

Excitation of different chromium centres by synchrotron radiation in MgO:Cr single crystals



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ARTICLE INFO

Article history:

Received 9 July 2015

Received in revised form

19 August 2015

Accepted 20 August 2015

Available online 22 August 2015

Keywords:

MgO

Luminescence

Impurity centres

Synchrotron radiation

ABSTRACT

The excitation spectra for the emissions of chromium-containing centres have been measured at 10 K using synchrotron radiation of 4–32 eV in MgO single crystals with different content of Cr³⁺ (5–850 ppm) and Ca²⁺ impurity ions. Both virgin crystals and the samples preliminarily irradiated with x-rays at 295 K have been studied. The role of complex chromium centres containing two Cr³⁺ and a cation vacancy (sometimes nearby a Ca²⁺ ion) on the luminescence processes and the transformation/creation of structural defects has been analysed. Such anharmonic complex centres could serve as the seeds for the creation of 3D defects that facilitate the cracking and brittle destruction of MgO crystals under their irradiation with ~GeV heavy ions providing extremely high excitation density within cylindrical ion tracks.

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1. Introduction

For more than a half of century face-centred cubic MgO single crystals have served as a model for theoretical and experimental investigations of numerous physical processes in a family of binary and complex wide-gap materials (WGMs, in MgO $E_g = 7.83$ eV at ~5 K) [1–19]. The growth of high-melting (~3100 K) MgO single crystals with a high level of perfection and purity (99.999, i.e. the concentration of cation and anion impurities down to 10^{-4} at%) is rather difficult and expensive procedure. Such single crystals exhibit extremely high resistance against irradiation with γ - or x-rays. In perfect regions of the MgO bulk, the formation energy of a Frenkel pair (vacancy-interstitial) significantly exceeds the value of E_g (see, e.g., [20,21]) and the recombination of completely relaxed conduction electrons (e) and valence holes (h) does not cause the creation of Frenkel defects.

However, surface corrosion of MgO takes place in a humid air atmosphere. In addition, radiation defects are created/transformed even under low-dense irradiation of MgO crystals containing in the bulk as-grown structural defects or traces of OH⁻ (substitute for oxygen ions), divalent ions Be²⁺, Ca²⁺, Fe²⁺, Ni²⁺, Sn²⁺ (substitute for Mg²⁺), Li⁺ and Na⁺ or trivalent Al³⁺, Cr³⁺, Fe³⁺ cation impurities with additional charge compensation. The

radiation-induced effects are more complicated under irradiation of WGMs containing nonisomorphic impurity ions (with respect to valence, ion radius as well as to atom mass) with fast neutrons, powerful electron pulses of 10^{-9} – 10^{-7} s or ~GeV swift heavy ions (SHIs) (see, e.g., [22–27]). Such SHIs spend more than 99% of their energy on ionisation losses providing a superhigh density of electronic excitations within overlapping cylindrical ion tracks and causing the cracking and even destruction of single crystals. Besides the knock-out (impact) mechanism universal for solids, radiation defects can also be formed at the decay of high-energy electronic excitations, recombination of long-lived ($\tau > \tau_{LO}$) core holes with conduction electrons or the recombination of non-relaxed (hot) e and h (see, e.g., [28,29]). Recently, the collapse of the so-called mobile discrete breathers (see, e.g., [30]) was considered as the reason for the rearrangement of many host ions and the formation of 3D defects in heavily irradiated materials predisposed to anharmonic interactions (see [31] and references therein). The creation of 3D defects, which serve as stoppers for dislocations impeding their movement to the surface and facilitating the cracking and brittle destruction of irradiated single crystals, was considered for metals and alloys in the framework of dynamical nonlinear theory of elasticity [31]. It was suggested that similar effects could cause the radiation damage and destruction of WGMs as well. Some experimental manifestations of the creation of 3D defects have been already detected in WGMs (see, e.g., [32]). The goal of the present study is to make an intermediate analysis of our recent experimental results connected with the influence of different luminescent impurity ions (especially pair

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Cr^{3+} centres containing in some cases also Ca^{2+}) on defect creation/transformation in MgO crystals.

2. Experimental

MgO single crystals were grown in Tartu from a highly pure starting material by a variation of the arc-fusion method. Nominally pure samples contain about 10 and 5 ppm of Ca^{2+} and Cr^{3+} impurity ions, respectively, while the concentration of Cr^{3+} ions in MgO:Cr equals 100 or 850 ppm. The photoluminescence experiments were carried out at 10 K at the SUPERLUMI station of HASYLAB at DESY, Hamburg [33]. This experimental set-up is unique tool for investigations of wide band gap materials [12,18,28,29,33–36]. The excitation spectra were normalised to equal the quantum intensities of the synchrotron radiation (4–32 eV) falling onto the crystal. The emission spectra of Cr^{3+} -related centres were recorded using a monochromator-spectrograph SpectraPro-308i equipped with a liquid nitrogen cooled CCD detector (typical resolution of 1 nm). Identical MgO:Cr crystals were investigated earlier under argon-ion laser pumping [16]. Some investigated crystals were previously irradiated by SHIs (~ 2 GeV, ^{238}U or ^{197}Au , range of 95 μm) at room temperature (RT) perpendicular to the (100) plane at the UNILAC linear accelerator of the GSI, Darmstadt [23,24].

3. Experimental results and discussion

Numerous impurity centres have been detected using EPR and optical methods in MgO crystals doped with trivalent Cr^{3+} ions [1,7,12,16–19,37]. A single Cr^{3+} substitutes for an Mg^{2+} forming a cubic impurity centre, while a nearby-located cation vacancy V_{Mg} lowers the symmetry to tetragonal or rhombic one. The radiative transitions ${}^2E \rightarrow {}^4A_2$ in cubic or tetragonal centres cause a series of narrow zero-phonon lines: R line at 1.776 eV and N line at 1.762 eV (lines of single- and pair-centres are not resolved in our case) as well as their broader phonon sidebands at 1.78–1.65 eV (698–750 nm, see Fig. 1). At chromium concentration of 850 ppm (Fig. 1c, f), the nonelementary broadband emission at 1.77–1.24 eV, tentatively connected with two-chromium centres with different rhombic microstructure has been also detected in a set of emission spectra measured by CCD detector at the excitation with 4–32 eV photons at 10 K. In contrast to the case of laser-excitation of MgO at RT [16], no broadband emission was observed in 100 ppm-crystals (Fig. 1b, e). The intensity of zero-phonon R and N

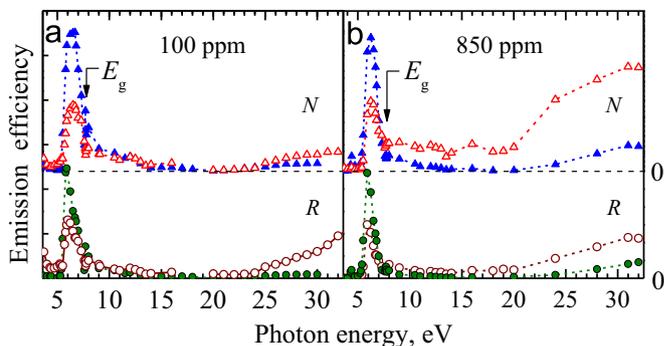


Fig. 2. Excitation spectra of N- (upper half) and R- emission lines (lower half) measured at 10 K for virgin (full symbols) and pre-irradiated (empty symbols) MgO crystals with 100 (a) or 850 ppm (b) of Cr^{3+} impurity ions (see text for details).

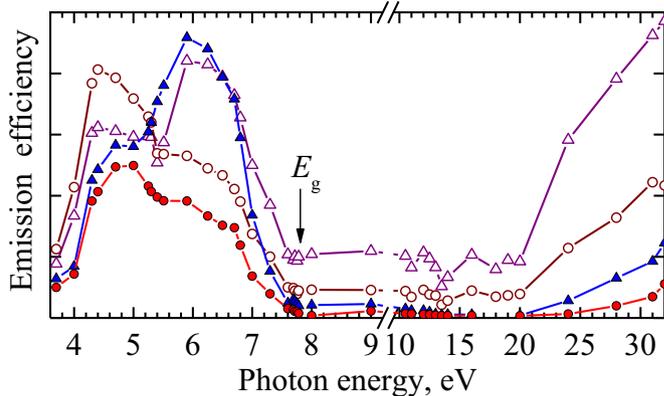


Fig. 3. Excitation spectra of the emissions at 1.6 eV ($\blacktriangle, \triangle$) and 1.42 eV (\bullet, \circ) measured at 10 K for virgin (\blacktriangle, \bullet) and x-irradiated (\triangle, \circ) MgO:Cr (850 ppm) crystals (see text for details).

emission lines or of the emission at 1.42 or 1.6 eV (the maxima of a rough decomposition of the broadband emission) was used for the construction of the excitation spectra for these emissions (see Figs. 2 and 3). The spectra were measured for two identical samples, one of which was preliminarily irradiated with x-rays at RT (50 keV, W, dose of ~ 10 kGy, 4–5 days before synchrotron measurements).

A preliminary x-irradiation of MgO:Cr $^{3+}$ (850 ppm) significantly changes the excitation spectra for the N- and R-lines (see Fig. 2b). In the x-irradiated sample, the efficiency of R- and N-emissions is halved in the region of intracentre excitation by

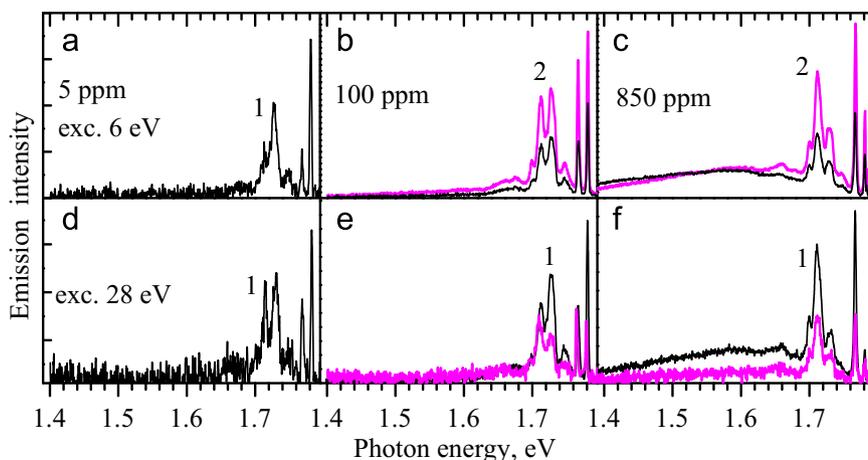


Fig. 1. Emission spectra measured at the excitation by the 6 eV (a–c) or 28 eV (d–f) photons at 10 K using CCD detector for x-irradiated (1) and virgin (2) MgO crystals containing ~ 5 ppm (a, d), 100 ppm (b, e) or 850 ppm (c, f) of Cr^{3+} ions. Curves 2 in (e) and (f) are multiplied by the factor of 2.

$h\nu=5.5-7.5$ eV photons, while the rise of $h\nu$ from 24 to 32 eV causes an increase in the excitation efficiency of the R- and N-lines by a factor of 5 or 3, respectively. The behaviour of the excitation spectra for R- and N-emissions in MgO:Cr³⁺ (100 ppm) is similar in favour of R-line (see Fig. 2a). At RT, x-ray-induced h become trapped on some centres (like Cr³⁺–V_{Mg} or a bivacancy V_{Mg}V_O) and e become trapped on Cr³⁺ ions converting them into Cr²⁺ centres, which are stable at RT and remain in this charge state after cooling down to 10 K. Cubic and tetragonal Cr-centres containing Cr²⁺ do not produce the Cr³⁺-emission at excitation energies below E_g , so the efficiency of Cr³⁺-centres emission is lower in the x-irradiated sample.

The situation changes when $h\nu > E_g$ and mobile charge carriers are created. Valence holes reach Cr²⁺ centres and recombine there with trapped electrons, thus creating excited Cr³⁺ centres, which relax with a characteristic emission. Moreover, the efficiency of R- and N-emissions at the excitation by the photons of $h\nu > E_g$ in the pre-irradiated sample (see curves with open symbols in Fig. 3) is even higher than that in a virgin crystal. Preliminary x-irradiation causes the filling of electron/hole traps and, as a result, decreases the efficiency of related channels of the absorbed energy transfer from a matrix, which are in competition with radiative electron–hole recombination near Cr³⁺ (i.e. excitation of the Cr³⁺-emission). It should be noted that the suppression of Coulomb-type traps with very high recombination cross-section, for instance positively double-charged cation (magnesium) vacancies that cannot be found in alkali halide crystals, has a determining effect on such competition in MgO:Cr crystals.

According to Fig. 3, the influence of preliminary x-irradiation on the excitation spectra for the emissions at 1.42 or 1.6 eV connected with pair chromium centres at $h\nu > E_g$ is approximately the same as in the case of R- and N-emissions. However, below 7 eV the spectra ratio for virgin and x-irradiated samples of MgO:Cr (850 ppm) is more complicated. It is worth noting that even prolonged irradiation with $h\nu \sim 20$ eV at 10 K causes the recharging of some Cr³⁺ into Cr²⁺. The intensity of Cr³⁺-emission (thoroughly studied at 77 K and RT in [8]) considerably decreases with a crystal cooling from 77 to 10 K. In our opinion, the effect is caused by the attenuation of the emission related to ⁵⁴Cr isotope with nuclear spin $I=0$, while MgO:Cr (850 ppm) contains also ~ 80 ppm of ⁵³Cr ($I=3/2$) ions the emission of which can be observed at 10 K.

Several types of pair chromium centres have been already observed in MgO:Cr single crystals [1,7,32]. Firstly, it is a tetragonal linear centre Cr³⁺–O²⁻–V_{Mg}–O²⁻–Cr³⁺, where two Cr³⁺ are spatially separated from each other. Fig. 4 presents two possible rhombic pair centres, the number of which significantly increases with the rise of Cr³⁺ concentration from 100 to 850 ppm. At the left, there is a triangular centre with two spatially close Cr³⁺ and V_{Mg}, which serves as an efficient trap for a radiation-induced hole at the oxygen ion depicted by a solid circle (see also [32]). At the right of Fig. 4 there is another linear rhombic centre. Recent

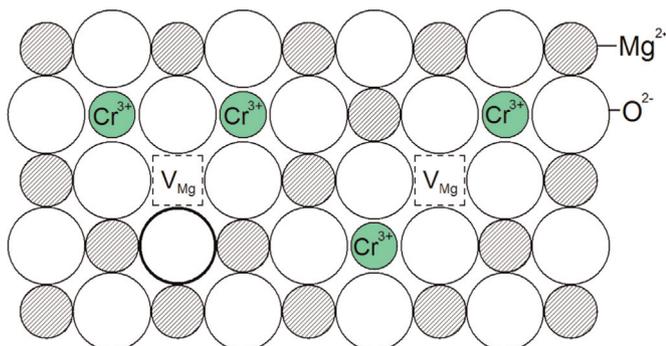


Fig. 4. Possible configurations of two-chromium rhombic centres in MgO.

theoretical studies confirm that in the case of single Cr³⁺–cation vacancy defect dipoles both C_{4v} and C_{2v} centres are existed in MgO:Cr³⁺ and the presence of the magnesium vacancy induces a significant structural relaxation [38,39]. Nevertheless, the theoretical analysis of complex centres, containing two or more Cr ions, is still absent in the literature.

From radiation damage standpoint of particular interest is one more complex two-chromium centre located nearby a Ca²⁺ impurity ion. For a large-size Ca²⁺ (3s²3p⁶3d⁰) it is energy-profitable to be located nearby a bivacancy V_{Mg}V_O within a complex centre. The optical characteristics of V_{Mg}V_O (similar to those in alkali halides [40]) have been revealed in MgO crystals grown from the melt [26]. It was shown earlier that a low-temperature emission peaked at 6.8 eV is related to the recombination of conduction electrons with the holes localised near Ca²⁺ in MgO:Ca (~ 100 ppm) [17]. The allowed $2p^6 \rightarrow 2p^5 3d$ electric dipole transitions take place in a Ca²⁺ ion at 27–30 eV. According to Figs. 2 and 3, just in the same spectral region there is a sharp rise of the emission efficiency of chromium centres in MgO:Cr (850 ppm) crystals (especially in the samples preliminarily exposed to x-irradiation at 295 K) – in the region of MgO fundamental absorption with small values of absorption constants for near-normal incidence [11], Ca²⁺ ensure the absorption of exciting photons and efficient energy transfer to chromium ions.

According to our experimental data [26,32,41], MgO single crystals containing minimum concentration of as-grown structural and impurity defects sustain SHI-irradiation (~ 2 GeV, ²³⁸U, ²⁰⁹Pb or ¹⁹⁷Au ions) with a fluence up to $\Phi=10^{13}$ ions/cm² that corresponds to average distance between neighbour tracks of $d=3.6$ nm. The sample cracking starts at the fluence of $\Phi=2 \times 10^{13}$ ions/cm² ($d=2.3$ nm) and brittle destruction of the irradiated crystal – at $\Phi=7 \times 10^{13}$ ions/cm² ($d=1.2$ nm) [42]. In MgO crystals with 850 ppm of Cr³⁺ and up to 50 ppm of Ca²⁺, there are anharmonic polyatomic centres each of which includes two Cr³⁺, Ca²⁺, an oxygen vacancy and magnesium vacancy and the initial stages of cracking begin already at $\Phi=10^{12}$ ions/cm² and $d=10$ nm.

4. Concluding remarks

The presence of certain impurity ions causes a dual influence on the creation efficiency of radiation defects in WDMs. The presence of even ~ 10 ppm of isovalent to Mg²⁺ light impurity ions (Be²⁺, Ca²⁺) decreases the radiation resistance of MgO single crystals. Such impurities serve as efficient traps for radiation-induced holes and, therefore, increase the probability of a sequent recombination of hot conduction electrons with trapped holes centres (the so-called hot e–h recombination) resulting in the creation of Frenkel defects (see [17,25] and references therein). In principle, the efficiency of defect creation via hot e–h recombination in some WGMs can be reduced by a light doping. In some cases, a hot conduction electron can spent its energy excess for the direct excitation of a certain impurity centre up to the excited state, while a subsequent recombination of the cooled carriers already provides insufficient energy for the creation of a pair of Frenkel defects. This solid-state analogue of the Franck-Hertz effect is considered as some kind of “luminescent protection” against radiation damage of WGMs [25,29,41,43,44]. However, at the rise of impurity concentration up to $\sim 1-2\%$ that is needed for the pronounced “luminescent protection”, the situation becomes more complicated – the formation of pair impurity centres increases the efficiency of radiation damage.

A complex impurity centre that incorporates two spatially close Cr³⁺, a cation vacancy and a Ca²⁺ ion could serve as an anharmonic seed for the formation of theoretically predicted [30,31] discrete breathers and their collapse with the creation of large 3D

defects. Under irradiation with \sim GeV SHIs providing extremely high excitation density ($\text{LET} > 20 \text{ keV/nm}$) within cylindrical ion tracks, such 3D defects are the stoppers for mobile dislocations and thereby facilitate the formation of dislocation loops, cracking and even brittle destruction of MgO single crystals.

Acknowledgements

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007–2013) under Grant agreement no. 226716, the Estonian Research Council – Institutional Research Findings IUT02-26. A.I. Popov thanks ESF Grant no. 2013/0046/1DP/1.1.1.2.0/13/APIA/VIAA/021.

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