

## Some Proposals for Transformation Mechanisms of the $\text{Li}_2\text{ZrF}_6$ , Trirutile and $\text{Na}_2\text{SiF}_6$ Structure Types: Simple Cation Rearrangements

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Under high pressure, rutile transforms into a structure of the  $\alpha\text{-PbO}_2$  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  $\text{Li}_2\text{ZrF}_6$ , trirutile,  $\text{Na}_2\text{SiF}_6$  and columbite structure types.

When  $\text{Li}_2\text{NbOF}_5$  was reported (2) as being isostructural with  $\text{Li}_2\text{ZrF}_6$  (3), a picture was made showing its relation to the rutile structure. In Figs. 2a and b, the structures of trirutile and  $\text{Li}_2\text{NbOF}_5$  are compared; Fig. 3 shows how the  $\text{Li}_2\text{ZrF}_6$  structure type can transform into the trirutile type if 50% of the cations are shifted in the way

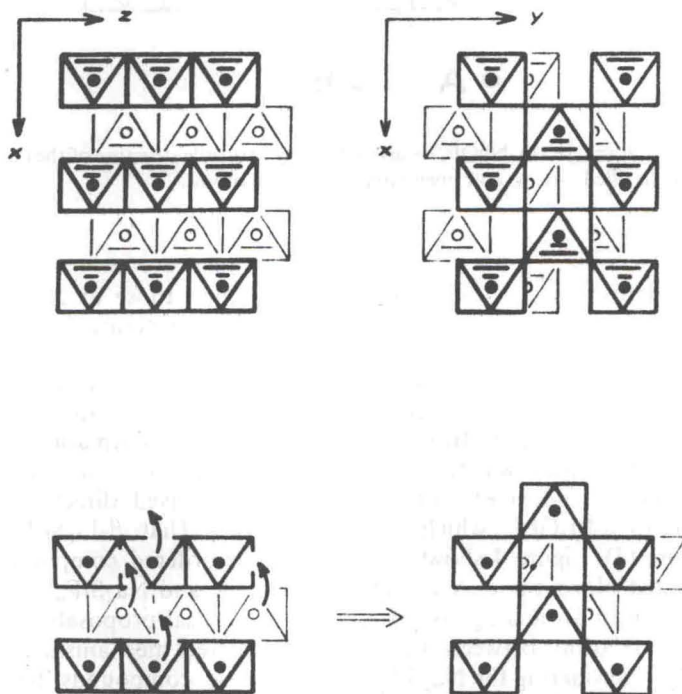


FIG. 1. The rutile structure (upper left) is compared with the  $\alpha\text{-PbO}_2$  structure type (upper right). Below is shown a possible mechanism for the rutile  $\rightarrow$   $\alpha\text{-PbO}_2$  transformation. Cation movements are indicated with arrows.

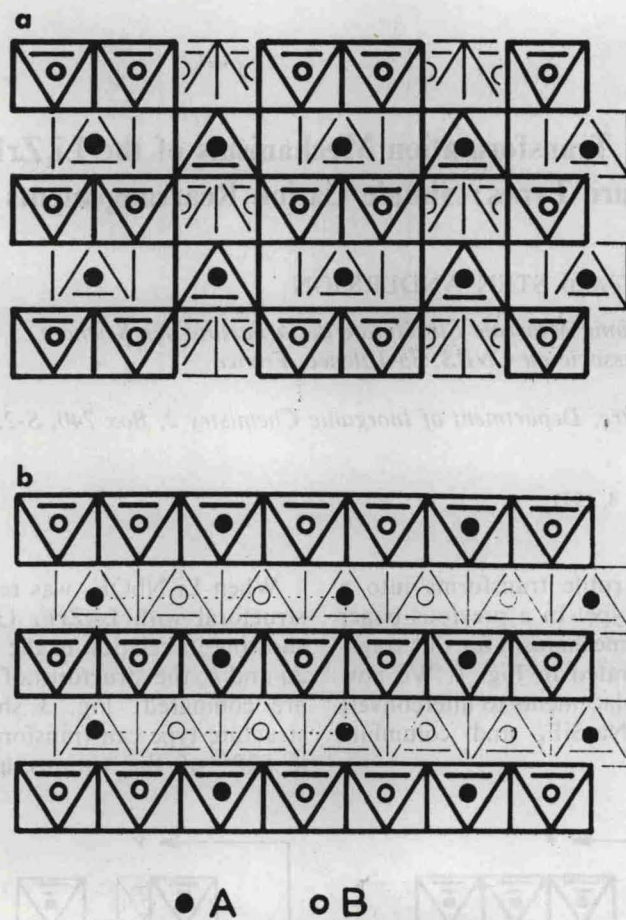


FIG. 2. In (a) the  $\text{Li}_2\text{ZrF}_6$  structure type ( $\text{Li}_2\text{NbOF}_5$ ) is given. In (b) the trirutile structure of the composition  $\text{AB}_2\text{X}_6$ . In both the structures, A corresponds to filled circles, and open circles are the B-atoms.

indicated by the curved arrows, and without disorder. To our knowledge, no such transformation has been reported for the compounds  $\text{Li}_2\text{NbOF}_5$  and  $\text{Li}_2\text{ZrF}_6$ . However,  $\alpha\text{-Li}_2\text{SnF}_6$  of the  $\text{Li}_2\text{ZrF}_6$  type has been found to transform to a structure of the trirutile type, designated  $\beta\text{-Li}_2\text{SnF}_6$  at  $510^\circ\text{C}$  (4).

Another interesting transformation was reported recently (5, 6). At about  $400^\circ\text{C}$ ,  $\alpha\text{-Li}_2\text{GeF}_6$ , of the trirutile type, transforms to  $\beta\text{-Li}_2\text{GeF}_6$  which has the  $\text{Na}_2\text{SiF}_6$  type structure (7). Figure 4 shows the  $\text{Na}_2\text{SiF}_6$  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  $\text{Na}_2\text{SiF}_6$  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  $\text{Na}_2\text{SiF}_6$  structure type may, in the reverse way, be geometrically derived directly from the ordered trirutile type. That  $\beta\text{-Li}_2\text{SnF}_6$  and  $\beta\text{-Li}_2\text{GeF}_6$  are formed as ordered compounds, with, respectively, the trirutile and  $\text{Na}_2\text{SiF}_6$  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  $\alpha\text{-PbO}_2$