Conference Paper

Optically Active Defects Induced by 10 MeV Electron Beam in Transparent $MgAl_2O_4$ Ceramics

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Abstract

In the synthesized $MgAl_2O_4$ ceramics, Raman scattering modes were detected due to the presence of random distribution of cations over structural positions (structural reversal effects). Irradiation by 10 MeV electron beam caused intensity redistribution of the fundamental bands in Raman spectrum. New optical absorption bands were registered. Observed features were attributed to the effect of radiation-induced 'ionic mixing' in cation sublattice. This effect is the formation of additional $[Al]_{Mg}$ and $[Mg]_{Al}$ anti-site defects. The obtained data on the defects in transparent ceramics are of interest for the creation of radiation-resistant electromagnetic radiation converters for alternative energy.

Keywords: aluminum magnesium spinel, anti-site defects, luminescence, transparent ceramics

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1. Introduction

Nowadays, study of aluminum–magnesium spinel (AMS) is carried out by many laboratories due to the fact that spinel is of practical interest for fiber optic temperature sensors, tunable solid-state lasers, matrices, manufacturing optical nanodevices, matrices for carrying out transmutation transformations, and filler material for disposal of radioactive waste [1–4]. Transparent ceramics of aluminum–magnesium spinel doped with ions of transition metals and rare earths can be used as radiation energy converters [5–7]. The polycrystalline structure of the magnesia spinel is optically isotropic. AMS undergoes no polymorphic transformations and, hence, is devoid of any thermally induced phase changes. Such ceramics have wide optical window (0.2–5.5 μm), high radiation and corrosion resistance, as well as mechanical strength, which is of great interest for many practical applications including alternative energy [8, 9].

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AMS belongs to the class of binary AB_2O_4 oxides (A-bivalent, B-trivalent cation) having cubic system. Single cubic unit cell contains 64 tetra- and 32 octahedral cationic positions. An important characteristic of spinel structure is cations positions distribution. Normal and inverse spinel structures are distinguished based on ions distribution in the cation sublattice [10]. An intermediate case is also distinguished, characterized by a partial inversion of the structure [11, 12]. It is known that degree of reversal in AMS structure increases together with rising of synthesis temperature and heat treatment at $\geq$ 1000 K [13]. Synthetic AMS always has replacement defects (so called anti-site defects – ADs) due to having low energy of formation and harsh conditions of synthesis (high temperature and pressure) [14, 15].

Impact of fast neutrons and gamma radiation on AMS leads to changes in cations structural positions. Such defects are characterized by an aluminum ion in the tetrahedral position of magnesium $[Al^{3+}]_{Mg}$ and vice versa [16, 17]. Anion vacancies are formed together with cation defects in $MgAl_2O_4$. The presence of the F and F^+ type centers was confirmed by the studies of thermochemically sintered polycrystalline $MgAl_2O_4$ [18] and investigation of single crystalline AMS irradiated by neutrons [19]. Activation of AMS and ceramics by ions of such transition 3d elements as Mn, Ti, Cr, Fe, etc. results in wide spectral range luminescence. At the same time, it should be noted that effect of radiation-induced substitution defects on spinel optical properties has not been sufficiently studied.

The aim of this work is to study formation and features of radiation-induced anti-site defects, as well as impurity ions Mn^{2+} and Cr^{3+} as factors influenced on the optical properties of AMS transparent ceramics.

2. Methods

Nanopowder of $MgAl_2O_4$ synthesized by Pechini method with additional heat treatment in liquid melt of inactive salt matrix with addition of 1 wt. % LiF was subjected to uniaxial hot pressing at 35 MPa with 1550°C soaking temperature for 1 h. Obtained ceramics were polished to decrease dispersion at the surface.

Optical absorbance spectrum was registered using Perkin Elmer Lambda 35 spectrophotometer. Absorbance centers concentration was calculated by means of Smakula–Dexter formula $n = 0.87{*}10^{17}(a_0/(a^2{}_0+2)^2)\ (\Delta E/f){*}k_0$, here n is amount of absorbance centers, a_0 is refractivity index around absorbance maximum (1.72 of single crystalline AMS), ΔE is full width at half maximum, *f* is oscillator power (taken as 1), k_0 is absorption constant at the maximum position.

Photoluminescence (PL) and Raman scattering spectra (Raman spectra) were recorded on a LabRam HR 800 Evolution spectrometer with an Olympus BX–FM microscope (50x and 100x lenses) with excitation by laser radiation with an energy of 2.54 eV (Ar-laser, radiation power on the sample $\sim$ 1.5 mW) and recording the Peltier-cooled CCD detector using a diffraction grating 600 ppm/mm at room temperature. The spectral resolution in the Raman scattering region of the spinel was $\sim$ 6–8 cm^{-1}, in the region of registration of the PL of chromium ions, 0.01 nm. Position of the RNC peaks is determined after adjusting the baseline by approximating the spectral profile with Voigt functions using Labspec® software. A sample of natural spinel (KOS-II) was used as an object for comparing the spectra of Raman and PL of transparent ceramics.

Irradiation by fast electrons was performed by means of UERL-10C linear electron accelerator at Ural Federal University (E = 10 MeV, fluence 10^{17} e/cm^2). Samples were placed in a chamber with water cooling. Temperature of samples during irradiation did not exceed 70 °C.

3. Results and Discussion

3.1. Optical absorbance

Initial AMS ceramics has high degree of transparency in wide spectral range. Great increase in optical absorption (OA) at photon energies above 6 eV is due to absorption in fundamental absorption edge range of material – E_g = 7.8 eV for single crystal (Figure 1(a)). Irradiation of ceramics by 10 MeV electron beam results in absorption growth in wide spectral range from 1.5 to 6 eV. It is known that 4.75 and 5.3 eV maxima can be attributed to F^+ and F-centers in aluminum magnesium spinel [18, 19]. Ones in 2.7 and 3.2 are due to extrinsic cation defects present in sample [20]. It is to be noted that there is no consensus about nature of 3.5–4.2 band in literature. According to researchers [20, 21], in the range from 3.5 to 4.2 eV, the absorption is caused by the formation of ADs with subsequent localization of charge carriers. However, there are works that connect the latter with anion dimers, that is, two closely situated oxygen vacancies – F_2-centers. [22]. Correlation of observed OA and Raman spectra supports ADs hypothesis. Origin of intensive band 6.2 eV requires additional investigations.

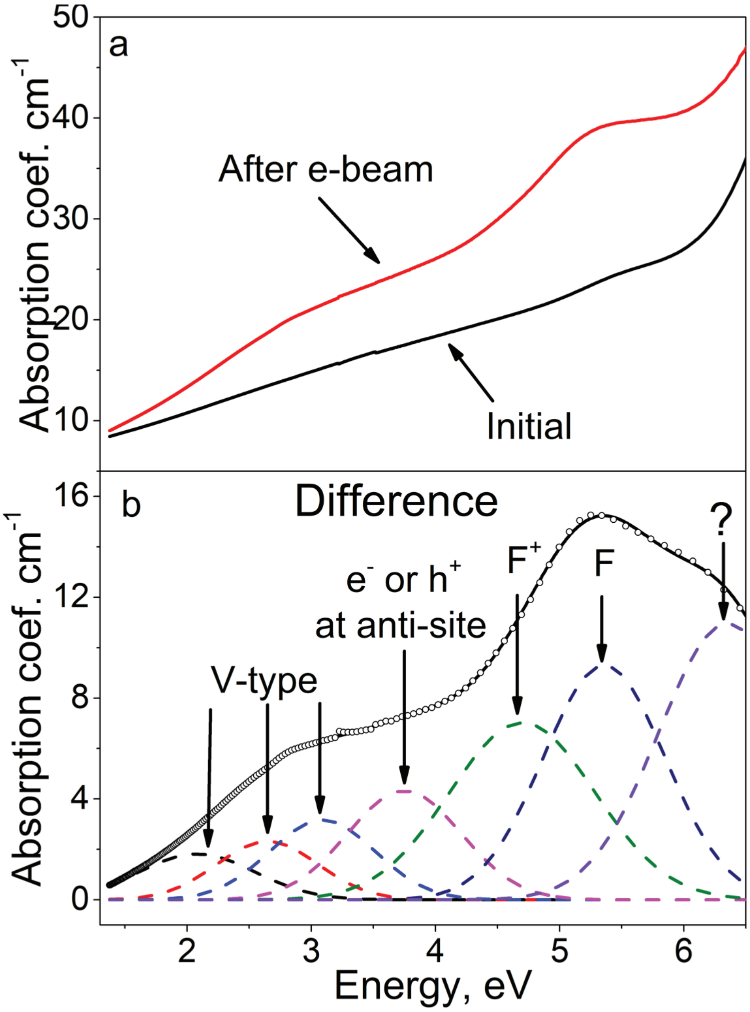

Figure 1: Optical absorption spectra of initial and irradiated AMS sample (a). The difference between optical absorption spectra (b). Solid line – resulting curve, dash line – Gaussians.

Concentrations of indicated defects were calculated using Smakula–Dexter formula according to experimental spectra (Table 1). Centers of F^+, F-type and unknown band have the highest concentration. The formation of V-type centers upon irradiation with accelerated electrons is caused by the formation of Frenkel defects of the cation sub-lattice by the mechanism of shock displacement with the formation of Al^{3+} and Mg^{2+} interstitials. Electron and hole centers can exist in ADs as a result of electron or hole localization at $[Al]^+{}_{Mg}$ or $[Mg]^-{}_{Al}$, accordingly with charge compensation. Centers of F^+ and F-type are formed due to dislodging of oxygen atom from its sublattice followed by capture of one or two electrons, respectively.

Table 1: The concentration of defects obtained by Smakula–Dexter formula.

Location, eV	2.15	2.7	3.1	3.75	4.7	5.3	6.2
n*10^{16}	**1,2**	**1,4**	**1,9**	**2,45**	**5,9**	**6,5**	**8,7**
Type of centrums	V	V	V	Electron or hole at ADs	F^{+}	F	?

3.2. Raman spectra

Raman spectra of initial and irradiated ceramics, as well as single crystalline of natural spinel are shown in Figure 2. In synthesized ceramics, as in natural spinel, four of the five vibrational modes (A_{1g}, E_g, F_{2g}(3), F_{2g}(1)) are observed, which are active according to the group theoretical analysis in Raman scattering of spinel with a normal cation distribution over the positions. Energy values of vibrational modes (Table 2) in synthesized and natural spinel are close to each other and consistent with literature data for $MgAl_2O_4$ [23]. Mode with E_g 407–408 cm^{-1} has the highest intensity. Low-intensity peak F_{2g}(2) at 562 cm^{-1} is not stationary.

Table 2: Vibrational modes in the Raman spectra of irradiated and initial ceramics of AMS, natural spinel. Comparison of the obtained results with the literature data for a synthetic single crystal $MgAl_2O_4$ (sh – shoulder; l/i – low intensity maxima; * – modes, associated in the literature with the inversion of the spinel structure).

Sample	The energy of vibrational modes of different type symmetry, cm^{-1}								
	F_{2g}(1)		E_g	**E_g**	F_{2g}(2)	**F_{2g}(2)**	**F_{2g}(3)**	A_{1g}	**A_{1g}**
Initial	**305**	366(sh)	*381(sh)	**406**	–	–	**669**	*722	**766**
e-beam (exposed by 10MeV electrons)	**304**	358(sh)	*380(sh)	**408**	–	–	**669**	*721	**766**
KOS-II	**312**	–	*~385(sh)	**407**	–	**~554(l/i)**	**666**	*~715(l/i)	**767**
$MgAl_2O_4$[23]	**308**	–	*375(sh)	**408**	*493	**562**	**670**	*720	**768**

Several additional maxima in Raman spectra of synthesized transparent ceramics are observed as well as broadening and intensity decrease of fundamental vibrational modes most explicitly expressed for the E_g mode. Measured width of this peak changes from ~ 8 cm^{-1} in natural spinel to ~ 35 cm^{-1} in synthesized ceramics. These spectral features of transparent ceramics are associated with reversal of the structure (presence of ADs) [23, 24].

Shape of Raman basic mode (E_g) in irradiated ceramics caused by formation of additional ADs is observed. Electrons with 10 MeV energy colliding with cation knock it out of sublattice to interstice or an adjacent cation position. Thus, the results of

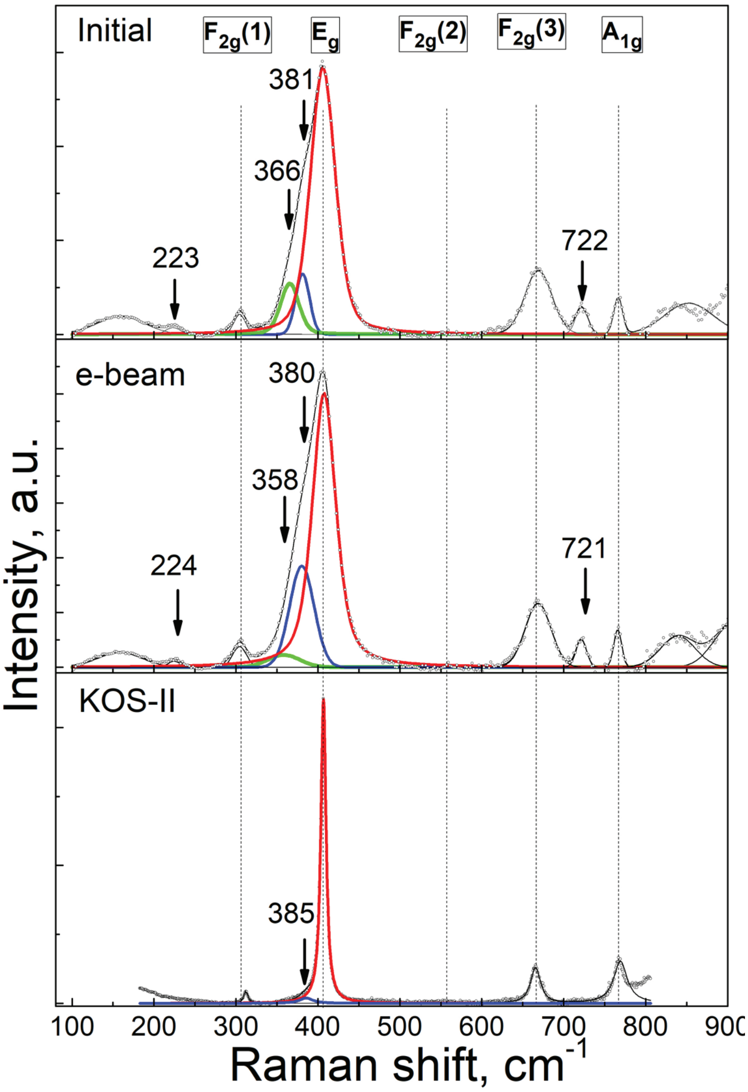

Figure 2: Raman scattering spectra of initial ceramics, irradiated one, and natural spinel. Dash lines – modes characteristic for natural spinel with normal structure.

synthesized AMS ceramics Raman analysis allow concluding that there is a substantial disorder associated with reversal of the structure. Irradiation by accelerated electrons leads to structural changes caused by formation of additional ADs.

3.3. Photoluminescence

Luminescence of natural spinel and AMS ceramics under 2.54 eV excitation is presented in Figure 3. Zero-phonon lines of chromium (R_1, R_2) radiative $^2E \rightarrow ^4A_2$ transitions, phonon wing in Stokes region (R-PSB), and region of zero-phonon N-lines associated with disorder of chromium environment are observed in luminescence spectrum of natural spinel (KOS-II) [16, 25].

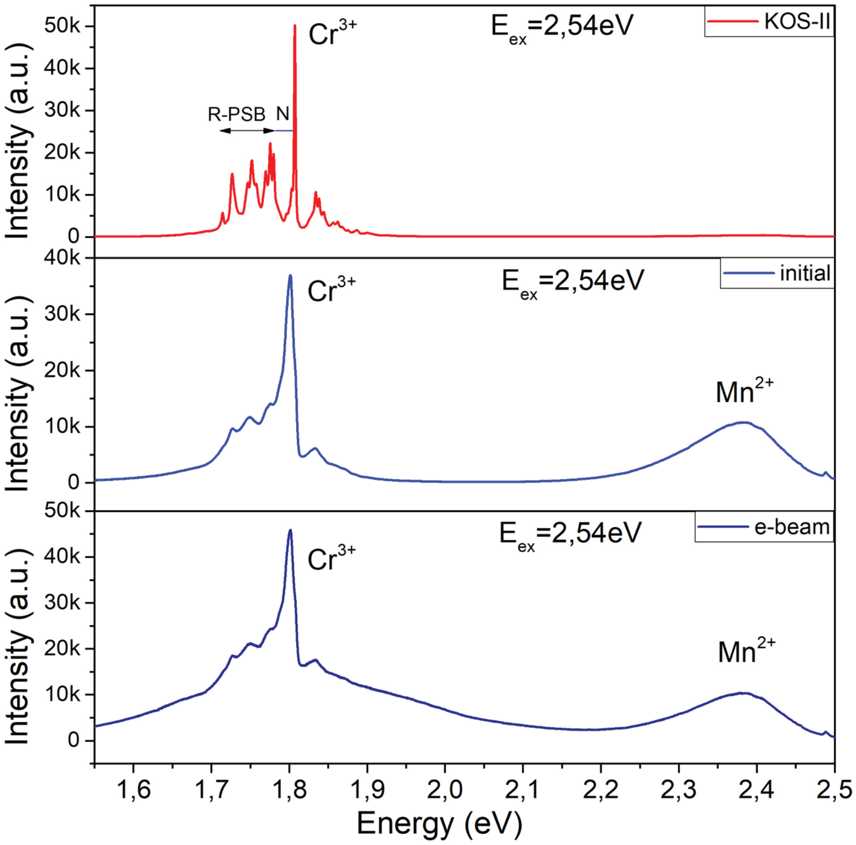

Figure 3: Luminescence spectra of initial ceramics, irradiated one, and natural spinel, RT.

Synthesized ceramics have broadened bands associated with luminescence of Cr ions in spinel matrix. A halo in 1.6–2 eV range is observed in spectra of spinel ceramics irradiated by electrons in addition to indicated luminescence. Irradiation by high-energy electrons leads to formation of ADs as it was shown in OA and Raman spectra. Growth of cation disordering leads to change of crystalline field local strength around Cr ion impurity. Such local distortions of matrix near chromium ion result in the luminescence bands broadening. It is noted that nonstoichiometry of AMS can have a significant effect on optical properties along with inversion of the structure [18].

On the luminescence spectra, an additional maximum of 2.4 eV caused by the presence of impurity Mn^{2+} in the tetrahedral position of Mg^{2+} is observed. There were no obvious changes in shape or intensity of the observed signal after irradiation.

Synthesized spinel has increased ADs concentration compared to natural crystals. On the other hand, irradiation by accelerated electrons also results in increase of ADs concentration. Thus, observed correlation between OA spectra (rise of absorption band in 3.7 eV), RS (decrease of main oscillation mode intensity in irradiated ceramics and redistribution of intensities of oscillation modes derived from deconvolution), and PL (widening of Cr^{3+} spectral lines) is due to effect of ADs on Cr^{3+} ions in octahedral aluminum cation position. Therefore, extrinsic cation center in transparent ceramics of aluminum magnesium spinel can act as indicator of ADs presence in cation sublattice.

4. Conclusion

Transparent $MgAl_2O_4$ ceramics were synthesized. Characterization of the samples was performed by optical absorption, Raman scattering, and photoluminescence methods. Relatively high stability to electron beams allows using transparent AMS ceramics as a functional material in alternative energy devices operating under extreme conditions.

Irradiation of aluminum magnesium spinel transparent ceramic by 10 MeV electrons results in formation of optically active defects in wide spectral range. Analysis of absorption, Raman scattering, and luminescence spectra allowed finding that irradiated samples have F^+, F-, and V-type anion defects. These defects in spinel are identified by the methods of OA and Raman scattering by the presence and broadening of characteristic bands.

It was found that effect of 'ionic mixing' in cation sublattice took place under 10 MeV electron beam irradiation. This effect is associated with the formation of point anti-site defects $[Al]_{Mg}$ and $[Mg]_{Al}$. There were no significant changes in the characteristic luminescence band of extrinsic Mn^{2+} ions according to spectroscopy data. It was shown that radiation-stimulated anti-site defects led to the formation of the halo induced by the growth of disordering in cation sublattice near the Cr^{3+} ions in the luminescence range 1.6–2 eV. Optical properties of Cr^{3+} ions can be utilized as indicators of cation disordering in the transparent ceramics structure.

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