Disorder in natrolites: structure determinations of three disordered natrolites and one lithium-exchanged disordered natrolite

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Abstract: Single crystal diffraction studies of three natrolite specimens from Uzabanya, Hungary (NaI, NaII, and NaII) were undertaken. In the study of NaI (a = 18.305(3), b = 18.632(3), c = 6.589(2) Å), 783 diffraction intensities were used (CAD-4 diffractometer, MoKα radiation (λMoKα = 0.71069 Å)) and the structure was refined to R (unweighted) = 0.020, R (weighted) = 0.026. In the study of NaII (a = 18.367(2), b = 18.583(1), c = 6.599(3) Å), 1304 diffraction intensities were used and the structure was refined to R (unweighted) = 0.025, R (weighted) = 0.027. In the study of NaII (a = 18.372(2), b = 18.576(2), c = 6.606(3) Å), 847 diffraction intensities were used and the structure was refined to R (unweighted) = 0.018, R (weighted) = 0.026. The three specimens differ in cell constants and in average Si-O and Al-O distances (in NaI Si-O (av) = 1.621 Å, Al-O (av) = 1.739 Å; in NaII Si-O (av) = 1.636 Å, Al-O (av) = 1.716 Å; in NaII Si-O (av) = 1.638 Å, Al-O (av) = 1.713 Å). The difference in cell constants and in Si-O and Al-O distances are related to the Si/Al order in the materials.

Crystals of NaII type were exchanged to the lithium form (LiI) in molten lithium nitrate (the crystals remained preserved). Single crystal studies of the exchanged material (a = 17.704(4), b = 18.540(5), c = 6.495(2) Å) used 775 diffraction intensities. The structure is similar to the structure of the sodium form. The structure was refined to R (unweighted) = 0.029, R (weighted) = 0.041. The lithium coordination is discussed.

Key-words: zeolites, natrolite, structure, disorder, lithium-coordination.

Introduction

There are several examples of minerals that have the same chemical composition and almost the same crystal structure, but which can nevertheless be distinguished by their lattice constants and sometimes by their crystal class. In the aluminosilicates listed in Table 1, the essential difference within a mineral type is the ordering of silicon and aluminium within the anion framework. This ordering may be complete as in microcline (usually called maximum microcline, maximum referring to order), or entirely absent as in sanidine. It is the complete disorder of silicon and aluminium on the available sites that causes the average symmetry of sanidine to be monoclinic. Bikitaite is another example. Ordered bikitaite is triclinic whereas the partially ordered material is monoclinic.

The asymmetric unit of the natrolite structure has three independent tetrahedral sites for silicon and aluminium (T(1), T(2) and T(3)). In Fig. 1a and 1b, the structure of the anion lattice of natrolite is shown. In these figures, the tetrahedra represent T(1)O₄, T(2)O₄ and T(3)O₄ units. The T(3)O₄ unit is shaded. Most natrolites are orthorhombic, and their anion lattice is arranged in such a way that T(1) and T(2) are predominantly occupied by silicon atoms and T(3) predominantly by aluminium atoms. If this order is complete, the material could be called maximum natrolite.

Natrolite can be tetragonal (e.g., the Tugtup Agtakorfi sample, Table 2). It has been suggested that sites T(2) and T(3) are occupied at random by silicon and aluminium in tetragonal natrolites (Pabst, 1971).

Some natrolites have lattice constants in the range between those for maximum natrolite and those for tetragonal natrolite. Five of the natrolites listed in Table 2 are of this intermediate type. Although the a and c axes increase from the top to the bottom of Table 2, the unit cell volume...