Influence of Rare Earth Cation size on the Crystal Structure in Rare Earth Silicates, $\text{Na}_2\text{RESiO}_4(\text{OH})$ (RE = Sc, Yb) and NaRESiO_4 (RE = La, Yb)

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Abstract

Crystals of $\text{Na}_2\text{ScSiO}_4(\text{OH})$ and $\text{Na}_2\text{YbSiO}_4(\text{OH})$ were synthesized at low temperatures using a sodium hydroxide based hydroflux, while crystals of NaLaSiO_4 and NaYbSiO_4 were grown at high temperatures using a sodium fluoride/sodium chloride eutectic flux. Both structure types were crystallized under reaction conditions that, when used for medium sized rare earths ($\text{RE} = \text{Pr}, \text{Nd}, \text{Sm} - \text{Tm}$) yield the $\text{Na}_5\text{RE}_4\text{X}[\text{SiO}_4]_4$, structure type, where X is OH in the hydroflux conditions and F in the eutectic flux conditions. Herein, we report the synthesis, structure, size effect, and magnetic properties of these compositions and introduce the new structure type of $\text{Na}_2\text{RESiO}_4(\text{OH})$, which crystallizes in the orthorhombic space group $Pca2_1$, of NaLaSiO_4 , which crystallizes in the orthorhombic space group $Pna2_1$, and of NaYbSiO_4 , which crystallizes in the orthorhombic space group $Pnma$, where both NaRESiO_4 compounds have one silicon structural analog.

Keywords

- $\text{Na}_2\text{RESiO}_4(\text{OH})$
- Hydroflux
- NaRESiO_4
- Crystal flux growth
- Single crystal

1. Introduction

Silicates are an expansive class of extended structures that are based on linked SiO_4 tetrahedral building blocks and that encompass many diverse compositions [1-6] including numerous examples of complex rare earth containing silicate structures. The presence of rare earth elements in the silicate structure can lead to interesting optical [5,7-10] and magnetic [4,11-14] properties. Furthermore, a unique feature of the rare earth silicates is the existence of a series of structural analogs and, at times, new structure types when a rare earth cation size limit is reached above or below the point at which a given structure ceases to form. Identifying such structural limits and exploring all the diverse structures that form for the rare earth group can lead to improved understanding of the overall crystal chemistry of silicates. While each case is unique, one can state that, in general, the rigidity of the crystal structure controls the size range of lanthanides that can be incorporated. Some structures, such as $\text{Na}_5\text{RE}_4\text{X}[\text{SiO}_4]_4$ ($\text{RE} = \text{Pr, Nd, Sm-Yb, Y; X} = \text{F, OH}$), are not very rigid and their rare earth coordination environment site is capable of accommodating a wide range of rare earths extending in size from 0.985 Å (Yb) to 1.126 Å (Pr) [13,15,16]. Other silicate structures that have a more rigid framework structure are often limited to only a small sub-set of rare earths and the structure tends to change when the next sized rare earth falls outside the size range that can be accommodated. Often, this results in a new composition at the same time.

The synthesis of new silicates can be accomplished by a number of methods, including solid-state reactions to obtain polycrystalline samples and solution based routes to obtain single crystals. For the latter case fluoride containing fluxes have been shown to be very effective means of dissolving SiO_2 as well as rare earth oxides to produce rare

earth containing compositions [12,17,18]. When using fluoride-containing fluxes with rare earths and silica, products are usually rare earth silicate oxides or oxyfluorides. For the particular system discussed in this paper, the large and small rare earths tend to form oxides, while the middle-sized rare earths tend to form oxyfluorides.

The hydroflux method is another approach to create single crystals, albeit one that operates in a much lower temperature regime. This new technique encompasses the best of many crystal growth techniques. By operating at a low temperature (180 °C – 240 °C) [13,15,19-24] and a low pressure, this technique allows for the preparation of materials that are stable only at low temperatures and that could not be obtained via the more traditional high temperature flux growth [17]. In addition, this method does not have the high pressure concerns found in traditional hydrothermal growth methods. The hydroflux occupies a place in the compositional regime that is between a wet flux and an aqueous solution, where its acid base properties are controlled by the Lux-Flood concept of oxo-acidity [25,26] and where unique compositions can be isolated as single crystals.

Herein we present the use of both the hydroflux method and the fluoride flux crystal growth approach for the synthesis of new complex rare earth silicates, NaLaSiO₄, NaYbSiO₄, Na₂YbSiO₄(OH), and Na₂ScSiO₄(OH), and discuss the effect of both the crystal growth temperature/method and the rare earth cation size on the structures that are obtained.

2. Experimental Section

2.1. Sample preparation

2.1.1. Materials preparation

Sc_2O_3 (>99%) was purchased from Aran Isles Chemical Inc., Yb_2O_3 and La_2O_3 (99.9%) were purchased from Alfa Aesar, NaOH (ACS grade) was purchased from Fisher Scientific, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (99+%) was purchased from EM Science, NaF (99% min.) was purchased from Alfa Aesar, and NaCl (99.9%) was purchased from Fisher Scientific. SiO_2 (99.99%) was purchased from Aldrich as fused pieces and ground to a powder in a ball mill.

2.1.2. Single crystals

$\text{Na}_2\text{RESiO}_4(\text{OH})$ ($\text{RE} = \text{Sc}, \text{Yb}$)

Crystals of $\text{Na}_2\text{ScSiO}_4(\text{OH})$ and $\text{Na}_2\text{YbSiO}_4(\text{OH})$ were grown in 23 mL polytetrafluoroethylene (PTFE)-lined stainless steel autoclaves by utilizing an NaOH hydroflux. For $\text{Na}_2\text{ScSiO}_4(\text{OH})$, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (1.91 mmol), Sc_2O_3 (1.03 mmol), NaOH (9.68 g), and deionized water (8.5 g) were loaded into a PTFE liner that was placed into a steel autoclave before being placed into a programmable oven that was ramped at 5 °C/min to 230 °C and held for 48 h before slow cooling to 80 °C at a rate of 0.1 °C/min. After reaching 80 °C, the oven was shut off. For $\text{Na}_2\text{YbSiO}_4(\text{OH})$, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (1.86 mmol), Yb_2O_3 (0.975 mmol), NaOH (9.24 g), deionized water (8.17 g), and WO_3 (1.1 mmol), which acted as a mineralizer, were added to a PTFE liner that was loaded into a steel autoclave that was placed into a programmable oven that was ramped at a rate of 5 °C/min. to 230 °C, where it dwelled for 48 h. After the dwelling period, the reaction was

quenched by removing it from the oven between 200 – 230 °C. If the reaction was pulled out after the flux had cooled below 200 °C, an impurity of YbO(OH) was consistently observed. Reactions quenched between 200 – 230 °C yielded phase pure crystals, albeit twinned, with no difference observed between different quenching temperatures above 200 °C. The crystals from these reactions were gently scraped from the inside of the PTFE liners and sonicated in methanol to remove the flux before being collected via vacuum filtration and then dried.

NaRESiO₄ (RE = La, Yb)

Crystals of NaLaSiO₄ were synthesized by loading La₂O₃ (1 mmol), Na₂CO₃ (1 mmol), and SiO₂ (2 mmol) into a silver crucible. The eutectic flux of NaF (1.41 g) and NaCl (0.96 g) was placed on top of the reactants. The crucible was then loosely fitted with a silver lid and placed into a programmable furnace that was programmed to ramp in 1.5 h to 900 °C where it dwelled for 48 h before slow cooling to 650 °C at a rate of 3 °C/h before the furnace was shut off. The flux was washed away by sonication in water to yield crystals of NaLaSiO₄.

Crystals of NaYbSiO₄ were synthesized by loading Yb₂O₃ (2 mmol), Na₂CO₃ (2 mmol), and SiO₂ (4 mmol) into a silver crucible. The eutectic flux of NaF (2.80 g) and NaCl (1.93 g) was added on top of the reactants. The crucible was loosely fitted with a silver lid and placed into a programmable furnace that was programmed to ramp in 1.5 h to 800 °C where it dwelled for 24 h before slow cooling to 600 °C at a rate of 6 °C/h. After reaching 600 °C, the furnace was shut off. Crystals were isolated by sonication in water to wash away the flux. The NaYbSiO₄ phase was the major product, with a minor amount of a second new ytterbium containing composition, Na₃YbSi₂O₇.

2.2 Characterization

2.2.1 Single Crystal X-ray Diffraction

Structure determinations were performed using single crystal X-ray intensity data from a colorless needle crystal [Na₂YbSiO₄(OH)], a colorless octahedral crystal [Na₂ScSiO₄(OH)], a colorless needle crystal [NaLaSiO₄], and a colorless rectangular block crystal [NaYbSiO₄]. The X-ray data of Na₂YbSiO₄(OH), Na₂ScSiO₄(OH), and NaYbSiO₄ were collected using a Bruker SMART APEX diffractometer (Mo K α radiation, $\lambda = 0.71073$ Å) [27] and the X-ray data from NaLaSiO₄ were collected using a Bruker D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an Incoatec microfocus source (Mo K α radiation, $\lambda = 0.71073$ Å) [28]. The raw area detector data frames were reduced and corrected for absorption effects using the SAINT+ and SADABS programs [27]. Final unit cell parameters were determined by least-squares refinement of large sets of reflections from the data sets. The initial structural models were obtained by direct methods using SHELXS [29]. Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2013/4 [29] using the ShelXle interface. The final structural models were checked for missed symmetry elements using the ADDSYM program in PLATON [30-33], which found no missed symmetry in any case.

NaLaSiO₄ crystallizes in the orthorhombic system. The space groups $Pna2_1$ and $Pnma$ were consistent with the pattern of systematic absences in the intensity data. The acentric group $Pna2_1$ was eventually determined to be correct by structure solution. NaYbSiO₄ also crystallizes in the orthorhombic system. The space groups $Pnma$ and $Pna2_1$ were consistent with the pattern of systematic absences in the intensity data. The

centrosymmetric group *Pnma* was confirmed by structure solution. For $\text{Na}_2\text{RESiO}_4(\text{OH})$, the compounds crystallize in the polar space group *Pca2₁* as determined by the pattern of systematic absences in the intensity data and by structure solution.

For $\text{Na}_2\text{RESiO}_4(\text{OH})$ the two unique hydrogen (hydroxyl) atoms necessary for crystal electroneutrality could not be reliably located or refined. They are presumably bonded to the two unique non-silicate oxygen atoms O9 and O10. Small residual electron density peaks were observed near the two oxygens, but did not give acceptable positional or displacement parameters, even with restraints applied. A soft restraint (SHELX ISOR instruction) was applied to the displacement parameters of one oxygen atom (O3) to prevent an oblate ellipsoid shape. The reason for this is not clear, but may be due to minor positional disorder of the silicate group [Si1/O1-O4] around the Si1-O4 bond, as the displacement ellipsoids for O1 and O2 are also slightly oblate. The absolute structure (Flack) parameter near convergence for the $\text{Na}_2\text{YbSiO}_4(\text{OH})$, $\text{Na}_2\text{ScSiO}_4(\text{OH})$, and NaLaSiO_4 compounds refined to 0.41(2), 0.49(10), and 0.50(2) respectively, indicating the data crystals are two-component inversion twins. An inversion twin law was included in the final refinement cycles.

2.2.2 Magnetic Property Measurements

The DC magnetic susceptibilities of $\text{Na}_2\text{YbSiO}_4(\text{OH})$ and NaYbSiO_4 were measured as a function of temperature using a Quantum Design MPMS 3 SQUID Magnetometer. 82.39 mg of a ground polycrystalline powder of $\text{Na}_2\text{YbSiO}_4(\text{OH})$ and 52.70 mg of a mixed ground polycrystalline powder of NaYbSiO_4 and $\text{Na}_3\text{YbSi}_2\text{O}_7$, the second new ytterbium containing composition mentioned earlier, were massed on a balance sensitive to 0.01 mg and loaded into a gelatin capsule for data collection. Zero-

field-cooled conditions from 2 – 300 K in an applied field of 1000 Oe were used to measure the temperature dependent susceptibilities of the samples. The raw magnetic moments were corrected for sample shape and radial offset effects using the method outlined by Morrison and zur Loye [34].

3. Results and Discussion

3.1 Structure Description

$Na_2ScSiO_4(OH)$ and $Na_2YbSiO_4(OH)$ crystallize in a new structure type in the orthorhombic space group $Pca2_1$. Within the structure are two unique silicon environments, two unique rare earth environments, four sodium environments, and ten oxygen environments. Both silicon environments result in isolated SiO_4 units that are corner shared to two RE(1) and to two RE(2) octahedra. Both rare earth environments consist of REO_6 octahedra that corner share to two Si(1) tetrahedra, two Si(2) tetrahedra, and to two of the other rare earth octahedra (**Figure 1**). The oxygen sites O(9) and O(10), which make up the corner-shared sites of the RE octahedra, are presumed to be the location of the hydroxyl groups. Na(1), Na(2), Na(3), and Na(4) sit in the channels between O(1), O(7), O(3), and O(6), respectively, where O(1) corner shares Si(1) and RE(2) polyhedra, O(7) corner shares Si(2) and RE(1) polyhedra, O(3) corner shares Si(1) and RE(2), and O(6) corner shares Si(2) and RE(1). The overall structural representation is shown in **Figure 2**, relevant crystallographic information is listed in **Table 1**, and rare earth – oxygen interatomic distances are collected in **Table 2**.

NaYbSiO₄ crystallizes in the orthorhombic space group *Pnma* in a structure type that is similar to one observed for the many other compositional analogs of this structure type, such as germanates. Known NaRETO₄ (RE = rare earth, T = tetragen) examples include NaREGeO₄ (RE = Sm-Tb, Ho-Lu) [35-37] and NaRESiO₄ (RE = La [38], Nd [39], Sm [40], Gd [41,42], Ho [39], Er [39], Lu [39,43], Y [44,45]), where the germanate examples crystallize in the orthorhombic space group *Pnma*, while the silicon examples are reported to crystallize in the orthorhombic space groups *Pmcn* (La), *Pna2₁* (Nd), *Pmnb* (Gd [42]), *Pbn2₁* (Er, Lu [39], Y [44]), *Pc2_{1n}* (Y [45]), and *Pnma* (Lu [43]), and in the tetragonal space group *I4/m* (Sm, Gd [41], Ho) . Since *Pmcn* and *Pmnb* are non-standard settings of *Pnma*, NaLaSiO₄, NaGdSiO₄, and a polymorph of NaLuSiO₄ crystallize in the same space group as the reported NaYbSiO₄.

NaYbSiO₄ crystallizes in the space group *Pnma* in the olivine structure type. As expected, it is isostructural with the known germanates. The structure contains one unique sodium, one unique silicon, one unique ytterbium, and three unique oxygen environments. The Yb atoms are located in a distorted YbO₆ octahedra that corner shares with other YbO₆ octahedra and corner and edge share to SiO₄ tetrahedra (**Figure 3**). The SiO₄ tetrahedra are isolated from each other and contribute to the overall structure only via corner and edge sharing with YbO₆ octahedra, which transforms the two-dimensional sheets of the Yb polyhedra along the *a* axis to a three-dimensional structure (**Figure 4**) while the sodium atoms fill the channels between the ytterbium and silicon polyhedra as shown in **Figure 5**. **Figure 4** shows the overall structure down the *c* axis. The relevant crystallographic information is listed in **Table 1**, and ytterbium – oxygen interatomic distances are collected in **Table 3**.

NaLaSiO₄

NaLaSiO₄ crystallizes in the space group *Pna*2₁, which is similar to the previously reported NaNdSiO₄, NaErSiO₄, and a polymorph of NaLuSiO₄ where the Er and Lu analogues are reported in the space group *Pbn*2₁, which is a non-standard setting of the space group *Pna*2₁ [39]. In this structure there are three unique lanthanum sites, three unique silicon sites, three unique sodium sites, and twelve unique oxygen sites. All three La sites are 8 CN where all are edge and corner shared to isolated SiO₄ units, and all are corner and face shared with other La polyhedra. The La polyhedra form face shared columns down the *a* axis where the columns corner share with each other, making it look as though the columns are overlapped when looking down the *c* axis (**Figure 6**). The Si form isolated SiO₄ units and the sodium atoms fill the channels in the structure where the Na(1) atoms sit in line with the Si(3) atoms down the *a* axis, the Na(2) atoms sit in line with the Si(2) atoms down the *a* axis, and the Na(3) atoms sit in line with the Si(1) atoms down the *a* axis. The relevant crystallographic information is listed in **Table 1**, and lanthanum – oxygen interatomic distances are collected in **Table 4**. Overall structural views down the *a* and *c* axis are shown in **Figures 7** and **8**, respectively.

Figure 9 depicts the range of synthetic conditions under which the different complex rare earth silicates can be synthesized. From the figure it is clear that both temperature and rare earth cation size play important roles in determining the structure that forms. It is interesting to note that for the middle range of rare earth cation radii, the Na₅RE₄X[SiO₄]₄ structure type forms, as the oxyfluoride when crystallized out of high temperature fluoride fluxes and as the oxyhydroxide when crystallized out of a low temperature hydroflux. Furthermore, the Na₅RE₄X[SiO₄]₄ structures are bracketed by

four other structure types for larger and for smaller rare earth cations: $\text{Na}_2\text{RESiO}_4(\text{OH})$ and NaLaSiO_4 for larger cations at low and high synthesis temperatures, respectively, and $\text{Na}_2\text{RESiO}_4(\text{OH})$ and NaRESiO_4 for smaller cations at low and high synthesis temperatures, respectively.

In this study we found that the fluoride/chloride eutectic flux growth conditions that yield the $\text{Na}_5\text{RE}_4\text{F}[\text{SiO}_4]_4$ structure for $\text{RE} = \text{Pr, Nd, Sm-Tm}$, surprisingly resulted in the formation of the NaRESiO_4 structure for $\text{RE} = \text{La, Yb, Lu}$ [43], for the larger and smaller rare earths, while the hydroflux and hydrothermal growth reaction conditions that form the $\text{Na}_5\text{RE}_4(\text{OH})[\text{SiO}_4]_4$ structure for $\text{RE} = \text{Pr, Nd, Sm-Yb, Y}$, unexpectedly resulted in the formation of the $\text{Na}_2\text{RESiO}_4(\text{OH})$ structure for $\text{RE} = \text{La}$ [46], Yb, Sc , for the larger and smaller rare earths, respectively. It should be noted that for the reported conditions and compositions, as a function of rare earth size, different structure types occur for larger and smaller rare earths with the NaRESiO_4 structure adopting the $Pna2_1$ space group for larger rare earths and adopting the $Pnma$ space group for smaller rare earths and the $\text{Na}_2\text{RESiO}_4(\text{OH})$ structure adopting the $Pnma$ space group for the larger rare earths and adopting the $Pca2_1$ space group for the smaller rare earths.

3.2 Magnetic Properties

The magnetic data of $\text{Na}_2\text{YbSiO}_4(\text{OH})$ and NaYbSiO_4 are summarized in **Table 5**. The NaYbSiO_4 sample used for the collection of the magnetic susceptibility data contained roughly a quarter of a second ytterbium silicate phase, $\text{Na}_3\text{YbSi}_2\text{O}_7$, to be reported on in detail in the near future. The magnetic data were corrected for the presence of the 2nd phase by determining the exact phase fraction, 75.2 % NaYbSiO_4 and 24.8 % of $\text{Na}_3\text{YbSi}_2\text{O}_7$, by analyzing powder X-ray diffraction data using the JADE

software package. The magnetic susceptibilities and the inverse susceptibilities for both compounds are shown in **Figure 10**. The samples are paramagnetic and the inverse susceptibilities were fit over the range of 100 – 300 K using the modified Curie-Weiss law $\chi = \chi_0 + C/(T-\theta)$, where χ is susceptibility, χ_0 is the temperature independent susceptibility, C is the Curie constant, and θ is the Weiss temperature. The χ_0 values from the fit (**Table 5**) were positive, as has previously been reported for ytterbium containing compounds, where the positive values were thought to arise from crystal field effects in the ytterbium [47,48]. The fit to the inverse magnetic susceptibility yielded effective moments of 4.20 μ_B for Na₂YbSiO₄(OH) and 4.18 μ_B for the NaYbSiO₄ mixed sample.

4. Conclusion

The new compositions Na₂YbSiO₄(OH) and Na₂ScSiO₄(OH) were synthesized using the hydroflux crystal growth method, while NaLaSiO₄ and NaYbSiO₄ were prepared using a traditional high temperature fluoride/chloride eutectic flux. Interestingly, these compositions all grow under the same conditions used to synthesize Na₅RE₄X[SiO₄]₄ (RE = Pr, Nd, Sm-Yb, Y; X = OH, F) indicating the substantial influence of rare earths size effects in silicate systems. Paramagnetic behavior was observed for both Yb analogues.

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Graphical Abstract

Figure 1. Visual representation of the two REO₆ octahedra and mode of octahedra corner sharing in Na₂ScSiO₄(OH), where RE(1) is represented in green, RE(2) is in orange, silicon is in blue, and oxygens are in red.

Figure 2. Overall representation of the structure of Na₂ScSiO₄(OH) where RE(1) are green, RE(2) are orange, Na are purple, silicon are blue, and oxygens are red.

Figure 3. Illustration of NaYbSiO₄ highlighting the edge- and corner-sharing of the SiO₄ tetrahedra to the REO₆ octahedra.

Figure 4. Structural image of NaYbSiO₄, which highlights the overall olivine structure down the *c* axis. Ytterbium is shown in orange, silicon is shown in blue, and sodium is shown in purple.

Figure 5. Visual representation of NaYbSiO₄ illustrating how the sodium atoms (purple) fill the channels created by the REO₆ octahedra (orange) and SiO₄ tetrahedra (blue).

Figure 6. Structural image of NaLaSiO₄ where the La columns along the *c* axis are shown. La polyhedra are shown in orange, Si is shown in blue, Na is shown in purple, and O is shown in red.

Figure 7. Structural representation of NaLaSiO₄ down the *a* axis where the color scheme is the same as Figure 6.

Figure 8. Structural representation of NaLaSiO₄ showing the structure down the *c* axis where the color scheme follows the one detailed in Figure 6.

Figure 9. Scheme to organize the reported phases based on their synthesis conditions and as a function of rare earth cation size.

Figure 10. Magnetic susceptibility and inverse magnetic susceptibility data of $\text{Na}_2\text{YbSiO}_4(\text{OH})$ (top) and NaYbSiO_4 (bottom).

Table 1. Crystallographic data for Na₂RESiO₄(OH) (RE = Sc, Yb) and NaRESiO₄ (RE = La, Yb).

Formula	Na ₂ ScSiO ₄ (OH)	Na ₂ YbSiO ₄ (OH)	NaLaSiO ₄	NaYbSiO ₄
Formula weight	200.04	328.12	253.99	288.12
Temperature (K)	296(2)	296(2)	301(2)	296(2)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>Pca</i> 2 ₁	<i>Pca</i> 2 ₁	<i>Pna</i> 2 ₁	<i>Pnma</i>
<i>a</i> (Å)	13.6153(7)	13.9074(5)	21.4726(10)	11.0329(3)
<i>b</i> (Å)	5.4215(3)	5.5366(2)	9.4441(4)	6.3536(2)
<i>c</i> (Å)	12.1083(7)	12.4876(5)	5.5008(3)	5.1054(2)
<i>V</i> (Å ³)	893.78(9)	961.54(6)	1115.50(9)	357.88(2)
<i>Z</i>	8	8	12	4
Density (Mg/m ³)	2.973	4.533	4.537	5.347
Absorption coefficient (mm ⁻¹)	2.027	19.806	11.786	26.440
Crystal size (mm ³)	0.06 x 0.06 x 0.05	0.08 x 0.03 x 0.02	0.05 x 0.04 x 0.01	0.08 x 0.040 x 0.03
2 theta range (°)	5.98 to 65.19	5.86 to 65.29	4.71 to 80.68	7.388 to 70.466
reflections collected	26026	27619	88663	9114
data/restraints/parameters	3246 / 1 / 164	3503 / 7 / 164	7027 / 1 / 192	860 / 0 / 41
R (int)	0.0796	0.0544	0.0404	0.0349
GOF (<i>F</i> ²)	1.081	1.048	1.203	1.133
R indices (all data)	R ₁ = 0.0626 <i>w</i> R ₂ = 0.1107	R ₁ = 0.0307 <i>w</i> R ₂ = 0.0527	R ₁ = 0.0226 <i>w</i> R ₂ = 0.0441	R ₁ = 0.0280 <i>w</i> R ₂ = 0.0444

Table 2. RE bond distances (in Å) for Na₂RESiO₄(OH) (RE = Sc, Yb).

	Na ₂ ScSiO ₄ (OH)	Na ₂ YbSiO ₄ (OH)
RE(1) – O(4)	2.057(5)	2.207(6)
RE(1) – O(2)	2.078(5)	2.204(7)
RE(1) – O(6)	2.120(12)	2.275(13)
RE(1) – O(7)	2.121(10)	2.200(9)
RE(1) – O(9)	2.128(5)	2.240(6)
RE(1) – O(10)	2.171(5)	2.262(6)
RE(2) – O(8)	2.069(5)	2.193(6)
RE(2) – O(5)	2.086(5)	2.190(6)
RE(2) – O(10)	2.119(5)	2.262(6)
RE(2) – O(1)	2.127(9)	2.261(8)
RE(2) – O(3)	2.129(10)	2.187(13)
RE(2) – O(9)	2.161(6)	2.287(6)

Table 3. Yb bond distances (in Å) for NaYbSiO₄.

NaYbSiO ₄	
Yb(1) – O(2)	2.170(3)
Yb(1) – O(3)	2.221(3)
Yb(1) – O(1)	2.235(2)
Yb(1) – O(1)	2.235(2)
Yb(1) – O(1)	2.235(2)
Yb(1) – O(1)	2.235(2)

Table 4. La bond distances (in Å) for NaLaSiO₄.

La(1)		La(2)		La(3)	
La(1) – O(3)	2.422(3)	La(2) – O(5)	2.442(2)	La(3) – O(9)	2.404(3)
La(1) – O(12)	2.452(3)	La(2) – O(4)	2.459(3)	La(3) – O(7)	2.488(3)
La(1) – O(4)	2.501(3)	La(2) – O(7)	2.490(3)	La(3) – O(6)	2.517(3)
La(1) – O(1)	2.521(3)	La(2) – O(10)	2.519(3)	La(3) – O(3)	2.525(3)
La(1) – O(2)	2.527(2)	La(2) – O(8)	2.545(2)	La(3) – O(12)	2.533(3)
La(1) – O(1)	2.555(3)	La(2) – O(2)	2.600(2)	La(3) – O(11)	2.547(2)
La(1) – O(11)	2.581(2)	La(2) – O(9)	2.658(3)	La(3) – O(8)	2.573(2)
La(1) – O(5)	2.619(3)	La(2) – O(6)	2.683(3)	La(3) – O(10)	2.763(3)

Table 5. Experimental magnetic moments (μ_{eff}) compared to calculated moments (μ_{calc}) for $\text{Na}_2\text{YbSiO}_4(\text{OH})$ and NaYbSiO_4 .

	$\text{Na}_2\text{YbSiO}_4(\text{OH})$	NaYbSiO_4
Fit Range (K)	100 – 300	100-300
χ_0	0.00085	0.0029
θ (K)	-95.92	-75.81
μ_{eff} (μ_{B}/RE)	4.20	4.18
μ_{calc} (μ_{B}/RE)	4.54	4.54