Exchange of Tetrapositive Cations into Zeolites for Zeolite-Based Inorganic scintillators. Crystal Structures and Scintillation Properties of Hf$^{4+}$- and Zr$^{4+}$-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$_2$ZrCl$_6$ and Cs$_2$HfCl$_6$ crystals.[1] High atomic number ions such as Zr$^{4+}$ and Hf$^{4+}$ 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$_4$ and ZrCl$_4$ are significant at a moderate temperature, it was hoped that Hf$^{4+}$ and Zr$^{4+}$ could be introduced into zeolites by the vapor-phase ion-exchange (VPIE) method.

2 Experiment
Fully dehydrated Tl$_{12}$-A and Cs$_7$Na$_5$-A were treated either with HfCl$_4$ (g, 7.9 $\times$ 10$^3$ Pa) (crystals a and b) or with ZrCl$_4$ (g, 3.7 $\times$ 10$^3$ 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 $R_1 = 0.072$, 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 the dehydrated zeolites Hf$_4$Cl$_{12}$, Tl$_{12}$-A, Hf$_4$Cl$_{12}$, Cs$_7$Na$_5$-A, Zr$_4$Cl$_{12}$, Tl$_{12}$-A, and Zr$_4$Cl$_{12}$, Cs$_7$Na$_5$-A are broad bands ranging from 300 to 720 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$_4$Cl$_{12}$, Tl$_{12}$-A and M$_4$Cl$_{12}$, Cs$_7$Na$_5$-A are similar, their decay patterns are quite different. The four zeolites, M$_4$Cl$_{12}$, Tl$_{12}$-A and M$_4$Cl$_{12}$, Cs$_7$Na$_5$-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$_6^{2-}$, (2) migration of charge carriers (hot electrons and holes) to activator ions, (3) luminescence through Na$^+$-perturbed excitons, and (4) secondary energy transfer by UV radiation, arising from...
charge transfer from $\text{M}^{4+}$ to $\text{O}^{2-}$, to surrounding luminescence centers.

![Fig. 2: (a) HfCl$_6^{2-}$ in Hf,Cl,Tl-A, (b) Cs$_3$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.](image)

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

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