

Synthesis, Crystal Structure, Fluorescent and Thermal Properties of Sodium Tridecafluorodizirconate $\text{Na}_5\text{Zr}_2\text{F}_{13}$ Compound

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ABSTRACT Crystals of sodium tridecafluorodizirconate $\text{Na}_5\text{Zr}_2\text{F}_{13}$ were synthesized under mild hydrothermal conditions, and the structure was refined by single-crystal X-ray diffraction. The compound crystallizes in monoclinic with crystallographic data: $M_r = 544.39$, $C2/m$ (No.12), $a = 11.5600(9)$, $b = 5.4759(4)$, $c = 8.3989(6)$ Å, $\hat{a} = 97.361(10)^\circ$, $V = 527.28(7)$ Å³, $Z = 2$, $D_c = 3.429$ g/cm³, $\bar{e} = 0.71073$ Å, $\bar{i} = 23.48$ cm⁻¹, $F(000) = 504$, $T = 295$ K, $R_1 = 0.0173$ and $wR_2 = 0.0449$ for 55 variables and 682 contributing unique reflections. The crystal structure is constituted with six- and eight-fold sodium atoms, forming irregular trigonal prisms and irregular cubes, respectively. Here, the zirconium atoms are connected with seven fluorine atoms to form a mono-capped trigonal prism. $[\text{Zr}_2\text{F}_{13}]^{5-}$ complex ions formed by corner-shared $[\text{ZrF}_7]^{3-}$ are corner- and edge-shared to $[\text{Na}_4\text{F}_{22}]$ and $[\text{Na}_5\text{F}_8]$ cages, leading to the network structure. Thermal analysis, X-ray excited luminescence and photoluminescence under UV light measurements were conducted on $\text{Na}_5\text{Zr}_2\text{F}_{13}$ crystals.

Keywords: sodium tridecafluorodizirconate, hydrothermal synthesis, crystal structure, luminescent

1 INTRODUCTION

Considerable research effort on the heavy metal fluoride glasses like barium, zirconium fluoride and a series of rare-earth fluorozirconate compounds during the last two decades was initiated by the broad optical transmission window of these glasses and thereby the potential for ultralow-loss optical fibers^[1~10]. The fluorozirconate of alkali metals was first reported in 1938^[11], and most of the sodium and potassium fluorozirconates were reported among

the 1940s and 1970s^[1, 2, 12~15], and the recently reported of the potassium fluorozirconate KZrF_5 was in 1997^[16]. The optical property and the structure of fluorozirconate glasses have received considerable attention since these glasses were discovered two decades ago^[11, 12, 17, 18, 20]. The chemical bonds in fluorozirconate glasses are more ionic than in traditional network oxide glasses, and the high coordination number of fluorine around zirconium differs widely from the classical tetrahedral network, *i.e.*, SiO_2 . Such high coordination numbers in glasses

Received 1 July 2005; accepted 8 October 2005 (CSD, 416158)

This study was supported by the Fund from the key project from the NSF of China.

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were relatively unknown before the discovery of the fluorozirconates in 1974. The study of the structure is of great importance in understanding, from a fundamental point of view, the reason for their relatively easy formation and their physical and chemical properties. The crystal structure of the title compound has been reported by Herak *et al* in 1965^[2], but its crystallographic data have low merit factor and not been given in the publication in detail, and very few chemical and physical property studies of this compound were carried out.

Here we report the synthesis, crystallographic studies, luminescence and thermal stability property investigations of the title compound.

2 EXPERIMENTAL

2.1 Synthesis

Na₅Zr₂F₁₃ was synthesized under mild hydrothermal conditions. The reaction was carried out with the mixture of ZrO₂, NaH₂PO₄ and H₃BO₃ in the molar ratio of 1:8:6 and 3 mL of hydrogen fluoride (40% concentration) in aqueous solution. The mixture was sealed in a Teflon-lined stainless steel autoclave (degree of filling 70%), and then placed in an oven with subsequent heating at 130 °C for 4 days. The starting materials are all of analytical grade and used without further purification.

2.2 Structure determination

A plate-like single crystal with dimensions of 0.31mm × 0.09mm × 0.24mm was mounted on a Bruker AXS CCD diffractometer and exposed to MoK α radiation with a graphite monochromator.

Crystallographic data for the titled compound are summarized in Table 1. A total of 3×600 frames (2198 reflections) were taken from 3.55° < θ < 28.37°, yielding 682 unique observed reflections with $R_{\text{int}} = 0.0236$ at 295(2) K. The intensity data were corrected for Lorentz and polarization effects, and the absorption correction was made at the end of the refinements. The anomalous-dispersion coefficients were taken into account during the data processing. Systematic absences led to the space groups $C2$ and $C2/m$ (International Tables for Crystallography, 1983, Vol. A). The structure was solved in space group $C2/m$ and confirmed by the full-matrix least-squares refinement on F^2 using SHELXL 97^[13]. 55 variables, including anisotropic displacement parameters were refined to $R = 0.0173$ and $wR = 0.0449$ ($w = 1/[\sigma^2(F_o^2) + (0.0156P)^2 + 0.7692P]$, where $P = (F_o^2 + 2F_c^2)/3$) considering 682 contributing unique reflections with $F_o > 4\sigma(F_o)$ and $S = 1.229$. The maximum shift/e.s.d in the last cycle was <0.001. Final residual electron density was +0.464 (−0.352) e/Å³, 0.92(1.19) Å distance from the zirconium atoms. The atom positional and displacement parameters are given in Table 2.

The anisotropic displacement parameters, which are all normal except the F(1), are given in Table 3. The largest component U22 (parallel to b axis) is nearly six times bigger than the smallest component U33 for F(1), resulting in the tighter bonds of F(1)–F(3) (F4) close to the c direction and located in the layers perpendicular to the b axis with cations of Zr⁴⁺ and Na⁺.

$${}^b wR 2 = \left[\frac{\sum_{hkl} w(F_o^2 - F_c^2)^2}{\sum_{hkl} wF_o^4} \right]^{\frac{1}{2}} \quad {}^a R 1 = \frac{\sum_{hkl} \left| |F_o| - |F_c| \right|}{\sum_{hkl} |F_o|}$$

Table 1. Crystallographic Data for Na₅Zr₂F₁₃

Formula	Na ₅ Zr ₂ F ₁₃
Formula weight/amu	544.39
Space group	$C2/m$

Z	2
$a/\text{\AA}$	11.5600(9)
$b/\text{\AA}$	5.4759(4)
$c/\text{\AA}$	8.3989(6)
a	97.361 (10)
$V/\text{\AA}^3$	527.28(7)
$D_s/\text{g}\cdot\text{cm}^{-3}$	3.429
Linear absorption coefficient μ/cm^{-1}	23.48
Temperature/K	295(2)
Radiation, monochromator	MoK α graphite
Crystal shape, color	Plate-like, colorless
2θ range/ $^\circ$	7.10–56.74
Total number of observed reflections	2198
Number of unique reflections	682
hkl range	–15 h 15, –7 k 7, –10 l 10
Number of parameters	55
$F(000)$	504.0
$^aR_1, ^b wR_2$ ($I > 2\sigma(I)$)	0.0173, 0.0449
$^aR_1, ^b wR_2$ (all data)	0.0173, 0.0449
Goodness-of-fit on F^2	1.229
Residual peaks (hole) $\text{e}\cdot\text{\AA}^{-3}$	0.464 (–0.352)
Software	Shelxl-97 ^[19]

Table 2. Atomic Positional and Displacement Parameters for Na₅Zr₂F₁₃ with Space Group C2/m

Atom	WP ^a	x	y	z	$U_{eq}^b/\text{\AA}^2$
Zr(1)	4i	0.07306(2)	0	0.24271(3)	0.01131(12)
Na(1)	4i	0.83779(11)	0.5	0.07034(14)	0.0197(3)
Na(2)	4i	0.77747(10)	0	0.34682(14)	0.0195(3)
Na(3)	2d	0.5	0	0.5	0.0253(4)
F(1)	2a	0	0	0	0.0384(8)
F(2)	8j	0.13239(10)	0.2246(2)	0.42835(14)	0.0213(3)
F(3)	8j	0.43945(11)	0.2639(3)	0.24821(16)	0.0264(3)
F(4)	8j	0.18097(11)	0.2354(2)	0.14391(14)	0.0220(3)

^aWyckoff positions.^b U_{eq} were defined as one-third of the trace of the orthogonal U_{ij} tensor.Table 3. Anisotropic Displacement Parameters for Na₅Zr₂F₁₃ with Space Group C2/m

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zr(1)	0.01059(16)	0.01324(17)	0.01009(16)	0.000	0.00127(9)	0.000
Na(1)	0.0221(6)	0.0202(6)	0.0168(6)	0.000	0.0021(4)	0.000
Na(2)	0.0200(6)	0.0191(6)	0.0190(6)	0.000	0.0005(4)	0.000
Na(3)	0.0251(9)	0.0173(8)	0.0361(10)	0.000	0.0135(8)	0.000
F(1)	0.0240(14)	0.077(2)	0.0130(12)	0.000	–0.0027(10)	0.000
F(2)	0.0248(6)	0.0205(6)	0.0177(6)	–0.0057(5)	–0.0010(5)	0.0004(5)
F(3)	0.0214(6)	0.0261(7)	0.0310(7)	0.0001(5)	0.0001(5)	–0.0092(5)
F(4)	0.0263(6)	0.0188(6)	0.0225(6)	0.0026(5)	0.0091(5)	–0.0039(5)

2.3 Thermal analysis

The TG-DSC curve was measured on a NETZSCH STA 409 PS/PG instrument under air atmosphere from room temperature to 800 °C at a heating rate of 10 °C/min. The sample remains stable up to 539.5 °C and begins to decompose. XRD pattern

of the heated samples shows the presence of Na₅Zr₂F₁₃ and Na₃ZrF₇ as well as a few unknown phases, indicating that Na₅Zr₂F₁₃ partly decomposes to Na₃ZrF₇ and this process will continue as judged from the TG-DSC curve.

3 RESULTS AND DISCUSSION

3.1 Structure description

Three different kinds of coordination polyhedra are present in the structure:

(1) Irregular trigonal prism $[\text{NaF}_6]$ (Fig. 1(a)). Na(1) is coordinated on one side by two F(4) anions

($d_{\text{Na-F}} = 2.369 \text{ \AA}$) with F(4)–F(4) distance of 2.577 \AA and on the other side by four anions, forming a square F(3)–F(4)–F(4)–F(3) face, closer to Na^+ ($d_{\text{Na-F}} = 2.291$ and 2.299 \AA) but rather far from each other ($d_{\text{F(3)-F(4)}} = 3.407$, $d_{\text{F(4)-F(4)}} = 2.899 \text{ \AA}$), and also from F(4) on the other side ($d_{\text{F(3)-F(4)}} = 3.077$, $d_{\text{F(4)-F(4)}} = 3.066 \text{ \AA}$).

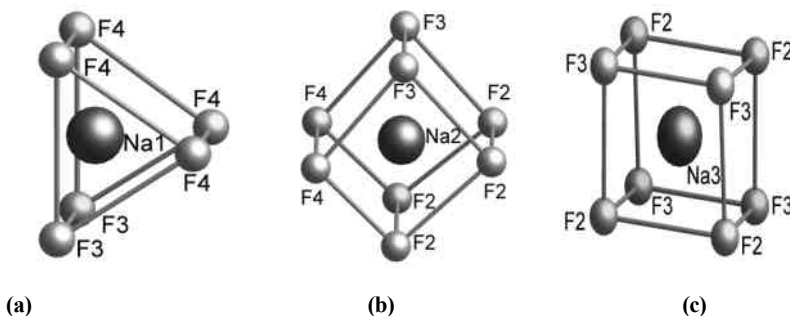


Fig. 1. (a) Irregular trigonal prism $[\text{NaF}_6]$ of Na(1) atom; (b) Irregular cube (face-sharing trigonal prism) $[\text{NaF}_8]$ of atom Na(2); (c) Irregular cube (face-sharing trigonal prism) $[\text{NaF}_8]$ of Na(3) atom.

(2) Irregular cube (face-sharing trigonal prism) $[\text{NaF}_8]$ (Fig. 1(b) and 1(c)). Na(2) has an eightfold coordination, forming a face-sharing irregular trigonal prism with shared face made up of two F(2) ($d_{\text{F-F}} = 3.014 \text{ \AA}$ and two F3 ($d_{\text{F-F}} = 2.585 \text{ \AA}$), and the distances between the two apical F(2) and F(4) in each side are 2.462 and 2.899 \AA , respectively. Na(3) occupies the right center of the rather regular face-sharing trigonal prism with F(2)–F(2)–F(2)–F(2) common face. F(3)–F(3) distances (2.819 \AA) in both F(2)–F(2)–F(2)–F(2) square sides are shorter than

those between the two edge F(2) (3.014 \AA) (with a mean Na–F distance of 2.425 and 2.433 \AA , respectively).

(3) Mono-capped trigonal prism (M.T.P) $[\text{ZrF}_7]^{3-}$ (Fig. 2). Both opposite triangular faces of the trigonal prism are F(2)–F(3)–F(4), and the square face F(3)–F(4)–F(4)–F(3) is capped by F(1) at the longest distance from Zr of $2.1044(3) \text{ \AA}$. The average Zr–F bond length (2.050 \AA) is slightly shorter than those ($2.06\text{--}2.08 \text{ \AA}$) usually encountered for sevenfold coordinated zirconium^[14].

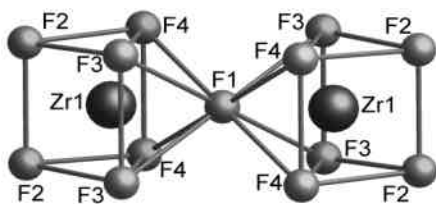
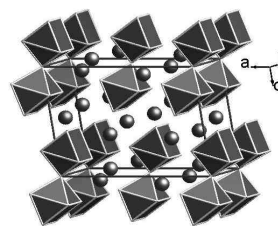


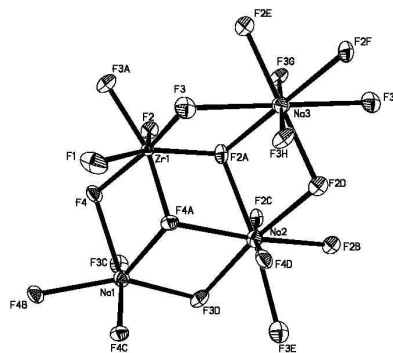
Fig. 2. $[\text{Zr}_2\text{F}_{13}]^{5-}$ complex ions formed by two monocapped trigonal prisms $[\text{ZrF}_7]^{3-}$

The whole structure of $\text{Na}_5\text{Zr}_2\text{F}_{13}$ results from the stacking, perpendicular to the *a* axis, of alternate single sheets of $[\text{Zr}_2\text{F}_{13}]^{5-}$ complex ions formed by corner-



(a)

(a) Polyhedral view of the $\text{Na}_5\text{Zr}_2\text{F}_{13}$ structure. The Zr mono-capped trigonal prisms form dimers by sharing the cap F atom. These polyhedral dimers are isolated by the matrix of Na cations shared $[\text{ZrF}_7]^{3-}$ M.T.P *via* F(1) atom (Fig. 2.). Sodium ions occupy the interstitial sites of the lattice, forming corner- and edge-sharing periodic groups.



(b)

Fig. 4. (a) Polyhedral view of the $\text{Na}_5\text{Zr}_2\text{F}_{13}$ structure (polyhedra are corner shared ZrF_7 , dark grey spheres are Na atoms); (b) The displacement ellipsoids of all the atoms drawn at the 50% level

3.2 Luminescence study

3.2.1 X-ray-excited luminescence (XEL)

XEL spectra were measured by using an X-ray-excited spectrometer, FluorMain, where an F-30 movable X-ray tube (W anticathode target) was used as the X-ray source and operated under the same condition (80 kV, 4 mA) at room temperature (RT). The luminescence spectra were obtained by 44 W plate grating monochromator and Hamamatsu R928-28 photomultiplier with the data acquired by computer.

The XEL spectra measured under $300 < \lambda < 775$ nm of $\text{Na}_5\text{Zr}_2\text{F}_{13}$ consist of two peaks (Fig. 4). The fluorescent intensity reveals that the fluorescent intensity increases roughly to maximum ($\lambda = 363.5$ nm with relative intensity 27.5 a.u.) with a followed broad band (with relative intensity 10 a.u.). The first peak with full-width at half-maximum (FWHM) of about 100 nm is rather asymmetric, and for further studies, it could be defined as two overlapped components due to the transition of two different energy levels.

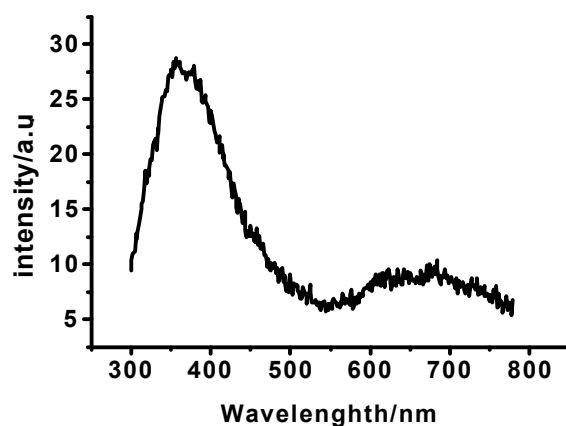


Fig. 4. X-ray excited luminescence (XEL) spectra of $\text{Na}_5\text{Zr}_2\text{F}_{13}$

Fluorescence of XEL due to bulk-emission instead of surface-excited-emission with essential difference can express the luminescent property of scintillator better. The emission corresponding to the first

peak is based on the charge-transfer transition so that the title compound can be used as the host of XEL material and scintillator matched effectively with electron-multiplier phototube because of its de-

tecting sensitive area between 300 and 500 nm. So it is possible to improve the luminescent capability of $\text{Na}_5\text{Zr}_2\text{F}_{13}$ crystal as scintillator *via* adjusting the proportion of start materials or adding doped element. Furthermore, we may control the proportion of fast- and slow-emission components of two peaks spectra system to get potential scintillator with appropriate decay time. Due to the essential difference between the bulk-emission and surface-emission in XEL, it is better to describe the obtained XEL property as bulk effect.

3.2.2 Photoluminescence (PL)

The absorption spectra measurements were carried out on a Cary 4000 UV-Vis spectrophotometer. A Perkin-Elmer LS-55 Fluorescent meter was applied to record the ultraviolet radiation excitation and emission spectra. The excitation spectrum (from 230 to 410 nm) in Fig. 5(a) shows that there exists a peak with maximum intensity at 240 nm. As shown in Fig. 5(b), the emission spectrum consists of two main peaks with maximum at about 380.5 and 424 nm excited by UV light 240 nm.

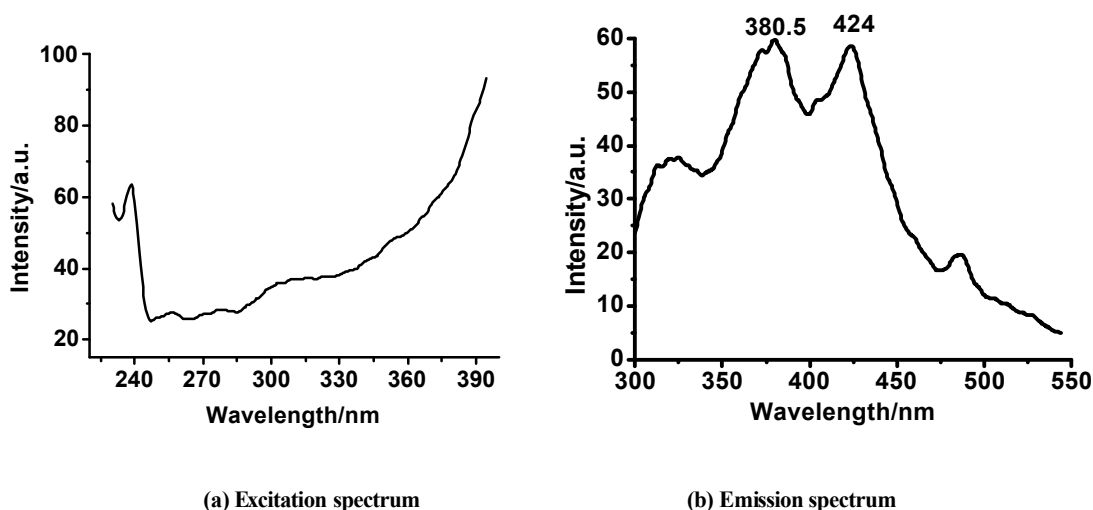


Fig. 5. Fluorescent intensities of $\text{Na}_5\text{Zr}_2\text{F}_{13}$ compound in function of wavelength

4 CONCLUSION

We synthesized crystals of sodium tridecafluorodizirconate $\text{Na}_5\text{Zr}_2\text{F}_{13}$ under mild hydrothermal conditions and refined the crystal structure by single-crystal X-ray diffraction method. In the title compound, $[\text{Zr}_2\text{F}_{13}]^{5-}$ complex ions formed by corner-shared $[\text{ZrF}_7]^{3-}$ are corner- and edge-shared to $[\text{Na}_4\text{F}_{22}]$

and $[\text{Na}_3\text{F}_8]$, leading to the network structure. Thermal analysis, X-ray excited luminescence and photoluminescence under UV light measurements were conducted on $\text{Na}_5\text{Zr}_2\text{F}_{13}$ crystals, indicating that the title compound is a potential scintillator with appropriate decay time by controlling the proportion of fast- and slow-emission components.

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