A₅RE₄X[TO₄]₄ Crystal Growth. Fluoride Flux Synthesis of Na₅Ln₄F[GeO₄]₄ (Ln = Pr, Nd), the First Quaternary Germanate Oxyfluorides

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Abstract:

Crystals of Na₅Pr₄F[GeO₄]₄ and Na₅Nd₄F[GeO₄]₄ were synthesized using a eutectic sodium fluoride, sodium chloride flux. Both compounds crystallize in the tetragonal space group *I*-4 with lattice parameters of $a = 12.1173(4)$ Å and $c = 5.6795(2)$ Å (Pr) and of $a = 12.0642(17)$ Å and $c = 5.6674(11)$ Å (Nd). The structure of the reported compounds is three-dimensional with face and corner sharing lanthanide polyhedra which edge and corner share with isolated germanium tetrahedra. These novel compositions represent the first example of quaternary germanium containing oxyfluorides.

Keywords

- Na₅Pr₄F[GeO₄]₄
- Na₅Nd₄F[GeO₄]₄
- Germanate oxyfluoride
- Fluoride flux
- Crystal growth

1. Introduction

Flux crystal growth is a versatile technique used for exploratory research [1], where typically the flux is a crucial part of the reaction. Throughout the literature, the use of different fluxes or conditions has been observed to yield different products, highlighting the importance of choosing an appropriate flux [2,3]. Fluoride fluxes have been demonstrated to readily dissolve starting material oxides, including rare earth oxides, silicon dioxide, and germanium oxide. Since it is known that rare earth silicate oxides and oxyfluorides have been grown out of alkali fluoride fluxes, these fluxes represent good choices when trying to grow new rare earth tetragen oxyfluorides [2,4-8].

The previously reported silicon analogues of the title compounds, $\text{Na}_5\text{RE}_4(\text{OH})[\text{SiO}_4]_4$ (RE = Pr, Nd, Sm, Eu, Tb-Yb, Y) and $\text{Na}_5\text{RE}_4\text{F}[\text{SiO}_4]_4$ (RE = Pr, Nd, Sm-Tm), were studied for their magnetic, luminescent, and SHG properties [4,6]. It was determined that in the oxyhydroxide analogues, the Tb analogue ordered antiferromagnetically, the Eu, Gd, and Tb members luminesce with fluorescence quantum yields from 2 – 21 %, and second harmonic generation (SHG) was not observed. In the oxyfluoride analogues, the Tb and Dy analogues were found to be antiferromagnetic, the Eu, Gd, and Tb members were found to be luminescent with fluorescence quantum yields from 5 – 17 %, and all but the Nd member were found to exhibit weak SHG. It is unknown if changing the tetragen changes the properties, however, with magnetic ordering occurring below 3 K, weak SHG, and fluorescence quantum yields below 25 % seen for the silicate analogues, synthesizing the germanate analogues is clearly of interest.

Various rare earth containing germanates have been found to exhibit magnetic properties, luminescence, and display ionic conductivity [9-13]. And yet, in spite of these properties, rare earth containing germanates have been studied far less extensively than the other tetragen family of rare earth containing silicates. In fact, $\text{Na}_5\text{Pr}_4\text{F}[\text{GeO}_4]_4$ and $\text{Na}_5\text{Nd}_4\text{F}[\text{GeO}_4]_4$ are the first quaternary germanium oxyfluorides that contain a rare earth element and either an alkali or alkaline earth element. This work reports only the second example of a germanium analogue from the $\text{A}_5\text{RE}_4\text{X}[\text{TO}_4]_4$ ($\text{A} = \text{Na}, \text{K}$; $\text{RE} =$ rare earth, $\text{X} = \text{F}, \text{OH}$; $\text{T} = \text{Si}, \text{Ge}$) family. The $\text{A}_5\text{RE}_4\text{X}[\text{TO}_4]_4$ family crystallizes in the noncentrosymmetric tetragonal space group $I-4$ [4-6,14-17].

2. Experimental Section

2.1 Synthesis

Crystals of $\text{Na}_5\text{Ln}_4\text{F}[\text{GeO}_4]_4$ ($\text{Ln} = \text{Pr}, \text{Nd}$) were grown via a sodium fluoride, sodium chloride eutectic flux growth. Ln_2O_3 (1 mmol), where Pr_2O_3 was reduced from Pr_6O_{11} (99.9 %; Alfa Aesar) and Nd_2O_3 (99.9 % Acros Organics) was used as received, Na_2CO_3 (1 mmol; ACS grade, Fisher Scientific), and GeO_2 (2 mmol; 99.98 %, Alfa Aesar) were loaded into a silver crucible and a eutectic flux mixture of NaF (2.81 g; 99 % min, Alfa Aesar) and NaCl (1.93 g; ACS grade, Fisher Scientific) were loaded on top of the reactants. The crucible was then loosely fitted with a silver lid and placed in a programmable furnace that was set to ramp to 800 °C where it dwelled for 24 h before being programmed to slow cool to 600 °C at a rate of 3 °C/h. After reaching 600 °C, the furnace was shut off. To isolate the crystals, the reactions were sonicated in water and the crystals were collected by vacuum filtration. $\text{Na}_5\text{Ln}_4\text{F}[\text{GeO}_4]_4$ ($\text{Ln} = \text{Pr}, \text{Nd}$) was determined to be the major product by powder X-ray diffraction analysis, with a small

amount GeO_2 ($> 5\%$) found in $\text{Na}_5\text{Pr}_4\text{F}[\text{GeO}_4]_4$ and Nd_2O_3 (approx. 6 % by JADE software analysis) found in $\text{Na}_5\text{Nd}_4\text{F}[\text{GeO}_4]_4$.

Polycrystalline samples of $\text{Na}_5\text{Ln}_4\text{F}[\text{GeO}_4]_4$ ($\text{Ln} = \text{Pr}, \text{Nd}$) were prepared using a solid state method to obtain phase pure samples for magnetic measurements. 1 mmol of Pr_2O_3 (reduced from Pr_6O_{11} and stored under a desiccator or Nd_2O_3 (prefired at 1000 °C for 12 h), 1 mmol Na_2CO_3 (ground and dried overnight at 100 °C), 0.5 mmol NaF (ground and dried overnight at 100 °C), and 2 mmol GeO_2 (ground and dried overnight at 100 °C) were weighed out and ground together for 30 minutes to promote intimate mixing. The sample was then pressed into a pellet and loaded into a copper tube that was crimped at both ends to avoid fluoride loss. The crimped copper tube was loaded into a flow-through furnace that was purged with N_2 gas. The reactions were then calcined at 600 °C for 10 h before ramping to 900 °C and dwelling there for 24 h. After 24 h at 900 °C the furnace was shut off and allowed to reach room temperature. The reactions were ground and characterized by powder X-ray diffraction and found to be phase pure.

2.2 Single Crystal X-ray Diffraction

X-ray intensity data were collected on a colorless prismatic crystal of $\text{Na}_5\text{Pr}_4\text{F}[\text{GeO}_4]_4$ and a blue-purple plate crystal of $\text{Na}_5\text{Nd}_4\text{F}[\text{GeO}_4]_4$ at 300(2) and 293(2) K, respectively, using a Bruker D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an Incoatec microfocus source (Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$)[18], and a Bruker SMART APEX CCD diffractometer (Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$), respectively [19]. The data collections covered 100 % of reciprocal space to $2\theta_{\text{max}} = 75.66^\circ$ and 56.6° , with $R_{\text{int}} = 0.034$ and 0.0425 after absorption corrections. The raw area detector frames were reduced and corrected for absorption effects using the

SAINT+ and SADABS programs [19]. Final unit cell parameters were determined by least-squares refinement of 9889 and 3488 reflections from each data set. Difference Fourier calculations and full-matrix least squares refinement against F^2 of the structural model were performed with SHELXL-2014/1 [20] using OLEX2 [21].

2.3 Magnetic Property Measurements

The magnetic properties of $\text{Na}_5\text{Ln}_4\text{F}[\text{GeO}_4]_4$ ($\text{Ln} = \text{Pr}, \text{Nd}$) were measured using a Quantum Design Magnetic Property Measurement System (QD-MPMS3 SQUID VSM). The zero-field cooled magnetic susceptibility was measured as a function of temperature between 2 and 300 K in an applied field of 1000 Oe. Radial offset and shape corrections were performed using the method outlined by Morrison and zur Loye [22].

3. Results and Discussion

3.1 Synthesis

An alkali fluoride/alkali chloride eutectic flux was used to grow crystals of $\text{Na}_5\text{Ln}_4\text{F}[\text{GeO}_4]_4$ ($\text{Ln} = \text{Pr}, \text{Nd}$). The eutectic mixture of NaF and NaCl was chosen to lower the melting point of the NaF flux in order to perform the reaction in a silver instead of a platinum vessel. By choosing the eutectic ratio of 33 % NaCl to 67 % NaF, which lowered the melting point of the flux from 996 °C (NaF) to 679 °C, the use of a reaction dwell temperature more than 100 °C above the melting point of the flux becomes feasible without coming close to the melting point of silver (962 °C).

Overall, germanate compounds are more difficult to synthesize due to the relative lower reactivity of germanium when compared to silicon. In this system, the identical conditions were used to grow $\text{Na}_5\text{Ln}_4\text{F}[\text{GeO}_4]_4$ ($\text{Ln} = \text{Pr}, \text{Nd}$) as were used to grow the $\text{Na}_5\text{RE}_4\text{F}[\text{SiO}_4]_4$ ($\text{RE} = \text{Pr}, \text{Nd}, \text{Sm} - \text{Tm}$) compounds [4]. However, only in the case of

Pr and Nd, was the desired phase obtained and even adaptations to the reaction did not result in the crystallization of any of the other rare earth analogues, while routinely yielding the known NaREGeO₄ germanate analogues [12,23].

3.2 Structure

Na₅Ln₄F[GeO₄]₄ (Ln = Pr, Nd) crystallizes in the tetragonal space group *I*-4, with the same structure as the other reported A₅RE₄X[TO₄]₄ (A = Na, K; RE = rare earth, X = F, OH; T = Si, Ge) [4-6,14-17]. The Na₅Ln₄F[GeO₄]₄ structure contains one unique lanthanide site, one unique germanium site, two unique sodium sites, one unique fluorine site, and four unique oxygen sites. The lanthanide site is eight coordinate with seven bonds to oxygen and one bond to fluorine. Each lanthanide polyhedron is face shared to two other lanthanide polyhedra. In total, four lanthanide polyhedra share the fluorine site, thereby creating the Ln₄O₂₀F unit shown in **Figure 1**. These lanthanide units stack down the *c* axis where down the column each Ln unit is connected through corner and edge sharing to GeO₄ tetrahedra as shown in **Figure 2**. Adjacent columns of Ln units are connected through edge sharing of Ln polyhedra and edge and corner sharing of Ln units with GeO₄ tetrahedra (**Figure 2**). The Na(1) atoms sit in line with the fluorine atoms down the *c* axis and fill the channels between the Ln units as shown in **Figure 3**. Four Na(2) atoms sit in the channels between the Ln columns down the *c* axis (**Figure 3**). The overall structure down the *c* axis is shown in **Figure 3** with crystallographic data presented in **Table 1** and Ln – O and Ge-O interatomic distances presented in **Table 2**.

3.3 Magnetism

In the A₅RE₄X[TO₄]₄ family, where A = Na, K; RE = Pr, Nd, Sm-Yb, Y; X = F, OH; and T = Si or Ge, reports of magnetism are solely focused on the A = Na and T = Si

compounds. Here, we report the first magnetic property measurements of the family when $T = \text{Ge}$ and the first magnetic property measurements ever reported on quaternary germanate oxyfluorides. In the previous magnetic studies when $T = \text{Si}$, it has been seen that unless the rare earth is small, like terbium or dysprosium, the resulting magnetism is paramagnetic. In the germanates this appears to be the case as well. Down to 2 K, $\text{Na}_5\text{Ln}_4\text{F}[\text{GeO}_4]_4$ ($\text{Ln} = \text{Pr}, \text{Nd}$) are both strictly paramagnetic with the magnetic data summarized in **Table 3** and the magnetic susceptibilities and inverse susceptibilities are shown in **Figure 4**. For both analogues, the inverse susceptibility was fit over the range of 100 – 300 K. The effective moments are $3.6 \mu_B$ (Pr) and $3.67 \mu_B$ (Nd) which compare well with the expected moments of $3.56 \mu_B$ (Pr) and $3.3 - 3.7 \mu_B$ (Nd).

4. Conclusion

$\text{Na}_5\text{Ln}_4\text{F}[\text{GeO}_4]_4$ ($\text{Ln} = \text{Pr}, \text{Nd}$) crystals were grown using a sodium fluoride, sodium chloride eutectic flux. Both compositions crystallize in the tetragonal space group *I*-4 like previously reported analogues. The compounds represent the second germanium analogues of this family reported and are the first germanium oxyfluoride analogues. Germanate oxides and oxyfluorides are not found often in literature due to the difficulty encountered when trying to synthesize germanates. These new compounds may indicate new pathways to synthesize future germanate compounds. Other members of this germanate oxyfluoride family could have the potential to exhibit SHG or interesting magnetic properties.

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Table 1. Crystallographic table for single crystal X-ray data for Na₅Nd₄F[GeO₄]₄.

Formula	Na ₅ Pr ₄ F[GeO ₄] ₄	Na ₅ Nd ₄ F[GeO ₄] ₄
Formula weight (g/mol)	1243.95	1257.27
Temperature (K)	300(2)	293(2)
Crystal system	Tetragonal	Tetragonal
Space group	<i>I</i> -4	<i>I</i> -4
<i>a</i> (Å)	12.1173(4)	12.0642(17)
<i>c</i> (Å)	5.6795(2)	5.6674(11)
<i>V</i> (Å ³)	833.92(6)	824.9(3)
<i>Z</i>	2	2
Density (Mg/m ³)	4.954	5.062
Absorption coefficient (mm ⁻¹)	18.772	19.754
Crystal size (mm)	0.10 x 0.04 x 0.03	0.14 x 0.04 x 0.04
2 theta range (°)	4.75 to 75.66	4.78 to 56.60
reflections collected	24672	3488
data/restraints/parameters	2244 / 0 / 32	1005 / 0 / 70
<i>R</i> (int)	0.0339	0.0425
GOF (<i>F</i> ²)	1.064	1.105
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0128 <i>wR</i> ₂ = 0.0209	<i>R</i> ₁ = 0.0212 <i>wR</i> ₂ = 0.0561

Table 2. Nd – O and Ge – O bond distances (in Å).

	Na ₅ Pr ₄ F[GeO ₄] ₄	Na ₅ Nd ₄ F[GeO ₄] ₄
<i>Ln</i> (1) – O(4)	2.4700(17)	2.320(9)
<i>Ln</i> (1) – O(1)	2.3403(19)	2.416(8)
<i>Ln</i> (1) – O(4)	2.4086(17)	2.431(9)
<i>Ln</i> (1) – O(1)	2.4415(19)	2.441(9)
<i>Ln</i> (1) – O(3)	2.6210(17)	2.451(8)
<i>Ln</i> (1) – O(2)	2.5566(16)	2.533(7)
<i>Ln</i> (1) – O(3)	2.4528(17)	2.604(8)
<i>Ln</i> (1) – F(1)	2.61981(14)	2.6037(6)
Ge(1) – O(1)	1.7479(18)	1.726(9)
Ge(1) – O(2)	1.7470(16)	1.740(7)
Ge(1) – O(4)	1.7391(17)	1.754(9)
Ge(1) – O(3)	1.7695(16)	1.773(8)

Table 3. Experimental magnetic moments (μ_{eff}) compared to calculated moments (μ_{calc}) for $\text{Na}_5\text{Ln}_4\text{F}[\text{GeO}_4]_4$ ($\text{Ln} = \text{Pr}, \text{Nd}$).

Compound	Fit Range (K)	θ (K)	μ_{eff} (μ_{B}/RE)	μ_{calc} (μ_{B}/RE)
$\text{Na}_5\text{Pr}_4\text{F}[\text{GeO}_4]_4$	100 – 300	-32.81	3.61	3.56
$\text{Na}_5\text{Nd}_4\text{F}[\text{GeO}_4]_4$	100 – 300	-36.59	3.67	3.3-3.7

Figure 1. $\text{Na}_5\text{Nd}_4\text{F}[\text{GeO}_4]_4$, representative of both compositions, showing the $\text{Ln}_4\text{O}_{20}\text{F}$ units formed through the face sharing of the Ln polyhedra where Ln is shown in orange, oxygen in red, and fluorine in green.

Figure 2. Representation of how the *Ln* unit columns are connected by corner and edge sharing Ge and how the adjacent columns are connected by Ge and *Ln* edge and corner sharing. *Ln* is shown in orange, Ge is shown in blue, oxygen is shown in red, and fluorine is shown in green.

Figure 3. Overall representation of $\text{Na}_5\text{Ln}_4\text{F}[\text{GeO}_4]_4$ down the c axis where the sodium atoms can be seen in purple while the other colors follow the scheme described in Figure 2.

Figure 4. Magnetic susceptibility and inverse magnetic susceptibility data of $\text{Na}_5\text{Pr}_4\text{F}[\text{GeO}_4]_4$ (top) and $\text{Na}_5\text{Nd}_4\text{F}[\text{GeO}_4]_4$ (bottom).