Comparison of the crystal chemistry of selected MSi₆O₁₅-based silicates

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ABSTRACT

The structures of four A₂MSi₆O₁₅·(nH₂O) silicates (A = Na or K, M = Nd or Y) recently determined by the authors are compared with one another and with the structures of related silicates. The 2:5 Si:O ratio in these compounds (silicate tetrahedra linked by sharing three O atoms per tetrahedron plus one unshared O atom) permits layer, double-chain, or double-ring configurations. In α-KNdSi₆O₁₅·2H₂O, β-KNdSi₆O₁₅, and Na₃NdSi₆O₁₅·2H₂O, the linkage is found to result in a corrugated layered structure, in β-NaYSi₆O₁₅, a double-chain structure, and in α-NaYSi₆O₁₅, a unique double-ring structure. Although the factors that govern the stabilities of ring vs. chain vs. layered structures remain to be completely elucidated, it is apparent in the layered structures that larger M cations (such as Nd and Ce) produce a greater degree of corrugation than do Zr and Ti cations. The more open structures of neodymium and cerium silicates contain large channels that may serve as pathways for fast alkali ion transport.

INTRODUCTION

All physical models for description of the response of a material to applied forces require knowledge of the crystal structure as a critical starting point. Yet, prediction of structure, given a composition, is a goal that still eludes solid-state chemists and physicists for all but the simplest of metals and binary compounds. In a contribution toward understanding the crystal chemistry of silicate compounds, we compare the recently determined structures of four silicates synthesized by the authors: α-KNdSi₆O₁₅·2H₂O, β-KNdSi₆O₁₅, Na₃NdSi₆O₁₅·2H₂O, and α-NaYSi₆O₁₅. Because these compounds were synthesized under similar hydrothermal conditions, as described below, differences in structure are directly attributable to differences between the cation species involved and, hence, are examined in detail. We also compare these structures with some related A₂MSi₆O₁₅ compounds (A = alkali metal or alkaline earth metal and M = Y, Zr, or Ti). Together, these compounds constitute a subset of Si₆O₁₅-based silicates that do not form flat silicate layers. In subsequent discussion these phases are designated simply by the A and M cations present in the composition; the Si₆O₁₅ anion that they have in common will be omitted for brevity. The properties of these compounds are of interest because the MSi₆O₁₅ complex anions tend to crystallize with open frameworks, creating channels that may serve as pathways for fast alkali ion transport.

SYNTHESIS AND PHASE IDENTIFICATION

All of the compounds prepared by us were grown by hydrothermal methods, as described in detail elsewhere (Haile et al. 1993a, 1993b). In general, the products were obtained in the form of microcrystalline powders from isothermal experiments, in which the temperature was held typically at 500 °C and the pressure at 825 bar. The precursor material was usually a finely ground glass of composition A₂O-M₂O₃·17SiO₂. The solvent was either deionized water or a 0.1 M solution of the hydroxide or carbonate of the appropriate alkali cation. As customary in the hydrothermal technique, just enough solvent was added to platinum capsules to balance the pressure applied during crystallization. They were filled to a fraction that ranged from 0.3 to 0.7 depending on the exact synthesis conditions. Synthesis was carried out in a Tuttle autoclave in experiments that extended from 7 to 12 d. The crystallization of NaNd and α-NaY (the latter is designated α to distinguish it from an isocompositional compound reported by Bourguiba and Dogguy 1994 and discussed below) was generally reproducible, but the stability range of both compounds in terms of pressure, temperature, and solution molarity was narrow. Consequently, they often appeared in conjunction with secondary phases. Slightly lower temperatures (350–500 °C) tended to produce NaNd as a single phase, whereas slightly higher temperatures (500–600 °C) and pressures (1400 bar) tended to favor crystallization of α-NaY as a single phase. A Bb₂,m form of KNd (designated β) was obtained in only three experiments out of more than 100 that were conducted in the K₂O-Nd₂O₃-SiO₂ system, suggesting that it may be a metastable phase. The synthesis of a KNd phase that was designated α was, in contrast, extremely reproducible and occurred over a wide range of synthesis conditions. It was possible to synthesize large crystals (0.1 × 2 × 1 mm³) in experiments that were
performed in a temperature gradient through use of a Morey autoclave (Haile et al. 1991).

The chemical compositions of the crystals so obtained were established with electron microprobe techniques. Data were collected with a JEOL Superprobe 733 equipped with a wavelength-dispersive detector. The intensities of the characteristic X-radiation peaks were converted to stoichiometric quantities using the ZAF data reduction procedure and appropriate standards. Where the microprobe measurements suggested the presence of H2O in the structure, the H2O content was also determined by thermogravimetric analysis combined with mass spectrometry of the emitted vapor. Crystal structures were determined by single-crystal X-ray techniques using diffraction data that were collected at room temperature in MoKα radiation. Crystallographic data are provided in Table 1. Complete structure determinations, reported elsewhere (Haile et al. 1995, 1997; Haile and Wuensch, unpublished manuscript), confirmed the ideal compositions deduced from the microprobe and thermogravimetric analyses.

**Overview of Structures to be Considered**

The main structural features of the four A,MSi6O18 (nH2O) silicates synthesized in the present work are summarized in Table 2 along with similar data for four related silicates: β-Na,YSi6O18 (Bourguiba and Dogguy 1994); dalyrite, K,ZrSi6O18 (Fleet 1965); armstrongite, CaZrSi6O18 (Kashaev and Sapozhnikov 1978); and K,CeSi6O18 (Karpov et al. 1976). All of the structures are based on linkages of SiO4 tetrahedra that share three of their four O corners with a corner of a neighboring SiO4 group. The fourth vertex is unshared, being bonded to M (and, in some cases, A as well) rather than a second Si atom. This proportion of “bridging” to “terminating” O atoms accommodates the overall Si:O ratio of 2:5. In general, the Si-O_termin_ bond distance is shorter than the Si-O_pre_ distance, reflecting a stronger bond between Si and O than between the M (or A) cation and O.

A stoichiometry of A,MSi6O18 provides six terminating O atoms per formula unit for each M cation. The ionic radius of the M cation, ~0.95 Å, suggests that this species is octahedrally coordinated by O (r_O ~ 1.36 Å). Thus, it is reasonable to expect that the six terminating O atoms available per M cation provide this coordination. In three of the compounds, α-K,Nd, β-K,Nd, and α-Na,Y (and in all four related compounds), octahedral coordination by terminating O atoms is indeed observed. In Na,Nd, however, the Nd atom is sevenfold coordinated (one of its seven vertices consists of a bridging O atom), with the unusual consequence that it shares one of its polyhedral edges with that of an SiO4 tetrahedron. As might be expected, the shared edge is shortened relative to other O-O distances in the structure, whereas the distances between the cations and the bridging O atoms are elongated. The increase in bond lengths results in a bond valence sum of 2.06 at the bridging O atom, which is only slightly greater than the average of 1.96(12) in the Na,Nd structure (Haile et al. 1997).

From the data provided in Table 2 it is evident that (MSi6O18)-based silicates readily adopt either single-layer structures in which isolated SiO4 layers are linked only by bonds with A or M atoms or double-chain structures in which two chains are linked together by bridging O atoms. In addition to the single-layer and double-chain structures, Table 2 reveals that one compound, α-Na,Y, adopts a double-ring structure and another, K,Ce, adopts a three-dimensional framework structure. Possible reasons for the appearance of these rare, and presumably unfavorable, silicate anion configurations are discussed below, including a detailed comparison of K,Ce with the single-layer silicates and α-Na,Y individually.

**Double-chain silicates**

Comparisons of the double-chain silicates have been made by others (see, for example, Ghose and Wan 1978) and we mention only briefly some key features that distinguish these from the single-layer silicates. First, the valences and sizes of the A and M cations appear to have little influence in determining which of these two general topologies is adopted: Both M^4+ and M^6+ cations appear in both types of structures, as do both A^+ and A^2+. The structural differences observed may, in fact, result from differences in synthesis conditions (layers tend to result from hydrothermal synthesis and chains from atmospheric, high-temperature crystallization), rather than differences in chemistry. It is also noteworthy that only one double-chain structure-type, that of zekezterite, LiNaZr, has been observed. Epididymite, Na,Be, and elpidite, Na,Zr, can be considered distortions of the zekezterite structure. In contrast, few of the single-layer compounds are isostuctural to one another. Indeed, of seven single-layer
MSiO₃ structures that have been reported only two pairs of isomorphs occur. The zekterite structure-type contains two large A cation sites (eight- to tenfold coordinated), one small A cation site (fourfold coordinated), and one M cation site (sixfold coordinated). These features provide a capacity for accommodation of cations of varying size and valence, attributed by Gunawardane et al. (1982) as the result of the unique ability of this structure to balance local distortions at the tetrahedral (A) and octahedral (M) sites in a manner that minimizes distortions of the silicate chain. Bourguiba and Doggy (1994) suggested that the chain itself is quite flexible. In the case of β-Na₂Y, the distortions at the usually tetrahedral site are so great as to cause the coordination at this site to become eightfold.

**Layered Structures**

The connectivity of tetrahedra in the silicate sheets

The single-layer structures of α-K₂Nd, β-K₂Nd, Na₂Nd, dalylite, and armstrongite have in common a wollastonite-type chain (Ohashi and Finger 1978), as the basic structural building block (Fig. 1a). In the terminology of Liebau (1985), this is a dreier-single chain, meaning that the translational repeat unit along the chain consists of three silicate tetrahedra and that the tetrahedra are linked only to others that extend along the direction of the chain. Viewed along the direction of the chain, the wollastonite-chain has a width of two silicate tetrahedra. Condensation of two wollastonite-type chains produces the xonolite-like chain (Kudoh and Takeuchi 1979), a dreier-double chain, shown in Figure 1b. This chain is characterized by the presence of eight-membered silicate rings. Further condensation of xonolite-like chains produces the connectivity of tetrahedra in the sheets found within all of the single-layer A,MSiO₃ (-nH₂O) structures under present consideration. Condensation of the xonolite-like chains in a direction normal to the chain results in the formation of alternating four- and six-membered rings at the interface between them, (Fig. 1c). Alternatively, the position of the xonolite-like chains can be sheared by one-half of the chain repeat distance prior to condensation. A sequence of five-membered rings then occurs along the interface (Fig. 1d), once the sheet is distorted to permit rejoining the bridging O atoms.

The layers revealed by the structure determinations are shown schematically in Figure 2. Severe corrugation of the layers was neglected in this representation. Unshaded tetrahedra indicate polyhedra for which the terminating or apical O atom is above the plane of the sheet (an “upward directed” tetrahedron), whereas shading indicates that the O atom resides below the plane (“downward directed”). In the two K₂Nd silicate structures (Figs. 2a and 2b) and in armstrongite, CaZr, (Fig. 2d) the xonolite-like chains condense in a direction normal to the chain as in Figure 1c. Disregarding the directness of the tetrahedra, neighboring xonolite-like chains are directly related by translation, and, for this idealized case, the periodicity perpendicular to the chains is equal to the width of four silicate tetrahedra (i.e., the width of the xonolite-like chain). The same is true in dalylite, K₂Zr (Fig. 2e), although in this structure the layer is significantly distorted from the idealized rectangular nets that are characteristic.
of the first three structures. The silicate sheets of Na,Nd (Fig. 2c) are somewhat more complex. Pairs of xonotlite-like chains again come together to form six- and four-membered rings at their interface as in the K,Nd phases, but alternate chains condense with shear so that five-membered rings are generated at the second interface as in Figure 1d. Repetition of these alternating modes of condensation produces a total offset equal to the chain periodicity and thus leads to centering of the face of the unit cell that is parallel to the layer. It is noteworthy that in the zirconium silicates armstrongite and dalyite, all tetrahedra along each wollastonite-type chain are pointed in the same direction, whereas in the neodymium silicates, the directedness alternates along the chain.

The coordination polyhedra around the rare-earth cation, M, link neighboring silicate sheets to form a threedimensional framework. In all but the sodium neodymium silicate, octahedra around these cations derive three of their O neighbors (i.e., one face) from a layer below and the remaining three (i.e., the opposite face) from a layer above the cation. Hence, the location and geometry of the M polyhedra are intimately tied to the directedness of silicate tetrahedra. Returning to the basic structural unit, the wollastonite-type chain, there are two apical O-O distances that are comparable to the lengths of typical edges in M polyhedra (Belov 1961). In the idealized geometry shown in Figure 2b, the distance between the apical O atoms of two neighboring SiO₄ tetrahedra with the same directedness is 3.05 Å; that between the apical O atoms of two tetrahedra separated by a third in different orientation is 4.16 Å. Again, it is assumed that the tetrahedra are pointed in the same direction. The former distance is essentially fixed by the geometry of the SiO₄ tetrahedra and the Si-O-Si angle. The latter distance, however, can vary because the two tetrahedra providing the coordinating, apical O atoms have no fixed relationship to one another. To complete a triangular face of the octahedron, a third O neighbor is needed. This derives from either a neighboring wollastonite-type chain or from a chain further removed. To bring this O atom to a reasonable distance from the M cation, all of the layers, shown in idealized form in Figure 2, become highly corrugated in the actual structures along the direction perpendicular to the wollastonite-type chains. In general, there is little corrugation along the length of the chains.

The positioning of the octahedral faces of the M polyhedron relative to the apical terminal O ions in the silicate layers of Figure 2 is depicted in Figure 3. The triangular faces in the neodymium silicates contain O atoms from neighboring wollastonite-type chains in accord with the distribution of upward- and downward-directed tetrahedra. This is true also of Na,Nd (Fig. 3c) but, as a consequence of the sevenfold coordination of Nd, a fourth bond to a bridging O is present within the triangle. The tetrahedra in neighboring chains all point in the opposite direction in the zirconium silicates. The triangular faces therefore join apical O atoms from every second chain (Figs. 3d and 3e). Consequently, the manner in
which the silicate layers are corrugated and the way in which neighboring layers are related in the Zr silicates are very different from that in the neodymium silicates. As can be seen in Figure 4, which provides idealized projections of the structures along the direction of the wollastonite-type chains, the corrugations are such that a neodymium polyhedron spans three silicate tetrahedra (in a direction normal to the wollastonite-type chain), whereas in the zirconium silicates the Zr octahedra span four. The degree of warping of the layers is therefore greater in the former than in the latter. Moreover, the layers in the zirconium silicates are stacked in a staggered, two-layer sequence that gives rise to a centered unit cell. In contrast, neighboring layers in the neodymium silicates are stacked essentially by translation normal to the layers. The structure of α-K,Nd is, however, somewhat more complicated than that of the other two neodymium silicates. The α-phase has a two-layer stacking sequence in which neighboring layers are related by a twofold rotation axis parallel to the corrugations, rather than by translation. The basic geometric features represented in Figure 4 remain present, however.

In both the neodymium and the zirconium silicates, the overall stoichiometry requires that there should be two MO₆ octahedra for every eight silicate tetrahedra along the direction of the corrugation. Hence, in the neodymium silicates a large channel is formed by the “non-participation” of two out of eight silicate tetrahedra (at least on one side of a given layer) in the formation of MO₆ octahedra (Fig. 4a). In the zirconium silicates, by contrast, no such channels are formed. Indeed, the small channels suggested for the zirconium silicates by Figure 4b are not really present in the true structures because of distortions from the idealized arrangement that is depicted. The greater openness of the neodymium-silicate frameworks over those of the zirconia silicates is evidenced by the significantly greater volumes per formula unit in the neodymium silicate structures (Table 2).

At first glance, it is somewhat counterintuitive that bonding across four tetrahedra (Fig. 4b) should be necessary to provide more favorable conformation with the shorter O-O distances of the ZrO₆ octahedra instead of bonding across three (Fig. 4a). However, bringing the O atoms closer together in the latter configuration would force the Si-O-Si angles to adopt small and energetically unfavorable values. That the neodymium-silicate framework is preferred by larger M cations is evidenced by the structure of sazhinite, HNa₃CeSi₄O₁₄ (Shumyatskaya et al. 1980). This compound is formed with a Ce³⁺ ion that has
a radius of 1.01 Å and displays a CeSi₆O₁₅ framework that is virtually identical to the NdSi₆O₁₅ framework of β-KNdSi₆O₁₅.

It is noteworthy that a silicate layer of the type observed in these MSi₆O₁₅ silicates is also found in K₃Be₂Si₆O₁₅ (Namaova et al. 1976), a compound that, strictly speaking, has no octahedrally coordinated M cation. The distribution of four-, six- and eight-membered rings and the directedness of silicate tetrahedra are identical to that in α-KNd. Two Be atoms are tetrahedrally coordinated and share an edge in such a way that six O atoms effectively form a distorted octahedron about each pair of Be atoms. As in the case of the MSi₆O₁₅ silicates, the six O atoms that form this octahedron are all terminating atoms with respect to the linkage of silicate tetrahedra. The Be₆O₆ pseudo-octahedron is, however, much smaller than the octahedra in the silicates described above. The average Be-O distance is 1.644 Å and the average length of an O-O edge of the polyhedron 2.678 Å. As might be expected on the basis of these local geometric differences, the manner in which the Be₆O₆ pseudo-octahedra are linked to the Si₆O₆ layers differs significantly from that of the MO polyhedra. Four of the six O atoms in Be₆O₆ derive from a layer below the Be atoms and two derive from a layer above. Consequently, two of the faces of the pseudo-octahedron are formed by O atoms within the same silicate layer (Fig. 5a). One of these faces is equivalent to that found in α-KNd, β-KNd, and NaNd (Fig. 3a) and the other to the octahedral face present in CaZr (Fig. 3e). The Be₆O₆ group thus spans four neighboring wollastonite chains and introduces an even higher degree of corrugation in the Si₆O₆ layer than the ZrO₆ octahedra in CaZr and K₃Zr. Neighboring silicate layers in K₃Be₂ are related by translation, and the remaining two O atoms of the pseudo-octahedra derive from downward-directed silicate tetrahedra that are translationally equivalent to two of those of Figure 5a. Specifically, the apices of two shaded tetrahedra that are vertically displaced from one another provide the remainder of the coordination. The two shaded tetrahedra that are horizontally displaced from one another form part of other Be₆O₆ groups. The Be₆Si₆O₁₅ framework of K₃Be₂ is shown in Figure 5b. The much greater extent of layer warping in this structure in comparison with the MSi₆O₁₅ structures (Fig. 4) is clearly evident.

Origin of the corrugations

On the basis of the six single-layer silicate structures that have been compared we conclude that as the octahedrally coordinated M cation decreases in size from Nd⁴⁺ to Zr⁴⁺ to (Be₂)⁴⁺ the degree of corrugation of the layers increases commensurably. This occurs because a high degree of corrugation permits terminating O atoms to come within sufficient proximity to one another to satisfy the coordination requirements of a small M cation.

Liebau (1985) has conducted a broad analysis of the impact of A and M cation species on silicate layer topology. His first observation, that for a fixed average valence smaller cations tend to induce greater degrees of layer warping, is entirely in agreement with the results presented here. Liebau’s second observation concerns the impact of A and M cation valence on layer topology. He noted that as the average valence of the A and M cations increases and, accordingly, the number of cations per silicate tetrahedra decreases, the compatibility of those cations with flat silicate layers decreases. Hence, the degree of layer warping increases. This second conclusion is only partially borne out by the silicates examined in the present work. The K₃Nd, NaNd, and α-NdY compounds have a lower average cation valence (0.67) and greater number of cations per six SiO₆ tetrahedra (4) than do the K₃Zr and CaZr compounds and indeed exhibit less corrugation in their layers than the latter. However, K₃Be₂ has the same average cation valence and number of cations per silicate tetrahedra as the neodymium silicates, yet has the most highly corrugated layers of the three types of single-layer silicates examined. Furthermore, one would expect K₃Zr and CaZr to have very different degrees of layer corrugation if one employed valence arguments alone, yet the corrugation in the respective layers is similar.

The framework structure of K₃Ce

The related compound K₃Ce takes on an “interrupted framework” structure rather than a single-layer motif, (Table 2). Karpov et al. (1976) identified xenotilite-like chains as the basic structural unit of this structure. The structure can also be understood in terms of (SiO₄) layers, containing six- and ten-membered silicate rings, that are linked together by bridging O atoms to form the three-dimensional silicate anion (Fig. 6). Although the position of the octahedral faces of the Ce polyhedron relative to the terminal O atoms cannot be described in terms of the geometries of Figure 3 (such groupings of silicate tetrahedra do not exist in K₃Ce), it is noteworthy that, as with the other MSi₆O₁₅ structures, three of the O atoms derive from a layer above the Ce atom and three from a layer below. The extreme elongation of the ten-membered rings leads to a structure in which terminating O atoms are within close enough proximity to form the face of a CeO₆ octahedron without significant corrugation of the layers. Moreover, as with K₃Zr (and unlike the other MSi₆O₁₅ compounds) two of the O-O edges in the
octahedron are formed by terminating O atoms that derive from neighboring (i.e., directly linked) silicate tetrahedra.

As discussed above, such a configuration provides a relatively short O-O distance and more readily accommodates the slightly smaller M cations in these structures.

The adoption of a framework structure by K$_2$Ce has been explained by Liebau in terms of a combined valence-cation size argument. He suggested that the high degree of layer warping that would be induced by the high average valence (low number of A and M cations per silicate tetrahedra) would result in the creation of interstitial sites between silicate layers that are too small for the Ce$^{4+}$ cation (sixfold coordination for an ion of 0.80 Å radius). Stated alternatively, although the large Ce$^{4+}$ cation may be stable in a layer structure with a relatively low degree of corrugation, the high valence is compatible only with a high degree of corrugation, and thus no layer can accommodate both the valence and the size requirements. Although this may be true, it is also quite possible that the absence of a single-layer structure for K$_2$Ce results from synthesis conditions that favored the observed framework structure. Indeed, in light of the similarity of the layers in K$_2$Zr and CaZr and the differences between the layers of the A$_2$Nd phases and K$_2$Be$_2$, it appears that size, not valence, determines the degree of layer corrugation. Therefore, under appropriate synthesis conditions it might be expected that the compound K$_2$Ce could adopt a single-layer structure in which the corrugation is similar to that in the A$_2$Nd structures, because these contain an octahedral site sufficiently large for the Ce$^{4+}$ cation.

This prediction is, to some extent, supported by the existence of corrugated layers in sazhinite, a cerium silicate isostructural to β-K$_4$Nd (Table 2). At first glance, the structural differences observed between the two cerium silicates are explained readily by the differences in stoichiometry and valence of the A and M cations: HNa$_2$Ce$^{4+}$ vs. K$_2$Ce. However, for neither structure determination was the assigned stoichiometry or valence confirmed by a chemical analysis. Indeed, in an earlier work, the chemical formula of sazhinite was reported as Na$_2$Ce$^{4+}$Si$_2$O$_6$.6H$_2$O (Es’kova et al. 1974). Furthermore, the assignment of an OH group to one of the terminating O sites in the later refinement is not justified in terms of the Si-O(H) and Ce-O(H) bond lengths. Normally, metal-hydroxyl group bonds are longer than metal-oxygen bonds, but no unusually long bonds are present in the model refined by Shumyatskaya et al. (1979). Thus, it is quite possible that the actual stoichiometry of this mineral is Na$_2$Ce$^{4+}$Si$_2$O$_6$.nH$_2$O. In such case, sazhinite would then provide an example of Ce$^{4+}$ existing in a single-layer silicate.

**The isolated Si$_4$O$_{15}$ unit**

The structure determined for α-Na$_2$YSi$_2$O$_6$ (Haile et al. 1995) contains an unusual, discrete Si$_4$O$_{15}$ unit that is shown in Figure 7a. It is, in the terminology of Liebau, a dreier-double ring, indicating that it is composed of two three-membered rings that share a common interfacial
The rarity of this unit results from the small Si-O-Si angles to which it gives rise. This may be seen from the data provided in Table 2. Indeed the Si-O-Si angle in α-Na,Y is substantially smaller in comparison with β-Na,Y. To accommodate this small angle, as is apparent from Table 2, the Si-Oa bond distances are elongated relative to the other structures investigated. Hill and Gibbs (1979) have examined the relationship between Si-O-Si angle and Si-Oa distance and concluded that the latter is linearly related to the secant of the angle. In Figure 8, we compare the average values obtained in our four silicates with the results of the linear regression analysis of Hill and Gibbs. It is evident that the data for our structures agree well with the relationship.

The SiO₄ units in α-Na,Y are linked by YO₆ octahedra to form a three-dimensional network (Fig. 7b). In this case, unlike that of the layered silicates, the octahedron is essentially free to take on the most favorable configuration without the need to conform to O-O distances in the silicate anion. This configuration, combined with the compactness of the dreier-double ring, turns out to provide a structure with a much denser arrangement than in the layered silicates, as evidenced by the much smaller volume per formula unit. The high density explains why higher pressures facilitated more ready synthesis of the α-Na,Y phase.

The higher density of α-Na,Y relative to that of the β form suggests that the nature of the conditions of synthesis may account for these strikingly different polymorphic forms. The dreier-double ring structure was formed from hydrothermal solutions at 500–600 °C and 1400 bar, the highest pressures used in our syntheses. In contrast, β-Na,Y was produced at 850 °C and ambient pressure by crystallization from a flux of Na₂MoO₄ and P₂O₅. In addition, β-Na,Y contains the M⁴⁺ ion of largest radius known to result in formation of the zekterite structure-type and thus may be at the limit of structural stability for this configuration. The large Si-O-Si angles that occur in the chain imply that strain is necessary to match the SiO₄ to a cation as large as Y⁴⁺. The existence of two polymorphs of Na,Y demonstrates that it can be misleading to attribute differences in structure solely to differences in chemistry when different synthesis conditions are used or when synthesis conditions are unknown.

The reasons for the gross differences between the α-Na,Y structure and those displayed by the three other A₃SiO₈₃ silicates examined in this work are not immediately apparent. We earlier suggested (Haile et al. 1995) that the greater electronegativity of Y relative to Nd resulted in an effectively smaller charge per silicate tetrahedron, permitting the silicate groups to come within closer proximity to each other. Alternatively (or perhaps additionally), it is possible that a layered yttrium silicate was not obtained because YO₆ cannot match either of the general motifs shown for the corrugated layers of Figure 4. The Y octahedron is perhaps too small for the neodymium configuration and too large for the zirconium model. However, given the many isomorphic zirconium and yttrium silicates (for example, the double-chain silicates listed in Table 2), it would be surprising if yttrium could not fit into the dalyite or armstrongite structure types. Indeed, any explanation based on size alone is somewhat unsatisfying. It is hard to imagine, given the myriad connectivities and modes of distortion with which an SiO₄ layer might be designed, that not a single one could conform to the geometry of the YO₆ octahedron.

Moreover, although the isolated dreier-double ring was observed only in the Na₃O-Y₃O₇-SiO₂ system, it may be premature to conclude that no layered silicate structures exist in this system. The structures of all compounds that we encountered in the sodium and potassium Nd₃O₇-SiO₂ systems have either been solved or found to possess previously known structure types. However several crystalline phases with structures that are as yet unsolved were reproducibly obtained in the Na₂O-Y₂O₃-SiO₂ system (Haile et al. 1993a). Several unique phases were identi-
fied on the basis of their powder diffraction patterns, but poor crystal quality precluded structure determinations. It is quite likely that some of these may be layered silicates.

**Conclusions**

The variety of silicate structures observed for these compositionally similar materials suggests that the energy differences between the various configurations are quite small. The reasons why a structure with the unique dreier-double ring was assumed by the phase with composition Na,YSiO₃ remain to be completely explained. In contrast to yttrium silicate, both neodymium and zirconium silicates readily crystallize as layered structures, despite the significant differences between these ions in terms of charge and size. The Si₆O₁₈ sheets in these structures assume highly corrugated configurations to conform to the geometry of the MO₃ (or MO₄) polyhedron. The differences in size between NdO₆ (or NdO₅) and ZrO₂ produce differences in the manner in which corrugation occurs, generating much more open structures in the case of the neodymium (and cerium) silicates than obtained in zirconium (and titanium) silicates. This openness results in large channels within the structures and suggests that layered neodymium and cerium silicates are, in general, more likely candidates for phases that may exhibit high ionic conductivity.

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