Review of effects of radiation damage on the luminescence emission of minerals, and the example of He-irradiated CePO₄

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Abstract The accumulation of structural damage that is created in minerals upon corpuscular irradiation, has two apparently contrarious effects on their luminescence behaviour. First, irradiation may cause the generation of luminescent defect centres, which typically results in broad-band emissions. Such defect emissions are characteristic of low levels of radiation damage. Second, radiation damage depletes in general the luminescence of minerals, which is associated with broadenings and intensity losses of individual emission lines. Minerals that have suffered elevated levels of irradiation hence tend to be virtually non-luminescent.

This review paper aims at giving an overview of the possible correlations of radiation damage and emission characteristics of minerals. After a brief, introductory summary of the damage-accumulation process and its causal corpuscular radiation, an array of examples is presented for how internal and/or external irradiation may change appreciably the emission of rock-forming and accessory minerals. As a detailed example for the complexity of changes of emissions upon damage accumulation, preliminary results of a case study of the photoluminescence (PL) of synthetic CePO₄ irradiated with 8.8 MeV He ions are presented. Irradiation-induced spectral changes include (i) the initial creation, and subsequent depletion, of a broad-band, defect-related PL emission of orange colour, and (ii) gradual broadenings and intensity losses of PL lines related to electronic transitions of rare-earth elements, eventually leading to gradual loss of their splitting into multiple Stark levels (shown for the $^4F_{3/2} \rightarrow ^4I_{9/2}$ transition of Nd³⁺).

Keywords Radiation damage • Ion irradiation • Defect centres • Radio-haloes • Photoluminescence • Cathodoluminescence

Introduction: Radiation damage in minerals

The common phenomenon of structural radiation damage in minerals is predominantly due to atomic displacements that are caused by alpha decays of radio-nuclides (i.e., uranium and thorium, and their instable daughter nuclei). The beta-decay events in the same decay chains, and gamma radiation, are in general considered insignificant for the creation of permanent structural damage though the displacement of lattice atoms. The spontaneous fission of ^{238}U , in contrast, produces a high amount of localised damage; this process is nevertheless negligible in considering bulk damage because of its relative rarity.

In discussing the action of alpha-decay events, two different types of radiation are to be considered (Fig. 1). An instable, heavy parent nucleus A emits spontaneously an alpha particle (i.e., a helium core) and hence transforms into a daughter nucleus B, according to:

A huge amount of energy, on the order of several millions of electron volts, is released in such an event. Its two main products, namely the alpha particle emitted and the heavy daughter nucleus, acquire the same impetus. Because of its ca. 50-fold higher weight, the heavy daughter nucleus carries away only about 2% of the energy (0.06–0.17 MeV), compared to that of the alpha particle (3.9–8.8 MeV). The recoil energy however still exceeds by several orders of magnitude the binding and displacement threshold energies of lattice atoms. The daughter nucleus is therefore displaced from the original lattice site of its parent, and travels through the host lattice.

To visualise, for the example of the alpha decay of ^{212}Po , the different trajectory lengths of the recoil nucleus and the alpha particle emitted, and the different profiles of their nuclear and electronic interactions (i.e., atomic displacements and lattice ionisation, respectively) in the host mineral, Monte Carlo simulations were done of the stopping of 0.17 MeV ^{208}Pb and 8.8 MeV ^4He ions in a CePO_4 target. The calculations were done using the SRIM–2008 code (Ziegler et al. 2008). This software package (SRIM = the Stopping and Range of Ions in Matter) is based on a full quantum-mechanical treatment of ion-atom collisions; it predicts, among others, the ranges of the ions irradiated, and density and distribution of the vacancies generated in the target (Ziegler et al. 1985). The density of atoms in the target was assumed to be $8.145 \times 10^{22} \text{ cm}^{-3}$ ($\rho = 5.3 \text{ g/cm}^3$). The SRIM default values were accepted for displacement threshold (Ce and P, 25 eV; O 28 eV), lattice binding (3 eV), and surface binding energies (3.3–4.2 eV). To reach high statistical precision, trajectories for 10,000 incoming ions, irradiated into the target perpendicular to its surface, were calculated. Selected results are presented in Fig. 1.

The 0.17 MeV recoil nucleus loses a significant fraction of its energy in nuclear interactions (i.e., elastic collisions with lattice atoms; Fig. 1). Including multiple atomic displacements within sub-branches created by the displaced lattice atoms, each recoiled nucleus thus creates a tiny damage cluster. This cluster is less than 100 nm in length (compare Weber 1990; Weber et al. 1994; Shpak et al. 2007). According to our SRIM results it contains an average of ~2000 atomic displacements (Fig. 1). The 8.8 MeV alpha particle, in contrast, travels more than 30,000 nm through the monazite target. Throughout its pathway it loses the vast majority of its high energy through electronic interactions, and ~200 scattered Frenkel-type defects (i.e., vacancy–interstitial pairs) are created predominantly near the far ends of the ion trajectories (cf. Weber et al. 1998; Ewing et al. 2003; Fig. 1). It should be noted that among the common alpha-decay events in the U–Pb and Th–Pb chains, the ^{212}Po decay

releases the highest energy. The recoiled ^{208}Pb therefore creates the largest defect cluster with the highest number of defects; the same is true for the alpha particle created in this event.

It should be noted that the number of defects in the ballistic collision cascade caused by a heavy recoil nucleus is still a contested issue. For instance, Devanathan et al. (2006) found that an average of ~6000 defects are created per alpha recoil in zircon, whereas SRIM calculations of Nasdala et al. (2001) predicted an average of only ~1000 defects per recoil cluster. Predictions of the amounts of defects based on SRIM calculations should therefore be considered as rather rough estimates (for instance, the anisotropy of the target lattice remains unconsidered, and default energies were used). More reliable predictions require the application of molecular dynamics (MD) simulations (Trachenko et al. 2004; Devanathan et al. 2006; Shpak et al. 2007). As an example for a MD result, a picture of the damage cluster created by a heavy nucleus is shown in Figure 2. It can be seen clearly that its central, density-depleted amorphous part is surrounded by a region where the host lattice is compacted and affected by shear stress and shows high concentrations of point defects (for details cf. Trachenko et al. 2002).

In spite of significant simplifications and the resulting uncertainties, our SRIM results (Fig. 1) nevertheless indicate that minerals incorporating the radio-nuclides U and Th in their lattices, suffer structural damage mainly due to the action of alpha recoils (cf. Wasiliewski et al. 1973). The alpha particles themselves have rather subsidiary contribution (i.e., ca. 10–15%) to the total bulk damage. Due to the comparably minor damage efficiency but much longer range of the alphas emitted, compared to the recoiled nuclei, alpha particle damage is mostly observed in non-radioactive minerals as a result of external irradiation. This irradiation may emanate either from U- or Th-containing phases that are included within the mineral, or radioactive sources (minerals or fluids) in close proximity. For U- or Th-bearing minerals, notable alpha-particle damage has been described only in few cases, for instance near boundaries between zones or interior regions that show huge relative differences in the radio-nuclide concentrations (for heterogeneous zircon shown by Nasdala et al. 2005).

The metamictisation process, i.e., build-up of bulk damage in actinide-bearing minerals, is based on the accumulation of numerous recoil clusters (plus scattered point defects) over geologic periods of time. The corpuscular irradiation itself – in mineralogical papers commonly expressed by the time-integrated alpha dose (Holland and Gottfried 1955; Murakami et al. 1991; Nasdala et al. 2001) – is however, inappropriate to “quantify” the radiation damage of a certain mineral. First, irradiation effects (i.e., the efficiency of a certain corpuscle in generating damage) may vary appreciably depending on the mineral species irradiated. Second, and most importantly, irradiation effects vary appreciably depending on the temperature (Meldrum et al. 1999; Nasdala et al. 2001). Note that a high number of alpha-decay events is merely an essential presumption for, but does not necessarily result in, the formation of bulk damage. Whether or not the structural damage created in alpha-decay events is stored and accumulated by the host mineral depends on the temperature-dependent ratio between damage generation and damage annealing.

We attempt to visualise the resulting different behaviours of minerals with two arrays of sketches in Figure 3. At temperatures where annealing is insignificant, or at least exceeded by the rate of damage creation, the recoil damage is accumulated (Fig. 3, upper row). At low irradiation levels, the crystalline host mineral shows isolated recoil clusters (plus scattered point defects). At elevated irradiation levels, the damage clusters inter-connect and form a three-dimensional network. This process is referred to as percolation transition (Salje et al. 1999; Trachenko et al. 2004); it is connected with dramatic changes in the diffusion

behaviour. Upon further damage accumulation, the bulk crystalline phase collapses and isolated crystalline remnants in an amorphous matrix are observed; and eventually the material becomes amorphised. This sequence (compare also Murakami et al. 1991) describes – widely simplified – the metamictisation process, as it is observed commonly for minerals such as pyrochlore, tetragonal ThSiO_4 , or zircon. The prerequisite for the damage accumulation is that these minerals must have spent a sufficiently long period at sufficiently low temperatures (for zircon below 150–200 °C; Meldrum et al. 1998; 1999). Still, the alpha dose experienced by the respective mineral since the time of its growth cannot be expected from the outset to correlate with the damage present. In fact, the majority of natural zircon was found to be less radiation-damaged than it would correspond to complete accumulation of the alpha-event damage (Nasdala et al. 2004).

At elevated temperatures, or for minerals that undergo self-annealing at low temperatures already (for instance monazite-group phosphate minerals or monoclinic ThSiO_4), the annealing rate exceeds the rate of creation of irradiation-induced damage. As a result, the damage cannot be accumulated (the structural recovery is visualised in Fig. 3, lower row, as “fading” of damage clusters). For example, monazite-(Ce) has, to the best of our knowledge, never been found in a severely radiation-damaged or even fully metamict state (Seydoux-Guillaume et al. 2007; Ruschel et al. 2012), in spite of the mostly much higher actinide concentrations and alpha doses of this mineral, compared to zircon.

Provided the thermal annealing does not prevail, the alpha-decay damage is accumulated. The above description is however guilty of some simplification, as in addition to the two competing processes of immediate annealing and crystalline-to-amorphous transition as a result of damage accumulation, other processes need to be taken into consideration also. First, there are always moderate irradiation-induced chemical changes, because in alpha-decay events the parent element transmutes into a daughter element and helium is produced. Also, the corpuscular “bombardment” of the target may result in segregation and phase or molecular decomposition. Examples include the irradiation-induced transformation of $\gamma\text{-Fe}_2\text{SiO}_4$ into Fe_3O_4 and SiO_2 (Wang et al. 1999), decomposition of HfSiO_4 and ZrSiO_4 into component oxides (Meldrum et al. 1999), or conversion of CO_2 molecules in cordierite into CO and O_2 (Nasdala et al. 2006a; Krickl et al. 2009b; Weikusat et al. 2010). In the study of radiation-damage effects, one is obliged to survey cautiously as to which degree such irradiation-induced changes may have affected the radiation-damaged mineral under investigation.

The structural and chemical changes caused by the self-irradiation result in dramatic changes of the mineral’s solid-state properties. Apart from significant changes of many physical parameters (such as refraction, hardness, density, and elastic moduli; see for instance Holland and Gottfried 1955; Vance and Milledge 1972; Chakoumakos et al. 1991; Dooley et al. 1993), the chemical resistance of radiation-damaged minerals is typically decreased, resulting in enhanced susceptibility to secondary alterations and chemical changes (e.g., Balan et al. 2001; Mathieu et al. 2001; Geisler et al. 2003; 2005; Nasdala et al. 2010b). Care should however be taken in discussing direct and indirect irradiation effects. The latter comprises changes that are not caused by the irradiation and the resulting structural damage itself, but by subsequent processes such as secondary alteration. However, radiation damage decreases a mineral’s chemical resistance and hence *favours* chemical alterations, but it does not *cause* such processes. Elemental, textural, and colour changes caused by a fluid-driven reaction, for instance, therefore cannot be considered as direct irradiation effects.

The decreased resistance of radiation-damaged minerals in potential post-growth processes is of enormous importance, as it for instance affects negatively their performance to immobilise radioactive elements (storage of nuclear waste) or to retain radiogenic nuclei (bias of geochronology results). The former is probably the main motivation for the extensive research done on radiation-damaged minerals and their synthetic analogues during the past two decades. Such secondary irradiation effects will nevertheless not be summarised here. The following discussion of irradiation-induced changes of the emission behaviour of minerals focuses on direct irradiation effects, i.e., changes in radiative electronic transitions that are due to modifications of the structure as caused by the impact of corpuscular radiation.

Radiation-damage effects on the luminescence of minerals

Possible effects of corpuscular radiation on the luminescence of minerals are still discussed somewhat controversially by Earth scientists. On the one hand, structural damage is known to suppress in general the emission performance of crystals (e.g., Vaz and Senftle 1971; Geisler and Pidgeon 2001; Seydoux-Guillaume et al. 2002; Nasdala et al., 2009; Ruschel et al. 2010). On the other hand, damage may enhance the emission, as observed from the strongly luminescent radio-haloes in naturally non- or weakly luminescent minerals (e.g., Smith and Stenstrom 1965; Mendelssohn et al. 1979; Schertl et al., 2004; Botis et al., 2005; Kagi et al. 2007). These two trends are only apparently contrarious; they are merely due to two different irradiation-induced phenomena which may even be affected simultaneously. They are summarised in the following and illustrated with examples (Fig. 4).

It is well-known that irradiation-damage in minerals may reduce notably their emission performance as detected by ionoluminescence (e.g., Garcia-Guinea et al. 2007; Nagabhushana et al. 2008) and thermoluminescence (e.g., Vaz and Senftle 1971). Please note, however, that these techniques are not discussed in detail here; our summary focuses on effects of irradiation damage in minerals on the two luminescence techniques that are used most commonly in the study of geological materials, namely, photoluminescence (PL) and cathodoluminescence (CL).

Most rock-forming and accessory minerals are insulator crystals. Such materials (provided they are chemically pure and well-crystalline) do not emit visible luminescence due to “intrinsic” band–band electronic transitions, because their forbidden band gap corresponds to quantum energies in the ultraviolet (UV) range. Luminescence of insulator-type minerals is however commonly observed owing to the presence of additional electronic levels within the band gap, which may for instance be caused by traces of non-formula chemical constituents, vacancies, or structural distortions. Such deviations from the ideal chemical and structural composition may also be created by the impact of radioactivity (or other forms of irradiation, such as the impact of the high-energy electron beam during electron probe micro-analysis). One potential effect of corpuscular irradiation is therefore the introduction of electronic activator levels into the band gap through the creation of defect centres (i.e., vacancies, interstitials, valence changes; or combinations of them).

One of the most common and striking example for defect luminescence is that of α -quartz. Structural damage in this mineral as caused by the impact of alpha-irradiation is easily detected in cathodoluminescence (CL) images obtained in CL systems attached to an optical microscope (OM–CL). Here, the damage is observed in the form of yellowish-orange radio-haloes (Owen 1988; Ramseyer et al. 1988; Meunier et al. 1990; Götze et al. 2001; Krickl et al.

2008; Okumura et al. 2008). The sources of the alpha radiation are mostly inclusions of actinide-bearing minerals (Fig. 4a), however external alpha-irradiation caused by neighbouring phases such as radioactive fluids (Fig. 4b) are also observed. As alpha particles in the natural U and Th decay chains penetrate about 10–45 μm in α -quartz, luminescent radio-haloes in this mineral typically have diameters of several tens of micrometres (Komuro et al., 2002; Botis et al., 2005; Krickl et al., 2008). The orange colour of the CL emission was assigned by Siegel and Marrone (1981) to non-bridging oxygen-hole centres generated by the impact of alpha particles. An analogous (however much more rarely observed) example for luminescent radio-haloes was documented by Schertl et al. (2004), namely, blue emission of kyanite related to alpha-particle damage in close proximity to radioactive monazite (Fig. 4c).

In addition to the investigation of radio-haloes in naturally irradiated minerals, defect-luminescence phenomena are studied increasingly from samples that were irradiated with beams of ions. As discussed above, the investigation of natural samples always bears the uncertainty that, due to a possibly unknown or uncertain thermal history, estimates of the amounts of irradiation that have caused effectively the defect luminescence observed are potentially biased. Irradiations in the laboratory (especially if done at very low temperatures), in contrast, allow one to exclude post-irradiation annealing and hence provide a more reliable tool for the quantification of irradiation effects. Examples for the generation of defect luminescence in irradiation experiments are presented in Figures 4 d–f.

Alpha irradiation of diamond followed by moderate heating at temperatures in the range 500–1000 $^{\circ}\text{C}$ causes, in addition to transformation of the green into orange-brown radio-colouration (Vance et al. 1973), intense yellowish green defect luminescence (Fig. 4d). The emission is mainly assigned to the H3 centre (i.e., two N atoms associated with a vacancy; see Zaitsev 2001, and references therein). This centre's zero-phonon line lies near 19870 cm^{-1} (503.2 nm wavelength), with several intense electron-phonon coupling bands in the range $>18900 \text{ cm}^{-1}$ ($<529 \text{ nm}$ wavelength). It forms when upon thermal annealing the irradiation-induced GR1 centre (i.e., a neutral vacancy) becomes mobile and is trapped at an A defect (i.e., a nitrogen pair; Alekseev et al. 2000; Collins et al. 2005; Collins and Kiflawi 2009). A similarly strong activation of defect luminescence (however of yellow colour) is observed upon alpha irradiation of zircon (Fig. 4e). The emission centre is related to point defects created by the alpha particles (Götze et al. 1999; Gaft et al. 2002; Nasdala et al. 2011); however its exact assignment is still somewhat controversial. The OM–CL image presented in Figure 4e shows a synthetic ZrSiO_4 crystal after comparably heavy He irradiation (fluence $10^{16} \text{ ions per cm}^2$). The surficial damaged volume emits intense defect luminescence. Nasdala et al. (2011) found in He-irradiation experiments that this broad-band yellow CL is generated at very low, and suppressed at moderate defect densities. This conclusion is underlined by the fact that the yellow emission has only been observed for natural zircon with very low degrees of radiation damage (Hanchar et al. 1997; Götze et al. 1999). A third example for irradiation-induced emission is shown in Fig. 4f. Though this example is not related to corpuscular but electron irradiation, we show it here because it demonstrates nicely how irradiation-related damage may result in significant defect luminescence. The surface of this polished epoxy mount, containing synthetic CePO_4 crystals, shows extensive electron-beam damage. Each single imaging scan in the scanning electron microscope (SEM) can be recognised as rectangular area. The intensity of the emission seems to correlate with the intensity of the beam impact and damage, as slower and hence longer scans have produced brighter rectangles (see especially the interlaced small rectangles near the bottom of the image).

Examples for the opposite effect of luminescence suppression due to irradiation damage are presented in Figs. 4g–j. Radio-haloes in feldspar do not show any radio-colouration (Fig. 4g, left part) but are characterised by CL colour changes (Fig. 4g, right part). In most cases a significant depletion of the CL emission intensity is observed. Un-irradiated feldspar typically shows pale blue CL. This emission colour is mainly due to a broad band near $20800\text{--}22200\text{ cm}^{-1}$ (450–480 nm wavelength), which is assigned to paramagnetic oxygen point-defects (such as the Al–O–Al centre; Finch and Klein 1999; Götze et al. 2000). In alpha haloes the intensity of this band is decreased appreciably (Krickl et al. 2009a) whereas a reddish-brown colour component of the emission is observed. The latter was found to be due to new radiation-induced bands near $16600\text{--}17800\text{ cm}^{-1}$ (560–600 nm wavelength; Krickl et al. 2009a) and $13300\text{--}14300\text{ cm}^{-1}$ (700–750 nm wavelength; Kayama et al. 2011); sound band assignments however cannot be given at present.

The irradiation-induced intensification of the emission of diamond has been described above (cf. Fig. 4d), the opposite effect is shown in Fig. 4h. Brown coloured radio-haloes at the surface of a rough diamond specimen appear dark under UV illumination; the blue PL of the un-irradiated host is depressed in these areas as a result of relatively strong alpha irradiation. More weakly alpha-irradiated areas, in contrast, show the yellowish-green defect PL (note that in Fig. 4h, all dark spots are surrounded by irregularly shaped PL haloes). Defect-PL in diamond seems hence to follow the same general behaviour as the defect-CL in zircon described above, namely, creation at very low defect densities and suppression at elevated defect densities. This was recently confirmed in ion-irradiation experiments on diamond conducted by Nasdala et al. (2013).

A typical example for the general inverse correlation of radiation damage and integral emission intensity is presented in Fig. 4i, which compares the birefringence and SEM–CL patterns of a complex zircon crystal containing an inner and an outer core. Only the outer core is mildly radiation-damaged, whereas inner core and outer regions are strongly damaged (Nasdala et al. 2005). Correspondingly, only the outer core shows “fresh” 3rd order interference colours (note that the birefringence decreases strongly with increasing radiation damage; Sahama 1981; Chakoumakos et al. 1987) and appears bright in the CL image. It could of course be speculated that the lowered CL of this crystal’s inner core and outer region is not due to their more elevated damage but alternatively caused by differences in the chemical compositions. Such uncertainties are excluded for the example presented in Fig. 4j, which is discussed in the following.

In addition to the artificial creation of radiation damage through ion-irradiation in the laboratory, the effect of radiation damage in minerals on their luminescence behaviour is studied commonly in thermal annealing experiments. It is well known that the structural reconstitution of initially radiation-damaged minerals results in significant increases of their integral emission (Geisler and Pidgeon 2001; Nasdala et al. 2002; Seydoux-Guillaume et al. 2002). In such studies, mineral samples are mostly analysed under the very same conditions before and after the annealing. Nasdala et al. (2006b) followed a different concept. In their study, accessory zircon grains were cut in half, one of the half-crystals was annealed (whereas the other half-crystal was left in the original, radiation-damaged state), and both half-crystals were then prepared close to each other in one mount. This procedural manner was connected with the two analytical advantages. First, two half-crystals of the same original (i.e., objects with corresponding internal textural patterns and chemical compositions) were compared. Second, the preparation provided the option to study the back-scattered electrons (BSE) and CL intensities of the two half-crystals simultaneously in one single imaging step, under truly

identical conditions. It can be seen in Fig. 4j that the structural reconstitution of zircon is not only connected with BSE decrease (assigned tentatively by Nasdala et al. 2006b to electron-channelling contrast) but also a significant increase of the CL.

The recovery of the emission behaviour upon structural reconstitution is also demonstrated in Fig. 5, showing three pairs of PL spectra of minerals rich in rare-earth elements (REE). Strongly radiation-damaged (amorphous) fergusonite-(Y) (Fig. 5a; Ruschel et al. 2010) and ekanite (Fig. 5c) are characterised by nearly complete suppression of REE-related emissions, which are recovered after annealing, leading to dramatic increases of the integral emission. Similar recovery of the REE-related CL (Nasdala et al. 2002) and PL emissions (Nasdala et al. 2004) was observed upon recrystallisation through thermal annealing of naturally amorphised zircon. Moderately radiation-damaged monazite-(Ce) shows REE more or less “intact” emissions (Fig. 5b). However individual Stark levels of electronic transitions are somewhat broadened, reflecting disturbance of the short-range order around the REE sites. Upon annealing, a general sharpening of the individual lines is observed, along with moderate intensity gain (Fig. 5b). Similar line sharpening and intensity gain of Nd³⁺-related emissions upon annealing of radiation-damaged aeschynite-group minerals has been reported already by Xue and Gong (2000).

The examples above covered effects of the main radiation-induced process, i.e., the gradual transformation of a crystalline material to its amorphous analogue, on its emission characteristics. Additional processes such as irradiation-induced chemical changes, irradiation-induced segregation, phase decomposition, or secondary chemical and structural changes, have not been underlined with examples; nevertheless they need to be considered, if applicable, in interpreting the emission phenomena observed. For instance, radiogenic daughter elements, implanted in the host mineral, could hypothetically form emission centres (for instance, Pb-related luminescence is well-known; Gaft et al. 2005 and references therein). Also, the secondary uptake of non-formula constituents upon chemical alteration may suppress the emission and/or introduce elemental species that form new emission centres. To give an example for the former, it is known that dehydration of solids may increase their emission intensity (Gutzov and Peneva 1995). The secondary uptake of water in a secondary, fluid-driven alteration of a radiation-damaged mineral may therefore be expected to result in suppression of the emission. Also, as the primary radiation-damaged phase is decomposed and a secondary phase crystallises, alteration events are typically connected with an increase of the crystallinity, which in turn may also increase the emission.

Most irradiation-induced changes of the luminescence of self- or externally irradiated, insulator-type minerals, however, are related to the introduction of defects in the structure due to atomic knock-ons. The spectral changes observed include (i) general intensity losses (generally assigned to either the decreasing short-range order around existing centres or the formation of non-radiative recombination centres) connected with broadenings of individual emission lines, and/or (ii) also intensity gains due to either irradiation-induced restructuring (e.g., Bhawe et al. 1999) or the creation of new emission centres.

Study of helium-irradiated CePO₄

Generalities and experimental details

Although the thorough characterisation of the luminescence of naturally radiation-damaged minerals may provide a wealth of useful information, the uncertainty remains how much of irradiation was needed to create the damage present, and hence the luminescence changes observed? This uncertainty is underlined by the consideration that the irradiation dose experienced by a certain sample, and the damage accumulated by this sample, do not necessarily correlate. Rather there is often a clear mismatch between damage creation and storage, due to thermal annealing and hence partial or even complete structural reconstitution. Quantitative studies, i.e. those addressing the question how much of corpuscular irradiation is needed to create certain changes of the luminescence behaviour, require samples with well-known thermal histories. This is the case for samples whose radiation damage was generated under controlled conditions in the laboratory, through irradiation with ion beams. As an example for the latter, preliminary results of a study of synthetic, monazite-structured CePO₄ irradiated with ⁴He ions, are reported in the following.

The sample investigated consisted of crystals of monoclinic CePO₄ (space group $P2_1/n$, $Z=4$), synthesised using a lithium molybdate flux-type method (Hanchar et al. 2001; Ruschel et al. 2012). Preliminary X-ray diffraction and spectroscopic analyses showed that the crystals are very well ordered. Helium-irradiation experiments were done using unprepared CePO₄ crystals, as these showed flat crystal faces of exceptionally high surface quality. Experiments were done at the nuclear reaction analysis beamline of the former 5 MV Tandem accelerator (in the meantime decommissioned and replaced by a 6 MV Tandatron accelerator) of the Helmholtz-Zentrum Dresden (formerly Forschungszentrum Rossendorf), Germany. Samples were attached to a copper sample-holder and loaded into a vacuum chamber ($\sim 10^{-8}$ mbar). Irradiations were done at liquid-nitrogen temperature (-196°C) to exclude local up-warming of the sample under the focused beam and hence immediate thermal annealing during the experiment. The ion beam was focused to a rectangular area of about 1 mm^2 size. Samples were irradiated with 8.8 MeV ⁴He²⁺ ions (this ion energy is equivalent to the energy of alpha particles produced in the ²¹²Po $\rightarrow$ ²⁰⁸Pb decay within the ²³²Th chain). Irradiation fluences were varied in the range $1 \times 10^{14} - 1 \times 10^{16}$ ions/cm², which was achieved by varying the irradiation times between ~ 30 seconds and ~ 50 minutes.

The crystals irradiated were embedded in epoxy and cut parallel to the direction of the ion beam (i.e., roughly perpendicular to the surface irradiated). Thin sections (thicknesses $\sim 25\text{ }\mu\text{m}$) attached to a glass slide but without glass cover were produced. Thin sections were inspected first under visible light using an optical binocular microscope. Second, PL images ($>400\text{ nm}$ wavelength) were obtained under broad UV ($<370\text{ nm}$ wavelength) illumination using a mercury lamp.

Photoluminescence spectra in the visible and near-infrared range (i.e., spectral range $21000\text{--}10600\text{ cm}^{-1}$) and Raman spectra, both including confocal point-to-point line-scans with a step width of $1\text{ }\mu\text{m}$, were obtained by means of a dispersive Horiba Jobin Yvon LabRam–HR spectrometer. This system was equipped with an Olympus BX41 optical microscope, a diffraction grating with 1800 grooves/mm in the optical pathway, a Si-based, Peltier-cooled charge-coupled device (CCD) detector, and a software-controlled x–y stage. The PL spectra were excited with the 473 nm emission of a diode laser (3 mW at the sample);

Raman measurements were made with He–Ne 632.8 nm excitation (8 mW). With a 100× objective (NA = 0.90) used, and the system operated in the confocal mode, the lateral resolution was ca. 1 μm . Spectra were calibrated using the Rayleigh line and neon lamp emissions. The wavenumber accuracy was better than 0.5 cm^{-1} , and the spectral resolution was determined at $\sim 1 \text{ cm}^{-1}$. Fitting was done assuming Lorentzian-Gaussian shapes of individual bands/lines. Fit results for the full width at half maximum (FWHM) of bands were corrected mathematically for the apparatus function according to the simplified procedure of Dijkman and van der Maas (1976).

Irradiation-induced damage

Thin-sections of irradiated samples, prepared parallel to the direction of the incident ion beam, were inspected under a high-power optical microscope. In plane-polarised light, the area irradiated with 10^{16} He/cm^2 showed a colourless but nevertheless clearly recognisable, narrow stripe-like feature parallel to the ion-irradiated surface (not shown). In the area irradiated with 10^{15} He/cm^2 , the stripe was still well recognised but faint, and in the area irradiated with 10^{14} He/cm^2 it was hardly observable. At high magnification, the stripes appeared to consist of two parallel lines (inter-distance on the order of only 1–2 μm) with mirror-inverted dark–bright contrast. In cross-polarised light, the narrow stripes showed significantly (10^{16} He/cm^2) to slightly (10^{15} He/cm^2) lowered interference colours, compared to the surrounding areas. Such features have been described already for other He-irradiated, colourless minerals such as α -quartz (Krickl et al. 2008) or zircon (Nasdala et al. 2011). The stripe is interpreted as a narrow zone with clearly higher defect concentration, compared to the neighbouring volume areas. It is observed in transmitted light because the correspondingly higher radiation damage results in lowered refraction and birefringence (Holland and Gottfried 1955) and may hence be interpreted as a close pair of (mirror-inverted) Becke lines. In view of the theoretical defect distribution of 8.8 MeV He ions in a CePO_4 target (see Fig. 1), the stripe marks the volume area near the ends of the ion trajectories, where most of the damage (i.e., the majority of scattered Frenkel defect pairs) is created. In our case, the distance of the stripe from the surface irradiated was about 33–34 μm , which corresponds very well with the depth of maximum damage as predicted by Monte Carlo calculation ($\sim 33.6 \mu\text{m}$; Fig. 1).

Monoclinic CePO_4 contains 24 atoms per unit cell (volume $\sim 300 \text{ \AA}^3$), which converts to $\sim 8 \times 10^{-2}$ lattice atoms per $\text{\AA}^3$. Our SRIM calculations predicted that in the depth range 33–34 μm below the sample surface, each 8.8 MeV He ion creates an average of 7×10^{-3} atomic displacements per $\text{\AA}$ of path length (Fig. 1). For the highest irradiation in our study (10^{16} He/cm^2), this value converts to a maximum defect concentration 7×10^{-3} defects per $\text{\AA}^3$. The ratio of the two values above (i.e., $\sim 8 \times 10^{-2}$ lattice atoms and 7×10^{-3} defects per $\text{\AA}^3$) suggests that the defect density within the stripe is ca. 0.09 displacements per lattice atom (dpa) in case of the sample irradiated with 10^{16} He/cm^2 . In spite of the relative impreciseness of such estimates based on SRIM results (as we have discussed above), the consideration above implies that a defect density of 0.09 dpa must be well below the amorphisation threshold for monoclinic CePO_4 . This assessment is supported by the detection of moderately broadened Raman bands of crystalline CePO_4 [Fig. 6; a maximum FWHM of only 6.1 cm^{-1} was determined for the $\nu_1(\text{PO}_4)$ band], which implies rather moderate structural damage

(compare Ruschel et al. 2012), and the observation of lowered interference colours but still no extinction.

Except from the stripe in the sample irradiated with 10^{16} He/cm², the ion-irradiated samples studied here represent in general low to very low levels of structural radiation damage. In the sample irradiated with 10^{16} He/cm², the volume range 0–32 μ m below the surface irradiated (i.e., the volume between surface and stripe) yielded very minor Raman band broadening of ca. +0.2–0.3 cm⁻¹ [Fig. 6; FWHMs of the $\nu_1(\text{PO}_4)$ Raman band were determined at 2.1–2.2 cm⁻¹, compared to 1.9 cm⁻¹ in the un-irradiated host beyond the stripe]. The sample irradiated with 10^{15} He/cm² experienced mild radiation damage within the stripe [maximum FWHM of the $\nu_1(\text{PO}_4)$ Raman band 2.7 cm⁻¹]. Potential structural changes of this sample in the depth range <32 μ m behind the surface irradiated, and throughout the sample irradiated with 10^{14} He/cm², were below the detection sensitivities of Raman spectroscopy (Fig. 6) and microscopy under cross-polarised light.

Irradiation-induced changes of the luminescence

The effects of the He irradiation on the luminescence of CePO₄ were investigated by obtaining PL photomicrographs and spectra. Colour images of the PL light obtained under UV illumination are dominated by an irradiation-induced emission of orange to brownish yellow colour. The emission patterns (i.e., the depth profiles of the PL intensity) observed vary appreciably with the ion fluence. In the sample irradiated with 10^{15} He/cm², only the stripe shows intense defect luminescence (Fig. 7, left image; a similar but extremely faint emission pattern was observed from the sample irradiated with 10^{14} He/cm²). In the sample irradiated with 10^{16} He/cm², the entire ion-irradiated volume, however except the stripe, emits orange light (Fig. 7, right image). Both luminescence patterns correspond to the predicted distribution pattern of point defects created by 8.8 MeV alpha particles. Our observations indicate first the creation of the orange emission centre at very low defect densities on the order of 4×10^{-5} Å⁻³ (or 0.0005 dpa). This centre is then suppressed at moderate defect densities exceeding ca. $1\text{--}2 \times 10^{-3}$ Å⁻³ (or exceeding ca. 0.02 dpa). This behaviour is similar to that of defect emissions of He-irradiated zircon (CL study by Nasdala et al. 2011) and diamond (PL study by Nasdala et al. 2013). The observation of onset and suppression of the defect luminescence of He-irradiated CePO₄ at comparably higher defect densities, compared to ZrSiO₄, does not necessarily indicate substantially different responses of the two phases to the He-irradiation but may perhaps be explained by the different luminescence techniques used. Further studies of ion-irradiated CePO₄, involving irradiations with a wider range of fluences and combined PL and CL analyses, are planned.

Comparison of the depth profiles presented in Figs. 6 and 7 shows that the orange emission is observed in mildly radiation-damaged micro-areas, characterised by low values of the FWHM of the $\nu_1(\text{PO}_4)$ Raman band in the range 2–3 cm⁻¹. More radiation-damaged CePO₄, in contrast, seems to be affected by general luminescence suppression. Ruschel et al. (2012) found in a comprehensive annealing study of a range of monazite–(Ce) samples from locations worldwide that the broadening of their $\nu_1(\text{PO}_4)$ Raman band due to the accumulated radiation damage (estimated roughly from the difference between total and chemical broadening) was between +6.6 cm⁻¹ and +12.8 cm⁻¹. Our results indicate that the generally poor luminescence emission of all samples of Ruschel et al. (2012) is probably explained by

the too high degree of radiation damage in these samples, well beyond the suppression of the orange band.

In PL spectra (Fig. 8a), the orange emission is evident as broad band with a maximum in the range $16000\text{--}18000\text{ cm}^{-1}$ (555–625 nm wavelength). Photoluminescence line-scans (Fig. 8b) showed that the depth profile of the intensity of the orange broad-band emission (see again Fig. 7, left image) correlates with the predicted defect distribution, whereas there is no clear correspondence to the ionisation distribution (compare Fig. 1). The creation of the orange emission centre consequently must be related to the formation of atomic point defects.

Superimposed on the orange broad-band emission there are groups of narrow emission lines, which are assigned to REE-related centres (Fig. 8a). These are dominated by Sm^{3+} in the visible range, potentially overlaid by Eu^{3+} and Pr^{3+} , and low-intensity emissions of Nd^{3+} near 11500 cm^{-1} (near 870 nm wavelength; Gaft et al. 2005, and references therein). Their origin is explained by very minor pollution of the commercial high-purity CeO_2 used as starting material for the synthesis. With increasing damage, the REE-related emissions show gradual intensity losses and broadening of individual lines (Fig. 8c). The Stark splitting of electronic transitions, observed as groups of individual lines, is however still preserved. This corresponds to the still preserved crystalline state (with mild to moderate disorder) of our samples. The gradual intensity losses with increasing damage are possibly due to simple destruction of radiative centres (for instance discussed by Tringe et al. 2007), resulting in an enhanced fraction of non-radiative energy releases (for instance through the generation of phonons) in the increasingly disturbed solid. Also, it needs to be considered that the creation of new defect related centres may cause partial energy release in radiative electronic transitions outside the visible range (due to the introduction of additional energetic levels within the forbidden band gap). Ionisation effects (i.e., the irradiation-induced transformation of Nd^{3+} to another valence state) may also reduce the Nd^{3+} emission. The latter however appears less significant, as the distribution patterns of intensity loss (Fig. 8d) and electronic stopping (Fig. 1, right part, dashed graph) do not correlate.

Depth profiles of spectral parameters of REE-related emissions (Figs. 8d–e) showed that especially the FWHMs of individual lines depend closely on the defect concentration in the sample. For instance, the line-broadening profile of the 11590 cm^{-1} (863 nm wavelength) Stark sub-level of the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ emission of Nd^{3+} shows a remarkably close match with the predicted defect profile (Fig. 8e). This observation is interpreted to reflect the increasing disturbance of the short-range order around the eight-fold REE³⁺ sites in the monazite-(Ce) structure.

Conclusion

Photoluminescence spectroscopy and imaging was proven again to be most sensitive in detecting minute amounts of defects and structural damages. In the case of PL emissions related to defect centres with $4f$ electronic configuration that consist of groups of narrow emission lines, the increasing widths of individual lines were found to be related most sensitively to structural disorder and defect concentration. It is therefore suggested that REE-related emissions may potentially be used to quantify the degree of radiation damage. For this, however, the availability of reliable calibration lines is a mandatory presumption. This includes the need of calibrations for (i) effects of the chemical composition (see the review

article by Lenz et al. in this special issue) and (ii) effects of structural irradiation damage on PL spectral parameters. The latter will be addressed in future irradiation experiments.

Such ion-irradiations for the establishment of a luminescence-versus-damage calibration will however not be done using light but heavy ions. First, damage produced by the latter corresponds more closely to the damage in natural minerals (please recall that most of the structural damage in natural minerals is created by alpha-recoils of the heavy daughter nuclei). Second, light ions, in contrast to heavy ions, create a narrow zone of heavy damage bracketed by mildly damaged areas (see again Fig. 1). The thinness of this zone, compared to the lateral resolution of modern spectrometers, and the strong damage-density gradient within this zone, make it most difficult to correlate observed changes of spectral parameters with their corresponding defect densities. Heavy-ion irradiation therefore appears much more promising for studying damage-dependent changes of the emission, especially if the experimental setup ensures that the entire target is damaged and not underlaid by undamaged sample volumes (discussed in detail by Nasdala et al. 2010a).

Potential analytical advantages of a PL-based damage-estimation technique include its high lateral resolution on the micrometre scale and the opportunity to perform analyses non-destructively. Similar to the Raman-based quantification of radiation damage, an analogous PL-based technique would for instance enable one to obtain information on the degree of radiation damage even for tiny accessories in rock thin-sections. The PL-based damage estimation appears promising, as an alternative to confocal Raman spectroscopy, especially in the case of REE-containing mineral species whose Raman spectrum is characterised by comparably broad bands. In such cases such as titanite or rutile, difficulties to monitor FWHM increases of initially broad vibrational bands

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Fig. 1. Simplified sketch (not to scale) of an alpha-decay event in monazite-(Ce) (CePO_4), for the example of the $^{212}\text{Po} \rightarrow ^{208}\text{Pb}$ decay in the ^{232}Th chain, along with distribution patterns of the electronic (dashed graphs) and nuclear stopping (solid graphs) of the recoil nucleus (left) and the ejected alpha particle (right) as predicted by SRIM calculation. Note the different lateral scales; the travel distance of the alpha particle exceeds that of the recoiled daughter nucleus ca. 1000 times

Fig. 2. Sketch (produced by MD simulation) of a damage cluster generated by a single recoil nucleus in zircon (ZrSiO_4). The recoil nucleus moved from the lower left to beyond the upper right corner of the pictured area. Image by permission of K. Trachenko

Fig. 3. Simplified visualisation of the metamictisation process. Recoil-damage clusters are shown as droplets-shaped areas, and scattered point defects generated by alpha particles are shown as small dots. The number (n) of events in the area shown is quoted. Upper row: Damage accumulation leads to a three-dimensional network through inter-connection of the recoil clusters ($n=100$) and eventually to a predominantly amorphous solid with isolated crystalline “islands” ($n=250$). This process may finally lead to an amorphous, metamict form (not shown). Lower row: Damage cannot be stored if the thermal annealing (visualised as fading of damage clusters and point defects) exceeds the accumulation rate

Fig. 4. Images of mineral samples whose luminescence emission is enhanced (a-f) or depleted (g-j), respectively, due to irradiation effects. **a** OM-CL photomicrograph of sandstone from the Espinaco formation, Minas Gerais, Brazil. Quartz shows orange defect-CL around two radioactive inclusions (arrows). Image courtesy J. Götze. **b** OM-CL photomicrograph of a quartz conglomerate from Witwatersrand, RSA. The orange defect-CL was generated from alpha particles emitted from U-bearing fluids. Image courtesy J. Götze. **c** OM-CL photomicrograph of a kyanite from the Dora Maira Massif. The kyanite shows blue defect-CL around a monazite inclusion (arrow). Image courtesy H.-P. Schertl. **d** PL image (<370 nm UV illumination) of a slice of a type IaA diamond after local irradiation with 22.5 MeV ^{12}C ions (irradiation along the direction of view) and subsequent heating at 1000 $^{\circ}\text{C}$. The irradiated spot shows intense yellowish-green defect luminescence. Sample courtesy

J.W. Harris. **e** OM–CL photomicrograph of a synthetic zircon crystal irradiated with 8.8 MeV ^4He ions (irradiation direction in the image plane; from the top). The volume area penetrated by the helium ions (thickness ca. 33 μm) shows yellow broad-band, defect emission. Sample courtesy J.M. Hanchar, image J. Götze. **f** PL photomicrograph of a thin section containing single crystals of synthetic, Gd-doped monazite embedded in araldite epoxy. Scanning the sample with an electron beam during SEM imaging has caused luminescent defect areas. **g** Combination of plane-polarised light (left) and OM–CL (right) photomicrographs of a K-feldspar containing a large monazite inclusion, from the Strangways Range, Australia. In the alpha halo surrounding the inclusion (arrows), the blue luminescence of the feldspar is decreased notably and shows a yellowish brown hue. Sample courtesy A. Möller, images J. Götze. **h** PL photomicrograph of the surface of a rough diamond from Namaqualand, RSA. In circular alpha haloes (having pale orange-brown radio-colouration), the blue luminescence of the diamond is virtually extinct. Sample courtesy J.W. Harris. **i** Combination of cross-polarised light (left) and SEM–CL photomicrographs of a heterogeneous zircon crystal from the Adirondack Mountains, New York State. The CL correlates inversely with the interference colours; the central low-actinide zone (3rd order pink interference colour) yielded the highest CL intensity. Sample courtesy J.M. Hanchar, CL image A. Kronz. **j** Combination of BSE and SEM–CL image of a cut-in-half zircon grain from the Bluffpoint quartz diorite, Ontario. One of the two half-crystals was annealed at 1300 °C to remove the radiation damage, which has resulted in dramatic recovery of its CL emission. Sample courtesy D.W. Davis, images A. Kronz

Fig. 5 Three examples for effects of radiation damage on REE-related emissions. **a** PL spectra of fergusonite-(Y) from Berere, Madagascar (mainly Er^{3+} and Ho^{3+}). **b** Monazite-(Ce) from Moss, Norway (all emission lines related to Nd^{3+}). **c** Ekanite from Ratnapura, Sri Lanka (affected mainly by Pr^{3+} and Sm^{3+}). In all three cases, notable recovery of REE-related emissions is observed after structural reconstitution of the host minerals upon dry thermal annealing. Sample courtesy C. Schnier (fergusonite), A. Massanek (monazite), and I.V. Pekov (ekinite)

Fig. 6 Raman line-scans of He-irradiated samples: FWHM of the symmetric PO_4 stretching band near (main A_g mode of monoclinic CePO_4 near 970 cm^{-1}) plotted versus penetration depth. Band broadenings indicates increasing disturbance of the short-range order; their depth profiles correlate very well with the defect distribution predicted by SRIM calculation (grey dash-dot graph shown for comparison; cf. Fig. 1)

Fig. 7 Dependence of the orange defect-luminescence in monoclinic CePO_4 on the irradiation fluence (8.8 MeV He irradiations). PL images ($<370\text{ nm}$ excitation) are compared with defect distributions predicted by SRIM calculation. The defect-PL is observed only in a relatively narrow range of defect densities (visualised as gray bar)

Fig. 8 Photoluminescence emission of a synthetic CePO_4 crystal irradiated with 8.8 MeV He ions (10^{15} and 10^{16} ions per cm^2). **a** PL spectrum (488 nm excitation) of the spot irradiated with 10^{15} He/cm^2 , obtained in the most damaged volume area (i.e., the stripe near ca. 33.5 μm below the surface); compared to the spectrum of the un-damaged host. Radiation damage results in the creation of an orange, broad-band defect emission whereas narrow emission bands of trace-REEs (mainly Sm^{3+}) start to become less defined and lose some intensity. Low-intensity Raman bands are marked with an asterisk. **b** Plot of the integral intensity of the orange defect-emission against depth (spot irradiated with 10^{15} He/cm^2). The emission intensity correlates well with the defect concentration predicted by SRIM calculation (grey dash-dot graph). **c** PL spectrum (633 nm excitation) of the most damaged region of the spot irradiated with 10^{16} He/cm^2 , in comparison with the un-damaged host, showing the damage-induced broadening of a Nd^{3+} emission in the NIR range. **d,e** Plots of intensity and FWHM of the 11590 cm^{-1} (863 nm wavelength) Stark sub-level of the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ Nd^{3+} emission against depth (spot irradiated with 10^{16} He/cm^2). Line broadening and intensity loss correlate again with the defect distribution (SRIM; grey dash-dot graph)