

## Exchange of Tetrapositive Cations into Zeolites for Zeolite-Based Inorganic scintillators. Crystal Structures and Scintillation Properties of Hf<sup>4+</sup>- and Zr<sup>4+</sup>-Containing LTA

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### 1 Introduction

Numerous new inorganic scintillator materials have appeared in the last several decades. They have been studied for use in precision calorimetry in high-energy physics, medical imaging, and homeland security. Recently, Saeki et al. completed an extensive and comparative study of the scintillation properties of Cs<sub>2</sub>ZrCl<sub>6</sub> and Cs<sub>2</sub>HfCl<sub>6</sub> crystals.[1] High atomic number ions such as Zr<sup>4+</sup> and Hf<sup>4+</sup> are important for inorganic scintillation because they serve as effective X-ray antenna by absorbing X-ray photons to produce fast electrons by the photoelectric effect.[2] Zeolites containing these ions might be exceptional and tunable scintillators. Unfortunately, it is difficult to introduce tetrapositive cations into zeolites by conventional liquid-phase ion-exchange (LPIE). Because the vapor pressures of HfCl<sub>4</sub> and ZrCl<sub>4</sub> are significant at a moderate temperature, it was hoped that Hf<sup>4+</sup> and Zr<sup>4+</sup> could be introduced into zeolites by the vapor-phase ion-exchange (VPIE) method.

### 2 Experiment

Fully dehydrated Tl<sub>12</sub>-A and Cs<sub>7</sub>Na<sub>5</sub>-A were treated either with HfCl<sub>4</sub> (*g*, 7.9 × 10<sup>3</sup> Pa) (crystals a and b) or with ZrCl<sub>4</sub> (*g*, 3.7 × 10<sup>3</sup> Pa) (crystals c and d) at 523 K under anhydrous conditions. The product crystals were all milky white. 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* = 12.065(2), 12.248(2), 12.215(1), and 12.230(1) Å) with all unique data to the final error indices *R*<sub>1</sub> = 0.072, 0.049, 0.47, and 0.069, respectively.

Their luminescence properties upon X-irradiation were explored. CCD images of the four crystals were obtained using synchrotron X-radiation at the Pohang Accelerator Laboratory (Figure 1).

The X-ray induced luminescence spectra of similarly prepared dehydrated 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.

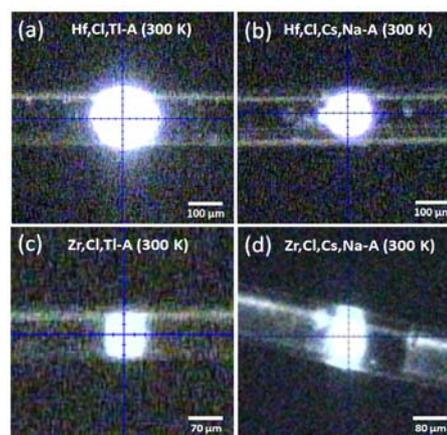


Fig. 1: CCD images of Zr<sup>4+</sup> and Hf<sup>4+</sup> containing LTA during exposure to synchrotron X-radiation (17.7 keV, 350 mA).

### 3 Results and Discussion

In M,Cl,Tl-A,[3,4] M = Hf and Zr, some M<sup>4+</sup> ions are 3-coordinate with three framework oxygen atoms of 6-rings. In Hf,Cl,Tl-A, octahedral HfCl<sub>6</sub><sup>2-</sup> ions are at the very centers of 7% of the large cavities within Tl<sub>14</sub>HfCl<sub>6</sub><sup>12+</sup> clusters (Figure 2a). MCl<sub>6</sub><sup>2-</sup> ions are also seen in Hf,Cl,Cs,Na-A[3] Zr,Cl,Cs,Na-A[5]; they occupy 7% and 14% of the large cavities and are members of Cs<sub>11</sub>MCl<sub>6</sub><sup>9+</sup> continua, respectively (Figure 2b). The remaining Tl<sup>+</sup>, Cs<sup>+</sup>, and Na<sup>+</sup> ions occupy well-established cation sites.

The X-ray induced luminescence spectra of the dehydrated zeolites Hf,Cl,Tl-A, Hf,Cl,Cs,Na-A, Zr,Cl,Tl-A, and Zr,Cl,Cs,Na-A are broad bands ranging from 300 to 720 nm peaking at 390, 410, 500, and 495 nm, respectively (Figure 2c). Although the X-ray induced luminescence spectral shapes and peak positions for the M,Cl,Tl-A and M,Cl,Cs,Na-A are similar, their decay patterns are quite different. The four zeolites, M,Cl,Tl-A and M,Cl,Cs,Na-A, appear to luminesce by different mechanisms. Four possible mechanisms are recognized for their scintillation processes. They are (1) self-trapped exciton luminescence of MCl<sub>6</sub><sup>2-</sup>, (2) migration of charge carriers (hot electrons and holes) to activator ions, (3) luminescence through Na<sup>0</sup>-perturbed excitons, and (4) secondary energy transfer by UV radiation, arising from

charge transfer from  $M^{4+}$  to  $O^{2-}$ , to surrounding luminescence centers.

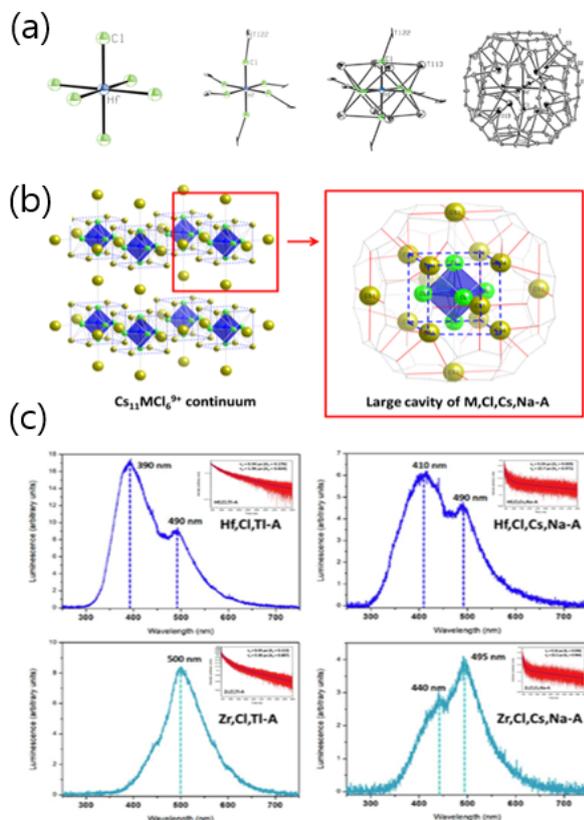


Fig. 2: (a)  $HfCl_6^{2-}$  in  $Hf,Cl,Tl-A$ , (b)  $Cs_{11}MCl_6^{9+}$  continua in  $M,Cl,Cs,Na-A$ , and (c) X-ray luminescence spectra and scintillation decay times of  $Hf^{4+}$  and  $Zr^{4+}$ -containing LTA.

The integrated light yields observed for  $M,Cl,Tl-A$  and  $M,Cl,Cs,Na-A$  powders are about 20% to 93% that of bismuth germanate, a commercially available scintillator whose light yield is well documented.[6] Under the same measurement conditions,  $Tl^+$ - and  $Cs^+,Na^+$ -exchanged zeolite LTA showed no radioluminescence.

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#### References

- [1] K. Saeki, Y. Fujimoto, M. Koshimizu, T. Yanagida and K. Asai, *Appl. Phys. Express*, 9 (2016) 042602.
- [2] C. Wang, O. Volotskova, K. Lu, M. Ahmad, C. Sun, L. Xing and W. Lin, *J. Am. Chem. Soc.*, 136 (2014) 6171.
- [3] J. Y. Kim, H. J. Kim, N. H. Heo and K. Seff, *J. Phys. Chem. C*, 121 (2017) 19619.
- [4] J. Y. Kim, J. M. Park, H. J. Kim, N. H. Heo and K. Seff, *J. Phys. Chem. C*, 119 (2015) 18326.

[5] C. W. Lee, J. Y. Kim, H. J. Kim, N. H. Heo and K. Seff, *J. Phys. Chem. C*, 120 (2016) 18682.

[6] P. A. Rodnyi, *Physical Processes in Inorganic Scintillators*, M. J. Weber, Ed.; CRC Press: Boca Raton, FL, 1997; pp 6-7.

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