# Cathodoluminescence and Raman Spectroscopic Characterization of Experimentally Shocked Plagioclase

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**Abstract.** Cathodoluminescence (CL) spectrum of plagioclase shows four emission bands at around 350, 420, 570 and 750 nm, which can be assigned to $Ce^{3+}$, Al–$O^-$–Al or $Ti^{4+}$, $Mn^{2+}$ and $Fe^{3+}$ centers, respectively. Their CL intensities decrease with an increase in experimentally shock pressure. The peak wavelength of the emission band related to $Mn^{2+}$ shifts from 570 nm for unshocked plagioclase to 630 nm for plagioclase shocked above 20 GPa. The Raman spectrum of unshocked plagioclase has pronounced peaks at around 170, 280, 480 and 510 $cm^{-1}$, whereas Raman intensities of all peaks decrease with an increase in shock pressure. This result suggests that shock pressure causes destruction of the framework structure in various extents depending on the pressure applied to plagioclase. This destruction is responsible for a decrease in CL intensity and a peak shift of yellow emission related to $Mn^{2+}$. An emission band at around 380 nm in the UV-blue region is observed in only plagioclase shocked above 30 GPa, whereas it has not been recognized in the unshocked plagioclase. Raman spectroscopy reveals that shock pressure above 30 GPa converts plagioclase into maskelynite. It implies that an emission band at around 380 nm is regarded as a characteristic CL signal for maskelynite. CL images of plagioclase shocked above 30 GPa show a dark linear stripe pattern superimposed on bright background, suggesting planer deformation features (PDFs) observed under an optical microscope. Similar pattern can be identified in Raman spectral maps. CL and Raman spectroscopy can be expected as a useful tool to evaluate shock pressure induced on the plagioclase in terrestrial and meteoritic samples.

**Keywords:** Cathodoluminescence, plagioclase, shock experiment, Raman spectroscopy, maskelynite, Planar Deformation Features
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## INTRODUCTION

Cathodoluminescence (CL) is the emission of photons with ultraviolet (UV) to infrared (IR) wavelengths from a material stimulated by an incident electron beam. CL spectroscopy and microscopy provide important information on the existence and distribution of defects and trace elements in materials, whereas it is quite difficult to obtain such factual evidence using other analytical methods. An advanced application of CL microscopy and spectroscopy to various minerals such as feldspar and silica minerals has been extensively reported in planetary and meteoritic sciences, e.g., determination of silica polymorphs [1] and interpretation of formation processes of the plagioclase in Lunar meteorite [2].

Since CL features of materials depend not only on varieties of emission centers but also on their host chemical composition, crystal fields, and sample temperature, it is closely related to geological condition during formation process and subsequent metamorphism such as shock events [2]. Extensive investigation on CL of shock-induced minerals has been conducted for high-pressure silica polymorphs to identify their minerals and clarify the shock metamorphic effect on CL [1,3], although very few studies have been reported in CL of feldspar minerals, which is the most important rock-forming mineral. In this study, CL and Raman measurements of plagioclase experimentally shocked at 0, 20, 30 and 40 GPa were carried out to evaluate shock metamorphic effect on them.

## SAMPLES AND METHODS

A single crystal of plagioclase from Sannidal, Norway was selected as starting material for shock experiment. This plagioclase has a composition of $Ab_{60}An_{40}$ as determined by electron microprobe analysis (EPMA). Shock experiments were carried out at 20, 30 and 40 GPa using a single-stage light-gas gun located at Tohoku University, Japan. Polished thin sections of recovered samples were used for polarized microscopic observation, EPMA and CL and Raman measurements.

Color CL images were captured using a cold-cathodoluminescence microscope (Luminoscope), consisting of an optical microscope, an electron gun, and a cooled charge-coupled device (CCD) camera. The instrument was operated at 15 kV accelerating voltage and 0.5 mA beam current with 100 s exposure. A scanning electron microscope-cathodoluminescence (SEM-CL) analysis was carried out using an SEM (JEOL: JSM-5410) combined with a grating monochromator (Oxford: Mono CL2), located at Okayama University of Science, Japan, to measure CL spectra ranging from 300 to 800 nm in 1 nm steps. The CL intensity emitted from the samples was collected using a retractable parabolic mirror collector coated with Al (collecting efficiency 75%). The collected CL was dispersed by the grating monochromator, which had the following characteristics: 1200 grooves/mm, a focal length of 0.3 m, F of 4.2, limit of resolution of 0.5 nm, and slit width of 4 mm at the inlet and outlet. The dispersed CL was collected by a photon counting method using a photomultiplier tube (Hamamatsu: R2228) and converted to digital data. All CL spectra were corrected for total instrumental response, which was determined using a calibrated standard lamp

(Eppley Laboratory: Quartz Halogen Lamp). CL images at high magnification were obtained with a MiniCL detector (Gatan) equipped with SEM-CL. Calibration curves of photomultiplier tubes attached with SEM-CL and MiniCL detector are shown in Figure 1. The correction of CL spectrum prevents errors in the peak position of emission bands and allows quantitative evaluation of CL intensity. Measured and corrected spectra of the plagioclase as a starting material are illustrated in Figure 2.

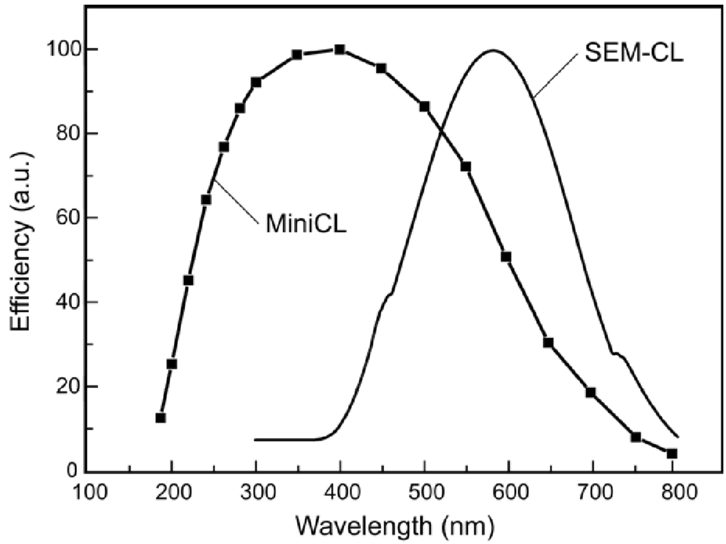


**FIGURE 1.** Calibration curves of photomultiplier tube (Hamamatsu: R2228) attached with secondary electron microscope-cathodoluminescence (SEM-CL) and sensitivity characteristic curve of MiniCL photomultiplier tube (Gatan).

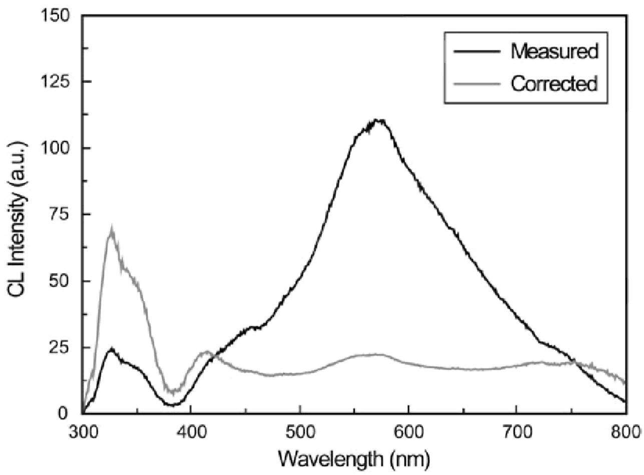


**FIGURE 2.** CL spectra of unshocked plagioclase measured and corrected for total instrument response.

## RESULT

An unshocked plagioclase exhibits a bright emission with homogeneous distribution of intensity in the CL image obtained by MiniCL imaging system, and has no characteristic features such as growth zonal structure or lamellae under optical microscope and in SEM and BSE images (Fig. 3a and b). Plagioclase experimentally shocked at 20 GPa, however, shows a heterogeneous distribution of CL intensity with bright core and dull rim which cannot be detected in SEM and BSE images (Fig. 3c and d). The CL image of plagioclase shocked at 30 GPa pictures dull linear stripes superimposed on more brightly luminescent background, which are corresponding to planar deformation features (PDFs) under optical microscope (Fig. 3f). PDFs occurs as one or multiple sets of narrow stripes (<2~3 μm) with spacing of 2 to 10 μm in shocked minerals under an optical microscope. Especially quartz is the mineral in which shock characteristic deformation is well developed and has been extensively studied, although a few PDFs in feldspar have been investigated up to now. Similar features related to PDFs were found in plagioclase shocked at 40 GPa under optical microscope and in CL and BSE images (Fig. 4a, b and d). SEM images of samples at 30 and 40 GPa, however, show no such features (Fig. 3e and 4c).

The CL spectrum of unshocked plagioclase has four emission bands at around 350, 420, 570 and 750 nm in the UV, blue, yellow and red-IR regions (Fig. 5). The shocked sample at 20 GPa also shows similar four emissions in CL spectroscopy, whereas it has lower CL intensities of all emissions than does unshocked plagioclase. Furthermore, the peak wavelength of the emission band in the yellow region shifts from 570 nm for unshocked plagioclase to 630 nm for shocked sample at 20 GPa. The CL spectrum of shocked sample at 30 GPa consists of two emission bands at 350-400 nm in the UV-blue region and 630 nm in the red region. All emission bands also have a low CL intensity compared to unshocked plagioclase. A bright UV-blue emission is observed only in CL spectrum of plagioclase shocked at 40 GPa. The emission band with a maximum at 380 nm in UV-blue region was recognized in CL of shocked samples only at 30 and 40 GPa.

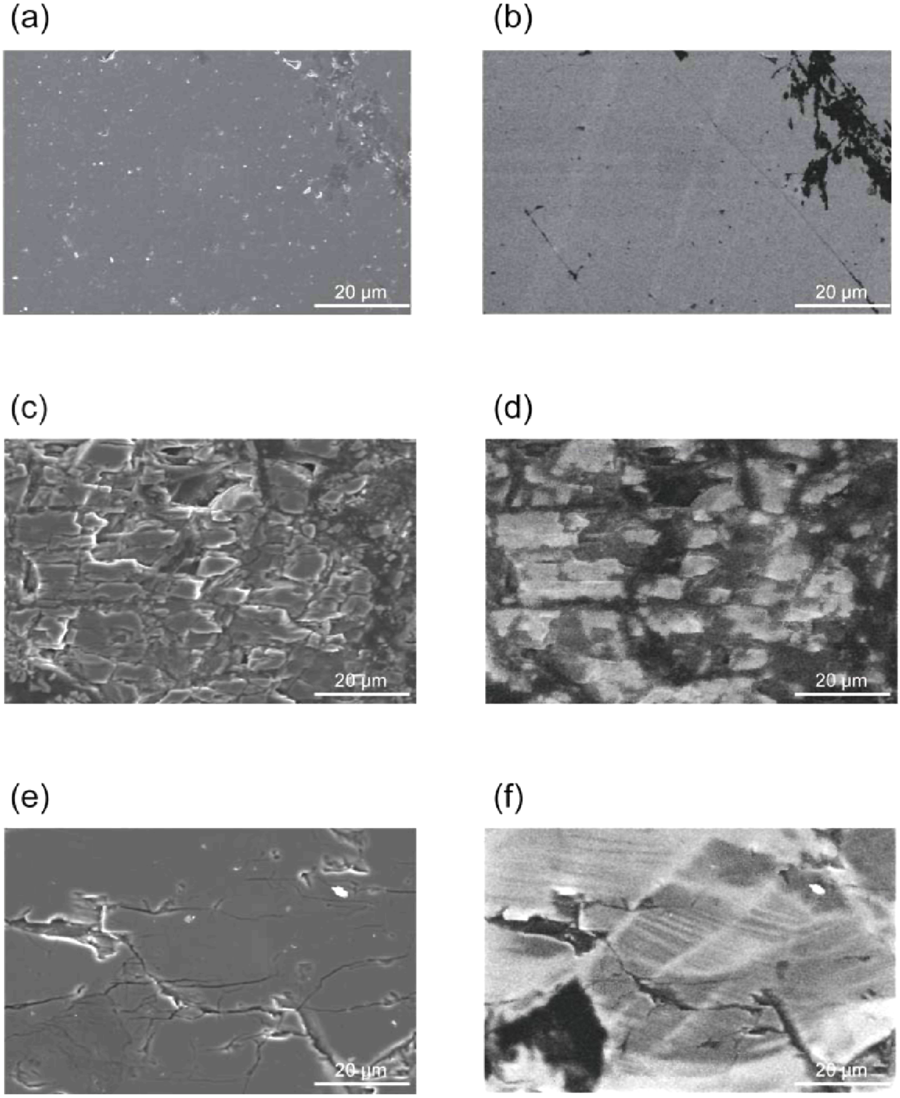


**FIGURE 3.** Unshocked plagioclase in (a) SEM image and (b) CL image, shocked sample at 20 GPa in (c) SEM image and (d) CL image, and shocked sample at 30 GPa in (e) SEM image and (f) CL image.

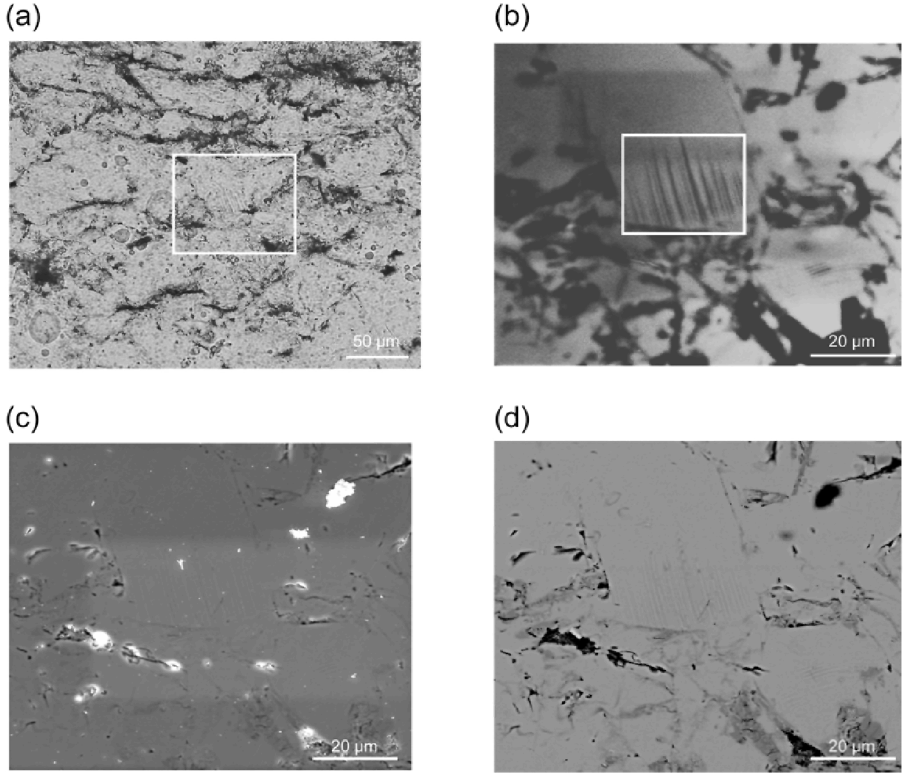


**FIGURE 4.** Plagioclase shocked at 40 GPa in (a) optical microscopic photograph, (b) CL image, (c) SEM image and (d) BSE image.

The Raman spectrum of unshocked plagioclase consists of pronounced peaks at around 170, 280, 480 and 510 $cm^{-1}$, whereas the shocked sample at 20 GPa shows two peaks at around 480 and 510 $cm^{-1}$ in its Raman spectrum (Fig. 6). Furthermore, shocked sample at 30 GPa has a weak and broad peak at 480 $cm^{-1}$ compared to unshocked and shocked samples at 20 GPa. The Raman intensity of a peak at 480 $cm^{-1}$ decreases with an increase in shock pressure. Plagioclase shocked at 40 GPa shows broadened peaks at around 500 and 580 $cm^{-1}$. 2D and 3D Raman spectral images pictured using relative intensity of highest peak at 505 $cm^{-1}$ over the area in plagioclase shocked at 40 GPa are shown in Fig. 7a and b, where sub-linear contrast in 2D and alignment of ridge and valley in 3D might correspond to the PDFs shown as straight line observed in optical image (Fig. 4a) and in CL image (Fig. 4b) as dark stripe superimposed on bright luminescent background.

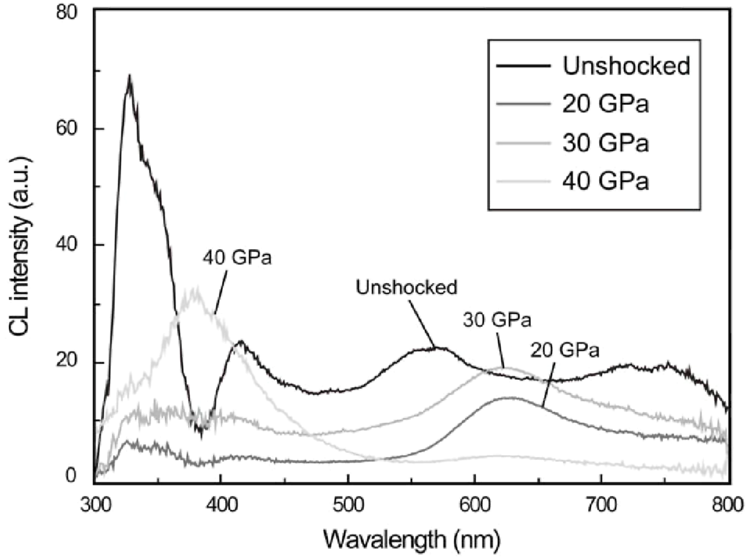


**FIGURE 5.** CL spectra of plagioclase unshocked and shocked at 20, 30 and 40 GPa.

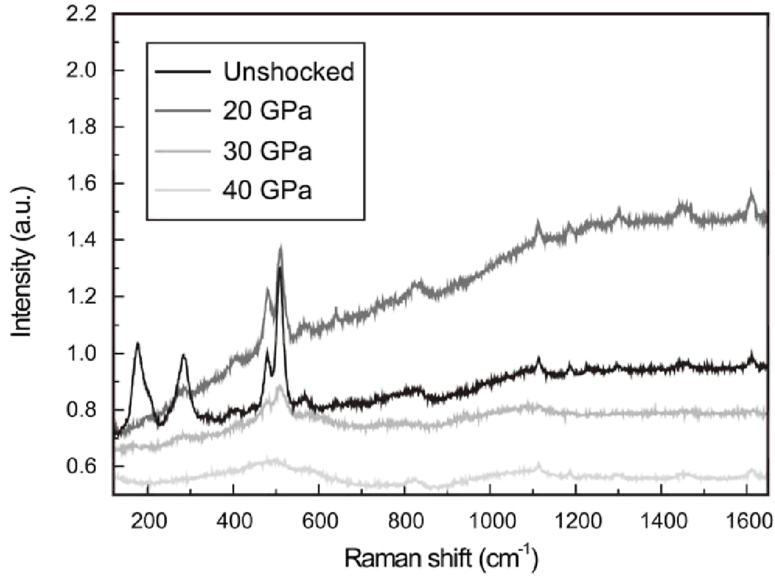


**FIGURE 6.** Raman spectra of plagioclase unshocked and shocked at 20, 30 and 40 GPa.

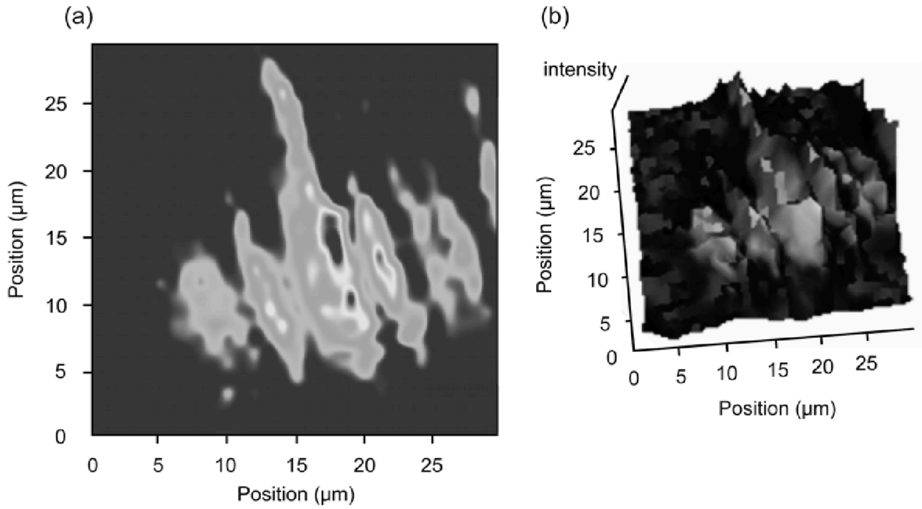


**FIGURE 7.** Plagioclase experimentally shocked at 40 GPa in (a) 2D Raman spectral image and (b) 3D Raman spectral image pictured using Raman peak intensity at 505 $cm^{-1}$.

## DISCUSSION

CL spectroscopy reveals that unshocked plagioclase exhibits four emission bands in UV, blue, yellow and red regions (Fig. 5). Similar emissions have been reported in various CL studies on feldspar. According to Laud et al. (1970), emission band at 350 nm observed in UV spectral region might be assigned to $Ce^{3+}$ center [4]. Alternatively, it could it be possible that there is also a structural defect, because of the fact that this UV emission disappears after shock.

Yellow and red-IR emission bands at around 570 and 750 nm have been found in not only natural plagioclase but also synthetic samples, and assigned to $Mn^{2+}$ and $Fe^{3+}$ centers, respectively [5,6]. CL emission bands of unshocked plagioclase in yellow and red-IR regions are assigned to $Mn^{2+}$ and $Fe^{3+}$ centers, respectively. CL spectra of plagioclase as well as alkali feldspar have an emission band at 450-480 nm [7,8]. Similar blue emission band is recognized in CL spectra of plagioclase measured here and might be related to Al–$O^{-}$–Al or $Ti^{4+}$ (more unlikely) center.

Plagioclase shocked at 20 GPa also consists of these four emission bands, whereas their CL intensities are quite lower than those of unshocked sample. At 30 GPa, CL spectrum of shocked plagioclase shows only an emission band in yellow region, and that of plagioclase shocked at 40 GPa has none corresponding to these four emission bands. These facts indicate that experimentally shock pressure reduces activities of these emission centers in plagioclase. CL spectroscopy for unshocked and shocked plagioclase also reveals that an induction of shock pressure has a critical influence on the wavelength of the emission band in the yellow region. Unshocked plagioclase has a maximum of emission peak at 570 nm, although CL spectra of the shocked samples at 20 and 30 GPa involve a peak centered at 630 nm. Furthermore, the peak wavelength of the yellow emission related to the $Mn^{2+}$ center shifts from 570 nm for unshocked plagioclase to 630 nm for shocked samples above 20 GPa.

The Raman spectroscopy reveals a mechanism of the decrease in CL intensity and peak shift in the yellow emission by high shock pressure. The Raman spectrum of unshocked plagioclase shows pronounced peaks at around 170, 280, 480 and 510 $cm^{-1}$, which can be assigned to T–O–T atomic vibrations (Fig. 6). Raman intensities of these peaks decrease with an increase in shock pressure. This fact suggests that shock pressure causes partly destruction of the framework structure in varying extents depending on the pressure induced on the sample. This structural breakdown might change frame work configuration around luminescence centers related to UV, blue, yellow and red emissions. It is responsible for a decrease in the CL intensity with an increase in shock pressure. The shift of peak wavelength in yellow region might be related to alteration of the crystal field around $Mn^{2+}$ center by shock pressure. An emission at around 570 nm is caused by the radiative transition of the electrons in $Mn^{2+}$ ions from $^4T_1$ to $^6A_1$[5]. The wavelength of this emission is actually affected by the strength of crystal field ($Dq$) around $Mn^{2+}$ ions [9]. The energy level of $^4T_1$ in $Mn^{2+}$ ion decreases with an increase in the $Dq$, where $^6A_1$ energy level is constant against the $Dq$. According to Blasse and Grabmaier (2002), $Mn^{2+}$ ion with weak $Dq$ emits green CL emission, whereas that with intense $Dq$ does yellow-red CL emission during radiative transition from $^4T_1$ to $^6A_1$ [10]. The unshocked plagioclase has shorter wavelength (570 nm) than do experimentally shocked samples (630 nm). It implies that shocked plagioclase has lower transition energy between $^4T_1$ and $^6A_1$ with higher $Dq$ than does unshocked sample. Shock-induced pressure might make an alteration of coordinate configuration around $Mn^{2+}$ ions, which causes a reduction of its $Dq$. This effect due to the increasing shock pressure results a peak shift from 570 nm for the unshocked plagioclase to 630 nm for shocked plagioclase. The change in wavelength of $Mn^{2+}$ emission might be applied to evaluate shock pressure induced on plagioclase up to 20 GPa.

The CL spectra of plagioclase shocked at 30 and 40 GPa only exhibit a UV-blue emission which has its maximum at around 380 nm. Such UV-blue emission has not been reported in natural and synthetic feldspar minerals up to now. The Raman spectrum of shocked sample at 40 GPa shows characteristic broadened peaks at 500 and 580 $cm^{-1}$. These peaks are also observed in the Raman spectrum of shocked samples at 30 GPa, whereas their intensities are apparently weakened. Similar spectral peaks at 500 and 580 $cm^{-1}$ have been reported in Raman spectroscopic studies for maskelynite in shergottites [11]. It suggests that shock-induced pressure converts plagioclase to maskelynite partly for 30 GPa and almost completely for 40 GPa. An emission band at 380 nm, therefore, may be used as a characteristic CL signal to identify the maskelynite. These results imply that CL and Raman spectroscopy of plagioclase is expected as an approved to evaluate shock pressure induced in the samples from impact creator and meteorites.

The unshocked plagioclase shows a bright emission with homogeneous distribution of intensity in the CL image (Fig. 3b). It also has no features or textures such as growth zonal structure or lamellae under optical microscope and in SEM and BSE images (Fig. 3a). The CL image of plagioclase shocked at 20 GPa, however, exhibits heterogeneous distribution of intensity, whereas SEM and BSE images show no such characteristics (Figs. 3a and b). Since CL intensities of all emissions decrease with an increase in shock pressure, their heterogeneous distribution of plagioclase shocked at 20 GPa might be caused by different shock effect on the CL in bright and dull emission area. Plagioclase shocked at 30 and 40 GPa only have a unique CL pattern with dark linear stripes on bright background. It corresponds to the PDFs under optical microscope (Fig. 3b and 4b). 2D and 3D Raman spectral images also can illustrate similar pattern (Fig. 7a and b). These facts imply that interference shock wave with high pressure could cause structural destruction with parallel array along wave front. CL and Raman methods, therefore, can be applied to the characterization of shock metamorphic features such as PDFs with micron meter sized resolution.

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