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Hydrothermal synthesis of new rare earth silicate fluorides: A novel class of polar materials

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ABSTRACT

Polar crystals provide an interesting avenue for materials research both in the structures they form and the properties they possess. This work describes the hydrothermal synthesis and structural characterization of three novel silicate fluorides. Compound (**1**), $LiY_3(SiO_4)_2F_2$ crystallizes in space group $C2/c$, with $a=17.651(4)$ Å, $b=4.8868(10)$ Å, $c=11.625(2)$ Å and $\beta=131.13(3)^\circ$. $BaY_2(Si_2O_7)F_2$ (**2**) crystallizes in space group $P-1$, with $a=5.1576(10)$ Å, $b=6.8389(14)$ Å, $c=11.786(2)$ Å, $\alpha=93.02(3)^\circ$, $\beta=102.05(3)^\circ$ and $\gamma=111.55(3)^\circ$. Finally, the structure of $Ba_2Y_3(SiO_4)_2F_5$ (**3**) was determined in the polar orthorhombic space group $Pba2$, having unit cell parameters $a=8.8864(18)$ Å, $b=12.764(3)$ Å and $c=5.0843(10)$ Å. The structures are compared based on their building blocks and long range polarities. Aligned silicate tetrahedra segregated into a single layer in (**3**) impart the observed polarity.

1. Introduction and brief review of rare earth silicate fluorides

Polar compounds are a fascinating canvas for materials research, both in their structural features and their unique physical and optical properties [1]. In particular polar solids have an enormous variety of optoelectronic properties. They can exhibit nonlinear optical effects, ferroelectric properties, domain engineering, surface acoustic waves, quasi-phase matching and numerous other physical manifestations of electro-optic behavior [2]. Of particular interest is the situation whereby a polar acentric structure also contains an ordered rare earth site, especially optically transparent ions like Y^{3+}. This enables the systematic substitution at the site with various laser active ions like Nd^{3+}, Yb^{3+} or Er^{3+}. In this case the material can serve the dual function as both the laser material and a second harmonic generator at the same time. Proper orientation of the polar axis helps to generate polarized laser light for subsequent operations like Q-switching. Such materials are called self-frequency doublers and have a number of practical applications [3,4].

In this paper we identify a novel and relatively unexplored class of compounds, namely the metal silicate fluorides, which have a considerable tendency to form polar structures. At the same time they contain an ordered rare earth ion (preferably yttrium) for systematic substitution, along with a polar axis for additional optical manipulation. We also focus on solids containing one or more alkali or alkaline earth ion, as these provide additional chemical knobs to turn, increasing our chemical and structural flexibility. The mineralogical literature is always a rich initial source of inspiration for functional solids, and the polar materials are no exception [5]. The rare earth element (REE) containing silicate fluorides are an excellent starting point [6]. However, while partial REE substitution can occur over a wide variety of crystallographic sites (especially substituting for Na, Ca or other rare earth elements) in natural silicate minerals, the occurrence of well-characterized compounds where a lanthanide is the primary occupant of a given site is confined to a much shorter set of silicate fluoride minerals. Several interesting minerals are based on La or Ce [7–15], and there are a number of synthetic lanthanide silicate fluorides [16–19] and alkali-containing lanthanide silicate fluorides [20–27] reported. Focusing on yttrium-based compounds for reasons just discussed we find nine examples among the naturally-occurring silicate fluorides, and these are summarized in Table 1.

Of these, cappelenite (Ba), hiortdahlite (Na, Ca), kapitsaite (Ba), miserite (K, Ca) and okanoganite (Na) also contain a site where an alkali or alkaline earth metal is the primary occupant. Also, cappelenite and kapitsaite are silico-borates, okanoganite is a silico-borate with phosphorous disorder and kuliokite is an aluminosilicate, so the mineralogical silicate fluorides can be quickly truncated by focusing the search on the alkali- and

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Table 1
Yttrium silicate fluoride minerals.

Mineral name	General formula	Space group	Ref.
Yftisite	$Y_4Ti(SiO_4)_2OF_6$	*Cmcm*	[28]
Fluorothalenite	$(Y,Er)_3(Si_3O_{10})F$	$P2_1/n$	[29]
Kuliokite	$Y_4Al(SiO_4)_2(OH)_2F_5$	*P*1	[30]
Britholite	$(Y,Ca,Lu)_5(SiO4)_3(OH,F)$	$P2_1$	[31]
Cappelenite	$Ba(Y,REE)_6(Si_3B_6O_{24})F_2$	*P*3	[32]
Hiortdahlite	$(Na,Ca)_4(Ca,Y)_8Zr_2(Y,Na)_2(Si_2O_7)_4O_3F_5$	$P-1$	[33]
Kapitsaite	$(Ba,K,Pb)_4(Y,Ca,Gd)_2(Si,B)_{12}O_{28}F$	$P-1$	[34]
Miserite	$(K,Ca)_{6.4}(Y,Ce)(Si,Al)_8O_{22.25}(OH)F$	$P-1$	[35]
Okanoganite	$(Y,Ce,Ca,Th)_{15}(Fe,Ti)Na(Si,P)_7B_3O_{34}(OH)_4F_{10}$	*R*3*m*	[36]

alkaline earth-yttrium silicate fluorides. The collection of yttrium-based silicate fluoride minerals exhibits an interesting structural feature in their propensity to crystallize in polar space groups (four of the nine are polar–cappelenite (*P*3), okanoganite (*R*3*m*), kuliokite (*P*1) and britholite ($P2_1$)).

Based on this tendency it would appear the alkali- and alkaline earth-yttrium silicate fluorides could be potentially rich areas for targeting new polar synthetic materials. These minerals exhibit a variety of means by which polarity can be achieved. For example, the polarities of cappelenite and okanoganite are most apparent by alignment of borate and silicate tetrahedra (where the direction of specific B–O or Si–O bonds collectively work in concert to impart polarity), respectively, in sheets or layers in the structure. Britholite is polar due to a shortening of certain rare earth oxide bonds which breaks the mirror symmetry of the apatite structure. Even with these interesting structural tendencies, there seems to be a somewhat limited precedent for synthetic yttrium silicate fluorides, with the only examples being the alkali metal-based compounds $Cs_2Y(Si_4O_{10})F$ [37] and $Na_5Y_4(SiO_4)_4F$ [38]. Synthetic alkaline earth-yttrium silicate fluorides appear completely neglected, and one must begin to consider other rare earth ions as in $Ba_2Ce_3(SiO_4)_3F$ [39] and $La_6Ba_4(SiO_4)_6F_2$ [40] in order to gain a foothold in this synthetic phase space. One possible reason for the lack of progress in the synthetic metal silicate fluoride systems is the tendency of silicates and silicate fluorides to form viscous liquids and glasses from their melts. Amphoteric oxides, however, tend to form high quality single crystals in hydrothermal fluids, so we felt confident that this promising class of compounds would lend themselves to this plan of attack.

The interplay of OH^- and F^- in the structures of many naturally occurring silicates and silicate fluoride species hints at their hydrothermal origins, and we have recently demonstrated that many fluoride-containing species resist hydrolysis during hydrothermal synthesis [41–45]. In particular, we recently isolated crystals of a new class of alkaline earth borate fluorides $M_3B_6O_{11}F_2$ (M=Sr, Ba) which crystallize in the polar space group $P2_1$ [46]. These structures exhibit a directed polarity based on the alignment of $[BO_3]$ triangles in the unit cell. Like B_2O_3, SiO_2 is an amphoteric oxide, so we have extended our hydrothermal exploration of phase space to seek novel silico-borates and silicate fluorides. In this paper we introduce three new members of this latter class of compounds, namely $LiY_3(SiO_4)_2F_2$ (**1**), $BaY_2(Si_2O_7)F_2$ (**2**) and $Ba_2Y_3(SiO_4)_2F_5$ (**3**). The structures are contrasted with one another, particularly in the aspects which affect (**3**) crystallizing in a polar space group.

2. Materials and methods

Single crystals of the title compounds were synthesized through a general two-step process of melt growth of starting materials followed by hydrothermal treatment. Starting materials were prepared from melts in platinum crucibles performed in air at 1000 °C for 24 h. For $LiY_3(SiO_4)_2F_2$ (**1**), the precursor powders were: 0.26 g (10 mmol) LiF, 1.1 g (7.5 mmol) YF_3, 0.30 g (5.0 mmol) SiO_2 and 0.092 g (2.5 mmol) NH_4F. For $BaY_2(Si_2O_7)F_2$ (**2**), the precursor powders were: 0.88 g (5.0 mmol) BaF_2, 1.1 g (7.5 mmol) YF_3 and 0.30 g (5.0 mmol) SiO_2. For $Ba_2Y_3(SiO_4)_2F_5$ (**3**), the precursor powders were: 0.88 g (5.0 mmol) BaF_2, 1.45 g (10 mmol) YF_3 and 0.06 g (1 mmol) SiO_2. The resulting powders in each case were then loaded (0.11 g) into individual silver ampoules along with 0.4 mL of an aqueous mineralizer solution. Mineralizers used were 2 M KF in the synthesis of (**1**) and (**2**), and 2 M KHF_2 was used to synthesize (**3**).The ampoules were weld-sealed and placed in an autoclave with excess water for counter pressure, and the autoclave was heated to 575 °C for 4 days, autogenously producing a pressure of 20 kpsi. The autoclave was then cooled to room temperature over 12 h and the crystals were harvested from the ampoules. Crystals of (**1**) formed as colorless diamond-shaped plates, while crystals of (**2**) and (**3**) formed as colorless rods. We note that while these products have not yet been synthesized in a phase pure yield (they are typically contaminated with binary fluoride crystals such as LiF, BaF_2 and YF_3), the variety of silicate fluoride products obtained in these preliminary reactions seem to suggest a rich hydrothermal phase space can be explored by varying the metal and silicate ratios in the reactions.

Single crystal x-ray diffraction of the resulting crystals was performed using a Rigaku AFC8S diffractometer equipped with Mo$K\alpha$ (λ=0.71073 Å) radiation and a Mercury CCD area detector. Data collection and processing, including corrections for absorption and Lorentz and polarization effects was performed using the CrystalClear software package [47]. Candidate space groups were identified based on the systematic absences of the data. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL software package [48]. All atoms were refined anisotropically in all structures. Elemental analysis by EDX was performed to confirm the presence of fluorine in each structure and to verify the approximate ratios of Ba:Y in compounds (**2**) and (**3**). Within the sensitivity of EDX we note good agreement in the compositions of the solved structures and the elemental analysis data (supporting information Table S1). In all cases, F atoms were crystallographically distinguished from O atoms by bond valence analyses of the atoms in question.

The structure of (**1**) was determined in the monoclinic space group $C2/c$, with a=17.651(4) Å, b=4.8868(10) Å, c=11.625(2) Å and β=131.13(3)°. Consecutive refinements resulted in a final R_1 value of 0.0407 based on the observed data. The structure of (**2**) was solved to a final R_1 value of 0.0292 in space group $P-1$, with a=5.1576(10) Å, b=6.8389(14) Å, c=11.786(2) Å, α=93.02(3)°, β=102.05(3)° and γ=111.55(3)°. The structure of (**3**) was solved in the polar, acentric orthorhombic space group *Pba*2, having unit cell parameters a=8.8864(18) Å, b=12.764(3) Å and c=5.0843(10) Å. A final R_1 value of 0.0273 was obtained after consecutive refinements and a Flack parameter of -0.027 also statistically suggested the acentricity and absolute structure (polarity). A summary of the crystallographic data for these structure determinations is given in Table 2.

3. Results and discussion

3.1. Crystal structure of $LiY_3(SiO_4)_2F_2$ (1)

To our knowledge this is the first reported single crystal structure of a lithium ytrrium silicate fluoride. The structure of (**1**) can be described as a framework of $[LiO_6]$, $[YO_6F_2]$ and $[YO_6F]$ polyhedra with small gaps that are occupied by $[SiO_4]$ tetrahedra