Large red-shift of luminescence from $BaCN_2:Eu^{2+}$ red phosphor under high pressure

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We report a new material, $BaCN_2:Eu^{2+}$ for a very sensitive optical pressure sensor, 50 times more sensitive than ruby. Photoluminescence spectra of the $BaCN_2:Eu^{2+}$ phosphor was measured under hydrostatic pressures from ambient pressure to 5.34 GPa at room temperature. The peak wavelength of the luminescence was drastically red-shifted at a rate of 19 nm/GPa, which is approximately 50 times larger than that of the ruby, most commonly used as a pressure sensor in the high-pressure experiments. This large shift of the luminescence wavelength is suitable for application in optical pressure sensors for the high-pressure experiments without a high-resolution monochromator.

High-pressure science has opened a vast new window of opportunities for surprising discoveries of new materials, such as superconducting superhydrides with extremely high transition temperature, different stoichiometric compounds, and solid-state "gas" molecules.[1-4] Several tools such as the diamond anvil cell (DAC) have been developed to achieve high-pressure experiments together with a pressure sensor using the luminescence of the R_1 spectral line of ruby ($Al_2O_3:Cr^{3+}$) due to the wavelength shift against pressure and bright luminescence. The pressure measurement system was first reported by Forman et al.[5] being followed by much effort to calibrate the real pressure of the system from the wavelength shift of the R_1-line of the ruby sensor.[6-8] Because of the small peak shift of the R_1-line, a spectrometer with very high wavelength-resolution is required to evaluate the pressure from the luminescence peak value of the spectra. Many alternative materials for optical pressure sensors have been proposed, such as oxides, fluorides, and sulfides.[9-13]

Metal carbodiimides are interesting inorganic materials because of their dumbbell-like triatomic anion NCN^{2-} which can replace O^{2-} anions. An orange luminescence at 603 nm has been reported for Eu^{2+}-doped $SrCN_2$ obtained from the reaction of SrI_2, EuI_2, CsN_3 and CsCN.[14] The rhombohedral $BaCN_2$ has been prepared from the reaction of Ba_3N_2 and melamine under an Ar flow.[15] We have recently reported large temperature dependence of red luminescence wavelengths from the tetragonal $BaCN_2:Eu^{2+}$ phosphor prepared by a simple ammonia nitridation reaction of $BaCO_3$.[16] In this phosphor, each Ba^{2+} ion is situated in the square antiprism of N atoms of the NCN^{2-} anionic group. Ba^{2+} and NCN^{2-} ions form a CsCl-type arrangement of both ions in conjunction with an ordered arrangement of the NCN^{2-} anions. Under excitation with blue or green light (from 400 to 500 nm) $BaCN_2:Eu^{2+}$ shows intense red luminescence band due to Eu^{2+}: $4f^65d^1 \rightarrow 4f^7$ transition at room temperature peaked at 660 nm. The peak wavelength varies from 680 nm at 80 K to 640 nm at 500 K without significant thermal quenching. The $BaCN_2$ host material has large thermal expansion coefficients of $\alpha_a = 1.5\times10^{-5}$ K^{-1} and $\alpha_c = 2.3\times10^{-5}$ K^{-1} at 290 K, which are almost one order of magnitude larger than those of Si_3N_4 and Al_2O_3 ceramics. This relatively soft host lattice for Eu^{2+} doping leads to a wide variation in the luminescence wavelength with temperature, which is probably induced also by changes in the crystal field splitting of the 5d energy levels of the Eu^{2+} ions as well as by Boltzmann distribution of excited states. In this context it is expected that static high pressure can induce a modulation of crystal field strength by compression of the $BaCN_2$ lattice.

In the present study, we present a significant change of luminescence wavelength observed from the $BaCN_2:Eu^{2+}$ under static high pressures up to 5.34 GPa. The pressure dependence of the peak wavelength was almost 50 times larger than that of the ruby R_1-line, which is most commonly used as an optical pressure sensor. Therefore, the large shift of luminescence wavelength under high pressure makes $BaCN_2:Eu^{2+}$ a very sensitive pressure sensor with potential application to high-pressure experimental physics.

A Eu^{2+}-doped $BaCN_2$ sample was prepared from a mixture of $BaCO_3$ (99.9%, Fujifilm Wako Pure Chemicals Co.) and Eu acetylacetonate hydrate (99.9%, Aldrich) at a Ba:Eu ratio of 99:1. The mixture was nitrided in an alumina boat under an NH_3 flow of 50 mL/min at 900 °C for 15 h in an alumina tube furnace, similar to our previously reported method.[16] Almost single-phase tetragonal $BaCN_2$ doped with Eu^{2+} was confirmed by X-ray diffraction (XRD; Rigaku Ultima IV) measurements with Cu Kα radiation. The photoluminescence (PL) properties of $BaCN_2:Eu^{2+}$ were measured using a fluorescence spectrometer (Jasco, FP-6500) equipped with a 150 W Xe lamp as an excitation source at room temperature and under ambient pressure. Figure 1 shows PL and excitation spectra for $BaCN_2:Eu^{2+}$. A strong red luminescence band peaked at 660 nm, which has a wide excitation band ranging from 250 to 550 nm. The broad luminescence band is attributed to the Eu^{2+}; $4f^65d^1$-$4f^7$ transitions in the host lattice, which was also supported by X-ray absorption data.

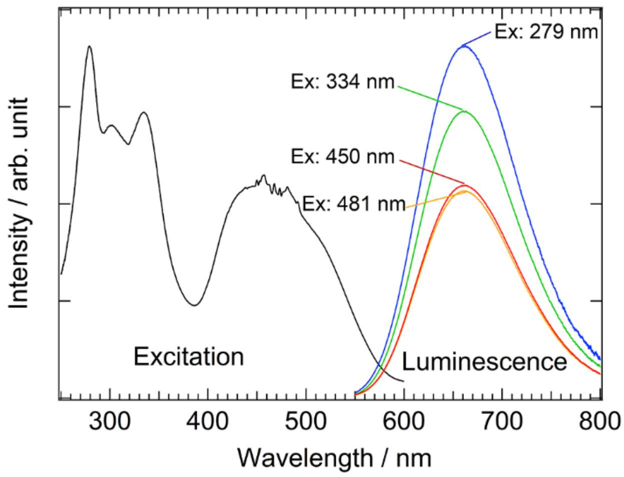

Figure 1 PL and PL excitation (PLE) spectra for $BaCN_2:Eu^{2+}$ at room temperature under ambient pressure. The excitation spectrum was monitored at a luminescence wavelength of 660 nm.

High-pressure luminescence measurements were performed using an in-house-built system. A Merrill Bassett type DAC system (TPSM3718, Syntek) was used to apply pressure with dimethylpolysiloxane as the pressure-transmitting medium. The pressure was measured by the shift of the R_1-line of ruby using Mao's equation.[7] The sample in the DAC was excited by a 450 nm laser (PL-450TB, Osram) and the luminescence from the sample was detected by a multichannel spectrophotometer (QE65 PRO, Ocean Optics). The fine structure of the R_1-line peak from the ruby was measured also by a high-resolution multichannel spectrophotometer (HR-4000, Ocean Optics) to evaluate the pressure from its peak wavelength.

Figure 2 shows the variations of PL spectra for $BaCN_2:Eu^{2+}$ with 450 nm excitation under pressures from ambient to 5.34 GPa. The luminescence peaks of the ruby R_1-line used as a pressure reference are superimposed on the broad emission spectra of the $BaCN_2:Eu^{2+}$. The luminescence intensity of the $BaCN_2:Eu^{2+}$ was almost comparable to that of the ruby reference. The intensities of all the spectra are normalized at their peak intensity. The luminescence peak wavelength shifted significantly from 660 nm at ambient pressure to 760 nm at 5.34 GPa. The original luminescence peak wavelength and band shape were reproduced again after decompression back to the ambient pressure.

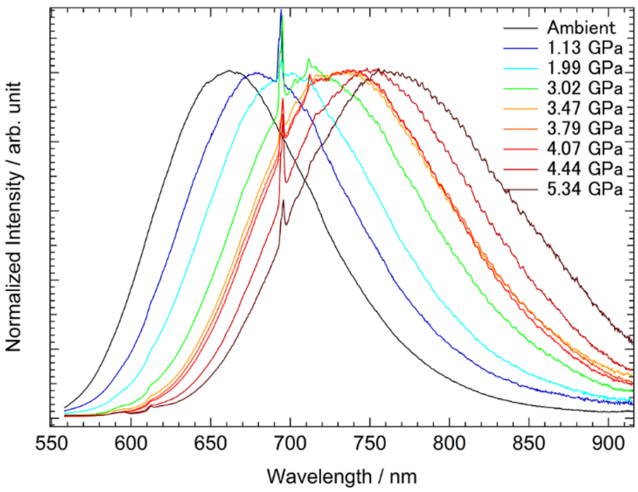

Figure 2 Luminescence spectra of $BaCN_2:Eu^{2+}$ under static high pressures at room temperature. The excitation wavelength was 450 nm. Luminescence intensities were normalized at the peak wavelengths. The sharp peaks at around 694 nm are due to the ruby R_1-line.

Figure 3 shows the pressure dependence of peak wavenumbers of the $BaCN_2:Eu^{2+}$ at high pressures up to 5.34 GPa. They shifted almost linearly toward lower energy with respect to the pressure. The luminescence wavenumbers recovered again by releasing the pressure. The linear fit of the pressure-dependent wavenumber of the peak gave a coefficient of -384 cm^{-1}/GPa, which is 50 times larger than -7.5 cm^{-1}/GPa for the R_1-line of ruby.[5)] The full width at half maximum (FWHM) values of the PL band of $BaCN_2:Eu^{2+}$ were almost unchanged against the applied pressures up to 5.34 GPa as shown in Fig. 3. The linear shift and reversible peak profile of the red luminescence band against pressure suggest that the basic crystal structure of $BaCN_2:Eu^{2+}$ remains unchanged, at least up to 5.34 GPa.

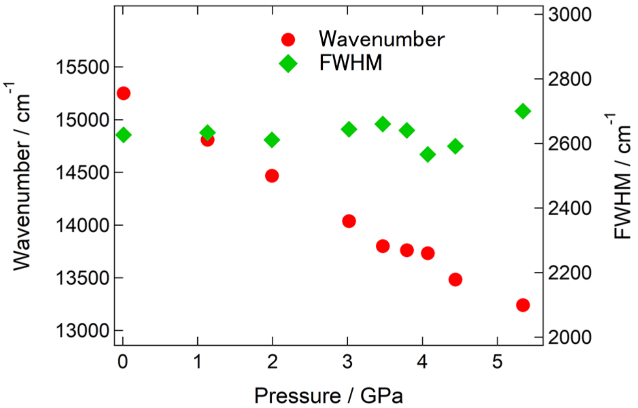

Figure 3 Pressure dependence of the maximum luminescence wavenumber and full width at half maximum (FWHM) of $BaCN_2:Eu^{2+}$.

The wavelength shift of the $BaCN_2:Eu^{2+}$ red luminescence is shown in Fig. 4, together with those of other potential alternative materials for optical pressure sensors and the ruby R_1 luminescence line. The reference lines are drawn by estimation of the luminescence wavelength using the respective pressure shift rates (spectral shift per pressure, nm/GPa). The $BaCN_2:Eu^{2+}$ phosphor shows the largest pressure shift of the luminescence wavelength; the shift rate was around 19.0 nm/GPa, which corresponds to -384 cm^{-1}/GPa. In a linear equation between pressure and luminescence wavelength, $P = A\times\Delta\lambda$, where P is the pressure in GPa and $\Delta\lambda$ is the wavelength shift between the ambient and the high pressures in nm, the coefficient A is 0.053 GPa/nm for $BaCN_2:Eu^{2+}$. This linear equation was applied to the R_1-line of the ruby below 19.5 GPa and the coefficient A was reported to be 2.74

GPa/nm.[6] Pressure sensitivity of peak wavelength of $BaCN_2:Eu^{2+}$ phosphor is almost 50 times higher than that of ruby.

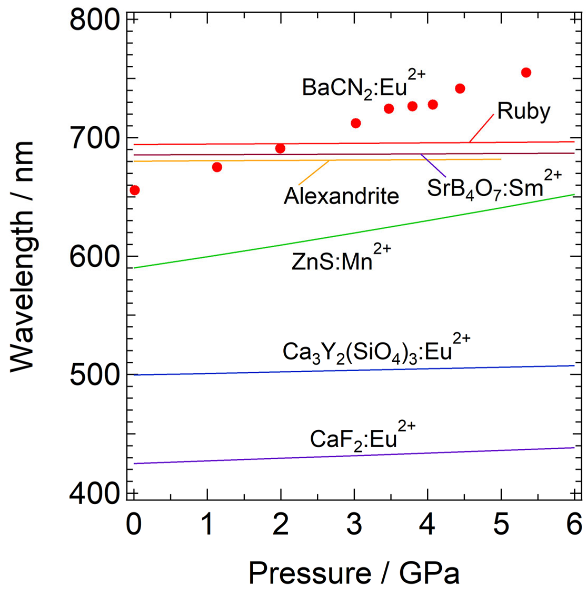

Figure 4 Pressure dependence of luminescence wavelength for $BaCN_2:Eu^{2+}$ and for other potential alternative materials for pressure sensor applications. [6,9-13]

Similar red-shifts have been observed in other Eu^{2+}-doped phosphors, such as $Ca_3Y_2(SiO_4)_3$ and CaF_2; their pressure shift rates were reported to be 1.4 nm/GPa and 2.2 nm/GPa, corresponding to -52 cm^{-1}/GPa and -115 cm^{-1}/GPa, respectively.[10,11] The luminescence band of the Eu^{2+}-doped phosphors correspond to the transition between the $4f^6 5d^1$ and $4f^7$ energy states. The luminescence of Eu^{2+} ions in a host material is influenced by structural parameters, including covalency, bond-length, and coordination number.[17] The red-shift of the Eu^{2+} luminescence indicates lowering of the lowest 5d excited state, $5d_1$, due to the increased crystal field splitting with pressure because of the compression of the lattice volume and bond length. The large pressure dependence of the $BaCN_2:Eu^{2+}$ phosphor is related to the pressure sensitive crystal lattice.

The $BaCN_2$ lattice has a large thermal expansion coefficient when compared to silicon nitride and aluminum oxide. The large temperature shift is thus attributed to the changes in the crystal field strength derived from the varying distance between Eu and N atoms. The “soft” host lattice can thus change the lattice volume and bond distances significantly by application of high pressure. Detailed analysis of the crystal structure of $BaCN_2$ under high pressure is required to understand the pressure dependence. The significant change in the PL wavelength of $BaCN_2:Eu^{2+}$ under pressure does not require a spectrometer with very high wavelength-resolution to evaluate the pressure. More precise control and calibration of pressure can be achieved using $BaCN_2:Eu^{2+}$ as an optical pressure sensor for high pressure experiments.

In summary, a large wavelength shift of the Eu^{2+} luminescence in $BaCN_2:Eu^{2+}$ was observed in the PL spectra under high pressures up to 5.34 GPa. The large red-shift is related to shrinkage of the Eu^{2+} ligand field and host lattice under high pressures. The present results reveal that the $BaCN_2:Eu^{2+}$ phosphor can be an alternative material for application as an optical pressure sensor for accurate pressure determination in the experimental high-pressure physics.

Acknowledgments

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Figure Captions

Fig. 1. PL and PL excitation (PLE) spectra for $BaCN_2:Eu^{2+}$ at room temperature under ambient pressure. The excitation spectrum was monitored at a luminescence wavelength of 660 nm.

Fig. 2. Luminescence spectra of $BaCN_2:Eu^{2+}$ under static high pressures at room temperature. The excitation wavelength was 450 nm. Luminescence intensities were normalized at the peak wavelengths. The sharp peaks at around 694 nm are due to the ruby R_1-line.

Fig. 3. Pressure dependence of the maximum luminescence wavenumber and full width at half maximum (FWHM) of $BaCN_2:Eu^{2+}$.

Fig. 4. Pressure dependence of luminescence wavelength for $BaCN_2:Eu^{2+}$ and for other potential alternative materials for pressure sensor applications. [6,9-13]

Fig.1.

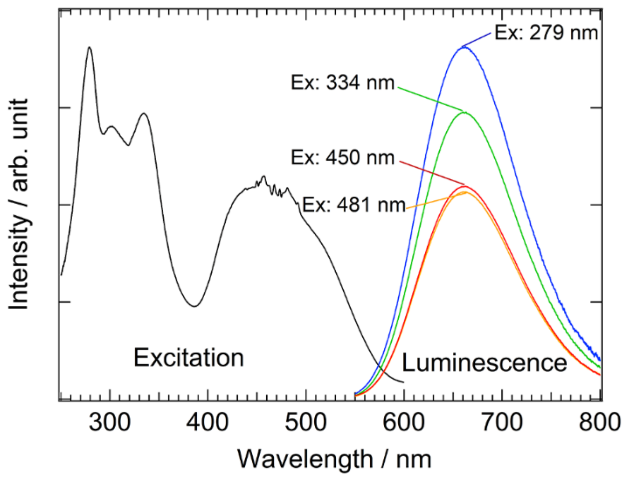
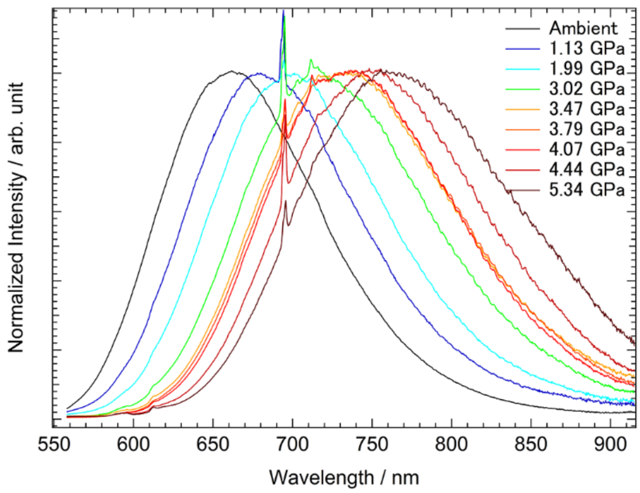

Ex: 279 nm
Ex: 334 nm
Ex: 450 nm
Ex: 481 nm
Intensity / arb. unit
Excitation
Luminescence
300
400
500
600
700
800
Wavelength / nm

Fig. 2.



Ambient
1.13 GPa
1.99 GPa
3.02 GPa
3.47 GPa
3.79 GPa
4.07 GPa
4.44 GPa
5.34 GPa
Normalized Intensity / arb. unit
550
600
650
700
750
800
850
900
Wavelength / nm

Fig. 3.

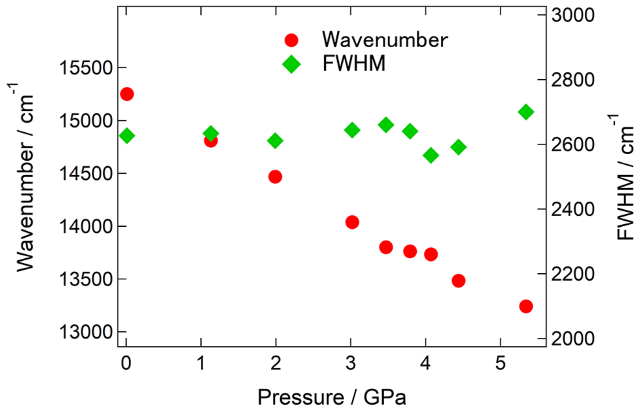
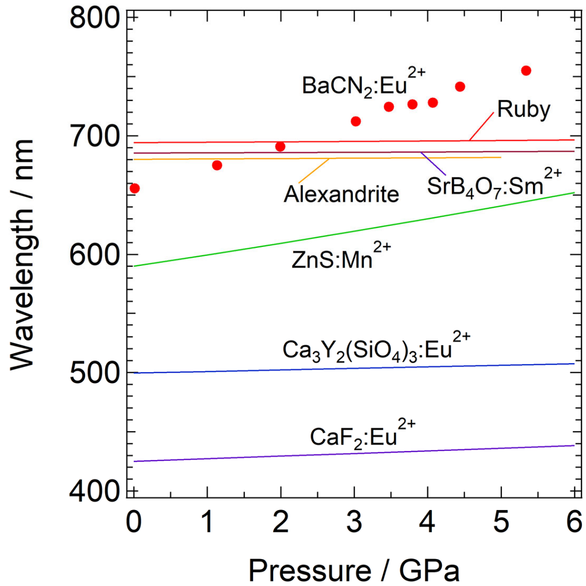

Wavenumber
FWHM
Wavenumber / cm^-1
FWHM / cm^-1
Pressure / GPa
15500
15000
14500
14000
13500
13000
3000
2800
2600
2400
2200
2000
0
1
2
3
4
5

Fig. 4.



800
700
600
500
400
0
1
2
3
4
5
6
Wavelength / nm
Pressure / GPa
BaCN2:Eu2+
Ruby
Alexandrite
SrB4O7:Sm2+
ZnS:Mn2+
Ca3Y2(SiO4)3:Eu2+
CaF2:Eu2+