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Crystal Structure and Scintillation Properties of Cs,Na-LTA Treated with Zirconium Chloride Vapor

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1 Introduction

Cs^+ ions assembled with X-ray absorbers like Zr or Hf, e.g., Cs_2ZrCl_6 and Cs_2HfCl_6, had scintillation properties [1]. Zeolites, because of their molecular dimensioned channels and cavities, can host relatively small molecules, relatively large cations, and continua. A broader range of compositions can be assembled within zeolites than those of pure and doped compounds, and this could lead to better scintillators. In this study, we expected that $ZrCl_4$ would be readily sorbed at a moderate temperature (523 K), where the vapor pressure of $ZrCl_4$ is reasonably high (3.7×10^3 Pa) and dehydrated Cs,Na-A is stable[2]. Zr^{4+} would be readily identifiable crystallographically because its ionic radius and scattering power are very different from those of any of the other ions in the expected product Zr,Cl,Cs,Na-A.

2 Experiment

Large colorless transparent single crystals of zeolite A ($|Na_{12}(H_2O)_x|[Si_{12}Al_{12}O_{48}]$–LTA, Na_{12}–A·$x$$H_2O$, or Na–A) was lodged in a thin Pyrex capillary. Aqueous $CsC_2H_3O_2$ (sigma-Aldrich, 99.99%+) (pH = 6.2) allowed to flow past it (dynamic ion exchange). A break-off sealed tube with anhydrous $ZrCl_4$ (sigma-Aldrich, 99.99%) was attached as a hydrated Cs,Na-A crystal prepared as above. After this crystal was fully dehydrated, the reaction vessel (the capillary containing the crystal, the tube above it, and the side arm containing the anhydrous $ZrCl_4$) was sealed off from the vacuum line. The internal seal was then broken and the $ZrCl_4$ was transferred to the tube. Finally, the side arm was sealed off. The resulting linear reaction vessel was heated to allow $ZrCl_4(g)$ to react with the zeolite. The diffraction intensities for the crystal was measured with synchrotron X-radiation at the BL-5A beam line of the Photon Factory, KEK, Japan.

3 Results and Discussion

$|Zr_{0.14}Cs_{5.69}Na_{4.13}Cl_{0.85}|[Si_{12}Al_{12}O_{48}]$–A (approximate formula, Table 1) was determined by single-crystal crystallography using synchrotron X-radiation. The structure of Zr,Cl,Cs,Na-A was refined in the space group $Pm\bar{3}m$ (a = 12.230(1) Å) with all unique data to the final error index $R_1 = 0.069$ for the 639 reflections for which $F_o > 4\sigma(F_o)$. Octahedral $ZrCl_6^{2-}$ ions center 14% of the large cavities; each Cl^- ion bonds to an 8-ring Cs^+ ion (See Fig. 1). These Cs^+ ions bridge between $ZrCl_6^{2-}$ ions to form a continuum with unit cell formula $Cs_3ZrCl_6^+$ in the near-surface volume of the crystal. Other Cs^+ ions lie opposite 6-rings in the sodalite and large cavities. Upon X-irradiation Zr,Cl,Cs,Na-A luminesces bright sky blue; the emission band is broad, ranging from 370 to 750 nm, peaking at 480 nm (See Fig. 2).

Table 1: Assignment of Oxidation States and Charge Budget

Atom	ions[a]	occupancy[b]	r,[c]Å	NC[d]	ΣCharges
Cs1	Cs^+	3.0	2.06	4	3.0
Cs2	Cs^+	0.74(4)	1.79	3	0.74(4)+
Cs3	Cs^+	0.82(14)	1.50	3	0.82(14)+
Cs4	Cs^+	1.13(14)	1.69	3	1.13(14)+
Na1	Na^+	4.13(15)	0.93	3	4.13(15)+
Zr	Zr^{4+}	0.142(17)		6	0.59(7)+
Cl	Cl^-	0.85(10)		2	0.85(10)-

ΣCs = 5.69(20) ΣNa = 4.13(15) Σ charges = 9.6(3)+
ΣZr = 0.142(17), ΣCl = 0.85(10)

[a]Extraframework ions [b]Occupancy, ions per unit cell. [c]Radii of M ions obtained by subtracting 1.32 Å from the shortest M-O bond lengths. [d]Coordination numbers.

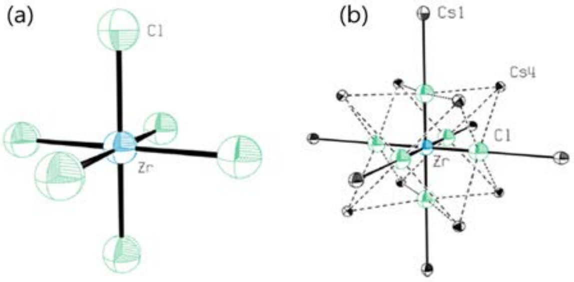
(a)
(b)

Fig. 1: Complexes and clusters in Zr,Cl,Cs,Na-A; (a) $ZrCl_6^{2-}$ and (b) the $Zr(ClCs)_6^{4+}$ unit associated further with eight surrounding Cs^+ ions.

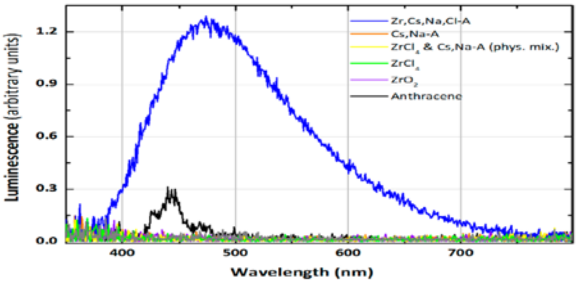

Fig. 2: Visible spectra of dehydrated Zr,Cl,Cs,Na-A powder and related materials upon irradiation with polychromatic X-rays (Cu target, 100 kV, 2mA)

References

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