Hydrothermal Synthesis, Structure, and Property Characterization of Rare Earth Silicate Compounds: $\text{NaBa}_3\text{Ln}_3\text{Si}_6\text{O}_{20}$ (Ln = Y, Nd, Sm, Eu, Gd)

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Abstract

A series of new lanthanide (Ln) silicates have been synthesized using high temperature hydrothermal techniques, and structurally characterized using single crystal and powder X-ray diffraction. The compounds have the general formula $\text{NaBa}_3\text{Ln}_3\text{Si}_6\text{O}_{20}$ (Ln = Y, Nd, Sm, Eu, Gd), and crystallize in the space group *Ama2* (No.40). As a representative example, the unit cell parameters of $\text{NaBa}_3\text{Gd}_3\text{Si}_6\text{O}_{20}$ are $a = 14.731(3) \text{ \AA}$, $b = 23.864(5) \text{ \AA}$, $c = 5.5449(11) \text{ \AA}$ and $Z = 4$. The title compounds adopt a three dimensional polar acentric framework made of Ln–O–Si bonding. The framework is comprised of LnO_8 and LnO_7 units forming edge-sharing infinite chains along the *c*-axis. These oxy-bridged infinite chains are also linked by $[\text{Si}_4\text{O}_{13}]$ tetrasilicate and $[\text{Si}_2\text{O}_7]$ disilicate units to form the three-dimensional framework structure, with Ba^{2+} and Na^+ cations residing inside channels of the framework. The polarity in the structure is imparted by the unusual tetrasilicate arrangement. The luminescence and magnetic properties were investigated on selected compounds. The temperature dependent magnetic susceptibility measurements on the Nd, Sm, and Gd derivatives reveal a Curie-Weiss behavior with an antiferromagnetic coupling parameter. For the Eu-derivative, the temperature dependent magnetic susceptibility deviates significantly from Curie-Weiss behavior. Luminescence properties of $\text{NaBa}_3\text{Eu}_3\text{Si}_6\text{O}_{20}$ and $\text{NaBa}_3\text{Sm}_3\text{Si}_6\text{O}_{20}$ compounds exhibited the characteristic transitions of Eu^{3+} ($^5D_0 \rightarrow ^7F_J$, $J = 0-4$) and Sm^{3+} ($^4G_{5/2} \rightarrow ^6H_J$, $J = 5/2, 7/2$), respectively, leading to strong visible red and orange emissions, respectively.

Keywords: Hydrothermal, rare earth silicate, lanthanide chains, X-ray diffraction

1. Introduction

The synthesis and characterization of silicates of rare earth elements have drawn considerable attention due to their interesting tunable optical properties ranging from visible to infrared luminescence.¹⁻⁴ Additionally, lanthanide silicates exhibit high thermal stability, ion exchange properties, and rich structural chemistry owing to great number of possible different coordination environments in lanthanide elements.⁵ Crystal growth of these silicates can typically be achieved via hydrothermal⁶⁻¹⁰ and flux¹¹⁻¹⁵ growth techniques. The chemistry of lanthanide-based silicates has been summarized by Wickleder in 2002,¹⁶ and that work identifies several mixed alkali-alkaline earth-rare earth silicates reported in the literature. Most of these structures are based on sodium or potassium alkali metal cations.¹⁷⁻¹⁹ Given the massive number of corresponding transition metal and main group metal silicates, the number of alkaline earth metal or mixed alkaline/alkaline earth metal containing rare earth silicates surprisingly is somewhat limited. This opens a promising avenue of investigation of a relatively undeveloped class of new single crystals with attractive physical properties. They also have an increased tendency to form polar acentric crystals with interesting optical magnetic properties. Such characteristics are well suited to form new important materials types such as multiferroics.²⁰⁻²³

In the family of alkaline earth metal based rare earth silicates, $\text{Ca}_3\text{Ln}_2(\text{SiO}_4)_3$ ($\text{Ln}^{3+} = \text{Y}^{3+} - \text{Lu}^{3+}$)²⁴⁻²⁶ is a promising group of compounds that has been studied for decades. These structures have been determined using single crystal and powder X-ray diffraction. These materials adopt a garnet type structure only when the size of the rare earth element is very small (i.e. Sc^{3+}). When the rare earth element is of intermediate size (Sm-Lu, Y) the structure adopts a carnotite-type structure ($\text{Ca}_5(\text{PO}_4)_2(\text{SiO}_4)$) with orthorhombic symmetry.²⁷ From spectroscopic point of view these carnotite analogs like $\text{Ca}_3\text{Y}_2(\text{SiO}_4)_3$, $\text{Ca}_3\text{Sc}_2(\text{SiO}_4)_3$ and $\text{Ca}_3\text{Lu}_2(\text{SiO}_4)_3$ exhibit excellent

luminescence properties when they are doped with trivalent lanthanide ions such as Ce^{3+} , Pr^{3+} , Eu^{3+} , Tb^{3+} and Sm^{3+} .²⁶

These interesting early results with calcium rare earth silicates motivate us to extend our own exploratory hydrothermal synthesis to a broader study of the alkaline earth lanthanide silicates, and in this study we employ barium as the alkaline earth building block. In general we find that the high temperature hydrothermal method is extremely versatile and useful with regard to the synthesis of single crystals of alkali and alkaline earth lanthanide oxyanions. Typically, varying the nature of the alkali ion used in the mineralizer as well as variation of the other metal ions can lead to a wide range of structural deviation, and we are in the process of determining the scope and limitations of the reactions of alkaline earth lanthanide silicates. In this contribution, we report the high temperature hydrothermal synthesis and single crystal structure characterization of a series of compounds with the formula of $\text{NaBa}_3\text{Ln}_3\text{Si}_6\text{O}_{20}$, where the rare earth ions are the larger-sized ions of the series ($\text{Ln} = \text{Y}, \text{Nd}, \text{Sm}, \text{Eu}$ and Gd).

The chemistry leads to the incorporation of the sodium ion from the mineralizer into the lattice along with the target barium ions. The work is a follow on of our previous report where we provided an initial preliminary description of $\text{NaBa}_3\text{Eu}_3\text{Si}_6\text{O}_{20}$ along with other europium-containing species.⁷ The title compounds crystallize in the non-centrosymmetric, polar space group *Ama2*, but there has so far been no significant property characterization studies on this compounds having this structure type. In the present investigation, we use hydrothermal synthesis to extend this series to the Y, Nd, Sm, and Gd analogs. Luminescence properties of $\text{NaBa}_3\text{Eu}_3\text{Si}_6\text{O}_{20}$ and $\text{NaBa}_3\text{Sm}_3\text{Si}_6\text{O}_{20}$ are reported, as well as preliminary magnetic properties of $\text{NaBa}_3\text{Ln}_3\text{Si}_6\text{O}_{20}$ ($\text{Ln} = \text{Nd}, \text{Sm}, \text{Eu}$, and Gd) series, which were measured because of their somewhat unusual Ln–O–Ln connectivity.

2. Experimental

2.1. Synthesis of $\text{NaBa}_3\text{Ln}_3\text{Si}_6\text{O}_{20}$ ($\text{Ln} = \text{Y}, \text{Nd}, \text{Sm}, \text{Eu}$ and Gd).

All reagents were analytical grade and used as purchased. The synthetic methods employed over the course of study used the following reagents: Y_2O_3 (Alfa Aesar, 99.9%), Sm_2O_3 (Alfa Aesar, 99.9%), Gd_2O_3 (Alfa Aesar, 99.9%), Eu_2O_3 (Alfa Aesar, 99.9%) and BaO (Alfa Aesar, 88%). The title compounds were all synthesized using similar hydrothermal methodology. As a typical example, the synthesis of $\text{NaBa}_3\text{Gd}_3\text{Si}_6\text{O}_{20}$ was achieved using the respective oxides (BaO ; 0.0733 g, Gd_2O_3 ; 0.0693 g, SiO_2 ; 0.0574 g) in a 6:3:12 molar ratio. These precursor powders were mixed thoroughly and placed in a silver ampoule with 0.4 mL of 5 M NaOH . The weld-sealed ampoules were loaded to into a Tuttle cold-seal autoclave, which contained additional deionized water to generate an appropriate counter pressure. The autoclave was heated at 600–620 °C for 6 days, typically generating a counter pressure of 25 kpsi. After cooling to room temperature, the contents of the ampoules were filtered and washed with deionized water. The reactions produced phase-pure yields of $\text{NaBa}_3\text{Gd}_3\text{Si}_6\text{O}_{20}$ as colorless columnar crystals up to 1-2 mm in length. The other analogs were prepared in similar fashion. The only material that did not form as a phase-pure product in this study was $\text{NaBa}_3\text{Y}_3\text{Si}_6\text{O}_{20}$, which grew as smaller crystals and was always contaminated with a minor amount of NaYSiO_4 .

2.2. X-ray Diffraction

Structure determination was carried out using single crystal X-ray diffraction. After initial microscopic inspection, the crystals were mounted on glass fibers and centered on a Rigaku AFC8-S diffractometer. Diffraction intensity data were collected using graphite monochromated

Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) and a Mercury CCD detector. Data were processed and corrected for absorption, Lorentz and polarization effects using the CrystalClear software package.²⁸ The structures were solved by direct methods and subsequently refined by full-matrix least-squares on F^2 using Fourier difference techniques using the SHELX software suite.²⁹ All atoms were refined anisotropically. Table 1 reports the crystallographic data of the NaBa₃Ln₃Si₆O₂₀ series. Selected interatomic distances and angles are reported in Table 2,

Table 1: Crystallographic data for NaBa₃LnSi₆O₂₀, Ln = Y, Nd, Sm and Gd.

chemical formula	NaBa ₃ Y ₃ Si ₆ O ₂₀	NaBa ₃ Nd ₃ Si ₆ O ₂₀	NaBa ₃ Sm ₃ Si ₆ O ₂₀	NaBa ₃ Gd ₃ Si ₆ O ₂₀
FW (g/mol)	1190.28	1356.27	1374.60	1395.30
crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
crystal dimension, mm	0.16 x 0.04 x 0.04	0.28 x 0.08 x 0.06	0.15 x 0.02 x 0.02	0.24 x 0.08 x 0.06
space group, Z	<i>Ama</i> 2, 4	<i>Ama</i> 2, 4	<i>Ama</i> 2, 4	<i>Ama</i> 2, 4
T (°C)	25	25	25	25
<i>a</i> (Å)	14.656(3)	14.831(3)	14.786(3)	14.731(3)
<i>b</i> (Å)	23.631(5)	24.163(5)	24.008(5)	23.865(5)
<i>c</i> (Å)	5.5139(11)	5.5901(10)	5.690(10)	5.5449(11)
<i>V</i> (Å ³)	1909.6(7)	2003.3(7)	1976.9(7)	1949.4(7)
2 θ range	2.21–25.05	2.17–25.04	2.76–25.05	1.71–25.04
No. Of reflections collected	8161	20870	8201	7996
μ (Mo K α) (mm ⁻¹)	15.660	13.912	15.130	16.513
<i>d</i> _{calc} (g cm ⁻³)	4.140	4.497	4.618	4.754
data/restraints/parameters	1764/1/163	1853/7/163	1669/1/163	1701/1/163
final R [<i>I</i> > 2 σ (<i>I</i>)] R ₁ , wR ₂	0.0303/0.0683	0.0134/0.0329	0.0274/0.0660	0.0293/0.0691
final R (All data) R ₁ , wR ₂	0.0326/0.0699	0.0134/0.0329	0.0275/0.0661	0.0296/0.0693
GOF	1.143	1.154	1.137	1.145
Flack parameter	-0.039(11)	-0.006(13)	0.01(2)	-0.03(2)

Table 2: Selected interatomic distances (Å) and angles (°) for NaBa₃LnSi₆O₂₀, Ln = Y, Nd, Sm, and Gd.

LnO₇	NaBa ₃ Y ₃ Si ₆ O ₂₀	NaBa ₃ Nd ₃ Si ₆ O ₂₀	NaBa ₃ Sm ₃ Si ₆ O ₂₀	NaBa ₃ Gd ₃ Si ₆ O ₂₀
Ln(1)–O(1)	2.336(6)	2.392(4)	2.379(7)	2.351(7)
Ln(1)–O(2)	2.398(7)	2.494(3)	2.464(6)	2.448(7)
Ln(1)–O(6)	2.484(7)	2.596(4)	2.567(6)	2.533(7)
Ln(1)–O(7)	2.259(7)	2.351(4)	2.322(8)	2.316(8)
Ln(1)–O(8)	2.237(6)	2.307(3)	2.285(6)	2.268(7)
Ln(1)–O(9)	2.401(8)	2.480(4)	2.455(6)	2.430(7)
Ln(1)–O(11)	2.265(7)	2.374(4)	2.344(6)	2.317(7)
LnO₈				
Ln(2)–O(1) x 2	2.212(6)	2.348(4)	2.300(7)	2.278(7)
Ln(2)–O(6) x 2	2.361(7)	2.467(4)	2.426(6)	2.410(7)
Ln(2)–O(9) x 2	2.368(7)	2.509(4)	2.466(6)	2.435(7)
Ln(2)–O(11) x 2	2.789(8)	2.703(4)	2.704(7)	2.701(8)
Si(1)O₄				
Si(1)–O(5)	1.671(6)	1.675(5)	1.683(8)	1.686(9)
Si(1)–O(8) x 2	1.630(7)	1.626(4)	1.634(6)	1.626(7)
Si(1)–O(10)	1.593(4)	1.602(5)	1.584(11)	1.582(7)
Si(2)O₄				
Si(2)–O(1)	1.609(6)	1.607(4)	1.607(6)	1.604(7)
Si(2)–O(2)	1.618(7)	1.616(4)	1.627(8)	1.627(9)
Si(2)–O(4)	1.646(7)	1.652(4)	1.649(6)	1.635(7)
Si(2)–O(7)	1.604(7)	1.610(4)	1.617(6)	1.611(8)
Si(3)O₄				
Si(3)–O(3)	1.655(2)	1.652(2)	1.650(3)	1.653(3)
Si(3)–O(6)	1.604(7)	1.619(4)	1.625(7)	1.619(8)
Si(3)–O(9)	1.622(8)	1.632(4)	1.647(7)	1.631(8)
Si(3)–O(11)	1.593(7)	1.606(4)	1.604(6)	1.603(6)
Si(4)O₄				
Si(4)–O(4) x 2	1.630(7)	1.623(4)	1.625(7)	1.625(7)
Si(4)–O(5)	1.652(8)	1.645(5)	1.638(9)	1.638(8)
Si(4)–O(12)	1.581(9)	1.581(5)	1.75(11)	1.578(8)
Ln(1)–O(1)–Ln(2)	112.1(3)	111.90(14)	112.29(2)	112.39(2)
Ln(1)–O(6)–Ln(2)	102.2(2)	101.73(12)	102.20(2)	101.95(2)
Ln(2)–O(9)–Ln(1)	107.4(3)	102.50(13)	103.80(2)	104.93(2)
Ln(1)–O(11)–Ln(2)	98.5(2)	99.84(13)	100.01(2)	99.56(2)

The powder X-ray diffraction data were collected using a Rigaku Ultima IV diffractometer equipped with Cu K α radiation ($\lambda = 1.5406$ Å). Diffraction patterns were collected in the range of 5–65° in 2 θ using a scan speed of 0.1 degrees per minute with a step size of 0.02°. The PDXL software package³⁰ provided by Rigaku was used for further data analysis. Additionally, the

elemental composition was confirmed by EDX measurements (Supplementary Information), using a Hitachi 3400N SEM.

2.3. Magnetic Property Characterization

Temperature-dependent magnetic susceptibility measurements of $\text{Ba}_3\text{NaLn}_3\text{Si}_6\text{O}_{20}$ ($\text{Ln} = \text{Nd}, \text{Sm}, \text{Eu}$ and Gd) were conducted using a Vibrating Sample Magnetometer (VSM) option on a Quantum Design PPMS from 10 K to 300 K in an applied field of 300 Oe. Crystals were individually selected from the reaction products and hand-ground into a powder sample. This powder (~30-40 mg) was loaded into a plastic capsule for each measurement. The magnetic susceptibility was corrected for the plastic capsule and core diamagnetism with Pascal constants.³¹

2.4. Photoluminescence studies

Photoluminescence (PL) excitation and emission spectra were recorded with a Horiba Jobin-Yvon Spex Fluorolog-3 fluorimeter equipped with a 450W xenon lamp as the excitation source in the range of 230-1800 nm wavelength. The fluorimeter is equipped with a double grating excitation and emission monochromators. All measurements were performed at room temperature.

3. Results and Discussion

3.1. Synthesis and Structural Description

The $\text{NaBa}_3\text{Ln}_3\text{Si}_6\text{O}_{20}$ family of compounds was first introduced in 1983,³² by a preliminary structure report of $\text{NaBa}_3\text{Nd}_3\text{Si}_6\text{O}_{20}$ in the non-standard space group $C2cm$, but no additional

characterization or phase exploration was reported. Because the structure exhibits several interesting features (*vide infra*), a more detailed investigation of the structure type and properties seemed warranted. In the present study, phase-pure yields of high quality single crystals of the $\text{NaBa}_3\text{Ln}_3\text{Si}_6\text{O}_{20}$ ($\text{Ln} = \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$) series of compounds were obtained from hydrothermal reactions using an aqueous sodium hydroxide mineralizer. Powder XRD patterns in Figure 1 indicate good agreement between the experimental and calculated patterns, and that the Nd, Sm, Eu and Gd analogs formed as phase-pure products. For reasons not clear to us, the $\text{NaBa}_3\text{Y}_3\text{Si}_6\text{O}_{20}$ crystals are very small compared to the other derivatives and also intermixed with minor amounts of NaYSiO_4 . It may be that both the small size and the lower yield of $\text{NaBa}_3\text{Y}_3\text{Si}_6\text{O}_{20}$ occurs due to a greater stability of the yttrium orthosilicate impurity phase, NaYSiO_4 , compared to the other NaLnSiO_4 phases under these hydrothermal conditions. If sodium is removed from the system by alternatively using 2.5 M $\text{Ba}(\text{OH})_2$ as a mineralizer, a complex rare earth silicate does not form, and the products are instead $\text{Ln}(\text{OH})_3$ and Ba_2SiO_4 .

Figure 1. PXRD analysis of the $\text{NaBa}_3\text{Ln}_3\text{Si}_6\text{O}_{20}$ series: (a) simulated PXRD of $\text{NaBa}_3\text{Gd}_3\text{Si}_6\text{O}_{20}$; experimental PXRD patterns of (b) $\text{NaBa}_3\text{Gd}_3\text{Si}_6\text{O}_{20}$, (c) $\text{NaBa}_3\text{Eu}_3\text{Si}_6\text{O}_{20}$, (d) $\text{NaBa}_3\text{Sm}_3\text{Si}_6\text{O}_{20}$, (e) $\text{NaBa}_3\text{Nd}_3\text{Si}_6\text{O}_{20}$.

Examination of the crystal structure of this family of compounds reveals several interesting features. This family of compounds crystallizes in space group $Ama2$. For simplicity, $\text{NaBa}_3\text{Gd}_3\text{Si}_6\text{O}_{20}$ will be used as the representative structural example here, as all others possess very similar structural feature. As a whole, the $\text{NaBa}_3\text{Ln}_3\text{Si}_6\text{O}_{20}$ series adopts a 3-D framework built from two unique Ln^{3+} sites, two unique Ba^{2+} sites and one unique Na^+ site, along with two different types of polysilicate building blocks ($[\text{Si}_2\text{O}_7]$ and $[\text{Si}_4\text{O}_{13}]$). The lanthanide silicate framework forms a series of channels along the c -axis that contain the Ba and Na atoms (Figure 2). The lanthanide sites both lack a center of symmetry, with Gd(1) located at a general position seven-coordinate with oxygen, and Gd(2) located at a $4a$ site having 2-fold rotational symmetry and eight-coordinate with oxygen. These site symmetries influence the observed spectroscopic properties, in particular for Eu-containing compounds where the emission wavelength can be quite sensitive toward site symmetry.

Figure 2. Perspective view of $\text{NaBa}_3\text{Gd}_3\text{Si}_6\text{O}_{20}$ along c -axis showing pseudo-one-dimensional channels where Ba^{2+} and Na^+ cations reside. The color scheme of the atoms is the same throughout this report.

Of additional interest to the present study is the connectivity of the lanthanide atoms with one another. As shown in Figure 3a, Gd(1)O₇ and Gd(2)O₈ polyhedra connect through shared oxygen edges to form infinite chains running parallel to the [001] direction. Each Gd(2)O₈ polyhedron connects to four Gd(1)O₇ polyhedra by shared oxygen edges, essentially fusing two zigzag chains into the observed one dimensional chains (Figure 3b). The infinite edge-sharing Gd–O–Gd chains are connected through both the tetrasilicate and disilicate building blocks in the structure (Figure 4). The [Si₂O₇] group is a common bridging silicate unit, and here it provides connectivity of neighboring chains along the *a*-axis. The [Si₄O₁₃] group in NaBa₃Ln₃Si₆O₁₂ is present as an isolated island. Aside from this family of compounds, this island unit is also present in Pb₂₁(Si₇O₂₂)₂(Si₄O₁₃) (though differing in the orientation of the apices of the silicate tetrahedra),³³ and thus there are very few examples of its structural behavior. Tetrasilicate groups in other lanthanide silicates are more often present as finite chains, as in Ba₂Nd₂(Si₄O₁₃),³⁴ Ba₂Gd₂(Si₄O₁₃),³⁵ and Na₄Sc₂(Si₄O₁₃),³⁶ or as a horseshoe shape as observed in La₆(Si₄O₁₃)(SiO₄)₂.³⁷ The [Si₄O₁₃] islands observed in the present study thus present a unique bridging mechanism for one dimensional lanthanide chains. These tetrasilicate groups bridge neighboring chains along the *a*- and *b*-axes. An additional feature of the [Si₄O₁₃] group is its role in imparting polarity on the structure. The individual silicate tetrahedra of these groups (Si(1), Si(2), and Si(4)) are arranged such that an apical oxygen atom extends approximately along the *c*-axis. Overall polarity is observed since this orientation is repeated for all [Si₄O₁₃] groups in the structure. Since the structure type lacks a center of symmetry, these compounds could be of interest to study for their nonlinear optical activity, particularly as candidates for self-frequency doubling when combined with a spectroscopically active lanthanide dopant. In addition the crystal forms in a potentially ferroic mm2 point group.

Figure 3. (a) Partial structure showing the edge-sharing connectivity of Gd(2)O₈ with Gd(1)O₇ to form the infinite Gd–O–Gd chains. (b) Infinite Gd–O–Gd chains propagate along the *c*-axis.

Figure 4. Partial polyhedral view of the extended structure of $\text{NaBa}_3\text{Gd}_3\text{Si}_6\text{O}_{20}$ showing the structural confinement of the Gd–O–Gd chains. The Gd–O–Gd chains are interconnected by $[\text{Si}_2\text{O}_7]$ and $[\text{Si}_4\text{O}_{13}]$ groups to form the 3-D framework type structure.

The bond distances and angles (Table 2) for the LnO_7 , LnO_8 , and SiO_4 units are within the expected range based on the sum of their Shannon crystal radii.³⁸ For instance, in $\text{NaBa}_3\text{Gd}_3\text{Si}_6\text{O}_{20}$, the GdO_7 bond distances range from 2.268(7)–2.533(7) Å and GdO_8 bond distances range from 2.278(7)–2.7013(8) Å. Additionally Gd–O–Gd bond angles are in the range of 99.56(2)–112.39(2)°. It is interesting to note that Gd(2)O_8 exhibits a rather distorted geometry by having two shorter (2.278(7) Å) and two longer (2.7013(8) Å) Gd–O bonds. The average Ln–O bond distances of LnO_7 and LnO_8 : 2.340(7)Å and 2.432(5)Å for Y^{3+} , 2.406(7)Å and 2.484(7)Å for Sm^{3+} , 2.379(7)Å and 2.436(7)Å for Eu^{3+} and, 2.380(7) Å and 2.484(7) Å, for Gd^{3+} are also in good agreement with the calculated Shannon crystal radii. It is also useful to

examine the Ln–O–Ln bond angles in correlation with the Ln–Ln magnetic interactions through Ln–O–Ln chains. Inter-chain magnetic interactions should be negligible due to their large separation provided by [Si₄O₁₃] and [Si₂O₇] groups and the ionic nature of the magnetic lanthanide centers.³⁹ In NaBa₃Gd₃Si₆O₂₀, the Ln–O–Ln bond angles within the chains are 112.39(2)° for Gd(1)–O(1)–Gd(2), 101.95(2)° for Gd(1)–O(6)–Gd(2), 104.93(2)° for Gd(2)–O(9)–Gd(1) and 99.56(2)° for Gd(1)–O(11)–Gd(2). The similarities in bond distances and angles within the Ln–O–Ln chains (Table 2) also suggests that the nature of the Ln–Ln magnetic interactions should be comparable within the series of compounds.

3.2. Magnetic properties

Because of the extended chain structure of the lattice we felt it suitable to determine the temperature dependent magnetic susceptibility of this paramagnetic series. The magnetic susceptibility, χ , versus temperature, T , was investigated for an applied magnetic field, H , of 0.03 T (Figure 5). As shown by χ^{-1} vs. T plot for Ln = Gd (Figure 5a inset), the Gd sample exhibits Curie-Weiss behavior with a negative inter-moment coupling at $H = 0.03$ T applied magnetic field. Further analysis of temperature-dependent magnetic susceptibility data of Ba₃NaLn₃Si₆O₂₀ (Ln = Nd, Sm, Eu and Gd) shows that all the samples except for NaBa₃Eu₃Si₆O₂₀ follow Curie-Weiss behavior. Fitting χ at higher temperatures (50–300 K) using the Curie-Weiss law yielded effective magnetic moments for Ln³⁺ cations of 3.66 ± 0.03 , 1.62 ± 0.02 , and $7.64 \pm 0.03 \mu_B$ per Ln³⁺ ion for the Nd-, Sm- and Gd-containing compounds, respectively. The theoretical effective magnetic moment of Nd³⁺, Sm³⁺, and Gd³⁺ are 3.62, 1.74, and 7.94 per Ln³⁺ ion. Further, θ values for Nd, Sm, and Gd-containing samples are -24.8, -25.0, -4.2 K, respectively. Such a negative magnitude is suggestive of an antiferromagnetic type coupling between magnetic

moments. Similar behavior has been observed in $\text{Na}_5\text{Ln}(\text{SiO}_4)_4(\text{OH})^{11}$ and the $\text{NaLn}_9(\text{GeO}_4)_6\text{O}_2$ series.⁴⁰

Figure 5. (a) χ vs. T for $\text{NaBa}_3\text{Ln}_3\text{Si}_6\text{O}_{20}$, ($\text{Ln} = \text{Nd, Sm, Gd}$). The inset in Figure 5a shows the inverse susceptibility of $\text{NaBa}_3\text{Gd}_3\text{Si}_6\text{O}_{20}$. (b) χ vs. T for $\text{NaBa}_3\text{Eu}_3\text{Si}_6\text{O}_{20}$.

In contrast, the magnetic susceptibility of $\text{Ba}_3\text{NaEu}_3\text{Si}_6\text{O}_{20}$ (Figure 5b) exhibits a very different temperature dependence. It increases quasi-linearly with decreasing temperature, forming a broad maximum around 100 K, before rapidly increasing with decreasing temperature below 25 K. This is reminiscent of what has been observed in low-dimensional spin systems with

domain formation.⁴¹ Similar types of deviation compared to other lanthanides have been observed in other europium-based systems, namely in recently published magnetic studies of $\text{Na}_5\text{Eu}(\text{SiO}_4)_4(\text{OH})$ ¹¹ and NaEuGeO_4 .⁴² It has been suggested that this increase in magnetic susceptibility at lower temperatures can be attributed to the presence of a small amount of Eu^{2+} impurity.⁴³ Our analysis of the temperature dependent magnetic susceptibility of $\text{NaBa}_3\text{Eu}_3\text{Si}_6\text{O}_{20}$ at 300 K shows that the magnetic moment is $3.87 \pm 0.02 \mu_B$ per ion, compared to a theoretical value $\mu_{\text{cal}} = 3.40 \mu_B$ per Eu^{3+} . The contrast between the susceptibility behavior of $\text{NaBa}_3\text{Eu}_3\text{Si}_6\text{O}_{20}$ and the other three structurally identical analogs warrants further study by neutron scattering and theoretical studies.

3.3. Photoluminescence studies of $\text{NaBa}_3\text{Eu}_3\text{Si}_6\text{O}_{20}$ and $\text{NaBa}_3\text{Sm}_3\text{Si}_6\text{O}_{20}$

Europium-containing structures are considered to be promising candidates as red phosphor materials due to the strong red emission of Eu^{3+} . Trivalent europium is also of interest due to its sensitivity as a probe of local site symmetry.^{44,45} Figure 6 shows the room temperature emission and excitation (Figure 6, inset) spectra of $\text{NaBa}_3\text{Eu}_3\text{Si}_6\text{O}_{20}$. The use of ground powder samples results in some slight broadening of the observed bands. The excitation spectrum (594 nm emission) is characterized with Eu^{3+} intra-4f⁶ transitions including $^5\text{D}_{1-4} \leftarrow ^7\text{F}_0$, $^5\text{L}_6 \leftarrow ^7\text{F}_0$ and $^5\text{G}_j \rightarrow ^7\text{F}_0$.^{9,10} The emission spectrum was recorded using 532 nm excitation ($^5\text{D}_1 \leftarrow ^7\text{F}_0$) and exhibits several emission bands between 550–750 nm. The presence of two crystallographically unique Eu^{3+} sites in the structure should generate two peaks for the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ emission. The observed splitting within the bands can likely be attributed to the different coordination geometries ($\text{Eu}(1)\text{O}_7$ and $\text{Eu}(2)\text{O}_8$) and the different abundances ($\text{Eu}(1) : \text{Eu}(2)$ is 2:1) of Eu^{3+} sites in the structure. The two Eu^{3+} sites can experience different dipole moments and hence

display bands with different absorption cross sections. Similar behavior has been observed in KEuGe_2O_6 ,⁴⁶ which also exhibits two different Eu^{3+} sites, namely EuO_6 -octahedra and EuO_8 -dodehedra. The greater intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission compared to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ emission is indicative of the lack of a center of symmetry of both europium sites in $\text{NaBa}_3\text{Eu}_3\text{Si}_6\text{O}_{20}$. The Eu(1) sites have no crystallographic site symmetry ($8c$) with $\text{Eu}(1)\text{O}_7$ bond distances ranging from 2.272(6) to 2.533(7) Å, and the Eu(2) sites have two-fold rotational symmetry ($4a$) with $\text{Eu}(2)\text{O}_8$ bond distances ranging from 2.279(6) to 2.715(8) Å.⁷ For comparison, the same transitions have nearly equal integrated intensities in $\text{Cs}_3\text{EuSi}_6\text{O}_{15}$,⁹ indicating that the EuO_6 polyhedron in that structure also lacks a center of symmetry, but is not as strongly distorted ($\text{Eu-O} = 2.27\text{--}2.34$ Å) as we observe in $\text{NaBa}_3\text{Eu}_3\text{Si}_6\text{O}_{20}$. This transition from the more highly distorted Eu(1) and Eu(2) sites in the present study could be useful for obtaining an intense red-emitting phosphor at 605–630 nm.

Figure 6. Room temperature emission spectrum of $\text{NaBa}_3\text{Eu}_3\text{Si}_6\text{O}_{20}$ excited at 532 nm. The inset shows the excitation spectrum obtained using $^7\text{F}_1$ manifold (594 nm emission).

Photoluminescence behavior was also studied in $\text{NaBa}_3\text{Sm}_3\text{Si}_6\text{O}_{20}$. Figure 7 shows the emission spectra obtained at a 404 nm excitation. The emission spectrum of $\text{NaBa}_3\text{Sm}_3\text{Si}_6\text{O}_{20}$ is characterized by major peaks at 564, 567, 600, 607, 647, and 656 nm which can be assigned as intra-4*f*-shell transitions. These peaks can be assigned to $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ (564 and 567 nm), $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ (600 and 607 nm), $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ (647 and 656 nm). The $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ and $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ transitions are the MD allowed transitions while $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ are due to ED allowed transitions. The peak splitting could be due to the crystal field effects and the different Sm geometries.^{47,48} The strongest emission from 404 nm excitation occurred via the $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ transition around 600 nm, corresponding to a visible orange output.

Figure 7. Room temperature emission spectrum of $\text{NaBa}_3\text{Sm}_3\text{Si}_6\text{O}_{20}$ excited at 404 nm. The inset shows the excitation spectrum of obtained using the emission from the $^5\text{G}_{5/2}$ manifold (601 nm emission).

4. Conclusions

This paper describes the synthesis of a series of new sodium barium rare earth silicates whereby sodium ions from the mineralizer become incorporated as part of the silicate lattice along with the barium and rare earth ion. The original concept was to generate new alkaline earth rare earth silicates but we found that the sodium ions are also readily incorporated in the lattice. The rare earths represent a range of ionic radii but the structure is the same in all cases. It is a polar acentric lattice type containing two different building blocks, a conventional disilicate and a unique $[\text{Si}_4\text{O}_{13}]$ tetrasilicate island. The structure further features one-dimensional lanthanide chains that share oxygen edges. The compounds can mostly be prepared as phase pure high quality single crystals enabling further investigation of physical properties including their magnetic and spectroscopic behavior. The magnetism of the various samples was studied, and most demonstrate a weak antiferromagnetic coupling as might be expected. The Eu analog displays unusual magnetic behavior that is not yet fully understood. Visible red and orange emissions have been obtained from Eu^{3+} - and Sm^{3+} -containing species, indicating their potential use as phosphor materials. The dependence of the structure on the sodium and barium ions suggests that many other rare earths silicates await discovery by continuing to manipulate the synthetic chemistry. This systematic variation of the alkali and alkaline earth ions is under investigation.

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