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Some Proposals for Transformation Mechanisms of the Li_2ZrF_6, Trirutile and Na_2SiF_6 Structure Types: Simple Cation Rearrangements

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Under high pressure, rutile transforms into a structure of the α-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 Li_2ZrF_6, trirutile, Na_2SiF_6 and columbite structure types.

When Li_2NbOF_5 was reported (*2*) as being isostructural with Li_2ZrF_6 (*3*), a picture was made showing its relation to the rutile structure. In Figs. 2*a* and *b*, the structures of trirutile and Li_2NbOF_5 are compared; Fig. 3 shows how the Li_2ZrF_6 structure type can transform into the trirutile type if 50% of the cations are shifted in the way

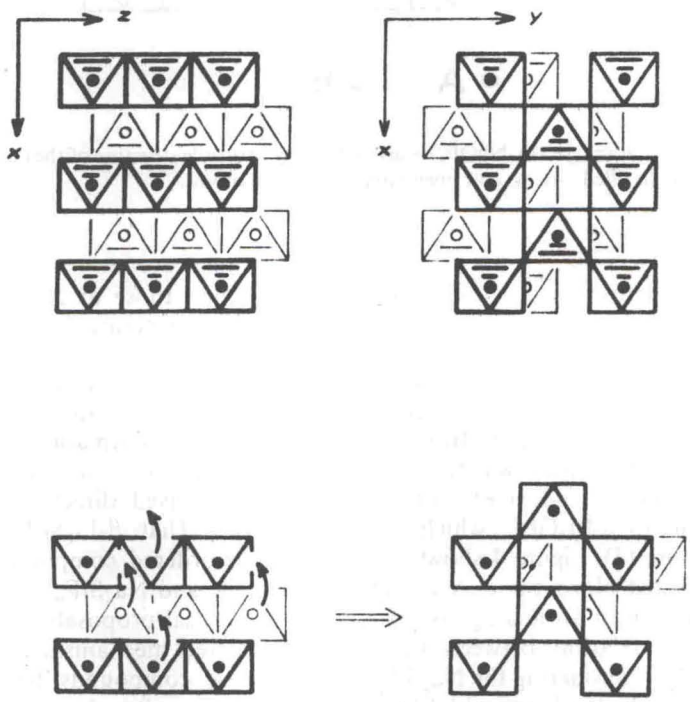

FIG. 1. The rutile structure (upper left) is compared with the α-PbO_2 structure type (upper right). Below is shown a possible mechanism for the rutile $\rightarrow$ α-PbO_2 transformation. Cation movements are indicated with arrows.

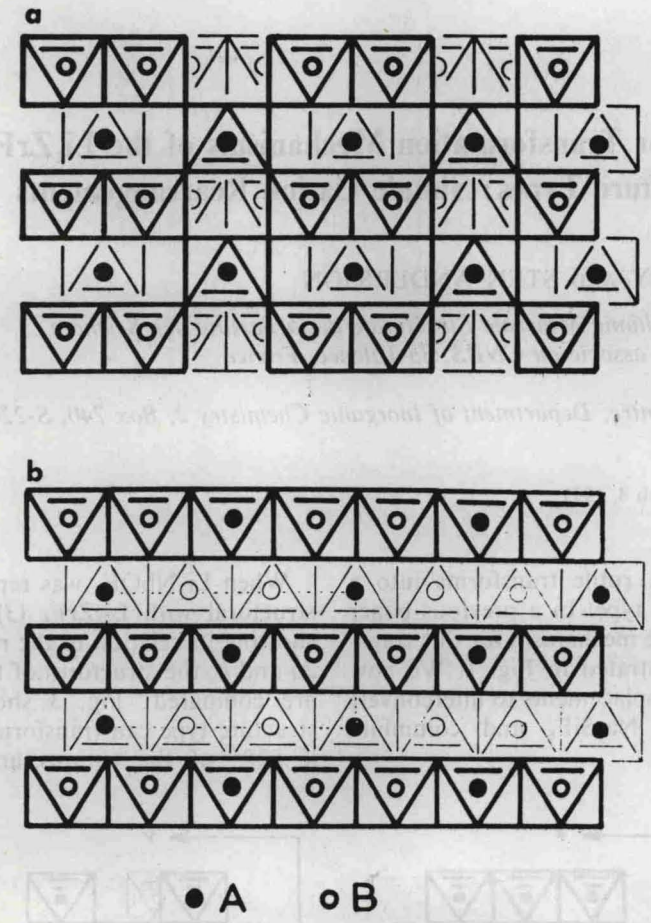

FIG. 2. In (*a*) the Li_2ZrF_6 structure type (Li_2NbOF_5) is given. In (*b*) the trirutile structure of the composition AB_2X_6. In both the structures, A corresponds to filled circles, and open circles are the B-atoms.

indicated by the curved arrows, and without disorder. To our knowledge, no such transformation has been reported for the compounds Li_2NbOF_5 and Li_2ZrF_6. However, α-Li_2SnF_6 of the Li_2ZrF_6 type has been found to transform to a structure of the trirutile type, designated β-Li_2SnF_6 at 510°C (*4*).

Another interesting transformation was reported recently (*5*, *6*). At about 400°C, α-Li_2GeF_6, of the trirutile type, transforms to β-Li_2GeF_6 which has the Na_2SiF_6 type structure (*7*). Figure 4 shows the Na_2SiF_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 Na_2SiF_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 Na_2SiF_6 structure type may, in the reverse way, be geometrically derived directly from the ordered trirutile type. That β-Li_2SnF_6 and β-Li_2GeF_6 are formed as ordered compounds, with, respectively, the trirutile and Na_2SiF_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 α-PbO_2

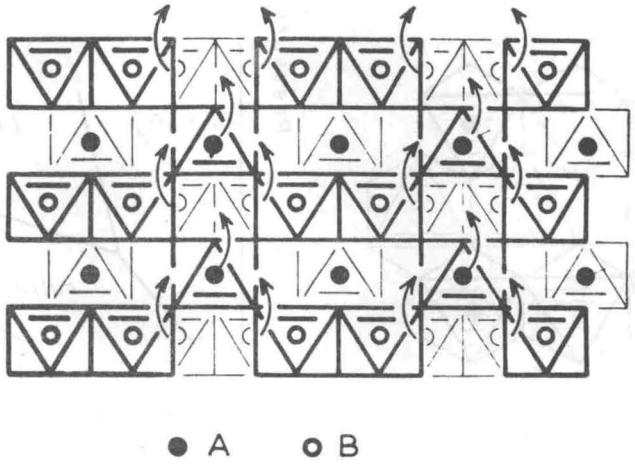

FIG. 3. If cations are shifted in the way described by arrows, the trirutile structure is formed from the Li_2ZrF_6 structure type.

structure type. Amongst the ternary compounds of general formula AB_2X_6 a similar arrangement of (ordered) cations occurs in columbite $FeNb_2O_6$. By analogy with the rutile $\rightleftarrows$ α-PbO_2 transformation, we might therefore expect the AB_2X_6 compounds discussed above to transform at high enough pressures to a ternary analog of α-PbO_2, possibly with the cations ordered as in $FeNb_2O_6$.

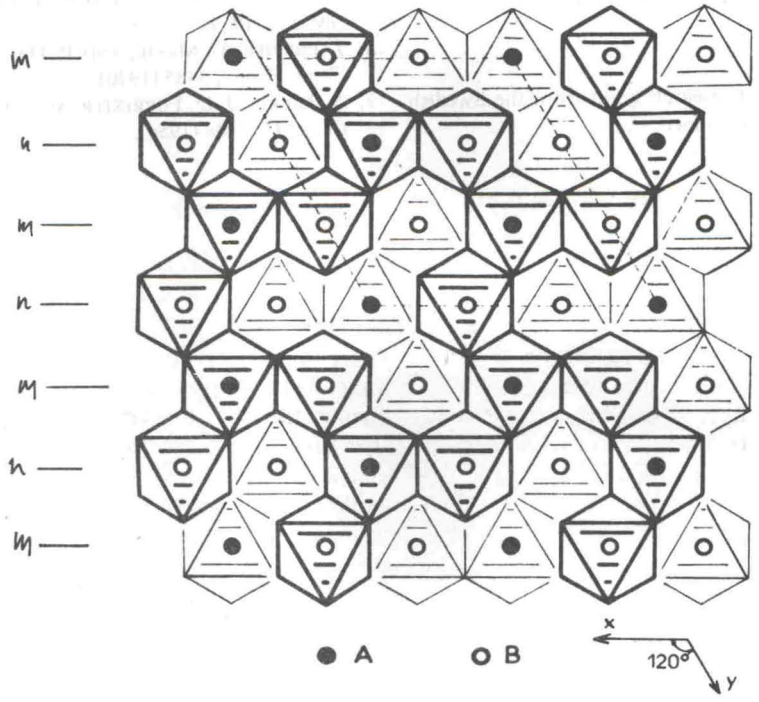

FIG. 4. The Na_2SiF_6 structure type.

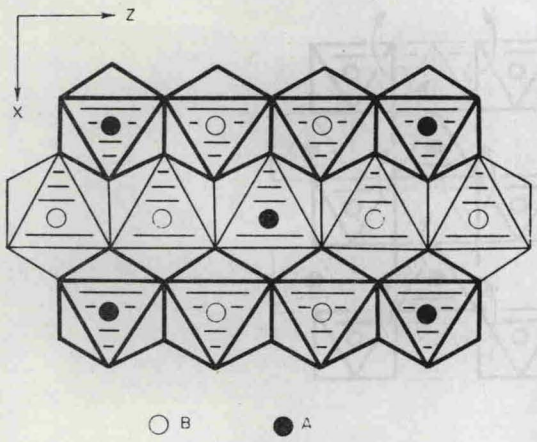

FIG. 5. The trirutile structure type.

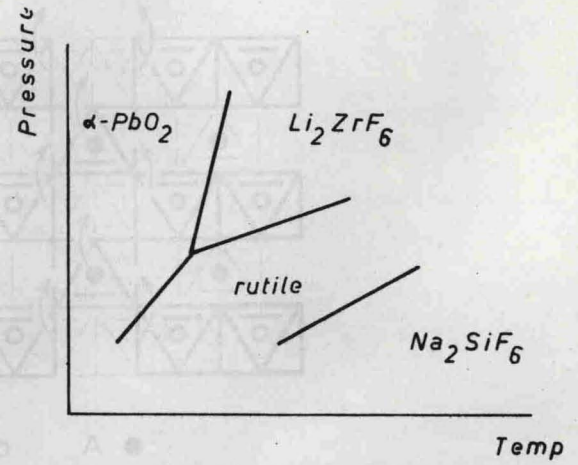

FIG. 6. Tentative temperature-pressure phase diagram for the various MX_2 structure types discussed.

It would be interesting to study the effects of applied pressure in the high temperature experiments referred to above.

In the meantime a tentative pressure-temperature phase diagram is given in Fig. 6. Its construction is based on the observations that

(a) α-$LiSnF_6$ transforms to β-Li_2SnF_6,
(b) α-Li_2GeF_6 transforms to β-$LiGeF_6$ at high temperatures and
(c) rutile transforms to a structure of the α-PbO_2 type at high pressure.

Acknowledgment

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