A new barium-containing alkali metal silicate fluoride $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$ with deep-UV optical property

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ABSTRACT A new silicate fluoride, $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$, has been successfully synthesized by a high-temperature solution method. It crystallizes in the orthorhombic space group *Cmcm* (No. 63). $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$ is the first barium-containing alkali metal silicate fluoride with the $[\text{NaO}_6]$ polyhedra, the $[\text{BaO}_8\text{F}]$ polyhedra and isolated $[\text{Si}_2\text{O}_7]$ units. The optical characterizations indicate that $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$ possesses wide transparent window and available luminescence properties. To confirm the coordination surroundings of anionic groups and its thermostability, infrared spectroscopy and thermal behaviors were also analyzed, which proved the existence of tetrahedrally coordinated silicon atoms and the good stability of $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$ at high temperature. First-principles calculation was also implemented for better understanding the relationship between the structure of $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$ and its property. Additionally, to further explore the structural novelty of $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$, the comparison of the anionic structures was carried out in mixed alkali and alkaline-earth metal silicate fluorides. Interestingly, the result indicates the isolated $[\text{Si}_2\text{O}_7]$ dimer is rare among the above systems, which enriches the structural chemistry of silicate fluorides.

Keywords: silicate fluoride, deep-ultraviolet transparent window, structure-properties relationship, structure comparison

INTRODUCTION

Silicon is one of the most affluent and extensive elements in the universe, on the basis of its total mass, phase numbers, occurrence frequencies, and distribution range. Furthermore, silica and silicates are the largest part in crust and mantle [1–3]. Especially, silicates are significant not only in natural minerals but also in industrial manufacture [4–10]. More recently, considerable advanced

applications of silicates in catalysis, molecular sieves, microelectronics, biomedicine, phosphors, laser hosts and ceramic materials have been established [11–17]. Generally, the immensely wide applications of silicates are derived from the diversity of their properties, which are essentially determined by their luxuriant structures [18–23]. For example, the artificial compounds Yb^{3+} : Sc_2SiO_5 , $\text{Lu}_{2(1-x)}\text{Ce}_{2x}(\text{SiO}_4)\text{O}$ and natural minerals monmorillonite $\text{Na}_x(\text{Mg},\text{Al})_2[\text{Si}_4\text{O}_{10}](\text{OH})_2 \cdot 4\text{H}_2\text{O}$, wollastonite $\text{Ca}_3[\text{Si}_3\text{O}_9]$, etc., play an important role in plenty of fields [24–28]. Herein, it makes sense to design and synthesize new promising silicates.

Because of the conspicuous influence on crystal structures and properties, it is worth to take the cationic selection into account when designing new silicates. The anionic structures depend on many factors, and the most important ones are: cationic size, valence, and electronegativity [29–37]. In terms of our research, the alkali and alkaline-earth metal atoms are ideal candidates, because there are no d-d or f-f electron transitions of the M–O (M means alkali or alkaline-earth metal atoms) bonds, which is beneficial to the transmission of UV light [37–45]. Additionally, introducing elements of halogen family may be an effective way to obtain better functional materials according to the previous report [46–50]. Particularly, introducing the F atoms into crystal can widen the transparency region and make the cutoff edge blue shift into ultraviolet (UV) or even deep-UV (DUV) region due to their large electronegativity [51–53].

Guided by the strategies above, a new compound, $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$, has been synthesized, which is the first barium-containing alkali metal silicate fluoride. Additionally, we find that there are certain associations

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between the polycondensation degree of the $[\text{SiO}_4]$ tetrahedra and the $n_{\text{M}}:n_{\text{Si}}$ in mixed alkali and alkaline-earth metal silicate fluorides. Therefore, we discussed the relationships between anion groups and the $n_{\text{M}}:n_{\text{Si}}$ about 47 compounds collected in the Inorganic Crystal Structure Database (ICSD), including the title compound $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$, concurrently. The synthesis, structure, spectroscopic properties, thermal stabilities and electronic band structure calculations of $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$ are reported in this paper. Besides, the silicates activated with lanthanide ions have been intensively studied due to high chemical stability and various crystal structures in photoluminescence field [11,54]. Therefore, to further explore the optical properties of $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$, doping Eu^{3+} into the pure powder of compound was carried out.

EXPERIMENTAL SECTION

Crystal synthesis

$\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$ was synthesized through the spontaneous nucleation method with $\text{BaF}_2\text{-B}_2\text{O}_3\text{-NaF-Na}_2\text{CO}_3$ as the flux system. A mixture of Na_2CO_3 , BaCO_3 , BaF_2 , B_2O_3 , NaF and SiO_2 in a molar ratio of 2:7:3:3:10:2 was ground adequately in an agate mortar and then placed into a platinum (Pt) crucible. The mixture was preheated to 550°C in 3 h, held at this temperature for 4 h to ensure the carbonates broken down completely, then heated to 870°C in 3 h, held at this temperature for 7 h to make the solution transparent and homogeneous. Afterwards, the mixture was cooled down to 770°C at a rate of 2°C h^{-1} , followed by cooling to 470°C at a rate of 5°C h^{-1} . Then the mixture was cooled down to room temperature at a rate of 30°C h^{-1} . Finally, the colorless crystals with the regular shape were obtained.

Solid-state synthesis

A polycrystalline sample of $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$ was prepared by the high temperature solid-state reaction. A mixture of NaF (0.445 g), BaCO_3 (6.280 g) and SiO_2 (1.275 g) with a molar ratio of 1:3:2 was ground thoroughly and placed in a Pt crucible. The mixture was heated to 650°C and then held for 100 h with several intermittent grindings. The phase purity was testified by the powder X-ray diffraction (XRD) in Fig. 1.

After that, the pure $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$ polycrystalline sample was doped with analytical purity Eu_2O_3 via the conventional solid-state reaction technique with a molar ratio of 18:1. Then the mixture was ground completely in an agate mortar and transferred into a Pt crucible. And the sample was calcined at 650°C , held for 24 h in air. Next, it was

Figure 1 Powder XRD patterns of $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$.

cooled to room temperature and reground into powder for subsequent measurement. The purity of the sample was confirmed by the powder XRD in Fig. S1 in the Supplementary information.

Single-crystal XRD

The transparent block crystal of $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$ was selected for the structure determination (Fig. S2). The single-crystal structure was determined by single-crystal XRD on an APEX II CCD diffractometer using monochromatic $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at $296(2) \text{ K}$ and integrated with the SAINT program [55]. The structure was solved with Olex2 and SHELXTL by direct methods [56–58]. All atoms were refined using full matrix least-squares techniques; final least squares refinement was on F_o^2 with data having $F_o^2 \geq 2\sigma(F_o^2)$. The structures were checked for missing symmetry elements by the program PLATON [59], and no higher symmetries were found. Relevant crystallographic data are listed in Table 1. Atomic coordinates and equivalent isotropic displacement parameters are shown in Table S1. Interatomic bond lengths and angles are given in Table S2.

Powder XRD

XRD patterns were obtained on an automated Bruker D2 X-ray diffractometer equipped with a diffracted beam monochromator set for $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature in the angular range of $2\theta = 15^\circ\text{--}80^\circ$ with a scan step of 0.01° and a fixed counting time of 1 s per step. The powder XRD patterns for the pure powder samples of $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$ and $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}:\text{Eu}^{3+}$ are displayed in Fig. 1 and Fig. S1, respectively. Fig. 1 shows that the experimental and calculated data of $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$ are

Table 1 Crystal data and structure refinement for NaBa₃Si₂O₇F

Empirical formula	NaBa ₃ Si ₂ O ₇ F
Formula weight	622.19
Temperature	296.15 K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, <i>Cmcm</i>
Unit cell dimensions	<i>a</i> = 5.780(2) Å <i>b</i> = 10.000(4) Å <i>c</i> = 14.612(6) Å
Volume	844.5(6) Å ³
<i>Z</i>	4
Calculated density	4.894 Mg m ⁻³
Absorption coefficient	14.193 mm ⁻¹
<i>F</i> (000)	1088
Crystal size	0.084 × 0.078 × 0.065 mm ³
Theta range for data collection	2.788° to 27.549°
Limiting indices	−7 ≤ <i>h</i> ≤ 7, −9 ≤ <i>k</i> ≤ 12, −19 ≤ <i>l</i> ≤ 18
Reflections collected/unique	2552/560 [<i>R</i> _{int} = 0.0266]
Completeness	100.00%
Max. and min. transmission	0.7455 and 0.5416
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	560/0/45
Goodness-of-fit on <i>F</i> ²	1.062
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^a	<i>R</i> ₁ = 0.0199, <i>wR</i> ₂ = 0.0478
<i>R</i> indices (all data) ^a	<i>R</i> ₁ = 0.0206, <i>wR</i> ₂ = 0.0482
Largest diff. peak and hole	0.996 and −1.082 e Å ⁻³

a) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w F_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

in good agreement, which demonstrates that the structural model is correct. And the powder XRD pattern of NaBa₃Si₂O₇F:Eu³⁺ (Fig. S1) reveals that the Eu³⁺-doped sample pattern matches with the standard ones. However, there are some impurity peaks, which are labeled by red circles, corresponding to the peaks of Ba₂SiO₄ or EuSiO₃.

The energy dispersive X-ray spectroscopy

Elemental analysis was carried on clean single crystal surfaces by the aid of a field emission scanning electron microscope (SEM, SUPRA 55VP) equipped with an energy dispersive X-ray spectroscopy (EDXS, BRUKER X-flash-sdd-5010).

Infrared spectrum

Infrared (IR) spectrum was recorded on a Shimadzu IR Affinity-1 Fourier transform IR spectrometer in the range of 400–4000 cm⁻¹ by mixing thoroughly with dried KBr

(5 mg of the sample and 500 mg of KBr).

UV-vis-NIR diffuse reflectance spectrum

The SolidSpec-3700DUV spectrophotometer was used to measure the spectrum of the NaBa₃Si₂O₇F powder sample ranging from 190 to 2600 nm at room temperature with tetrafluoroethylene as the standard. The reflectance spectrum was converted to absorption spectrum using the Kubelka-Munk function: $F(R) = (1-R)^2 / 2R = K / S$, where *R* is the reflectance, *K* is the absorption, and *S* is the scattering [60].

Photoluminescence (PL) measurements

Steady-state, room-temperature luminescence spectra were obtained by an Edinburgh Instruments FLS920 fluorescence spectrometer equipped with a 450 W xenon lamp as excitation source and a R928 photomultiplier tube as detector.

Thermal analysis

The thermal behavior was investigated by thermogravimetry and differential scanning calorimetry (TG-DSC) using a NETZSCH STA 449 F3 simultaneous thermal analyzer. The sample was placed in a Pt crucible and heated at a rate of 5°C min⁻¹ in the range of 40–1400°C under nitrogen gas flow.

Theoretical calculations

The CASTEP package based on density functional theory (DFT) was employed to demonstrate the relationship between the electronic-structure and the optical properties of the title compound [61]. Norm-conserving pseudopotentials (NCP) were chosen to describe the core-electron interactions. The exchange-correlation functional was disposed using the generalized gradient approximation (GGA) with Perdew-Buker-Ernzerhof (PBE). Then geometry optimization in unit cell of NaBa₃Si₂O₇F was performed with a good converged criterion fixing to the origin structure. The valence states are as follows: Na 3s¹, Ba 5s²5p⁶6s², Si 3s²3p², O 2s²2p², and F 2s²2p⁵. The plane-wave cut-off energy of 940 eV was used to ensure a small plane-wave basis set without compromising the accuracy required by our study. And 7 × 7 × 2 Monkhorst-Pack *k*-point meshes were selected in the Brillouin zone for the electronic structures and band structures.

RESULTS AND DISCUSSION

Crystal structure of NaBa₃Si₂O₇F

NaBa₃Si₂O₇F crystallizes in orthorhombic system, space

group *Cmcm* (No. 63). In the asymmetric unit, there are one unique Na atom, two crystallographically different Ba atoms, one unique Si atom, three unique O atoms and one unique F atom (Table S1). In the crystal structure, the Si atoms are bonded to four O atoms to form the $[\text{SiO}_4]$ tetrahedra. Furthermore, two $[\text{SiO}_4]$ units polymerize to form isolated $[\text{Si}_2\text{O}_7]$ dimer by sharing O atom (Fig. S3a) with the Si–O distances ranging from 1.613(4) to 1.650(2) Å and the O–Si–O angles in the range of $107.39(18)^\circ$ – $113.0(3)^\circ$. The Na^+ cations coordinate with six O atoms to form isolated $[\text{NaO}_6]$ polyhedra with the Na–O bonds ranging from 2.346(3) to 2.421(4) Å (Fig. S3b and Table S2). Furthermore, the $[\text{Si}_2\text{O}_7]$ dimers connect with $[\text{NaO}_6]$ to build a 3D $\infty[\text{NaSi}_2\text{O}_7]$ framework (Fig. S3f). Interestingly, as can be seen from Fig. 2, there are two different channels (type A and type B) in the 3D $\infty[\text{NaSi}_2\text{O}_7]$ network along the *a* axis. Type A channels with larger size are filled by the $\text{Ba}(2)^{2+}$ cations and the F^- anions, and type B channels are filled by two $\text{Ba}(1)^{2+}$ cations. The $\text{Ba}(1)^{2+}$ cations are nine-fold coordinated, connecting with eight O atoms and one F^- anion, with the Ba(1)–O bonds ranging from 2.857(3) to 2.9446(15) Å and Ba(1)–F showing 2.5001(16) Å (Fig. S3c). The coordination of the $\text{Ba}(2)^{2+}$ cations is consistent with that of $\text{Ba}(1)^{2+}$. The bonds lengths of Ba(2)–O range from 2.706(4) to 3.111(3) Å, and Ba(2)–F showing 2.802(8) Å (Fig. S3d). Besides, the one unique F^- anion is only bonded to the Ba atoms, namely, two Ba(1) and one Ba(2) atoms, respectively (Fig. S3e). There are no bonds between the F^- anions and the Na^+ cations. The sums of the bond valence of each atom in $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$ were calculated, and are listed in Table S1. The sums of these valence agree with the expected oxidation states. Additionally, if the F atom was replaced by an O atom, the atomic valence of the new O atom would be -1.366 eV [51]. And the valence of the replaced compound $\text{NaBa}_3\text{Si}_2\text{O}_8$ will also be out of balance, which is apparently unreasonable. In addition, EDXS was performed on a clean and block single crystal of the title compound which further confirmed the existence of the F atoms (Fig. S4). These all prove that the crystal structure is correct.

Crystal structure comparison

In order to investigate the diverse structures of silicate fluorides, the available alkali- and/or alkaline-earth metal cations-containing silicate fluorides are chosen according to the ICSD. On the basis of the research, there are 47 compounds including the title compound $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$, which meets the above criteria (Table S3). The anionic

Figure 2 The $\text{Ba}(1)^{2+}$, $\text{Ba}(2)^{2+}$ cations, and the F^- anions filled in the 3D $\infty[\text{NaSi}_2\text{O}_7]$ framework along the *a* axis.

groups display several different characteristics with zero-dimensional (0D) units, one-dimensional (1D) chains, and two-dimensional (2D) layers in different M/Si molar ratios, as summarized in Fig. S5. (1) In these 47 compounds, 19 (46%) cases have isolated $[\text{SiO}_4]$ tetrahedra with $n_{\text{M}}:n_{\text{Si}}$ ranging from 2.25 to 3.33. (2) There are only 5 cases possessing isolated $[\text{Si}_2\text{O}_7]$ dimers formed by two vertex-sharing $[\text{SiO}_4]$ tetrahedra. The anionic groups of the title compound $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$, $\text{Ca}_4(\text{Si}_2\text{O}_7)_2\text{F}_2$ [62] and $\text{Ca}_4(\text{Si}_2\text{O}_7)(\text{F}_{1.5}(\text{OH})_{0.5})$ [62] only possess $[\text{Si}_2\text{O}_7]$ anionic groups. As one can see from Table S3, the $n_{\text{M}}:n_{\text{Si}}$ are equal to 2 in these three compounds. While $\text{K}_{1.37}\text{Ca}_{6.90}(\text{Si}_8\text{O}_{22})\text{F}_{1.91}(\text{H}_2\text{O})_{0.264}$ and $\text{K}_{1.37}\text{Ca}_{6.57}(\text{Si}_8\text{O}_{22})\text{F}_{1.97}(\text{H}_2\text{O})_{0.106}$ [63] contain not only isolated $[\text{Si}_2\text{O}_7]$ dimers but also $[\text{Si}_{12}\text{O}_{30}]$ chains, whose $n_{\text{M}}:n_{\text{Si}}$ are 1.034 and 0.993, respectively. (3) The anionic groups are mostly 1D chains when $n_{\text{M}}:n_{\text{Si}}$ is in the range of 0.65 to 1.50. The exclusive $\infty[\text{Si}_2\text{O}_6]$ chains in $\text{NaBeCa}(\text{Si}_2\text{O}_6)\text{F}$ [64–65] are built by infinite vertex-sharing $[\text{SiO}_4]$ tetrahedra and the $n_{\text{M}}:n_{\text{Si}}$ is equal to 1.5. Another type of chain is $\infty[\text{Si}_4\text{O}_{11}]$ which exists in $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}\text{F}_2$ [66], $\text{K}(\text{NaCa})\text{Mg}_5(\text{Si}_8\text{O}_{22})\text{F}_2$ [67], $\text{Mg}_7\text{Si}_8\text{O}_{22}\text{F}_2$ [68] and $\text{Na}(\text{NaCa})\text{Mg}_5(\text{Si}_8\text{O}_{22})\text{F}_2$ [67]. Especially, it is easy to observe that there are inter-connecting rings by sharing the four edge-Si atoms in $\infty[\text{Si}_4\text{O}_{11}]$ chains. Interestingly, in $(\text{K}_{13.16}\text{Sr}_{1.38})(\text{Ca}_{24}\text{Na}_{7.32})\text{Si}_{70}(\text{O}_{166.4}(\text{OH})_{13.6})(\text{F}_2(\text{OH})_2)\cdot 0.82\text{H}_2\text{O}$ [69], there are three different kinds of chains ($\infty[\text{Si}_6\text{O}_{17}]$, $\infty[\text{Si}_{12}\text{O}_{30}]$, and $\infty[\text{Si}_{17}\text{O}_{43}]$) concurrently, which are formed by endless corner-sharing $[\text{SiO}_4]$ tetrahedra with $n_{\text{M}}:n_{\text{Si}}$ equaling to 0.655. (5) When $n_{\text{M}}:n_{\text{Si}}$ are below 0.65, the Si–O structures feature 2D layers. There are 7 compounds which contain $\infty[\text{Si}_4\text{O}_{10}]$ layers made up by $\infty[\text{Si}_6\text{O}_{15}]$ rings with $n_{\text{M}}:n_{\text{Si}}$ over the range of 0.60–0.65. Another type of layers $\infty[\text{Si}_8\text{O}_{19}]$ is in $(\text{K}_{1.65}\text{Na}_{0.83})(\text{Ca}_{4.52}\text{Na}_{2.48})\text{Si}_{16}\text{O}_{38}(\text{F}(\text{OH}))$

H₂O [70], (Na_{1.54}K_{0.80})(Ca_{4.03}Na_{2.97})Si₁₆O₃₈F₂·3.69H₂O [71] and (Na_{1.29}K_{0.79})(Ca_{4.48}Na_{2.52})Si₁₆O₃₈F₂·3.47H₂O [71] with $n_M:n_{Si}$ below 0.60.

In addition, taking all the compounds (47 cases) into consideration, it is clear to find that there are three cases containing unique [Si₂O₇] dimers. It is worth noticing that the title compound is the first anhydrous and disorder-free mixed alkali and alkaline-earth metal silicate fluoride containing exclusive [Si₂O₇] groups. Moreover, as mentioned above, one may find some rules about the formation of anion groups and the $n_M:n_{Si}$. When $n_M:n_{Si}$ is greater than 2, the anion structures feature 0D units. While $n_M:n_{Si}$ decreases to 0.65–2, the high polymerized Si–O groups appear, such as 1D chains and 2D layers. As $n_M:n_{Si}$ is lower than 0.65, there are only 2D layers in Si–O groups. And there is no 3D anion structure in mixed-alkali- and/or alkaline-earth-metal silicate fluorides.

Optical properties analyses

IR spectroscopic measurement was carried out to confirm the existence of tetrahedronally coordinated silicon atoms in NaBa₃Si₂O₇F. The IR spectrum and the assignment of the absorption peaks are shown in Fig. S6. The peaks at 1005, 968, 931 and 857 cm^{−1} are attributed to the stretching vibration of the [SiO₄] tetrahedra. The peak at 667 cm^{−1} is related to bending vibrations of the [SiO₄] tetrahedra. At 503 cm^{−1}, it can be attributed to the rocking vibration of the [SiO₄] tetrahedra. The assignments are consistent with those previously reported [19,72–73]. The results of the IR spectroscopic measurement are consistent with the analysis of crystal structure which verifies the correctness of the structure, concurrently.

The UV–vis–NIR diffuse reflectance spectrum of NaBa₃Si₂O₇F shown in the Fig. 3 has no absorption in the

Figure 3 Diffuse reflectance absorption curve of the powder sample of NaBa₃Si₂O₇F.

range of 6.55–0.478 eV (corresponding to 190–2600 nm). The result indicates that the material may have potential applications in the DUV region. As for the broad transparent region, it may be related to the crystal structure. Namely, the alkali and alkaline-earth metal cations without d-d or f-f electron transitions as well as the F atoms with large electronegativity often contribute to the cutoff edges shifting to the UV or even DUV region.

The PL analyses (Fig. 4a and b) indicate that NaBa₃Si₂O₇F displays a respectable performance on photoluminescence properties [74–76]. When monitored with the red emission of Eu³⁺ (615 nm), the PL excitation spectrum of NaBa₃Si₂O₇F:Eu³⁺ (Fig. 4a) ranging from 300–420 nm exhibits some peaks at 318, 362, 379, 394, 413 nm due to the transitions of the Eu³⁺ ions from the ground state ⁷F₀ to ⁵H₃, ⁵D₄, ⁵L₇, ⁵L₆ and ⁵D₃ excited states, respectively. As depicted in Fig. 4b, the emission spectrum excited at 394 nm consists of many sharp peaks ranging from 560 to 675 nm corresponding to the tran-

Figure 4 The excitation (a) and emission (b) spectra of NaBa₃Si₂O₇F:Eu³⁺.

sitions from the excited 5D_0 level to the 7F_J ($J=0, 1, 2, 3, 4$, and 5) levels of Eu^{3+} . As a result, the transferred energy from the transitions of the Eu^{3+} ions in $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}:\text{Eu}^{3+}$ yields appropriate color emissions in the visible region, which indicates that the title compound is a moderate luminescence host material and $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}:\text{Eu}^{3+}$ may be used as a red emitting phosphor for near-UV based white LEDs.

Thermal analysis

The TG-DSC curves of polycrystalline samples of $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$ are shown in Fig. S7. There is an obviously endothermic peak at 1147°C accompanying with the weight loss on the TG curve. To further verify its thermal property, the solid sample of $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$ was put into a Pt crucible, heated up to 1350°C , and maintained at this temperature for 24 h. Then it was slowly cooled down to room temperature. During the above process, the samples were not melted. The residuals were not $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$ but Ba_2SiO_4 confirmed by the powder XRD (Fig. S8). The result is consistent with the TG-DSC curves, which further proves that $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$ melts incongruently.

Electronic structure

As shown in Fig. 5, the valence band maximum (VBM) and the conduction band minimum (CBM) are located at the Γ point of the Brillouin zone which proves that $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$ is a direct band-gap compound with a dense bands distribution. The optical band gap for $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$ obtained by experiment is larger than 4.36 eV got *via* calculating. In general, the deficient accuracy of the exchange correlation energy is one of the most important reasons for the underestimation of the band gap by DFT methods [77]. Therefore, the calculation results are fairly

Figure 5 Calculated band structures of $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$.

reasonable.

The total and partial densities of states (TDOS and PDOS) can be observed in Fig. 6, it can be found that the top region of the VBs extends in a wide range from -10.0 eV to the VBM. These bands mostly originate from the Si $3s3p$, F $2s2p$ and O $2s2p$ states. It is worth noting that strong hybridizations occur among the Si $3s3p$, and O $2s2p$ states in the range of -8.0 to 0 eV . The conduction bands from the CBM to 10.0 eV are derived from the Ba $5d6s$ and Si $3s3p$ states, implying interactions in the Ba–O and Si–O bonds in the compound. The bands near the gap are dominated by O $2p$ and Ba $5d$, respectively. Accordingly, the absorption spectrum near the UV-visible cutoff wavelength can be assigned as the charge transfers among the states of O to those of Ba and Si.

CONCLUSIONS

$\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$, the first barium-containing alkali metal silicate fluoride, has been acquired by the high temperature solution method. It only possesses $[\text{Si}_2\text{O}_7]$ anionic groups

Figure 6 The total and partial densities of states of $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$.

which are rare in mixed alkali and alkaline-earth metal silicate fluorides. The IR spectrum, BVS calculations and the EDXS analyses further confirm the validity of the $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$ structure. The UV-vis-NIR diffuse reflection spectrum confirms that $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$ possesses excellent DUV transparent window, which is a promising candidate for the application in DUV field. The PL analyses indicate that $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$ is a moderate luminescence host material, and the $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}:\text{Eu}^{3+}$ exhibits its great potential as a red emitting phosphor for near-UV based white LEDs. Thermal analyses and melt experiment verify that it remains stable under 1147°C . Also, the relationship between anionic groups and molar ratios of M/Si for all the available alkali- and/or alkaline-earth metal cations-containing silicate fluorides has been discussed. These discoveries will enlighten subsequent studies on designing novel inorganic functional crystals which feature different structures and functional properties.

Received 25 April 2019; accepted 28 May 2019;
published online 3 July 2019

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Acknowledgements This work was supported by the National Natural Science Foundation of China (U1703132, 51872325 and 61835014), Tianshan Innovation Team Program (2018D14001), Xinjiang International Science & Technology Cooperation Program (2017E01014), the National Key Research Project (2016YFB0402104), the Science and Technology Project of Urumqi (P161010002), Xinjiang Key Research and Development Program (2016B02021), Major Program of Xinjiang Uygur Autonomous Region of China during the 13th Five-Year Plan Period (2016A02003), and West Light Foundation of the Chinese Academy of Sciences (2016–YJRC–2).

Author contributions Miao Z, Yang Y and Abudouwufu T performed the experiments, data analysis, and paper writing; Wei Z and Yang Z performed the theoretical data analysis; Pan S designed the concept and supervised the experiments. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information The supporting data are available in the online version of the paper. Accession Codes: CCDC 1888162 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +441223 336033.

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具有深紫外光学性能的含钡碱金属硅酸盐氟化物 $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$

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摘要 本文采用高温熔液法成功合成了新型硅酸盐氟化物 $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$. 它结晶于正交晶系, 空间群为 Cmcm (No. 63). $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$ 是已知的第一例含钡碱金属硅酸盐氟化物, 它包含了 $[\text{NaO}_6]$ 多面体、 $[\text{BaO}_8\text{F}]$ 多面体和孤立的 $[\text{Si}_2\text{O}_7]$ 二聚体. 光学表征表明该化合物具有宽的透过窗口和良好的荧光性质. 为了确定该化合物的阴离子基团的配位环境及热稳定性, 还对其进行了红外光谱测试和热学行为分析, 结果证明其结构中存在硅氧四面体且该化合物具有良好的热稳定性. 为了更好地理解结构和性能之间的关系, 对该化合物进行了第一性原理计算. 与此同时, 为了进一步探索 $\text{NaBa}_3\text{Si}_2\text{O}_7\text{F}$ 的结构新颖性, 我们还对混合碱金属和/或碱土金属硅酸盐氟化物的阴离子结构进行了比较, 结果表明孤立的 $[\text{Si}_2\text{O}_7]$ 二聚体在上述体系中较为少见, 这一研究结果丰富了硅酸盐氟化物的结构化学.