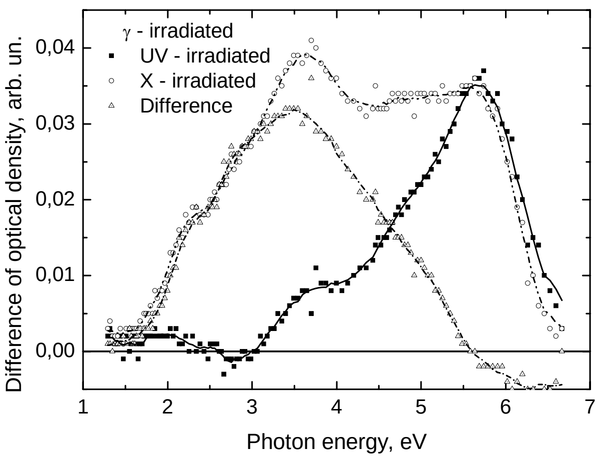

Fig. 6. Difference of absorption spectra of the gamma-irradiated and subsequent UV- and X-irradiation in spinel ceramics

The additional UV irradiation leads to appear absorption bands at 5.65 and 3.8 eV. As it was discussed before the first high intensity band could be related to electron centers at fluorine incorporated anion vacancies captured electron (F_O^+), the band at 3.8 eV is related to hole centers at anti-site defects [5]. The additional irradiation with X-rays leads to formation whole spectrum of absorption bands related to electron and hole optical centers. The difference between the X-ray and UV-induced absorption in gamma-irradiated samples show the main contribution of bands related to hole centers of different origins leading to very wide band in the spectral range of 2…5 eV.

CONCLUSIONS

There were investigated the radiation-induced optical center in magnesium aluminate spinel ceramics doped with LiF after different types of irradiation. After irradiation with UV-light we registered some absorption bands arising from charge exchange between nearest neighbor defects or defects and impurities. Irradiation with X-rays leads to generation of free charge carriers in conduction band of this insulator and subsequent capture them by different defects or impurities which gives additional absorption bands. Gamma-rays (maximal energy of E_{γ}~7 MeV) ensure also formation of new lattice defects with subsequent formation of optical centers by free charge carriers. The existence of radiation induced absorption bands was identified which were found in irradiated single crystals and identified with F- (5.3 eV), F^{+}- (4.75 eV), V-type (3.1 eV) centers. Also there is indication on the presence of bands at 4.2 and 3.8 eV which were previously identified with electron and hole centers at anti-site defects. In spinel ceramics doped with LiF evidently there was observed absorption band at 5.65 eV which absent in nominally pure spinel crystals and tentatively was identified with complex F-type centers consisting of anion vacancies with incorporated fluorine ion (F^{-}) and captured one electron. It was revealed that disk of transparent spinel ceramics prepared by hot-pressing technology has ununiformly distributed defects of different origin indicating the existence of uncontrolled variation of technological parameters or composition in pressing technique. Results of this research evidently show the possibility of differential optical spectroscopy of radiation induced centers to control the degree of perfection of transparent ceramics and predict behavior of this material in radiation fields.

Acknowledgments

This work was supported in part by Science and Technology Center in Ukraine (STCU) Project #2058, and by Ministry of Education and Science of Ukraine Project #7-13-06.

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Статья поступила в редакцию 29.09.2008 г.

РАДИАЦИОННО-ИНДУЦИРОВАННЫЕ ОПТИЧЕСКИЕ ЦЕНТРЫ В КЕРАМИКЕ МАГНИЙАЛЮМИНИЕВОЙ ШПИНЕЛИ

В.Т. Грицына, Ю.Г. Казаринов, А.А. Москвитин, И.Е. Рейманис

Исследовано образование оптических центров поглощения в керамике магнийалюминиевой шпинели при облучении УФ-светом, рентгеновскими или гамма-квантами. Керамика шпинели с добавками фторида лития была приготовлена с помощью технологии горячего прессования. Обнаружено, что вызванные облучением изменения в оптических центрах поглощения могут быть использованы для детектирования невидимых точечных дефектов в полученной керамике, их распределения по объему керамического диска, а также для предсказания поведения керамики в различных радиационных полях.

РАДІАЦІЙНО ІНДУКОВАНІ ОПТИЧНІ ЦЕНТРИ В КЕРАМІЦІ МАГНІЙАЛЮМІНІЄВОЇ ШПІНЕЛІ

В.Т. Грицина, Ю.Г. Казарінов, А.А. Москвітін, І.Є. Рейманіс

Досліджено утворення оптичних центрів поглинання в кераміці магнійалюмінієвої шпінелі під дією УФ-світла, рентгенівських та гама-квантів. Кераміка шпінелі з добавками фториду літію готувалась методом гарячого пресування. Знайдено, що зміни в спектрах оптичного поглинання, які виникли при опроміненні, можуть бути використані для виявлення невидимих точкових дефектів в кераміці, їх розподілу по об’єму керамічного диску, а також прогнозувати поведінку кераміки в різних радіаційних полях.