Cathodoluminescence properties of radiation-induced alkali feldspars

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ABSTRACT

Cathodoluminescence (CL) spectroscopy provides useful information about the existence of radiation-induced defect centers with a few micrometer resolutions and therefore has great potential to estimate the accumulated dose of natural radiation in micron-ordered mineral grain from radioactive decay. Although great scientific interest exists concerning the CL of various types of minerals, very few investigation have been conducted on the luminescence properties of radiation-induced alkali feldspars. This study, therefore, has sought a clarification of radiation effects on emission centers detected by CL analysis of alkali feldspar implanted with He\(^+\) ions at 4.0 MeV, which corresponds to the energy of an \(\alpha\) particle derived from radioactive decay of \(^{238}\text{U}\) and \(^{232}\text{Th}\).

Panchromatic CL images of cross-sections of sanidine, orthoclase and microcline show a dark line with \(~1 \mu\)m width on the bright luminescent background at 12–15 \(\mu\)m beneath the implanted surface, of which behavior may be corresponding to the electronic energy loss process of 4.0 MeV He\(^+\) ion. CL and Raman spectroscopy
revealed that He\(^+\) ion implantation may lead to a partial destruction of the feldspar framework and Na\(^+\) migration, resulting in a quenching of CL emission from alkali feldspar, in proportion to the radiation dose. CL spectra of unimplanted and He\(^+\)-ion-implanted sanidine, orthoclase and microcline have emission bands at ~400–410 nm and at ~730 nm. Deconvolution of the CL spectra can successfully separate these emission bands into emission components at 3.05, 2.81, 2.09, 1.73 and 1.68 eV. These components are assigned to the Ti\(^{4+}\) impurity, Al-O–Al/Ti defect, a radiation-induced defect center, and Fe\(^{3+}\) impurities on the T1 and T2 sites, respectively. The intensity at 3.05 eV negatively correlates with radiation dose owing to decreases in the luminescence efficiency. A slight Na\(^+\) diffusion and breaking of the linkage between Ti\(^{4+}\) and oxygen as a ligand might reduce the activation energy, which decreases availability of radiative energy in luminescence process of Ti\(^{4+}\) impurity center. Furthermore, He\(^+\) ion implantation causes electron holes to be trapped at and released from Löwenstein bridges as a consequence of Na\(^+\) migration and leads to a partial destruction of Al-O bond, which might be responsible for an increase and decrease in the intensity of emission component at 2.81 eV. With an enhanced radiation dose, there is a decrease in intensity at 1.73 eV and an increase in intensity at 1.68 eV. Deconvoluted CL spectra of the alkali feldspars reveal a positive correlation between
intensity at 2.09 eV and the radiation dose, which may be due to the formation of a radiation-induced defect center. These correlations can be fitted by an exponential curve, where the gradients differ between the alkali feldspars studied, and are largest for the microcline, followed by the orthoclase and then the sanidine. The intensity at 2.09 eV has the potential to be used in geodosimetry and geochronometry.

Keywords: cathodoluminescence, alkali feldspar, quenching, radiation-induced defect center, He⁺ ion implantation

INTRODUCTION

Luminescence of minerals has been extensively applied in geosciences for geodosimetry and geochronometry (e.g. Smith and Stenstrom 1965; Marshall 1988; Gaft et al. 2005). The accumulated doses of natural radiation that have been accumulated by rock-forming minerals such as quartz and feldspar can be quantitatively estimated using thermoluminescence (TL) and optical stimulated luminescence (OSL) spectroscopy. If the annual dose rate is known, these techniques can then be used to determine the luminescence dating of the minerals in sedimentary rocks and volcanic ejecta. Electron spin resonance (ESR) analysis also enables the detection of lattice
defects in minerals, where intensity of ESR from the radiation-induced defect center has been used as an indicator for geodosimetry and geochronometry. It is, however, necessary for estimating the accumulated dose or dating the geological age by TL, OSL and ESR methods to extract a large amount of mineral from the target sediment, so that these techniques are difficult to apply to micrometer sized grains. Cathodoluminescence (CL) spectroscopy also provides useful information about the existence and distribution of radiation-induced defect centers in quartz and feldspar, and with a spatial resolution of a few micrometers (Owen 1988; Komuro et al., 2002; Okumura et al., 2008; Kayama et al. 2011a; Kayama et al. 2011b), suggesting a potential for geodosimetry and geochronometry with respect to a micron-ordered heterogeneous minerals or single grain analysis.

The effect of ion implantation on CL emissions from quartz has been investigated to explore the processes whereby radiation-induced defect centers are formed and to estimate the accumulated dose of natural radiation from radioactive decay (e.g. Owen 1988; Komuro et al., 2002; Okumura et al., 2008; Krickl et al., 2008; King et al., 2011). According to Komuro et al. (2002) and Okumura et al. (2008), He$^+$-ion-implanted quartz at 4.0 MeV shows a bright luminescent band of $\sim$ 14 $\mu$m width from the implanted surface as a CL halo, within which the intensity positively correlates with
radiation dose. A similar CL halo with \(~45 \, \mu m\) width from the implanted surface has been also recognized in He\(^{2+}\)-ion-implanted quartz and SiO\(_2\) glass at 8.8 MeV, where the intensities increase with radiation dose (Krickl et al., 2008). Although these previous CL studies of ion-implanted quartz have demonstrated a good correspondence between CL intensity and radiation dose, the dose response to ion implantation differs between quartz samples of various origins, suggesting that the use of CL of quartz in geodosimetry is not straightforward. Okumura et al. (2008) concluded that the CL intensity of quartz depends on not only the radiation dose, but also other factors such as density of defect centers (e.g., [AlO\(_4/\)M\(_{\text{+}}\)]\(^0\) defect, self-trapped exciton, non-bridging oxygen hole centers) and on the concentration of impurity centers (e.g., Ge\(^{4+}\) and Fe\(^{3+}\) impurities). Accordingly, further work is required to elucidate how CL of radiation-induced quartz can be used in geodosimetry.

CL has also been used to detect radiation-induced defect centers in He\(^{+}\)-ion-implanted albite (Kayama et al. 2011a; Kayama et al., 2011b). In this case, radiation resulted in a characteristic red emission, whose intensity increased with radiation dose. Deconvolution of CL spectra by Gaussian fitting revealed an emission component at 1.861 eV that was assigned to a radiation-induced defect center produced by He\(^+\) ion implantation. No investigations of ion implantation on the CL properties of alkali
feldspars (e.g. sanidine, orthoclase and microcline) have been performed. Most alkali feldspars show a blue CL emission assigned to Al-O⁻-Al defect center, and the intensity depends on the natural radiation dose (Finch and Klein, 1999). Ion implantation corresponding to α particle radiation, therefore, potentially affects the CL emissions assigned to Al-O⁻-Al defect centers as well as other emission centers such as Ti⁴⁺ and Fe³⁺ impurities, which should be interpreted in detail for the application of CL to geodosimetry and geochronometry.

In this study, CL of He⁺-ion-implanted alkali feldspars at 4.0 MeV, corresponding to energy of α particle from radioactive decay of ²³⁸U and ²³²Th, was measured to clarify the effect of ion implantation on luminescent emissions derived from defect and impurity centers. Raman spectroscopy was also conducted for the implanted alkali feldspar to investigate a formation process of radiation-induced defect centers produced by He⁺ ion implantation.

**SAMPLES AND METHODS**

CL and Raman analyses were carried out for unimplanted and He⁺-ion-implanted samples of single crystals of sanidine (Sa) (Or₈₇Ab₁₃) phenocrysts from syenite and
phonolite xenoliths in Quaternary diatreme from Eifel, Germany, microperthitic
orthoclase (Or) (Or$_{93}$Ab$_{7}$) from Late Variscan granite in the Karlovy Vary Massif from
Karlovy Vary, Czech Republic and microperthitic microcline (Mi) (Or$_{89}$Ab$_{11}$) as
pegmatite minerals from Naegi granite in Late Cretaceous Sanyo-type granitic zone
from Nakatsugawa, Gifu, Japan. These alkali feldspars were identified by X-ray
diffraction analysis. Microstructures and microtextures associated with exsolution,
micropores and twining were located by optical microscopy and backscattered electron
SEM imaging of the plagioclase grains and avoid in subsequent CL work owing to their
potential impact on the results. The sliced samples (10 × 10 × 1 mm) were cut
perpendicular to c-axis for CL and Raman measurements in order to avoid a polarization
effects as suggested by Finch et al. (2003). The sliced samples were polished and
finished with a 1 μm diamond abrasive. CL microscopy and spectroscopy were
preliminarily conducted on the surface of the sliced samples to select the areas with
comparable CL intensity and homogeneous distribution of the intensity before the He$^+$
ion implantation experiments.

He$^+$ ion implantation was conducted perpendicular to their surface using a 3M-tandem
ion accelerator located at Takasaki Research Center of the Japan Atomic Energy
Research Institute. The ion-beam condition had a 4.0 MeV implantation energy,
corresponding to the energy of alpha particles from $^{238}$U and $^{232}$Th disintegrations, where a specific dose density was set in the range from $2.18 \times 10^{-6}$ to $6.33 \times 10^{-4}$ C/cm$^2$ for the sanidine and $4.83 \times 10^{-6}$ to $4.64 \times 10^{-4}$ C/cm$^2$ for the orthoclase and microcline (Table 1). The implanted samples for sanidine, orthoclase and microcline were numbered in order of dose density, e.g., Sa00 for unimplanted sanidine and Sa10 for the highest dose. CL spectra were acquired from the implanted surface of the samples, which is indicated by the postscript “S”, e.g., Or01S for orthoclase implanted at the lowest dose and Or08S for oligoclase implanted at the highest dose. The implanted samples were also cut perpendicular to their exposed surface to enable CL line analysis and high-resolution CL imaging of the surface in cross-section. The sectional samples are denoted by the postscript “C”, e.g., Mi00C for unimplanted microcline and Mi10C for microcline implanted at the highest radiation dose. Further details of the He$^+$ ion implantation experiment and sample preparation can be found in Okumura et al. (2008) and Kayama et al. (2011a).

A scanning electron microscopy-cathodoluminescence (SEM-CL) instrument was carried out using a JEOL: JSM-5410 SEM combined with a grating monochromator (Oxford: Mono CL2) to measure CL spectra. All CL spectra obtained in the range from 300 to 800 nm in 1 mm steps were corrected for the total instrumental response, which
was determined using a calibrated standard lamp. CL line analysis was measured across a profile from He$^+$ ion implanted surface (0 μm) to a depth of 20 μm with 0.25 μm steps, where the bulk intensity of the panchromatic CL (300 to 800 nm) was obtained. The operating conditions were set as follows: an accelerating voltage of 15 kV and a beam current of 2.0 nA in scanning mode with a 220 × 185 μm scanning area, which was established based on the preliminary CL spectroscopy for prevention of electron irradiation damage and enhancement of the signal/noise (S/N) ratio. According to Kayama et al. (2010), the corrected CL spectra in energy units were deconvoluted into the Gaussian components corresponding to each emission center using the peak-fitting software (Peak Analyzer) implemented in OriginPro 8J SR2. Peak position and integral intensity of the Gaussian component were acquired from each five deconvoluted CL spectra of unimplanted and He$^+$ ion-implanted sanidine, orthoclase and microcline at different radiation dose. High-resolution CL images were obtained using the Gatan:MiniCL imaging system under the same condition as CL spectral analysis by SEM-CL. More details of the equipment construction and analytical procedures are in Ikenaga et al. (2000) and Kayama et al. (2010).

A laser Raman microscope (Thermo Electron; Nicolet: Almega XR) was used for Raman spectral measurements, where the Nd:YAG laser (532 nm excitation line) was
selected and controlled at 20 mW with a $\sim$1 $\mu$m spot size. The operating conditions were set as five accumulations of 10 s each in the range 120 to 900 cm$^{-1}$ in steps of 1 cm$^{-1}$. Raman bands were calibrated by monitoring the position of the O-Si-O stretching vibration (464 cm$^{-1}$) in reference to a standard high optical grade quartz before and after the measurements. Details of instrument construction and analytical procedures can be found in Kayama et al. (2009).

RESULTS

CL microscopy

Panchromatic CL images of cross-sections of sanidine implanted at $3.03 \times 10^{-4}$ C/cm$^2$ (Sa09C) and of orthoclase (Or08C) and microcline (Mi08C) both implanted at $4.64 \times 10^{-4}$ C/cm$^2$ show a dark line with $\sim$1 $\mu$m width on the bright luminescent background at 12–15 $\mu$m beneath the implanted surface (Fig. 1). Similar dark lines occur in CL images of all other implanted samples, but they are absent from unimplanted alkali feldspars. The reduction in CL intensity that produces the dark line is more obvious for high dose than low dose implanted samples. Optical microscopy, and secondary electron (SE), and
backscattered electron (BSE) imaging reveal no microstructures or textures corresponding to the dark line observed in the CL image (Fig. 1).

**CL line analysis**

CL line analyses were carried out on cross-sections of Sa09C, Or08C and Mi08C (Fig. 2). The analysis line is shown in Fig. 1, and extends from the implanted surface to a depth of 20 μm, which includes the dark line at 12–15 μm. CL intensities of Sa09C appear to slightly decrease with the implantation depth, show a drastic drop at 12–15 μm, then increase to 16 μm (Fig. 2). Similar changes in intensity were found in CL line analyses of other sanidine cross-section samples. All implanted orthoclase and microcline samples also show similar depth-dependent change in CL intensities (Fig. 2).

**CL spectroscopy**

CL spectra of unimplanted sanidine (Sa00S) and microcline (Mi00S) have emission bands in the blue (~410 nm) and red-IR regions (~730 nm) (Figs. 3a and c). A UV emission at ~320 nm also occurs in the spectrum of Mi00S, and the intensity of this
peak is appreciably lower than of the emission bands in the blue and red-IR regions (Fig.
3c). Unimplanted orthoclase (Or00S) has similar UV, blue and red-IR emission with
higher intensities than Sa00S and Mi00S. CL spectroscopy of Sa09S reveals emission
bands at ~410 and ~730 nm, similar to those of Sa00S, whereas CL intensity of the blue
emission in Sa09S is lower than in Sa00S (Fig. 3a). Also, CL of Sa09S exhibits a
yellow-orange emission from 550 to 600 nm overlapped and concealed by the blue and
red-IR emissions. The intensity of the yellow-orange emission increases with the
radiation dose. CL spectra of Or08 and Mi08 consist of emission bands at ~320 nm in
the UV, ~410 nm in the blue and ~730 nm in the red-IR regions, and these spectral
patterns are similar to unimplanted orthoclase and microcline (Figs. 3b and c). The
implanted orthoclase and microcline show a decrease in the blue emission intensities
and an increase in the yellow-orange ones with an increase in radiation dose.

Raman spectroscopy

Raman spectra of unimplanted sanidine, orthoclase and microcline have pronounced
peaks at ~160, ~285, ~455, ~480 and ~515 cm\(^{-1}\), and weak ones at ~360, ~405, ~750
and ~810 cm\(^{-1}\). Similar peaks are also observed in Raman spectra of dark line areas at
12–15 μm depth in Sa09C, Or08C and Mi08C, which have lower intensities, larger bandwidths and high background compared to those of unimplanted samples. Raman line analyses of Sa09C, Or08C and Mi08C that were obtained from the implanted surface to the inside with 20μm depth reveal that the integral-peak intensities at 515 cm⁻¹ slightly decrease at 12–15 μm depth, then increase with greater depth (Fig. 4).

DISCUSSION

Characteristics of CL on implanted surface

Panchromatic CL images of the cross-sections show a dark line at 12–15 μm beneath the implanted surface (Fig. 1), and this distance is close to the maximum of electronic energy loss (~12.5 μm) of 4.0 MeV He⁺ ion in alkali feldspars (Bragg and Kleeman 1905; Nogami and Hurley 1948; Faul 1954; Owen 1988; Komuro et al., 2002; Okumura et al., 2008). By monochromatic CL imaging, Kayama et al. (2011a) found a similar dark line beneath the implanted surface of albite, again, corresponding to the range of He⁺ ion implantation at 4.0 MeV. CL line analyses acquired through the cross-sections of all implanted alkali feldspars also reveal decreases in emission intensities at 12–15
μm (Fig. 2). However, the distance at 12–15 μm is not completely concordant with the
maximum of electric energy loss process, which may be due to He\(^+\) ion implantation
condition or spatial resolution of CL microscopy proposed by Okumura et al. (2008).
Nevertheless, it is noteworthy that He\(^+\) ion implantation definitely make a quench of CL
emission from alkali feldspar around the end of the ion track, in proportion to the
radiation dose.

Raman spectra acquired from the dark line in CL imaging of Sa09, Or08 and Mi08
are of a lower peak intensity, broader bandwidth and high background than those seen in
unimplanted samples. Raman line analyses of Sa09C, Or08C and Mi08C show a slight
decrease in the integral-peak intensity at 515 cm\(^{-1}\) in the dark line at 12–15 μm,
assigned to T-O stretch and O-T-O deformation modes in TO\(_4\) group (Fig. 4) (von
Stengel 1977; Freedman et al. 2003). A similar phenomenon has been recognized in the
Raman spectra of He\(^+\)-ion-implanted albite (Kayama et al., 2011a; Kayama et al.,
2011b). These facts imply that He\(^+\) ion implantation may destroy the linkage between
TO\(_4\) tetrahedra or induce a strain, and consequently quenches CL in alkali feldspar. This
has been also observed in zircon, where the luminescence and Raman intensity is
reduced in proportion to metamictization (Nasdala et al. 2002; Kempe et al. 2010).

According to the previous studies, ion implantation also results in the migration of
monovalent cations in alkali feldspar. Monovalent cations such as Na\(^+\) migrate in the lattice of feldspar during Pb ion implantation (Petit et al., 1987). The extent of lattice damage caused by ion implantation and its consequent diffusion are determined by the implantation dose (Watson and Dohmen 2010). According to Jambon and Carron (1976), diffusion coefficient of alkali element in feldspar may depend on the defect density. Lineweaver (1963) demonstrated that electron irradiation transfers alkali elements into unirradiated areas due to formation of the electric fields produced by defection of oxygen. Although the cation migration potentially occurs in associated with ion implantation, it may be slight effective because there is almost no difference of Na\(^+\) content, obtained from chemical analysis by wavelength dispersive X-ray spectroscopy (WDS), between unimplanted and the implanted alkali feldspars. Taken together these findings indicate that the partial destruction, introduction of strain and the slight Na\(^+\) migration due to He\(^+\) ion implantation may be the cause of quenching of CL in alkali feldspar rather than the Na\(^+\) migration. This CL quenching may be responsible for a conversion of emission center related to the present alkali feldspar into non-luminescent center due to an alteration of the energy state or a change of luminescence efficiency due to a variation of the activation energy, as will be described in the section of “Radiation effects on each emission center”.
With an increase in the radiation dose on alkali feldspars, emission intensities of blue CL decrease sharply, whereas yellow-orange emissions intensities increase and red-IR intensities slightly decrease or increase depending on the samples (Fig. 3). This pattern indicates that He$^+$ ion implantation effect on CL vary depending on type of emission center. Although CL line analysis reveals a decrease in the intensity at 12–15 μm caused by an elimination of the emission center due to the partial destruction, introduction of strain or the Na$^+$ migration, there should also be an accumulation of radiation-induced defect centers related to the brightening CL emission around the end of the ion track. Therefore, CL halo in feldspars may be produced and characterized by both elimination and creation of the emission centers due to radiation, where the former should be the dominant process for the present alkali feldspar with the dark line and the later should be for albite with bright luminescent band reported by Kayama et al. (2011a).

Assignment of emission centers

The blue emission at 400–410 nm, shown in Fig. 3, is assigned to the following centers; (1) an oxygen defect associated with the electron hole trapped Löwenstein bridge (Al-O’-Al defect center) formed with two Al atoms, one of which is structural Al
and the others is impurity Al (Marfunin 1979; Finch and Klein 1999; Götze et al. 2000; Slaby et al. 2008; Kayama et al. 2010) and (2) Ti\(^{4+}\) incorporated with Al sites, which act as impurity center and/or oxygen defect associated with Al-O-Ti bridges (Marfunin and Bershov 1970; Mariano et al. 1973; Mariano and Ring 1975; Speit and Lehmann 1976; Kirsh et al. 1987; Smith and Brown 1988; Ginibre et al. 2004; Lee et al. 2007; Parsons et al. 2008; Kayama et al. 2010). According to Kayama et al. (2010), the blue emission band consists of an overlap of two components, namely the oxygen defect centers associated with Al-O-Al and Al-O-Ti bridges (Al-O-Al/Ti defect center) and the Ti\(^{4+}\) impurity center. The alkali feldspars also have the red-IR CL emission attributed to a Fe\(^{3+}\) impurity that substitutes for Al\(^{3+}\) ions in tetrahedral sites for the luminescence caused by the radiative transition of the electrons from \(^4T_1\) to \(^6A_1\) (Telfer and Walker 1978; Finch and Klein 1999; Götze et al. 2000). Kayama et al. (2010) clarified the suggestion of Finch and Klein (1999) that the red-IR CL emission is composed of two components assigned to Fe\(^{3+}\) impurity centers on T1 and T2.

CL spectra of the implanted alkali feldspars have yellow-orange emission from 550 to 600 nm (Fig. 3), of which intensities increase with radiation dose. Ionoluminescence (IL) spectrum of alkali feldspar shows a similar increase in the intensity depending on the radiation dose (Brooks et al. 2002). A comparable increase in the CL intensity with
radiation dose has been also observed in red emissions from He\(^+\)-ion-implanted albite, which is characteristic of the radiation-induced defect center (Kayama et al. 2011a; Kayama et al. 2011b). Krickl et al. (2008) also demonstrated a similar yellow emission assigned to the radiation-induced defect center in He\(^{2+}\) irradiated natural and synthetic SiO\(_2\) phase as well as natural \(\alpha\)-quartz with radiohaloes. This suggests the formation of radiation-induced defect center in alkali feldspar by He\(^+\) ion implantation and/or change in quantum efficiency of the recombination site.

According to deconvolution method suggested by Stevens-Kalceff (2009) and Kayama et al. (2010), the emission bands in CL spectra from the sanidine, orthoclase and microcline can be separated into five Gaussian components, at 3.05, 2.81, 2.09, 1.73 and 1.68 eV, where their peak position and integral intensity are obtained from each five deconvoluted CL spectral of unimplanted and the implanted alkali feldspar at different radiation dose. The emission components at 3.05 and 2.81 eV are constituents of the emission bands in the blue spectral region, where the former is assigned to Ti\(^{4+}\) impurity center and the latter to Al-O\(^-\)-Al/Ti defect center (Kayama et al. 2010). The red-IR emission comprises the components at 1.73 and 1.68 eV that Kayama et al. (2010) attributes to the Fe\(^{3+}\) impurity centers on the T1 and T2 sites, respectively. Intensity of the component at 2.09 eV increases with radiation dose, implying a characteristic CL
signal of the radiation-induced defect center (Fig. 5). The emission component assigned
to the radiation-induced defect center is also detectable in the deconvoluted CL spectra
of He$^+$-ion-implanted albite, but the peak wavelength (1.861 eV) is distinct from that
obtained from the alkali feldspar in the present study (2.09 eV). According to Blasse
and Grabmaier (1994), Götze et al. (2000) and Stevens-Kalceff et al. (2000), the peak
position of an emission band varies with chemical composition, crystal structure in host
lattice, and type of emission center. Therefore, further studies such as annealing
experiment and ESR analysis will be necessary for an identification of type of
radiation-induced defect center.

**Radiation effects on each emission center**

Figures 6, 7, 8 and 9 plot intensities of Gaussian components at 3.05 eV, 2.81 eV, 2.09
eV, 1.73 eV and 1.68 eV against dose density of He$^+$ ion implantation on the sanidine,
orthoclase and microcline, where the averaged intensities and the standard deviations
are obtained from five deconvoluted CL spectra of each of these feldspar implanted at
respective radiation dose. They elucidate radiation effects on CL of alkali feldspar
activated by each emission center, as follows.
**Ti⁴⁺ impurity center**

Intensities of the emission component at 3.05 eV decrease sharply with increasing radiation doses up to $1.07 \times 10^{-4}$ C/cm² for sanidine and $9.42 \times 10^{-5}$ C/cm² for orthoclase and microcline, then decrease more gradually above that threshold. As described above, He⁺ ion implantation potentially leads to the partial destruction, introduction of strain and the slight Na⁺ migration in the alkali feldspars judging from the present results obtained by Raman spectroscopy and EPMA analysis and the previous studies, which may be responsible for quenching of the CL activated by Ti⁴⁺ impurity center. According to Brooks et al. (2001), ion implantation reduces activation energy associated with hopping between adjacent channels, which is a function of the luminescence efficiency (Curie 1963). Kayama et al. (2009) demonstrated that the activation energy depends on the structural state in SiO₂ polymorphs, which may be due to a change of the energy state in host. Therefore, luminescence efficiency as well as the activation energy varies depending on the structural state in the host, as suggested by Blasse and Grabmaier (1994). A change of the structural state by partial destruction, introduction of strain or the Na⁺ migration during He⁺ ion implantation may decreases a
luminescence efficiency of Ti$^{4+}$ impurity center in the alkali feldspars due to a change in the activation energy. Alternatively, it may lead to an alteration of the energy state in Ti$^{4+}$ impurity center, resulting in a conversion of the emission center into non-luminescent center. Nevertheless, these outcomes of these processes may quench the blue CL in alkali feldspars. The energy used as CL activated by the Ti$^{4+}$ impurity center might be transferred into lattice vibration as phonon, or applied for radiative transition of the electron at other emission centers. However, further works will be necessary to validate an adequacy of this model.

**Al-O–Al/Ti defect center**

The emission components at 2.81 eV increase in intensity with an increase in low radiation level of He$^+$ ion for sanidine and microcline (Figs. 6b and 8b). IL spectroscopy of alkali feldspar also revealed an increase in the blue emission intensity with the radiation dose, which may be due to a formation of defect or vacancy in the structure (Brooks et al. 2002). Finch and Klein (1999) modeled the CL intensity of the blue emission in feldspar scales with the percentage of Löwenstein bridges with electron holes (Al-O$^-$-Al defect center) in the structure, which is closely related to natural
radiation dose received by the feldspar during its geological history. ESR analysis demonstrated that electron holes at oxygen positions (e.g., Al-O–Al) in feldspars are produced by natural gamma ray and X-ray radiation (Petrov et al., 1989). Furthermore, the diffusion of monovalent cations in quartz in response to ion implantation converts the [AlO₄/M⁺]₀ defect (M: H⁺, Li⁺, Na⁺ and K⁺) into the [AlO₄]₀ defect (equivalent to the Al-O–Al defect in feldspar), resulting in an increase in the blue emission intensity with elevated radiation doses (King et al., 2011). Electron holes may be derived from the slight Na⁺ migration in sanidine and microcline with He⁺ ion implantation and subsequently trapped in Löwenstein bridges in various extents depending on the radiation dose, which might be responsible for an increase in the blue CL intensity at a relatively low radiation level.

The intensities at 2.81 eV, however, decrease with as a function of radiation dose up to 2.41 × 10⁻⁵ C/cm² for orthoclase (Fig. 7b). The emission intensity is substantially higher in unimplanted orthoclase than unimplanted sanidine and microcline (Fig. 6, 7 and 8), which, taking the Finch and Klein (1999) model at face value, implies that the orthoclase may have quite high percentage of Löwenstein bridges with electron holes. The sanidine at 1.07 × 10⁻⁴ C/cm² and the microcline at 9.42 × 10⁻⁵ C/cm² have a maximum intensity at 2.81 eV in Figure 6b and 8b, implying their sufficient high
percentage of Löwenstein bridges. Electron holes, therefore, may have been already
trapped in almost all Löwenstein bridges in the orthoclase before He\textsuperscript{+} ion implantation
and in the sanidine and microcline after the implantation at relatively high radiation
dose, which may contributes to no increase in the intensity at 2.81 eV for the orthoclase
as well as the implanted sanidine and microcline at high level of radiation dose.

According to King et al. (2011), a mobility of an electron in quartz by ion implantation
also changes [AlO\textsubscript{4}]\textsuperscript{0} defect into [AlO\textsubscript{4}]\textsuperscript{-} defect, where the former acts as emission
center, but latter as non-luminescent center. Al-O-Al/Ti defect centers in the orthoclase,
and the implanted sanidine and microcline at relatively high radiation dose might be
eliminated and converted into non-luminescent centers due to the Na\textsuperscript{+} migration by He\textsuperscript{+}
ion implantation, which quenches their blue CL. Furthermore, Raman spectroscopy
shows a slight decrease in the integral-peak intensity at 515 cm\textsuperscript{-1} in the dark lines.
Radiation dose leads to a breaking of many Al-O bond in framework structure of the
alkali feldspar and then eliminating a large amount of Al-O-Al/Ti defect centers. An
introduction of strain of AlO\textsubscript{4} tetrahedra due to He\textsuperscript{+} ion implantation may be also due to
a change of the energy state in Al-O-Al/Ti defect centers. These processes might be
also responsible for the quenching effect on the blue CL.
Fe$^{3+}$ impurity center

The radiation doses on sanidine up to $1.07 \times 10^{-4}$ C/cm$^2$ decrease the intensity of emission components at 1.73 eV assigned to the Fe$^{3+}$ impurity center on T1 sites. This effect is also seen to doses of up to $9.42 \times 10^{-5}$ C/cm$^2$ for the microcline. The component at 1.68 eV, which is the Fe$^{3+}$ impurity center on T2 sites, increases in intensity with the radiation dose up to $1.07 \times 10^{-4}$ C/cm$^2$ in sanidine, $4.83 \times 10^{-5}$ C/cm$^2$ in orthoclase and $2.50 \times 10^{-4}$ C/cm$^2$ in microcline (Figs. 6, 7 and 8). This may contribute to an energy transition between Fe$^{3+}$ impurity centers on T1 and T2 sites.

The minimal partial destruction, introduction of strain or slight Na$^+$ migration may causes a decrease in the luminescence efficiency of Fe$^{3+}$ impurity center on T1 site as a consequence of a change of activation energy or a conversion of the emission center into non-luminescent center by an alteration of the energy state, the same as in the case of Ti$^{4+}$ impurity center. Consequently, the red-IR CL in alkali feldspar may be quenched by these processes derived from He$^+$ ion implantation. These results are concordant with IL spectral data of Fe$^{3+}$-activated emission obtained from alkali feldspar (Brooks et al. 2002). A part of energy for luminescence emission from the Fe$^{3+}$ impurity center on the T1 site should be consumed by radiative transition of Fe$^{3+}$ impurity center on T2 site as
the energy transition process, resulting in an enhancement of the red-IR CL intensity.

The rate of increase of emission intensity at 1.68 eV is lower for orthoclase than for sanidine and microcline (Figs. 6c, 7c and 8c). This may be due to the low concentration of Fe$^{3+}$ impurity centers on the T1 site judging from undetectable emission component at 1.73 eV in orthoclase, although further works will be necessary for an establishment of this model.

The emission component at 1.68 eV in sanidine shows a decrease in the intensity with an increase in the radiation dose above $1.07 \times 10^{-4}$ C/cm$^2$ (Fig. 6c). According to Kayama et al. (2009), a change in framework configuration by partial destruction of its structure alters the emission centers into non-luminescent centers with consequent quenching of CL due to an increase in the population of non-radiative transition. This is observed in other mineral systems, for example, Nasdala et al., (2002) demonstrated that natural radiation destroys the structure of zircon, leading to a decrease in emission intensity depending on the radiation dose. These facts indicate that the linkages between the Fe$^{3+}$ ions on T2 site and oxygen as their ligands might be appreciably broken or strained by He$^+$ ion implantation at relatively high radiation dose, and consequently the emission center is converted into non-luminescent center. Similarly, such change of the energy state of the emission center should be caused by the slight Na$^+$ migration, which
also results in a quenching of CL activated by Fe$^{3+}$ impurity centers on the T2 site. On the other hand, the intensities at 1.68 eV for orthoclase and microcline increase with radiation dose up to $4.64 \times 10^{-4} \text{ C/cm}^2$ and reach a the saturation level above $4.83 \times 10^{-5} \text{ C/cm}^2$ for orthoclase and $2.50 \times 10^{-4} \text{ C/cm}^2$ for microcline. Since Raman spectroscopy indicates that the framework of the disordered feldspar appears to be more prone to damage than ordered feldspar (Fig. 4), He$^+$ ion implantation effects of the structure-breaking may be potentially exerted to the sanidine rather than the orthoclase and microcline. Most Fe$^{3+}$ impurity centers on the T2 site act as an emission center in orthoclase and microcline, but not in the sanidine at relatively high radiation dose, which might explain the lack of a decrease in intensity at 1.68 eV in the orthoclase and microcline with the enhanced radiation dose.

**Radiation-induced defect center**

The emission components at 2.09 eV exponentially increase in intensity with radiation dose in the low radiation level, although the gradients differ between the alkali feldspars, and are largest for the microcline, followed by the orthoclase and then the sanidine (Fig. 9). Saturation of the intensity is reached at $4.02 \times 10^{-6} \text{ C/cm}^2$ for sanidine, above $2.41 \times 10^{-5} \text{ C/cm}^2$.
10^{-5} \text{ C/cm}^2 \text{ for orthoclase and above } 4.83 \times 10^{-5} \text{ C/cm}^2 \text{ for microcline; the saturated intensity of the ordered alkali feldspar tends to be higher than that of the disordered one. This pattern implies that an increase in the CL intensity of the yellow-orange emission assigned to the radiation-induced defect center might be closely related to the degree of Si-Al order. ESR studies on feldspar have also demonstrated that signals attributed to oxygen vacancies linked between Si and Al tetrahedra vary depending on natural gamma and X-ray radiation doses and the degree of Si-Al ordering (Matyash et al., 1982; Petrov et al., 1989). The emission component at 2.09 eV in the alkali feldspar, therefore, might be assigned to one or more of the oxygen vacancy centers. Further investigations such as annealing experiment and ESR analysis of radiation-induced alkali feldspars will allow us to specify type of the oxygen vacancy centers.

Figure 9 reveals that there is no decrease in the intensity at 2.09 eV with the enhanced radiation dose up to \(6.33 \times 10^{-4} \text{ C/cm}^2\) for sanidine and up to \(4.64 \times 10^{-4} \text{ C/cm}^2\) for the orthoclase and microcline. The components at 2.81 eV, however, decrease sharply in intensity in the range of relatively high radiation doses, which might be due to breaking of Al-O bonds related to the Al-O=Al/Ti defect center by He\(^+\) ion implantation. These results indicate that formation of the radiation-induced defect center assigned to component at 2.09 eV in the alkali feldspar should be a dominant process rather than an
elimination of the center due to the partial breaking of the structure in the present range of the radiation dose.

The dose response of intensity at 2.09 eV appears to be mainly controlled only by the degree of Si-Al ordering, even though other properties including chemical composition, crystal structure, concentration and distribution of other emission centers and the presence of microstructures or microtextures also differ between the alkali feldspars. Kayama et al. (2011b) demonstrated that several albite from different localities show almost same dose response of the intensity at 1.86 eV, not depending on other properties of these albite crystals. In the case of alkali feldspar, therefore, a quantitative estimation of α radiation dose from natural radionuclides using the intensity at 2.09 eV requires a correction for the CL spectral data on the basis of the degree of Si-Al ordering, but probably not to other mineralogical features. Eventually, the intensity at 2.09 eV may be used as an indicator for geodosimetry, and then geochronometry based on the additive dose method, which provide progressive application in geoscience and planetary science, e.g. clarification of space weathering on lunar regolith and micron-order grain recovered from Itokawa asteroid, sedimentary dating in wide applicable range, estimation of leakage of nuclear waste from geologic disposal facilities and atomic power plant.
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**FIGURE AND TABLE CAPTION**

**Figure 1.** (a) Panchromatic CL image of a cross-section of He⁺-ion-implanted (a)
sanidine (Sa09C), (b) orthoclase (Or08C) and (c) microcline (Mc08C). White lines indicate trace of CL and Raman line analyses for the alkali feldspars, shown in Figures 2a and 4d. Scale bars are 20 μm.

Figure 2. Plot of the relationship of CL emission intensity over the 300–800 nm range obtained by CL line analysis from the He⁺-ion-implanted surface to 20 μm. The samples analyzed are Sa09C, Or08 and Mi08. The path of the line analysis is indicated by the white lines in Figure 1.

Figure 3. CL spectra of (a) unimplanted (Sa00S) and He⁺-ion-implanted sanidine (Sa09S), (b) unimplanted (Or00S) and He⁺-ion-implanted orthoclase (Or08S), and (c) unimplanted microcline (Mi00S) and He⁺-ion-implanted microcline (Mi08S).

Figure 4. Plot showing the change in intensity of the Raman peak at 515 cm⁻¹ from the implanted surfaces of cross-section samples of Sa09C, Or08C and Mi08C to 20 μm depth. A slight decrease in the intensity at 515 cm⁻¹ is observed at ~10 μm, which is responsible for the cracks. Measured areas of the Raman line analysis are indicated in Fig. 1 as white lines.
Figure 5. Deconvolution of CL spectra in energy units obtained from He$^{+}$-ion-implanted (a) sanidine (Sa09S), (b) orthoclase (Or08S) and microcline (Mi08S). Data are fitted by several Gaussian curves.

Figure 6. A plot of the intensity of the Gaussian component at 2.09 eV obtained using CL spectral deconvolution against dose density of He$^{+}$ ion implantation for the sanidine (Sa00S to Sa10S), orthoclase (Or00S to Or08S) and microcline (Mi00S to Mi08S).

Figure 7. Plots of intensities of Gaussian components at (a) 3.05 eV, (b) 2.81 eV, (c) 1.68 eV and (d) 1.73 eV obtained using CL spectral deconvolution for the sanidine (Sa00S to Sa10S) against dose density of He$^{+}$ ion implantation.

Figure 8. Plots of intensities of Gaussian components at (a) 3.05 eV, (b) 2.81 eV and (c) 1.68 eV obtained using CL spectral deconvolution for the orthoclase (Or00S to Or08S) against dose density of He$^{+}$ ion implantation.

Figure 9. Plots of intensities of Gaussian components at (a) 3.05 eV, (b) 2.81 eV, (c)
1.68 eV and (d) 1.73 eV obtained using CL spectral deconvolution for the microcline (Mi00S to Mi08S) against dose density of He$^+$ ion implantation.

Table 1. Samples of alkali feldspars for CL and Raman measurements.

<table>
<thead>
<tr>
<th>No.</th>
<th>Dose density (C/cm$^2$)</th>
<th>No.</th>
<th>Dose density (C/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sa00</td>
<td>Unimplanted</td>
<td>Or00</td>
<td>Mi00 Unimplanted</td>
</tr>
<tr>
<td>Sa01</td>
<td>2.18 × 10$^{-6}$</td>
<td>Or01</td>
<td>Mi01 4.83 × 10$^{-6}$</td>
</tr>
<tr>
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<td>4.02 × 10$^{-6}$</td>
<td>Or02</td>
<td>Mi02 9.65 × 10$^{-6}$</td>
</tr>
<tr>
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<td>2.54 × 10$^{-5}$</td>
<td>Or03</td>
<td>Mi03 2.41 × 10$^{-5}$</td>
</tr>
<tr>
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<td>Or04</td>
<td>Mi04 4.83 × 10$^{-5}$</td>
</tr>
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<td>Mi05 9.42 × 10$^{-5}$</td>
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<td>Or06</td>
<td>Mi06 1.77 × 10$^{-4}$</td>
</tr>
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<td>Or07</td>
<td>Mi07 2.32 × 10$^{-4}$</td>
</tr>
<tr>
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<td>Or08</td>
<td>Mi08 4.64 × 10$^{-4}$</td>
</tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>Sa10</td>
<td>6.33 × 10$^{-4}$</td>
<td></td>
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</tr>
</tbody>
</table>

Sa, Or and Mi indicate sanidine, orthoclase and microcline, respectively.
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7
Figure 8
Figure 9

Intensity at 2.09 eV (a.u.)

Dose density (C/cm²) × 10⁻⁴

- Sanidine
- Orthoclase
- Microcline