Cathodoluminescence characterization of enstatite

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Enstatite in meteorite shows various emissions of cathodoluminescence (CL), and CL emission in terrestrial enstatite has been confirmed in this study. The CL spectra of these enstatite exhibit two broad emission bands at around 400 nm in a blue region and at around 670 nm in a red region. The emission components obtained by a spectral deconvolution can be assigned to impurity centers of Cr³⁺ (1.70–1.75 eV) and Mn²⁺ (1.85–1.90 eV) and to three defect centers (2.72–2.75, 3.18, and 3.87 eV). The emission component at 3.18 eV might be associated to the defect center derived from structural distortion by the substitution of Al for Si in a tetrahedral site. Extraterrestrial enstatite gives a characteristic emission at 3.87 eV in a blue to UV region, which is not detected in the terrestrial enstatite, suggesting radiation-induced defect by cosmic rays.

Keywords: Enstatite, Cathodoluminescence, Enstatite chondrite, Aubrite

INTRODUCTION

Enstatite is one of the most important rock-forming minerals in the terrestrial and extraterrestrial materials and commonly occurred in igneous and metamorphic rocks and various types of meteorite. Luminescent enstatite has been confirmed only in the meteorites of enstatite chondrite (E-chondrite), enstatite achondrite (Aubrite) and synthetic samples (e.g., Derham et al., 1964; Reid et al., 1964). Major silicate phase in E-chondrite and Aubrite is a near endmember of enstatite (FeO <1.0%), which shows various luminescence.

Cathodoluminescence (CL) of the enstatite has been investigated mainly in E-chondrite and Aubrite (e.g., Zhang et al., 1996). CL, a visible light of emissions when a material is irradiated by an electron beam, has a high advantage to reveal growth textures in the crystals of enstatite such as domain and zonation, most of which are difficult to be identified by conventional optical examinations. Therefore, CL of enstatite in E-chondrite has been used for the identification of its petrographic type and the studies of its thermal history (e.g., Zhang et al., 1996). Enstatite in meteorites occasionally shows various CL emissions with red, purple and blue (Reid et al., 1964), whereas terrestrial enstatite has no CL emission. In this study, we have confirmed luminescent enstatite in terrestrial materials for the first time. We have conducted to clarify the luminescence centers of CL emissions in the terrestrial and extraterrestrial enstatite by using a spectral deconvolution method.

SAMPLES AND METHODS

Single crystals of luminescent enstatite from Tanzania and Sri Lanka were selected for CL spectral measurements. The enstatite (Tan) from Mbeya, Tanzania occurred in ultramafic inclusions in alkaline olivine basalt, and the enstatite (Sri) from Sabaragamuwa, Sri Lanka were collected in the placer deposits originated from metamorphic sedimentary rocks with a high-grade in the Highland Complex (Dissanayake et al., 2000). Sahara 97096 (Sah97096), Sahara 97121 (Sah97121) and Yamato 86004 (Y–86004) for E-chondrite and Al Haggounia001 (Aub) for aubrite were chosen for a comparison with terrestrial enstatite. The polished samples finished with a diamond paste of 1 μm were coated with a 20 nm layer of carbon and employed for a CL examination.

Color CL images were obtained using a cold-cathode type Luminoscope (ELM-3) with a cooled charge-coupled device CCD camera. The identifications of constituent minerals in terrestrial and extraterrestrial samples were carried out using an electron probe microanalyzer (EPMA) and Raman spectroscopy after a polarizing-mi-
microscopic examination. CL spectroscopy was made by a SEM–CL system, which is comprised of SEM (JEOL: JSM-5410LV) combined with a grating monochromator (OXFORD: Mono CL2). The dispersed CL was recorded in the range of 300–800 nm by a photon-counting method using a photomultiplier tube and converted to digital data. All CL spectra were corrected for total instrumental response, which was determined using a calibrated standard lamp. Detailed construction of the equipment and analytical procedure can be found in Ikenaga et al. (2000).

RESULTS AND DISCUSSION

Color CL imaging reveals various types of CL emissions with red, red-purple, bluish-purple and blue in the terrestrial and extraterrestrial enstatite (Fig. 1). Extraterrestrial enstatite has been reported as a variety of CL colors emitted with red, magenta and blue (e.g., Zhang et al., 1996).

Figure 1. Color CL images of terrestrial enstatite (Tan1 and Sri1-3) and extraterrestrial enstatite (Sah97096 and Aub1).
In the previous studies (Crookes, 1879; Reid et al., 1964), however, terrestrial enstatite has not emitted any luminescence even by the excitation of any energy sources such as ion and X-ray beams. Most of terrestrial enstatite have the FeO contents above ~3 wt% (e.g., Deer et al., 1978), where Fe$^{2+}$ can act as a quencher to reduce the luminescence activated by impurity centers such as Mn$^{2+}$. In this study, we have first confirmed CL emissions with blue and red from the terrestrial samples (Tan1 and Sri1–3) with their low contents of FeO.

CL of enstatite is controlled mainly by activators of Mn$^{2+}$ and Cr$^{3+}$, and quencher of Fe$^{2+}$. Therefore, Fe ions of terrestrial enstatite should diminish luminescence efficiency derived from activators even with high density. Extraterrestrial enstatite with low FeO contents (<5 wt%) in E-chondrites shows obvious CL caused by various emission centers due to a negligibly small of quencher (Keil, 1968; Leitch and Smith, 1982; McKinley et al., 1984; Weisberg et al., 1994; Zhang et al., 1996). Terrestrial enstatite with luminescence have considerably low FeO contents (<1 wt%) on the same level with that of extraterrestrial enstatite (Sah97096a and Aub1), suggesting almost absence of quenching effect in the luminescent process (Table 1). Enstatite in E-chondrite and Aubrite are regarded as the minerals formed under highly-reducing conditionson their parent bodies judged by their mineral assemblages and compositions (e.g., Keil, 1968). However, terrestrial enstatite with low Fe has been reported in metamorphic rocks formed in the process of epithermal metamorphism (e.g., Dobrokhotova et al., 1967), which may be in a same case of the samples employed here. Most luminescent enstatite in the meteorites (Sah97096 and Aub1) show compositional variations of Al$\text{\textsubscript{2}}$O$\text{\textsubscript{3}}$, FeO, Cr$_2$O$_3$, MnO, and CaO contents with the ranges of five analyses in the table 1. The enstatite with red and red-purple CL (Tan1 and Sri1) have slightly higher MnO and Cr$_2$O$_3$ contents than blue CL enstatite.

The CL spectra of terrestrial and extraterrestrial enstatite show two broad emission bands at around 400 nm in a blue region and at around 670 nm in a red region (Fig. 2), both of which were detected in most enstatite sample-shaving various ratios of the CL intensities between red and blue regions. The difference of color tone in the CL such as red-purple (Sri1) and bluish-purple (Sri2) should depend on the ratio between blue and red emissions in enstatite. A red emission at around 670 nm in the synthetic enstatite is assigned to an impurity center derived from activated Mn$^{2+}$ substituted for Mg as an electron transition of $^4T_{1g}$ (G) $\rightarrow$ $^6A_{1g}$ (S) (Catalano et al., 2014). This electron transition similar to those in olivine and calcite is affected by the crystal field of the ligant oxygens coordi-
nated to the host Mn ion (Marfunin, 1979; Götte et al., 1999). Lofgren and DeHart (1992) confirmed that synthetic enstatite without impurities of Mn and Cr emits blue CL, suggesting other emission centers not related to impurity centers.

The CL spectral data obtained here were converted into energy units for spectral deconvolution using a Gaussian curve fitting because one Gaussian curve in energy units should correspond to one specific type of emission center (Yacobi and Holt, 1990; Stevens–Kalceff, 2000, 2009). Figures 3 and 4 show CL spectral patterns in energy units and the components deconvoluted by a Gaussian fitting using the peak–fitting software (Peak Analyzer) implemented in OriginPro 9.1, where a number of the component was determined using a statistical test of $\chi^2$ factor proposed by Stevens–Kalceff (2009). It results in five Gaussian components indicated in Figures 3 and 4, which can be identified to corresponding emission centers.

Terrestrial enstatite (Sri2) has two emission components related to impurity centers of Cr$^{3+}$ at 1.70 eV and Mn$^{2+}$ at 1.85 eV in a red region by referring to the results of the synthetic samples (e.g., Steele, 1988; Catalano et al., 2014), and two components at 2.72 and 3.10 eV in a blue region (Fig. 3), whereas extraterrestrial enstatite (Y–86004) has a characteristic component at 3.86 eV in a near–UV region in addition to those obtained in terrestrial one (Fig. 4). The emission components at 729 nm (1.70 eV) and 663–670 nm (1.85–1.87 eV) are assigned to Cr$^{3+}$ and Mn$^{2+}$, individually, according to Steele (1988) and Catalano et al. (2014).

The emission component at 2.72 eV might belong to the defect center, which is analogous to the defect center of the component at 2.75 eV detected in synthetic forsterite (Gucsik et al., 2012). Furthermore, this component has been confirmed in both terrestrial and extraterrestrial enstatite, suggesting a defect center possibly assigned to ‘intrinsic defect’ center formed during crystal growth. The synthetic enstatite without any activator and quencher ions emits a blue emission (e.g., Lofgren and DeHart, 1992). The same case of blue luminescence has been reported in several minerals (e.g., quartz) without any activators (e.g., Marshall, 1988).

The emission component at 3.18 eV might be due to the defect center associated with structural distortion by the substitution of Al for Si in a tetrahedral site. Emission bands at around 400 nm (3.10 eV) in a blue region were detected in most of the luminescent forsterite in meteorites as well as synthetic forsterite, while their CL intensities change depending on the samples (e.g., Gucsik et al., 2012, 2013). Steele et al. (1985) and Benstock et al. (1997) indicate that a blue CL emission in forsterite correlates with the concentrations of refractory–lithophile elements such as Ca, Al, and Ti, and could be derived by the distortion of T(Si, Al)–O chain when Al substitutes for Si and/or deformation of the lattice due to an incorporation of Ca and Ti ions. Such distortion involved with defects and unpaired electrons is caused by the substitutions of Si by Al and Ti and of Mg by Ca. Al$_2$O$_3$ contents in terrestrial enstatite increases with an increase in the intensity of the component at 3.10 eV when the CL color changes red to blue. A major emission center at 3.10 eV in a blue region has a correlation with the concentrations of Al$_2$O$_3$ in the enstatite, but not clearly with CaO and TiO$_2$ contents, suggesting a control of blue CL mostly by the Si–Al substitution in a tetragonal site.

Extraterrestrial enstatite (Y–86004) gives an additional emission component at 3.87 eV in a blue to UV region, which had not been found in enstatite so far. It is

**Figure 3.** CL spectrum in energy units of enstatite for terrestrial enstatite (Sri2) with their emission components deconvoluted by a Gaussian curve fitting.

**Figure 4.** CL spectrum in energy units of enstatite for extraterrestrial enstatite (Y–86004) with their emission components deconvoluted by a Gaussian curve fitting.
not detected in any terrestrial enstatite, suggesting a characteristic emission near UV probably related to the origin in a cosmic environment through the course of formation and progression of the enstatite in meteorite. Cosmic ray has extremely high-energy particles with intrinsic mass so that it flicks out oxygen which consists of enstatite crystal structure and forms oxygen vacancy responsible for defect center with a near-UV emission. Therefore, the total exposure of cosmic rays induced on the enstatite might be monitored using the intensity of the emission component at 3.87 eV.

Raman spectroscopy referred to the method by Ulmer and Stalder (2001) shows that all terrestrial enstatite with CL are identified only to orthoenstatite (Oen), but extraterrestrial enstatite to Oen and clinoenstatite (Cen). In the CL spectrum of extraterrestrial enstatite (Sah97096b and Sah97121), the peak position of emission band in a red region is located at around 670 nm for Oen, while at around 650 nm for Cen. The result of spectral deconvolution in a red region reveals that the positions of emission components differ between Oen and Cen (Figs. 5 and 6). An emission component related to Mn$^{2+}$ is centered at 1.85 eV for extraterrestrial Oen (Sah97096b) and at 1.85 eV terrestrial Oen (Sri2), but at 1.90 eV for extraterrestrial Cen (Sah97121). It suggests that the energy of the emission component activated by Mn$^{2+}$ might be used to identify the Oen and Cen, in which most of Mn$^{2+}$ occupies M2 site. According to Koto (1967), the nearest-neighbor distances between ligant oxygen and M2 ion is 1.985 Å for Oen and 2.02 Å for Cen. Sommer (1972) and Marfunin (1979) concluded that the strength of crystal field (Dq) around the transition metal elements such as Mn is enhanced in inverse proportion to the fifth power of metal-ligands (oxygen) distance. In the case of Mn ion octahedrally-coordinated with oxygen, the energy level of $^4T_{1g}$ ($^4G$) with excited-state Mn$^{2+}$ decreases with an increase in the Dq (Marfunin, 1979). Therefore, the emission energy specified by the distance between excited state ($^4T_{1g}$) and ground state ($^4A_{1g}$) reduces with increasing Dq. In the case of enstatite, therefore, the Mn-ligant distance for Oen is longer than that for Cen, resulting in the spectral–peak position of Mn activation for the Oen is located at a longer–wavelength side than that of the Cen as obtained in this study. Therefore, CL feature of red emission could be useful to distinguish between Oen and Cen phases with a micro-meter size in the enstatite.

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