Single crystal growth and characterization of the reduced barium sodium siliconiobate,
 $\text{Ba}_3\text{Na}_{0.32}\text{Nb}_6\text{O}_{12}(\text{Si}_2\text{O}_7)_2$

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Abstract

Single crystals of $\text{Ba}_3\text{Na}_{0.32}\text{Nb}_6\text{O}_{12}(\text{Si}_2\text{O}_7)_2$ were grown for the first time. The use of an alkali/alkaline earth eutectic flux facilitated the crystal growth. $\text{Ba}_3\text{Na}_{0.32}\text{Nb}_6\text{O}_{12}(\text{Si}_2\text{O}_7)_2$, a mixed valent Nb(V)/Nb(IV) compound, crystallizes in the noncentrosymmetric hexagonal space group $P-62m$ with $a = 8.9998(10)$ Å and $c = 7.8119(17)$ Å. The temperature dependence of the magnetic susceptibility was measured and found to be paramagnetic across the entire 2-300 K temperature range measured. Although noncentrosymmetric, $\text{Ba}_3\text{Na}_{0.32}\text{Nb}_6\text{O}_{12}(\text{Si}_2\text{O}_7)_2$ was not found to be second harmonic generation active. $\text{Ba}_3\text{Na}_{0.32}\text{Nb}_6\text{O}_{12}(\text{Si}_2\text{O}_7)_2$ was further characterized by IR and UV/Vis spectroscopies.

1. Introduction

The investigation of complex oxides containing early transition metals in reduced oxidation states remains a relatively unexplored area in materials science due to the difficulty of preparing such materials. Interest in these materials arises from the expectation that the different coordination environments of these early transition metal oxides can promote the formation of new structure types. In addition, the introduction of *d*-electrons, the number of which scales with the degree of reduction, coupled with the extended *d*-orbitals typical for early transition metal oxides, can lead to interesting physical properties including magnetism and/or metallic conductivity.¹⁻³

A limited number of complex reduced niobium oxides have been synthesized, typically via methods that have involved extreme temperatures and/or the use of specialized equipment and techniques for the exclusion of oxygen from the reaction environment.^{4, 5, 6} The most common approach has relied on the use of sealed niobium or tantalum tubes to exclude oxygen from the reaction mixture.⁷⁻⁹ An attractive alternative to metal tubes is the use of fused silica tubes filled with a redox stable flux containing the reagents plus a reducing agent. A number of papers describe such an approach^{4, 10} that, while attractive in theory, does not always succeed in practice. For example, the attempt by Shannon and Katz to prepare a reduced niobate containing Nb(IV) utilizing BaO, Nb₂O₅, Nb metal, and a BaF₂ mineralizer reacted in a sealed, evacuated fused silica tube, resulted in the Nb(V) containing Belkovite-type structure, Ba₃Nb₆O₁₂(Si₂O₇)₂.¹¹ This outcome may well have been a result of the kinetically slow reduction of Nb(V) to Nb(IV) using the high melting point metallic niobium reducing agent. Limited reactant/reducing agent contact does not favor fast kinetics and allows other processes that result in the formation of

complex oxides containing fully oxidized niobium to take place first. The use of a molten (at the reaction temperature) reducing agent can overcome this limitation.

The utilization of molten fluxes is well known as one of the most effective approaches for crystal growth because it lowers the reaction temperature and allows for the dissolution of a wide range of elements and precursors.¹² Careful selection of flux to assure redox stability is an important factor to consider when attempting the preparation of reduced species. Alkali metal chlorides fall into that category and the combined use of such fluxes with a molten reducing agent has enabled our group to prepare a variety of reduced oxides. Specifically the use of molten zinc metal as a reducing agent has been very effective. The operating temperatures for halide fluxes range from 600 to 1100°C, which makes zinc, with its relatively low melting point of 419°C, an attractive reducing agent that will be liquid/gaseous under the reaction conditions.

Using an alkali/alkaline earth halide eutectic melt, we successfully crystallized $\text{Ba}_3\text{Na}_{0.32}\text{Nb}_6\text{O}_{12}(\text{Si}_2\text{O}_7)_2$, a partially reduced siliconiobate, that contains a small amount of Nb(IV). Herein we detail the crystal growth, structure, magnetic and optical properties of the Belkovite-type $\text{Ba}_3\text{Na}_{0.32}\text{Nb}_6\text{O}_{12}(\text{Si}_2\text{O}_7)_2$.

2. Experimental details

2.1 Reagents

$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (Alfa Aesar, 99+%), NaCl (Fisher, ACS grade), and NaNbO_3 (Strem Chemicals, 99.9%) were dried at 260°C for a minimum of 24 hours before use. Zinc powder (Alfa Aesar, 99.9%) was used as received.

2.2 Synthesis

Single crystals of $\text{Ba}_3\text{Na}_{0.32}\text{Nb}_6\text{O}_{12}(\text{Si}_2\text{O}_7)_2$ were grown out of a molten barium chloride/sodium chloride eutectic flux. In a typical procedure, 1.5 mmol of NaNbO_3 (dried at

260°C for 24 hours), 2 mmol of Zn powder, and a 10x excess by weight of BaCl₂/NaCl (dried at 260°C for 24 hours) were placed in a 8'' long fused silica tube of ½'' diameter. The tube was evacuated via a vacuum manifold to a pressure of 10⁻⁴ torr and flame sealed. The tube was heated in a programmable furnace to 1050°C at a rate of 15°C/min, held for 48 hours, and then cooled to 550°C at a rate of 6°C/hr. At this point the furnace was shut off and allowed to cool to room temperature. The chloride flux was dissolved in water aided by sonication. Residual zinc powder was removed via sonication of the product in dilute HCl. The crystals were isolated via vacuum filtration yielding a phase pure product in approximately 75% yield based on NaNbO₃. Figure 1 shows an optical image and a scanning electron microscopy (SEM) image of the crystals. Figure S1 shows a powder X-ray diffraction pattern (PXRD) of ground crystals, demonstrating the phase purity of the product crystals.

2.3 *Energy-dispersive spectroscopy (EDS)*

Elemental analysis was performed on the single crystals using a TESCAN Vega-3 SBU SEM with EDS capabilities. The crystals were mounted on carbon tape and analyzed using a 20 kV accelerating voltage and an accumulation time of 1 minute. As a qualitative measure, EDS confirmed the presence of each reported element in the title compound.

2.4 *Single crystal X-ray diffraction (SXRD)*

X-ray intensity data from a dark blue hexagonal rod crystal were collected at 294(2) K using a Bruker SMART APEX diffractometer (Mo K α radiation, $\lambda = 0.71073$ Å).¹³ Larger crystals appear lustrous black, but are blue in color when thinner. The raw area detector data frames were reduced and corrected for absorption effects with the SAINT+ and SADABS programs.¹³ Final unit cell parameters were determined by least-squares refinement of 6599 reflections from the data set. An initial structural model was obtained with direct methods.

Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2014¹⁴ using the ShelXle interface.¹⁵

The compound crystallizes in the hexagonal system. No pattern of systematic absences was observed in the intensity data, leaving 16 possible space group choices. The non-centrosymmetric group $P-62m$ (No. 189) was eventually confirmed by structure solution and by reference to previously published data. There are nine atomic positions in the asymmetric unit: one barium atom, one niobium atom, one silicon atom, five oxygen atoms and one partially occupied position modeled as sodium. Barium Ba(1) and oxygen O(3) are located on site $3g$, and O(4) on site $3f$, both with $m2m$ site symmetry. Nb(1) and O(2) are located on a mirror plane (site $6i$, $..m$ site symmetry). Si(1) is located on a three-fold axis (site $4h$, $3..$ site symmetry), oxygen O(1) is on a general position, and O(5) is located on site $2c$, with $-6..$ site symmetry. After location and normal refinement of atoms of the $Ba_3Nb_6Si_4O_{26}$ framework described above, a residual electron density peak of magnitude $2.95 \text{ e}^-/\text{\AA}^3$ was observed in the difference map. This peak occupied a chemically sensible location in a cavity bounded by seven oxygen atoms within a range of $2.55 - 3.04 \text{ \AA}$. The next largest residual electron density peak was $0.83 \text{ e}^-/\text{\AA}^3$. The peak was refined as a fractionally occupied sodium atom originating from the reaction flux, as indicated by elemental analysis (EDS) data. The two shortest distances of $2.55 \text{ \AA}$ suggest this atom is not barium. Including this atom in the refinement reduced the R -factors from $R1/wR2 = 0.0213 / 0.0472$ to $0.0193/0.0394$ (all data) and flattened the difference map. All atoms were refined with anisotropic displacement parameters except for the partially occupied sodium. No deviation from full site occupancy was observed for Ba(1), Nb(1) or Si(1). The final absolute structure (Flack) parameter refined to $0.42(2)$, and the structural model was refined as an

inversion twin with this value as the minor twin fraction. Crystallographic data, equivalent atomic positions, and selected interatomic distances are listed in Tables 1-3.

2.5 Powder X-ray diffraction (PXRD)

PXRD data were collected on a Rigaku D/Max-2100 powder X-ray diffractometer using Cu K α radiation. The step scan covered the angular range 5-65° 2 θ in steps of 0.04°. No impurities were observed and the experimental and calculated PXRD patterns are in excellent agreement (see Figure S1).

2.6 UV-vis diffuse reflectance spectroscopy (UVVis)

UV-vis diffuse reflectance spectroscopy data of ground crystals were obtained using a PerkinElmer Lambda 35 UV-Vis scanning spectrophotometer equipped with an integrating sphere accessory in the range of 200-900 nm. Reflectance data were transformed to absorbance via the Kubelka-Munk function.¹⁶

2.7 Infrared spectroscopy (IR)

An IR spectrum of ground crystals was recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer fitted with an ATR accessory in the range of 650-4000 cm⁻¹.

2.8 Magnetic Susceptibility

The magnetic susceptibility was measured using a Quantum Design MPMS 3 SQUID magnetometer. The zero-field cooled magnetic susceptibility was measured as a function of temperature between 2-300K in an applied field of 1000 Oe. The measured magnetic data were corrected for shape and radial offset effects using the method reported by Morrison et al.¹⁷

2.9 Second Harmonic Generation (SHG)

Powder SHG measurements were performed on a modified Kurtz nonlinear-optical (NLO) system using a pulsed Nd:YAG laser with a wavelength of 1064 nm. A comparison with

a known SHG material was made using ground crystalline α -SiO₂. A detailed description of the equipment and methodology has been published elsewhere.^{18, 19}

3. Results and discussion

3.1 Synthesis

Crystals of Ba₃Na_{0.32}Nb₆O₁₂(Si₂O₇)₂ were grown out of a chloride flux, which are known to be redox stable solvents suitable for the crystal growth of reduced oxides.²⁰⁻²² In this work a BaCl₂/NaCl eutectic flux was used to ensure a long liquid range and, furthermore, to function as a source of barium and sodium ions during the crystallization process. Excluding potential oxidizing species, such as oxygen or water, from the reaction is crucial to promote a reducing environment. For this reason the reaction was performed in an evacuated sealed fused silica tube and all reagents except for the zinc powder were dried for 24 hours in an oven at 260°C to exclude water from the reaction. At a dwell temperature of 1050°C, the zinc metal is above its boiling point of 907°C and generates a vapor pressure significant enough to establish a uniform reducing atmosphere within the tube, but not so great as to rupture the fused silica tube.

At elevated temperatures Group 5 oxides are known to attack fused silica and, in this regard, NaNbO₃ serves as a mineralizer for silicon, which is leached from the interior walls of the fused silica tube. It was found that the addition of dry, powdered SiO₂ as a more finely divided source of silicon in fact worsened the yield and crystal quality of the product. We postulate that the slow dissolution of silicon from the interior wall of the fused silica tube allows for a more controlled crystallization, which results in a phase pure sample. The PXRD pattern of the ground crystals, shown in Figure S1, is in excellent agreement with the powder pattern calculated from single crystal data, confirming the phase purity of the sample. Attempts to crystallize compositions with higher sodium content were unsuccessful.

3.2 Structure

The structure of $\text{Ba}_3\text{Na}_{0.32}\text{Nb}_6\text{O}_{12}(\text{Si}_2\text{O}_7)_2$ is based on the Belkovite structure type which exhibits a three dimensional crystal structure consisting of corner- or edged-sharing BaO_{10} , NbO_6 , and SiO_4 polyhedra that form a siliconiobate framework with barium cations residing within large cavities of the framework.¹¹ This structure is similar to the known hexagonal tungsten bronzes, which contain a framework of corner-sharing tungsten polyhedra with alkali cations residing in channels within the structure.²³ In $\text{Ba}_3\text{Na}_{0.32}\text{Nb}_6\text{O}_{12}(\text{Si}_2\text{O}_7)_2$, additional smaller cavities exist in the framework that cannot accommodate a large barium cation and are unoccupied in the fully oxidized structure. In $\text{Ba}_3\text{Na}_{0.32}\text{Nb}_6\text{O}_{12}(\text{Si}_2\text{O}_7)_2$, fractionally occupied NaO_7 polyhedra reside in these smaller cavities. The barium and sodium cavities stack in an alternating AB sequence down the c axis and are easily distinguished when viewing the structure along the c axis, as shown in Figure 2. By doping in positive charge in the form of Na^+ , we are able to partially reduce the Nb(V) to Nb(IV). As sodium is significantly smaller than barium, its presence does not significantly alter the unit cell parameters, which are consistent with those of the fully oxidized structure.^{11, 24} Ba(1) is located in a ten coordinate distorted pentagonal prism, shown in Figure 3, with Ba-O distances between 2.864 Å – 3.122 Å. Ba(1) shares edges with itself, Si(1), and Nb(1) through O(1) and O(2). Ba(1) also shares a corner with the fractionally occupied Na(1) through O(2). Nb(1) is located in a six coordinate distorted octahedron, shown in Figure 4, with Nb-O distances between 1.935 Å – 2.041 Å. Nb(1) shares corners with itself through O(2) forming Nb_3O_{15} trimeric clusters, shown in Figure 5, and with itself through O(4) forming columns of trimeric clusters, shown in Figure 6. These trimeric columns are linked via Si(1) with corner sharing through O(1). Nb(1) also shares a corner with fractionally occupied Na(1) through O(2). Si(1) is located in a four coordinate tetrahedral coordination environment

with Si-O distances ranging from 1.603 Å – 1.622 Å. Si(1) shares a corner with itself through O(5) forming pyrosilicate groups, shown in Figure 7. Si(1)O₄ tetrahedra share an edge with Ba(1) and Nb(1) through O(1) and corner shares with fractionally occupied Na(1). Na(1) is fractionally occupied in a seven coordinate irregular coordination environment, shown in Figure 8, with Na-O distances ranging from 2.550 Å – 3.103 Å. The Na(1)O₇ polyhedron shares corners with Ba(1), Nb(1), and Si(1) through O(2), O(4), and O(5), respectively, and edges with Nb(1) through O(2) and O(4). Na(1) resides in cavities that are empty in the fully oxidized parent compound Ba₃Nb₆O₁₂(Si₂O₇)₂. As a consequence of this sodium doping, a small but not negligible amount of the niobium in Ba₃Na_{0.32}Nb₆O₁₂(Si₂O₇)₂ must be reduced from +5 to +4. The blue color of the compound provides evidence for this, as previously reported mixed Nb^{+4/+5} compounds are often blue. Based on the chemical composition of the title compound, the average oxidation state for niobium is +4.94 with 94.67% Nb(V) and 5.33% Nb(IV).

3.3 *UV-vis diffuse reflectance spectroscopy (UV/Vis)*

UV-Vis absorbance data shown in Figure 9 were collected using ground crystals. The absorption edge is clearly observed in the UV region, and the band gap estimated by the onset of the absorption edge is approximately 3.4 eV, indicating insulating behavior for the siliconiobate. A broad absorbance ranging from 900 nm – 400 nm is observed, with a maximum at 882 nm and shoulders at approximately 560 nm and 450 nm, that is consistent with the presence of Nb(IV) based on reports in the literature describing the UV-Vis absorption of niobium(IV) containing compounds.²⁵

3.4 *Infrared spectroscopy (IR)*

The IR spectrum, which is shown in the supplemental information section, Figure S2, was collected between 650 – 4000 cm⁻¹. The bands between 1200 cm⁻¹ – 850 cm⁻¹ correspond to

asymmetric Si – O – Si stretching modes and symmetric and asymmetric stretching modes of SiO₃.²⁶ The band observed at 736 cm⁻¹ corresponds to the NbO₆ symmetric stretching mode.²⁶

3.5 Magnetic Susceptibility

The unpaired electrons in Ba₃Na_{0.32}Nb₆O₁₂(Si₂O₇)₂ can be observed in magnetic susceptibility measurements. The temperature dependence of the magnetic susceptibility of Ba₃Na_{0.32}Nb₆O₁₂(Si₂O₇)₂ measured in an applied field of 1000 Oe is shown in Figure 10. In Ba₃Na_{0.32}Nb₆O₁₂(Si₂O₇)₂ the amount of Nb(IV) is small and is therefore magnetically dilute, thus no magnetic coupling is expected or observed. Down to 2K, the data do not reveal any long-range magnetic order and follow the Curie-Weiss (C-W) law as expected for simple paramagnetic species. The magnetic moment calculated from the inverse susceptibilities is 1.75 μ_B/mol Nb(IV), which is in good agreement with the expected spin only value for Ba₃Na_{0.32}Nb₆O₁₂(Si₂O₇)₂ of 1.73 μ_B/mol Nb(IV).²⁷

3.6 Second Harmonic Generation (SHG)

Although Ba₃Na_{0.32}Nb₆O₁₂(Si₂O₇)₂ belongs to the noncentrosymmetric space group *P*-62*m*, no detectable SHG response was observed when measuring a ground polycrystalline sample.

4. Conclusion

We successfully synthesized a new barium sodium siliconiobate, Ba₃Na_{0.32}Nb₆O₁₂(Si₂O₇)₂ via a molten salt flux technique and characterized its structure and physical properties. By utilizing a flux containing sodium we were able to fractionally dope sodium into cavities that remain empty in the fully oxidized parent compound, Ba₃Nb₆O₁₂(Si₂O₇)₂. Niobium in this structure is slightly reduced with an average oxidation state of +4.94 and a Nb(IV) content of 5.33%. As a result of the diluteness of the Nb(IV) in the

compound, only simple paramagnetic behavior is observed. The agreement of the experimental and theoretical magnetic moments confirms the presence and quantity of Nb(IV) in the structure.

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Table 1. Crystallographic data for Ba₃Na_{0.32}Nb₆O₁₂(Si₂O₇)₂

Formula	Ba ₃ Na _{0.32} Nb ₆ O ₁₂ (Si ₂ O ₇) ₂
Formula Weight	1505.25
Color and habit	Dark blue hexagonal rod
Crystal System	Hexagonal
Space group	<i>P</i> -62 <i>m</i>
Temperature (K)	294(2)
<i>a</i> (Å)	8.9998(10)
<i>c</i> (Å)	7.8119(17)
Volume (Å ³)	547.96(17)
<i>Z</i>	1
ρ_c (g/cm ³)	4.561
μ (mm ⁻¹)	8.660
<i>F</i> (000)	682
Crystal size (mm)	0.120 × 0.080 × 0.080
2 θ range (°)	2.607 – 35.427
Index ranges	-14 ≤ <i>h</i> ≤ 14, -13 ≤ <i>k</i> ≤ 14, -12 ≤ <i>l</i> ≤ 11
Reflections collected	15798
Independent reflections	953 [R(int) = 0.0321]
GOF (<i>F</i> ²)	1.179
<i>R</i> (<i>F</i>) ^{<i>a</i>}	0.0189
<i>R_w</i> (<i>F_o</i> ²) ^{<i>b</i>}	0.0381
Flack parameter	0.42(2)
Largest diff. peak and hole (e Å ⁻³)	0.813 and -1.105
^{<i>a</i>} <i>R</i> (<i>F</i>) = $\Sigma F_o - F_c /\Sigma F_o $. ^{<i>b</i>} <i>R_w</i> (<i>F_o</i> ²) = $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.	

Table 2. Atomic Coordinates and equivalent isotropic displacement parameters *U*_{eq} for Ba₃Na_{0.32}Nb₆O₁₂(Si₂O₇)₂. *U*_{eq} is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

	Occupancy	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Ba(1)	1	0.6006(1)	0	½	0.011(1)
Nb(1)	1	0.2376(1)	0	0.2440(1)	0.015(1)
Si(1)	1	⅓	⅔	0.2051(2)	0.007(1)
O(1)	1	0.1815(3)	0.4881(3)	0.2838(3)	0.011(1)
O(2)	1	0.8194(4)	0	0.2336(4)	0.010(1)
O(3)	1	0.2259(6)	0	½	0.013(1)
O(4)	1	0.2768(6)	0	0	0.012(1)
O(5)	1	⅓	⅔	0	0.018(1)
Na(1)	0.107	0.6210(30)	0	0	0.010(7)

Table 3. Selected interatomic distances (Å) for $\text{Ba}_3\text{Na}_{0.32}\text{Nb}_6\text{O}_{12}(\text{Si}_2\text{O}_7)_2$.

Ba(1)-O(1) x 4	2.864(3)	Si(1)-O(5)	1.6025(16)
Ba(1)-O(2) x 2	2.865(4)	Si(1)-O(1) x 3	1.622(3)
Ba(1)-O(1) x 4	2.984(3)	Na(1)-O(2) x 2	2.550(19)
Nb(1)-O(2) x 2	1.9352(12)	Na(1)-O(5) x 2	2.819(10)
Nb(1)-O(4)	1.9385(12)	Na(1)-O(4) x 2	3.054(19)
Nb(1)-O(3)	2.0027(8)	Na(1)-O(4)	3.10(3)
Nb(1)-O(1) x 2	2.041(3)		

Figure 1. Optical image of $\text{Ba}_3\text{Na}_{0.32}\text{Nb}_6\text{O}_{12}(\text{Si}_2\text{O}_7)_2$ grown out of a barium chloride/sodium chloride melt and SEM image of $\text{Ba}_3\text{Na}_{0.32}\text{Nb}_6\text{O}_{12}(\text{Si}_2\text{O}_7)_2$.

Figure 2. A. $\text{Ba}_3\text{Na}_{0.32}\text{Nb}_6\text{O}_{12}(\text{Si}_2\text{O}_7)_2$ viewed down the c axis. B. $\text{Ba}_3\text{Na}_{0.32}\text{Nb}_6\text{O}_{12}(\text{Si}_2\text{O}_7)_2$ viewed along the c axis. Ba, Na, Nb, Si, and O shown in pink, yellow, cyan, blue, and red, respectively. Fractional Na shown in full occupancy in figure for clarity. Unit cell shown as black solid line.

A.

B.

Figure 3. Local coordination environment of Ba(1). Ba, Na, Nb, Si, and O shown in pink, yellow, cyan, blue, and red, respectively.

Figure 4. Local coordination environment of Nb(1). Ba, Na, Nb, Si, and O shown in pink, yellow, cyan, blue, and red, respectively.

Figure 5. Nb_3O_{15} trimeric cluster. Nb and O shown in cyan and red, respectively.

Figure 6. Column of stacked Nb_3O_{15} trimeric clusters. Nb and O shown in cyan and red, respectively.

Figure 7. Local coordination environment of $\text{Si}(1)_2\text{O}_7$ pyrosilicate group. Ba, Na, Nb, Si, and O shown in pink, yellow, cyan, blue, and red, respectively.

Figure 8. Local coordination environment of Na(1). Ba, Na, Nb, Si, and O shown in pink, yellow, cyan, blue, and red, respectively.

Figure 9. UV/Vis absorbance spectrum for $\text{Ba}_3\text{Na}_{0.32}\text{Nb}_6\text{O}_{12}(\text{Si}_2\text{O}_7)_2$.

Figure 10. Magnetic susceptibility plot for $\text{Ba}_3\text{Na}_{0.32}\text{Nb}_6\text{O}_{12}(\text{Si}_2\text{O}_7)_2$. χ and $1/\chi - \chi_0$ are shown in blue and red, respectively.