Some Proposals for Transformation Mechanisms of the Li2ZrF6, Trirutile and Na2SiF6 Structure Types: Simple Cation Rearrangements

JEAN GALY AND STEN ANDERSSON

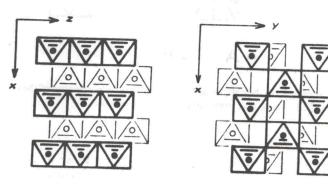
Service de Chimie Minérale Structurale de la Faculté des Sciences de Bordeaux associe au CNRS, 33-Talence, France

Chemical Centre, Department of Inorganic Chemistry 2, Box 740, S-220 07 Lund 7, Sweden.

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Under high pressure, rutile transforms into a structure of the α-PbO₂ type. In a previous paper (1) we proposed a simple mechanism for this transformation which is illustrated in Fig. 1. We now suggest similar cation displacements to interconvert the Li₂ZrF₆, trirutile, Na₂SiF₆ and columbite structure types.

When Li₂NbOF₅ was reported (2) as being isostructural with Li₂ZrF₆ (3), a picture was made showing its relation to the rutile structure. In Figs. 2a and b, the structures of trirutile and Li₂NbOF₅ are compared; Fig. 3 shows how the Li2ZrF6 structure type can transform into the trirutile type if 50% of the cations are shifted in the way



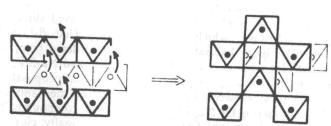
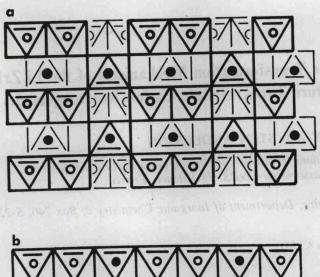


Fig. 1. The rutile structure (upper left) is compared with the α-PbO₂ structure type (upper right). Below is shown a possible mechanism for the rutile $\rightarrow \alpha\text{-PbO}_2$ transformation. Cation movements are indicated with arrows.



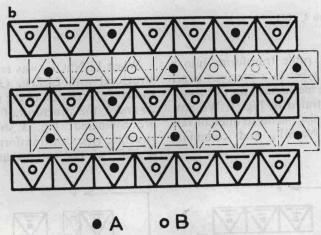


Fig. 2. In (a) the Li₂ZrF₆ structure type (Li₂NbOF₅) is given. In (b) the trirutile structure of the composition AB₂X₆. In both the structures, A corresponds to filled circles, and open circles are the B-atoms.

indicated by the curved arrows, and without disorder. To our knowledge, no such transformation has been reported for the compounds Li₂NbOF₅ and Li₂ZrF₆. However, α -Li₂SnF₆ of the Li₂ZrF₆ type has been found to transform to a structure of the trirutile type, designated β -Li₂SnF₆ at 510°C (4).

Another interesting transformation was reported recently (5, 6). At about 400° C, α -Li₂GeF₆, of the trirutile type, transforms to β -Li₂GeF₆ which has the Na₂SiF₆ type structure (7). Figure 4 shows the Na₂SiF₆ structure projected along the c-axis, and Fig. 5 the trirutile structure in an analogous projection. The geometrical relation between these structures can be shown by considering the Na₂SiF₆ type. The cations in the octahedra drawn with heavy lines are at $z = \frac{1}{2}$, those in the lighter octahedra at z = 0. If the metal atoms at z = 0 in m-planes move

to $z=\frac{1}{2}$, and those at $z=\frac{1}{2}$ in *n*-planes to z=0, the trirutile structure is obtained. This involves half the cations passing through octahedral faces along half the *c*-axis; the anion lattice remains intact. If the A and B atoms keep their relative order during the transformation, the ordered Na₂SiF₆ structure type may, in the reverse way, be geometrically derived directly from the ordered trirutile type. That β -Li₂SnF₆ and β -Li₂GeF₆ are formed as ordered compounds, with, respectively, the trirutile and Na₂SiF₆ structures, indicates that the geometrical proposals described here may very well be correct mechanisms.

All these compounds have approximately the same (hexagonally close packed) anion arrangement. At very high pressures the preferred cation arrangement seems to be like that in the α-PbO₂