The 13th Pacific Rim Conference of Ceramic Societies (PACRIM13)
October 27 - November 1, 2019, Okinawa Convention Center, Japan

Photoluminescence of sol−gel-derived transparent silica−(Gd,Pr)PO_4 glass-ceramics under excitation with a KrCl excimer lamp

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Gd^{3+} ions exhibit a sharp ultraviolet (UV) photoluminescence (PL) band at ~313 nm originating from the $^6P_{7/2} \rightarrow {}^8S_{7/2}$ 4f−4f transition, which has therapeutic effect for several skin diseases. This PL band can be effectively sensitized by codoping Pr^{3+} ions and exciting their 4f−5d transition at ≲ 240 nm in several inorganic rare-earth (RE) compounds including (La,Gd,Pr)PO_4 [1]. We have found that RE−P codoped silica glasses prepared by a cosolvent-free sol−gel method [2] were transparent glass-ceramics containing $REPO_4$ nanocrystals [3], and transparent silica−(Gd,Pr)PO_4 glass-ceramics exhibit an intense UV emission at ~313 nm via the excitation of Pr^{3+} ions [3,4]. However, the emission properties were examined using a monochromated Xe lamp and conventional light sources were not employed. A KrCl excimer lamp emits light with a narrow spectral width at 222 nm and is expected to be suitable for the excitation of silica−(Gd,Pr)PO_4 glass-ceramics. The purpose of this study is to examine the UV PL properties of transparent silica−(Gd,Pr)PO_4 glass-ceramics under excitation with a KrCl excimer lamp.

Dilute of nitric acid was added to 25 mmol of tetraethoxysilane (TEOS) and stirred for 55 min at 20 °C, followed by the addition of triphenylphosphine oxide (TPPO) and stirring for another 5 min. Then an aqueous solution of ammonium acetate ($AcONH_4$) and RE acetates were added to form a solution with an overall TEOS : H_2O : HNO_3 : $AcONH_4$: $(AcO)_3RE$: TPPO molar ratio of 1 : 10 : 0.002 : 0.01 : 0.01 : 0.01 (= $z_{RE} = z_{Gd} + z_{Pr}$). The value of z_{Pr}/z_{RE} was fixed at 0.05 because photoluminescence efficiency decreases at $z_{Pr}/z_{RE} >$ 0.1 [3]. The wet gel was aged for 24 h at 60 °C and gently dried at 60 °C. The dried gel was sintered in He at 1200 °C.

Fig. 1 shows photograph and optical absorption spectrum of a glass-ceramic obtained in this study. It was highly transparent and UV absorption edge attributed to the 4f−5d transition of Pr^{3+} ions was observed at ~240 nm. Fig. 2 shows PL spectra of the glass-ceramic measured under excitation at 220 nm with a monochromated Xe lamp and 222 nm with a KrCl excimer lamp. In both spectra UV PL band originating from the $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition of Gd^{3+} ions was observed. The internal and external quantum efficiencies (IQE and EQE, respectively) of UV PL were ~0.98 and ~0.92, respectively, under the excitation with a monochromated Xe lamp, and ~0.99 and 0.85, respectively, under the excitation with a KrCl excimer lamp. The value of IQE was ~1. These observations demonstrate that KrCl excimer lamps can be promising candidates of the excitation sources of silica−(Gd,Pr)PO_4 glass-ceramics.

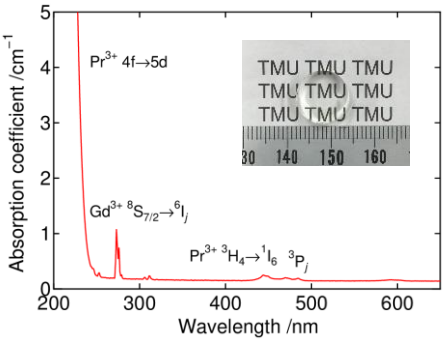

Fig. 1 Optical absorption spectrum and photograph of silica−(Gd,Pr)PO_4 glass-ceramic prepared in this study.

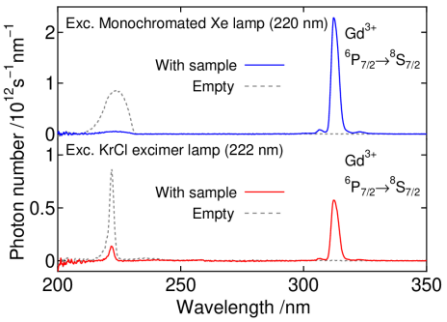

Fig. 2 PL spectra of silica−(Gd,Pr)PO_4 glass-ceramic measured under excitation at 220 nm with a monochromated Xe lamp and 222 nm with a KrCl excimer lamp.

Acknowledgement
We wish to thank ORC Manufacturing Co. Ltd for the provision of a KrCl excimer lamp.

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