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Identification and structures of the X-ray induced luminescence centers in the zeolites Zr,X,Cs,Na-LTA, X = Cl, Br, and I

Hyeon Seung Lim[1], Joon Young Kim[1], Gi Beom Park[1], Jae Gwon Jeong [1], Nam Ho Heo[1,*],
and Karl Seff[2]
[1]Department of Applied Chemistry, School of Applied Chemical Engineering, Kyungpook National University, Daegu, 41566, Korea
[2]Department of Chemistry, University of Hawaii, 2545 The Mall, Honolulu, Hawaii, 96822, U. S.

1 Introduction

X-ray induced luminescence (XIL) has been extensively utilized in medical imaging, physics, homeland security, and related industries.[1] In applications it is critical that the XIL wavelengths be well matched with optical sensors such as photomultiplier (PMT) and silicon photomultiplier (SiPM) tubes for the efficient conversion of light to electronic signals. However, unless the luminescent materials are doped with rare earth elements, this optimization is methodologically limited.

Recently, Sun et al. reported that color-tunable $CsPbX_3$-zeolite Y (X = Cl, Br, and I), where “quantum dots of perovskite” are encapsulated in the pores of the zeolite, luminesced upon ultraviolet (UV) irradiation. They found that the emission spectra of that zeolite could be tuned throughout the visible spectral range by varying its halide anion composition.[2]

In this work, we report the preparation, structures, and luminescent properties of three Cs,Na-A zeolites containing Zr^{4+} and different halide anions, Zr,X,Cs,Na-A where X = Cl, Br, and I.

2 Experiment

Single crystals of Zr,Cl,Cs,Na-A,[3] Zr,Br,Cs,Na-A, and Zr,I,Cs,Na-A were prepared from Cs,Na-A (Cs_7Na_5-LTA) as follows. Fully dehydrated single crystals of Cs,Na-A were exposed to $ZrCl_4(g)$, $ZrBr_4(g)$, and $ZrI_4(g)$ at 523 K, 543 K, and 573 K, respectively, for 48 h. Their crystal structures were determined by single-crystal crystallography using synchrotron X-radiation and their compositions were confirmed by SEM-EDX analyses. Their structures were refined in the space group $Pm\bar{3}m$ (a = 12.230(1), 12.235(2), and 12.210(2) Å), with all unique data to the final error indices R_1 = 0.069, 0.051, and 0.072, respectively. XIL images (CCD) of the three crystals were obtained using synchrotron X-radiation (Figure 1a).

The X-ray induced luminescence spectra of similarly prepared anhydrous powder samples were recorded at 293 K with a Flame-T spectrometer (Ocean optics, 50 kV, 30 mA). The scintillation decay times were measured by directly coupling the vessel containing each powder to the entrance window of the photomultiplier tube (PMT, H6610). Each sample was excited with a XR200 pulsed X-ray beam.

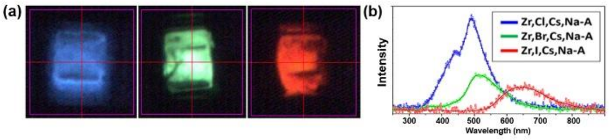

Fig 1. CCD images of anhydrous Zr,X,Cs,Na-A single crystals luminescing upon synchrotron X-irradiation at 298 K (Photon Factory, Tsukuba, Japan, 16.5 keV, 450 mA): Zr,Cl,Cs,Na-A (blue), Zr,Br,Cs,Na-A (green), and Zr,I,Cs,Na-A (red). (b) X-ray induced luminescence spectra of anhydrous Zr,Cl,Cs,Na-A, Zr,Br,Cs,Na-A, and Zr,I,Cs,Na-A powder samples.

3 Results and Discussion

The XIL domain peaks have red-shifted from 495 nm for Zr,Cl,Cs,Na-A, to 520 nm for Zr,Br,Cs,Na-A, and to 640 nm for Zr,I,Cs,Na-A (Figure 1b). This may be because the self-trapped excitons (STE) of $ZrBr_6^{2-}$ and ZrI_6^{2-} have smaller band gaps than that of $ZrCl_6^{2-}$, a result of the valence band maximum 4p energy level in Br^- being higher (5p in I^- even higher) than the 3p energy level in Cl^-. In the three structures, most Na^+ and Cs^+ ions occupy positions similar to those in Cs,Na-A. About 14%, 9%, and 6% of the large cavities of Zr,Cl,Cs,Na-A, Zr,Br,Cs,Na-A, and Zr,I,Cs,Na-A are centered by $ZrCl_6^{2-}$, $ZrBr_6^{2-}$, and ZrI_6^{2-} ions, respectively. These octahedral ZrX_6^{2-} ions are each held in place and stabilized at the centers of their large cavities by 24 bonds between all six of its halide ions and a cube of eight surrounding Cs^+ ions. They are further bridged by 8-ring Cs^+ ions to form a 3-dimensional $Cs_{11}ZrX_6^{9+}$ continuum in the surface volume of the crystal (Figure 2).

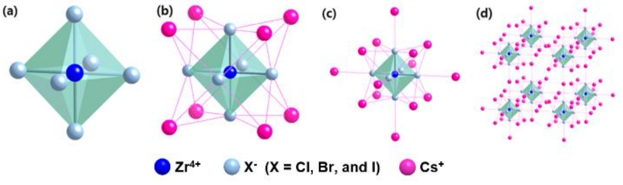

Fig 2. Complexes and clusters in Zr,X,Cs,Na-A: (a) ZrX_6^{2-}, (b) each ZrX_6^{2-} ion associates further with a cube of eight surrounding Cs^+ ions (Cs4), (c) six bridging Cs^+ ions associate with each $Cs_8ZrX_6^{6+}$ group to give $Cs_{14}ZrX_6^{12+}$, and (d) eight ZrX_6^{2-} ions (alternatively $Cs_8ZrX_6^{6+}$ groups) are bridged by 12 Cs^+ ions to show a portion of the cationic $Cs_{11}ZrX_6^{9+}$ continuum.

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* nhheo@knu.ac.kr