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Crystal growth, structures, magnetic and photoluminescent properties of $NaLnGeO_4$ (Ln = Sm, Eu, Gd, Tb)

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ABSTRACT

Single crystals of $NaLnGeO_4$ (Ln = Sm, Eu, Gd) were grown out of a molten sodium hydroxide flux, and their crystal structures were determined by single crystal X-ray diffraction. The lanthanide containing germanates crystallize in the orthorhombic space group of *Pnma*, and exhibit a complex three-dimensional structure consisting of corner- or edge-shared LnO_6, GeO_4, and NaO_6 polyhedra. UV–vis diffuse reflectance spectra indicated that the reported oxides are insulating materials with wide band gaps. The magnetic susceptibility data shows paramagnetic behavior. For the $NaEuGeO_4$ and $NaTbGeO_4$ compositions intense room temperature photoluminescence was observed.

1. Introduction

Oxide materials containing lanthanide elements continue to attract significant interest because they are used in many technologically important applications, such as optical converters, scintillators, phosphors, and LEDs [1–13]. One well-studied area consists of oxides containing both rare earths and main group elements, specifically lanthanide silicates and germanates [14–25]. In contrast to the lanthanide silicates, the germanium analogs have been less investigated, although both exhibit high thermal stability and useful optical properties [26]. One of the lanthanide germanate families, $NaLnGeO_4$ (Ln = lanthanide elements), is particularly interesting due to the presence of intense luminescent behavior. The family crystallizes in the orthorhombic space group of *Pnma*, and is based on the Olivine-type [27] structure composed of corner- and edge-shared LnO_6, GeO_4, and NaO_6 polyhedra. There exist a number of reports in the literature describing the synthesis, structures, and luminescent properties of selected members of this family [28–38]. Interestingly, a different space group for $NaSmGeO_4$ than what we observed has been previously reported [38]. Recently a structural phase transition and a change in photoluminescence as a function of pressure was reported for $NaEuGeO_4$ [28]. The optical properties of $NaGdGeO_4$ doped with other lanthanide elements (Nd^{3+}, Eu^{3+}, or Tb^{3+}) were investigated and reported recently [29–31,33–35].

Many compositions were prepared as single crystals utilizing typically high temperature hydrothermal (supercritical) conditions using the metal oxides and aqueous sodium hydroxide as starting reagents. This approach to crystal growth utilizes fairly high temperatures (>450 °C) and high pressures (>100–340 MPa) due to the low solubility of the starting oxides. Although $NaEuGeO_4$ was recently obtained via hydrothermal crystal growth at the low temperature of 230 °C using $Eu(NO_3)_3(H_2O)_6$ instead of Eu_2O_3 as the europium source, a homogeneous gel precursor was required for the reaction that took two weeks [28]. These methods are not as facile as one might like and hence we explored other routes for obtaining members of the $NaLnGeO_4$ family in single crystal form.

The use of molten fluxes is well known to be one of the most promising approaches for the crystal growth of oxides because it can lower reaction temperature and thus minimize the loss of volatile starting reagents. A number of compositions have been synthesized via flux crystal growth, which was recently reviewed [39].

We have focused on using hydroxide fluxes for the synthesis of a large number of new mixed metal oxides containing lanthanide elements [40–56]. The acid–base chemistry of molten hydroxide

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Table 1
Crystallographic data for $NaSmGeO_4$.

Formula	$NaSmGeO_4$
Fw	309.93
Temperature (K)	294(2)
Crystal system	Orthorhombic
Space group	*Pnma*
A (Å)	11.6351(5)
B (Å)	6.6042(3)
c (Å)	5.3041(2)
V (Å^3)	407.57(3)
Z	4
Density (g/cm^3)	5.051
Absorption coefficient (mm^{-1})	21.617
Crystal size (mm^3)	0.16 × 0.13 × 0.13
2 theta range (°)	7.00 to 56.52
Completeness (%)	100
Reflections collected	5146
R (int)	0.0298
GOF (F^2)	1.354
$R(F)^a$	0.0138
$R_w(F_o^2)^b$	0.0342
Largest diff. peak and hole (e Å^{-3})	1.060 and −0.579

$R(F)^a = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $R_w(F_o^2)^b = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

fluxes, best described by the Lux-Flood concept of oxoacidity [57,58], is thought to be one of the best media for oxide crystal growth, as it readily dissolves oxides, which is essential for their incorporation into a crystal. The autodissociation of molten hydroxide fluxes produces H_2O and O^{2-} as the acidic and basic species, respectively. The solubility of metal cations in the reaction mixture is strongly dependent on the acidity of the melt, which influences the crystallization of a wide range of complex oxides. Thus, controlling the water content of the reaction mixture, for example, adding water to increase the acidity or employing an open reaction vessel to increase the basicity by evaporation of water, impacts the crystal growth of various oxides. Using a sodium hydroxide melt, we successfully crystallized a series of $NaLnGeO_4$ (Ln = Sm, Eu, Gd) oxides, thereby establishing a new route for their crystal growth, compared to the methods that were used in the past. As a part of this work, we prepared polycrystalline powders of the known composition $NaTbGeO_4$ to investigate its physical properties, because other than its crystal structure, no characterization of this composition has been reported [59]. Herein we detail the crystal growth, the structures, the magnetic and the optical properties of the Olivine-type $NaLnGeO_4$ (Ln = Sm, Eu, Gd, Tb).

2. Experimental section

2.1. Reagents

Sm_2O_3 (Alfa Aesar, 99.9%), Eu_2O_3 (Alfa Aesar, 99.99%), Gd_2O_3 (Alfa Aesar, 99.99%), Tb_2O_3 (prepared from Tb_4O_7 (Alfa Aesar, 99.9%) at 1000 °C under a 5% H_2/N_2 gas flow), GeO_2 (Alfa Aesar, 99.99%), Na_2CO_3 (Alfa Aesar, 99.997%), and NaOH (Fisher, ACS grade) were used as received.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters U_{eq} for $NaSmGeO_4$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	X	*y*	*z*	U_{eq}
Sm(1)	0.2792(1)	0.25	0.4988(1)	0.006(1)
Ge(1)	0.5956(1)	0.25	0.5601(1)	0.005(1)
Na(1)	0	0	0.5	0.013(1)
O(1)	0.4561(3)	0.25	0.6814(7)	0.009(1)
O(2)	0.3299(2)	0.5459(4)	0.2913(4)	0.009(1)
O(3)	0.1083(3)	0.25	0.2653(7)	0.011(1)

Table 3
Selected interatomic distances (Å) for $NaSmGeO_4$.

Sm(1)–O(1)	2.275(3)
Sm(1)–O(2)	2.319(3)
Sm(1)–O(2)	2.319(3)
Sm(1)–O(2)	2.416(2)
Sm(1)–O(2)	2.416(2)
Sm(1)–O(3)	2.343(4)
Ge(1)–O(1)	1.745(3)
Ge(1)–O(2)	1.786(2)
Ge(1)–O(2)	1.786(2)
Ge(1)–O(3)	1.732(4)
Na(1)–O(1)	2.417(3)
Na(1)–O(1)	2.417(3)
Na(1)–O(2)	2.529(2)
Na(1)–O(2)	2.529(2)
Na(1)–O(3)	2.421(3)
Na(1)–O(3)	2.421(3)

2.2. Synthesis

Single crystals of $NaLnGeO_4$ (Ln = Sm, Eu, Gd) were grown out of a molten sodium hydroxide flux. The sodium hydroxide is commercially available and contains approximately 15% water by weight. In a typical procedure, 0.5 mmol of Ln_2O_3 (prefired at 1000 °C for 24 h), 2 mmol of GeO_2, and 4 g of NaOH were placed together into silver tubes approximately 10 cm long with a diameter of 1.25 cm, which had been flame-sealed at one end. After loading the reagents in to the vessel, the silver tubes were crimped shut and folded over twice before heating. For all compositions, the reaction mixtures were heated to 600 °C at a rate of 10 °C/min, held for 12 h, and then cooled to 400 °C at a rate of 4 °C/h. At this point the furnace was shut off and allowed to cool to room temperature. The hydroxide flux was dissolved in water, aided by the process of sonication, and the crystals were washed with water and acetone and isolated by vacuum filtration. For the Sm member, the product contained only crystals of $NaSmGeO_4$, while the Eu and Gd reactions yielded mixed phase products.

Polycrystalline samples of $NaEuGeO_4$, $NaGdGeO_4$ and $NaTbGeO_4$ were synthesized via conventional solid state methods. Stoichiometric amounts of Na_2CO_3, Ln_2O_3, and GeO_2 were thoroughly ground together and loaded into alumina crucibles. The mixtures were heated to 950 °C, held for 2d, and cooled to room temperature, with intermittent grindings. The purity of ground crystals and powder sample was confirmed by powder X-ray diffraction as seen in Fig. S1.

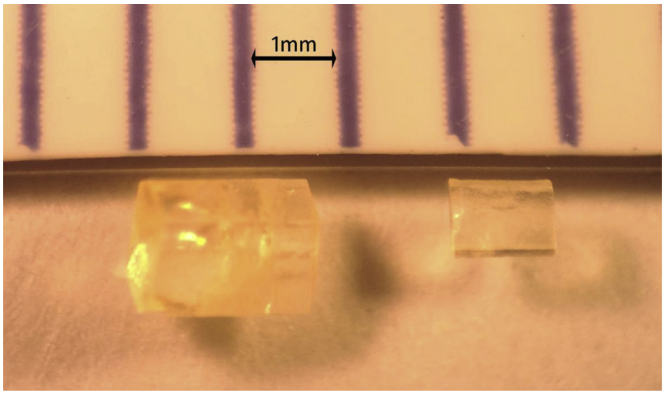

Fig. 1. Optical image of single crystals of $NaSmGeO_4$ grown out of a sodium hydroxide melt.