Comparison of the crystal chemistry of selected MSi$_6$O$_{15}$-based silicates

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Abstract

The structures of four A$_5$MSi$_6$O$_n$($n$H$_2$O) 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-K$_3$NdSi$_6$O$_{15}$·2H$_2$O, β-K$_3$NdSi$_6$O$_{15}$, and Na$_3$NdSi$_6$O$_{15}$·2H$_2$O, the linkage is found to result in a corrugated layered structure, in β-Na$_3$YSi$_6$O$_{15}$, a double-chain structure, and in α-Na$_3$YSi$_6$O$_{15}$, 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-K$_3$NdSi$_6$O$_{15}$·2H$_2$O, β-K$_3$NdSi$_6$O$_{15}$, Na$_3$NdSi$_6$O$_{15}$·2H$_2$O, and α-Na$_3$YSi$_6$O$_{15}$. 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 A$_5$MSi$_6$O$_n$ compounds (A = alkali metal or alkaline earth metal and M = Y, Zr, or Ti). Together, these compounds constitute a subset of Si$_6$O$_{15}$-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 Si$_6$O$_{15}$- anion that they have in common will be omitted for brevity. The properties of these compounds are of interest because the MSi$_6$O$_{15}$ 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 A$_5$O-M$_2$O$_3$·17SiO$_2$. 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 Na$_3$Nd and α-Na$_3$Y (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 Na$_3$Nd as a single phase, whereas slightly higher temperatures (500–600 °C) and pressures (1400 bar) tended to favor crystallization of α-Na$_3$Y as a single phase. A Bb$_2$m form of K$_3$Nd (designated β) was obtained in only three experiments out of more than 100 that were conducted in the K$_2$O-Nd$_2$O$_3$·SiO$_2$ system, suggesting that it may be a metastable phase. The synthesis of a K$_3$Nd 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 mm$^3$) in experiments that were...