LETTER

Photoluminescence properties of gypsum

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The photoluminescence (PL) properties of four gypsums from three localities, namely, Inner Mongolia (China), Turkey, and Canada, are investigated at room temperature. Under 365-nm excitation, two types of gypsums from Inner Mongolia exhibit different luminescence colors, namely, yellow and cyan-white, and gypsums from Turkey and Canada exhibit yellow and bluish-white luminescence, respectively. The PL spectra of these gypsums consist of continuous sub-bands distributed in all visible wavelengths, and the excitation spectra of these gypsums consist of continuous sub-bands distributed in a wide range of wavelengths, i.e., 200–500 nm. The features of PL and excitation spectra suggest that the origin of luminescence from these gypsums may be luminescent organic substances included into crystals in the growth process rather than the impurity ions substituted for Ca²⁺.

Keywords: Gypsum, Selenite, Luminescence spectra, Hourglass pattern

INTRODUCTION

Gypsum or selenite, the transparent variety of gypsum (CaSO₄·2H₂O), is a well-known luminescent mineral. Hourglass patterns are observed in images of some luminescent gypsums var. selenites. The hourglass pattern in selenite has been explained by sector zoning, which may be described as the existence of different luminescence centers in different growth sectors of a single crystal (Kastner, 1970; Dowty, 1976; Robbins, 1994; Rakovan and Waychunas, 1996). The different colors of luminescence from gypsum under ultraviolet (UV) light excitation have been reported as baby blue, creamy green, greenish white, yellow green, and yellow. Some investigators synthesized gypsum crystals (Kastner, 1970; Cody, 1976; Cody and Cody, 1988; van der Voort and Blasse, 1989; de Meer et al., 2000), and many investigators studied the luminescence properties of alkaline-earth sulfates activated with rare-earth (RE) ions (Nambi and Bapat, 1980; Yamashita et al., 1985; van der Voort and Blasse, 1990; Lakshmanan, 1999; Yamashita et al., 2001). However, the origin of luminescence from natural gypsum has not been identified (Robbins, 1994). Few reliable studies have been conducted on the PL properties of natural gypsum, besides the short report (Kono et al., 2010) on the PL properties of

gypsum from Inner Mongolia, China.

The objectives of this investigation are to carry out a detailed study of the PL and excitation spectra of gypsums from different localities, and to obtain results that help to clarify the origin of luminescence from natural gypsum.

SAMPLES

Four gypsum samples, namely, A1 and A2 from Inner Mongolia, China, B from Sivas, Turkey, and C from Alberta, Canada, were used in this study. Samples A1 and A2 were collected from Jirantai Saline Lake, Inner Mongolia, China. Luminescent specimens, A1 and A2, were selected from over 200 specimens found near the artificial bank of salt at Jirantai Saline Lake. The details of these crystals were described in our previous report (Kono et al., 2010). Sample B was collected in Sivas Province, Central Anatolia Region, Turkey. In ancient times, the Anatolia Region was immersed in a huge saline lake, and modern Sivas is famous for deposits of salt and gypsum. The gypsum specimen, quarried from a large gypsum lump with a size of 2 to 3 m, was a crystal aggregate consisting of a large number of transparent gypsum crystals with sizes as large as 1 to 4 cm. The type of the transparent gypsum crystal was allotriomorphic. After the aggregated crystal was smashed, only the pieces of transparent gypsum were manually selected as Sample B. Sample C

was selected from commercial specimens of fluorescent minerals. It was collected from Willow Creek near Nanton, Alberta, Canada. The transparent crystal with an idiomorphic type was a typical gypsum var. selenite. Through powder X-ray diffraction analysis, all the specimens were confirmed to be gypsum without any significant impurities.

EXPERIMENTAL

Luminescence spectra were measured at the Faculty of Education, Okayama University. The details of the system used for measuring the PL and excitation spectra are described in previous papers (Aierken et al., 2002, 2003, 2010). Before the measurement of luminescence spectra, the powdered specimen was packed into a sample holder with a synthetic quartz-glass cover. In the measurement of PL spectra, a 200-W deuterium lamp and a 500-W xenon short-arc lamp were used as excitation light sources. An excitation wavelength with a bandwidth of 2 to 5 nm was selected using a Ritsu MC-50L grating monochromator; the bandwidth was dependent on the luminescence efficiency. An observation wavelength with a bandwidth of 2 to 3 nm was selected using a Ritsu MC-50 grating monochromator. The PL spectral intensity was measured using a Hamamatsu Photonics R955 photomultiplier. PL spectra were corrected for the spectral sensitivity of the measuring system using a standard tungsten lamp calibrated in line according to the National Bureau of Standards, U.S.A.

For the measurement of optical excitation spectra, the same system as that used for the measurement of emission spectra was employed; however, the excitation bandwidth was 2 to 3 nm, depending on the luminescence efficiency, and the observation bandwidth was 5 nm. For the visible-light excitation, a 50-W halogen tungsten lamp was used. The ordinate of the excitation spectra was plotted against the relative excitation efficiency, after correction for optical excitation energy distribution.

RESULTS

The photoluminescence properties of the four gypsum samples were as follows:

Sample A1

Figure 1 shows Sample A1 under short-wave UV-light (Hg 253.7 nm) excitation. In Figure 1a, the bright yellow luminescence appears as an hourglass pattern. As the violet light from the Hg lamp and the yellow luminescence are scattered by the naturally etched crystal surface, the whole surface appears to be faintly luminescent. In Figure 1b, the $\{110\}$ sectors are nonluminescent and the

Figure 1. Gypsum var. selenite from Inner Mongolia, China (Sample A1), under UV-light (Hg 253.7 nm) excitation, as observed (a) from a normal direction to the a - b plane and (b) along the b axis; for obtaining the image shown in (b), the sample was cut along the a - c cleavage plane to a thickness of approximately 0.3 mm.

Figure 2. PL emission (Em) and excitation (Ex) spectra of gypsum var. selenite $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Sample A1) from Inner Mongolia, China, as measured at 300 K; the Em spectra were obtained under (1) 300-, (2) 360-, and (3) 436-nm excitations, and the Ex spectrum was obtained by monitoring the red luminescence at 660 nm.

$\{111\}$ sectors exhibit faint yellow luminescence. Parts of the $\{103\}$ sectors exhibit bright yellow luminescence that forms the pattern of the mathematical integral symbol. Figure 2 shows the PL and excitation spectra of Sample A1, as measured at 300 K. The relative intensities of the three PL spectra at 660 nm were corrected for the relative

Figure 3. Gypsum var. selenite from Inner Mongolia, China (Sample A2), under UV-light (Hg 253.7 nm) excitation, as observed along the *b* axis; the sample was cut along the *a-c* cleavage plane to a thickness of approximately 0.3 mm.

Figure 4. PL emission (Em) and excitation (Ex) spectra of gypsum var. selenite $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Sample A2) from Inner Mongolia, China, as measured at 300 K; the Em spectra were obtained under (1) 300-, (2) 360-, and (3) 436-nm excitations, and the Ex spectrum was obtained by monitoring the green luminescence at 550 nm.

PL efficiencies using the excitation spectrum. The PL intensities in the PL spectra of other samples were corrected in a similar manner. The PL spectra consist of an extremely broad band with a peak located at approximately 654 nm, 663 nm, and 678 nm under 300-, 360-, and 436-nm excitations, respectively, and are spread over the green, red and infrared wavelength regions. The peak shifts under these excitations are small. Under these excitations, the luminescence appears yellow to the naked eye. The excitation spectrum in Figure 2 consists of several sub-bands with a maximum peak at 394 nm, and the sub-bands are distributed in not only the UV region but also the blue region.

Sample A2

Figure 3 shows Sample A2 under short-wave UV-light excitation. In Figure 3, the $\{111\}$ and $\{\bar{1}03\}$ sectors exhibit cyan-white luminescence. The nonluminescent $\{110\}$ sectors exhibit an hourglass pattern. Figure 4 shows the PL and excitation spectra of Sample A2, as measured at 300 K. PL spectra consist of an extremely broad band with a peak located at approximately 524 nm, 492 nm,

Figure 5. PL emission (Em) and excitation (Ex) spectra of gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Sample B) from Sivas, Turkey, as measured at 300 K; the Em spectra were obtained under (1) 300-, (2) 360-, and (3) 436-nm excitations, and the Ex spectrum was obtained by monitoring the red luminescence at 660 nm.

and 533 nm under 300-, 360-, and 436-nm excitations, respectively. The peak positions are strongly dependent on the excitation wavelengths. The PL spectra under 300-nm excitation are spread over the long UV region and the entire visible wavelength region. Under 300- and 360-nm excitations, the luminescence color appears cyan-white to the naked eye. The excitation spectrum in Figure 4 consists of several sub-bands with a maximum peak at 425 nm, and the sub-bands are distributed in not only the UV but also the blue region. The excitation and emission spectra overlap with each other. It should be noted that the luminescence color (cyan-white) of Sample A2 is different from that (yellow) of Sample A1, even though both samples were collected from the same saline lake.

Sample B

The gypsum specimen from Turkey consisted of a large number of transparent crystals (Sample B). Under UV-light excitation, Sample B exhibited yellow luminescence. In the case of Sample B, the hourglass pattern was not observed. Figure 5 shows the PL and excitation spectra of Sample B, as measured at 300 K. The PL spectra consist of an extremely broad band with a peak located at approximately 628 nm, 635 nm, and 645 nm under 300-, 360-, and 436-nm excitations, respectively. The features, including the peak wavelengths, of these PL spectra are similar to those of the spectra of Sample A1, even though both samples were collected from different localities. Under these excitations, the luminescence appears yellow to the naked eye. The excitation spectrum in Figure 5 consists of several sub-bands with a maximum peak at 382 nm, and the sub-bands are distributed in not only the UV but also the blue region.

Sample C

Figure 6 shows Sample C under short-wave UV-light excitation; the sample was observed along the *b* axis. The {111} sectors in this figure exhibit bright blue-white luminescence, and this explains the typical hourglass pattern observed in the nonluminescent sectors. Figure 7 shows the PL and excitation spectra of the luminescent sector of Sample C at 300 K. The PL spectra consist of an extremely broad band with a peak located at approximately 444 nm, 453 nm, and 530 nm under 300-, 360-, and 436-nm excitations, respectively. The features, including the peak wavelengths, of these PL spectra are similar to those of the PL spectrum of Sample A2. The peak positions strongly depend on the excitation wavelengths. The PL spectra under 300-nm excitation are spread over the

Figure 6. Gypsum var. selenite from Alberta, Canada (Sample C), under UV-light (Hg 253.7 nm) excitation, as observed along the *b* axis.

Figure 7. PL emission (Em) and excitation (Ex) spectra of gypsum var. selenite $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Sample C) from Alberta, Canada, as measured at 300 K; the Em spectra were obtained under (1) 300-, (2) 360-, and (3) 436-nm excitations, and the Ex spectrum was obtained by monitoring the blue-green luminescence at 500 nm.

long UV region and the entire visible wavelength region. Under 300- and 360-nm excitations, the luminescence appears cyan-white to the naked eye. The excitation spectrum in Figure 7 consists of several sub-bands with a maximum peak at 388 nm, and the sub-bands are distributed in not only the UV but also the violet region. The excitation and emission spectra overlap with each other.

DISCUSSION

Luminescence from minerals is frequently ascribed to the following three causes: (i) intrinsic luminescence, (ii) impurity luminescence, and (iii) luminescence from inclusions; the luminescence spectra of minerals that exhibit luminescence due to the three causes have the respective characteristics. The intrinsic luminescence is due to the composition of the host crystal, e.g., the WO_4 center in scheelite (Gaft et al., 1998) and the TiO_6 centers in titanium minerals (Aierken et al., 2010). The emission spectrum due to intrinsic luminescence consists of a broad band, and the shape of the spectrum does not change when the excitation wavelength changes. The impurity luminescence is due to RE ions or heavy metal ions. The emission spectra of the RE^{3+} (except for Ce^{3+}) centers consist of characteristic narrow bands, and emission bands due to some RE ions, e.g., Ce^{3+} , Eu^{2+} , and Yb^{2+} , and heavy metal ions, e.g., Mn^{2+} , Fe^{3+} , and Pb^{2+} , are approximated to Gaussian curves when the emission spectra are drawn against a photon energy scale (Machel et al., 1991; Aierken et al., 2002, 2003). The PL and excitation spectra of our gypsum samples show continuous broad bands, and the shapes of the PL spectra depend on excitation wavelengths (Figs. 2, 4, 5, and 7). This is not consistent with the characteristics of the spectra corresponding to (i) intrinsic luminescence or (ii) impurity luminescence. As described in the following paragraph, the cause of luminescence from our gypsum samples seems to be (iii) luminescence from inclusions.

Many researchers have investigated fluid inclusions in minerals (Roedder, 1984; Pironon and Pradier, 1992; Kihle, 1995; O'Reilly and Parnell, 1999; Volk et al., 2002; Li and Parnell, 2003; Kono et al., 2011), but there are few reliable reports on the luminescence spectra of fluid inclusions. Kono et al. (2011) reported on the PL and excitation spectra of petroleum inclusions as large as $3 \times 2 \times 0.3 \text{ mm}^3$ in quartz from Pakistan. The petroleum inclusions exhibit bright bluish-white luminescence under UV-light excitation and yellow luminescence under visible-light excitation at 500 nm. The PL spectrum corresponding to 360-nm excitation and the excitation spectrum obtained by monitoring green luminescence at 520 nm from the petroleum inclusions are in good agreement with the Em

(Curve 3) and Ex spectra of Sample A2, respectively (Fig. 4). On the other hand, many investigators observed the PL and excitation spectra of crude oils and aromatic hydrocarbons (Thruston, Jr., and Knight, 1971; Wakeham, 1977; Burruss, 1991). Wakeham (1977) observed synchronous spectra of oils and aromatic hydrocarbons. The spectra were obtained by synchronously scanning both excitation and emission monochromators. The shapes of the synchronous spectra of oils and aromatic hydrocarbons are similar to those of the Em spectra of Samples A2 and C (Figs. 4 and 7, respectively), although the peak wavelengths of the Em spectra of our gypsums are longer than those of the synchronous spectra. Burruss (1991) presented the PL and excitation spectra of crude oil; these spectra are in good agreement with the Em (Curve 2) and Ex spectra of Sample A2, respectively (Fig. 4). Although optical microscopy did not indicate that our gypsum samples contained inclusions such as petroleum, the above discussion suggests that the origin of luminescence from our gypsums may be inclusions such as undetectable organic substances. As suggested by Dana et al. (1997), our gypsum samples probably contained organic substances when they were grown in a wet environment. Cody and Cody (1988) revealed that gypsum crystals synthesized in the presence of polytannate ions exhibit the same yellow-green luminescence characteristic of natural gypsums in their collections. The experimental results obtained by Cody and Cody (1988) support our hypothesis on the origin of luminescence from gypsum or selenite. In our results, the peak wavelengths of the PL and excitation spectra of Samples A1 and A2, which were collected from the same saline lake, are different (Figs. 2 and 4), while the PL and excitation spectra of Sample A1 obtained from Inner Mongolia, China (Fig. 2), are similar to those of Sample B obtained from Sivas, Turkey (Fig. 5). In the future, these facts should be verified and the origin of luminescence from gypsum must be identified.

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