

Table I

patient nr	phase composition	
	outer part	central part
1	WEW	HAPA+UA
2	WED+WEW	WEW+HAPA+UA
3	WEW+WED	WEW
4	HAPA+STRU	WEW+HAPA
5	WEW+WED+HAPA+STRU	WEW+HAPA+UA
6	WEW+HAPA	HAPA
7	WEW+WED	WEW+WED+HAPA+UA+STRU

Table II

patient nr and stone nr	phase composition	patient nr and stone nr	phase composition
I-1	WEW+WED	III-1	WEW
I-2	WEW	III-2	WEW+WED+UA
I-3	WEW+HAPA	IV-1	HAPA+STRU
II-1	WEW+HAPA+UA+STRU	IV-2	HAPA+STRU+WEW
II-2	WEW+HAPA+STRU		

coordinate respectively.

The second compound, $\text{BaTiAl}_5\text{O}_{12}$ is orthorhombic, $a = 4.862(1)$, $b = 7.136(2)$, $c = 13.598(3)$ Å, Pnn2. Its structure consists of ribbons of octahedra joined by sheets of tetrahedra to form parallel 'six-sided' tunnels. The barium ions in the tunnels are ten-coordinate.

In the first structure the tunnels are interconnected whereas in the second they are not. A full description of the structures will be presented together with their relevance to the SYNROC process.

References:

1. Ringwood, A.E. Safe Disposal of high level nuclear reactor wastes: A new strategy. Australian National University Press, Canberra (1978); and Ringwood, A.E., Kesson, S.E., Ware, N.G., Hibberson, W.O. and Major, A. *Geochem. J.*, **13**, 141 (1979)
2. Kesson, S.E. *Rad. Waste Manag. and the Nuclear Fuel Cycle*, **4**, 1, 53 (1983); and Kesson, S.E., Sinclair, W.J. and Ringwood, A.E. *Nucl. Chem. Waste Manag.*, In press, 1984.
3. G.D. Fallon and B.M. Gatehouse, *J. Solid State Chem.*, **49**, 59 (1983)
4. Guha, J.P., Kolar, D. and Volavsek, B. *J. Solid State Chem.*, **16**, 49 (1976); and Guha, J.P., *J. Solid State Chem.*, **34**, 17 (1980)

08.2-39

NEW STRUCTURES IN THE $\text{BaO-Al}_2\text{O}_3\text{-TiO}_2$ SYSTEM OF SIGNIFICANCE TO THE SYNROC PROCESS

B.M. Gatehouse, Chemistry Department,
Monash University, Clayton,
Victoria, 3168, Australia.

Interest in the alkaline earth aluminium titanates, especially the $\text{BaO-Al}_2\text{O}_3\text{-TiO}_2$ system, has heightened due to the work of Professor Ringwood and coworkers (1) on their proposed SYNROC process for the long term storage of radwaste. SYNROC consists principally of three minerals, hollandite ($\text{BaAl}_2\text{Ti}_6\text{O}_{15}$), perovskite (CaTiO_3) and zirconolite ($\text{CaZrTi}_2\text{O}_7$). Each of these synthetically formed mineral species has been shown to incorporate different radwaste ions in varying proportions (2).

The structure of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ was determined recently (3) and shown to contain blocked tunnels or cavities of the hollandite type in which barium ions are situated, and as a result of this finding other phases that might be of significance to the SYNROC process have been sought.

The structures of two compounds in the $\text{BaO-Al}_2\text{O}_3\text{-TiO}_2$ system, whose compositions were previously known but whose crystal systems and symmetries had been incorrectly reported (4), have been determined. The first, $\text{Ba}_3\text{TiAl}_9\text{O}_{20}$ is monoclinic, $a = 15.631(4)$, $b = 11.373(2)$, $c = 4.981(1)$, $\beta = 107.77(2)^\circ$ C2/m. The structure consists of sheets of corner-shared AlO_4 tetrahedra, two deep, linked by corner-sharing to parallel ribbons of edge-shared octahedra. Each ribbon forms part of four separate tunnels of two different types. One is 'five-sided' and the other 'six-sided'; both accommodate barium ions that are ten- and eight-

08.2-40 NEW COMPOUNDS WITH Ge_4^{4-} TETRAHEDRANE-ANIONS. By J. Llanos, R. Nesper and H.G. von Schnering, Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80.

I-IV-compounds of Na, K, Rb and Cs are not precisely characterized up to now [1,2,3,4]. Besides some clathrate compounds of the M_2X_6 and M_2X_{136} type, only the MX-compounds are observed. Their common unit is the X_4^{4-} tetrahedrane anion which is always coordinated by four metal atoms in form of a distorted cubane M_4X_4 . Different crystal structures arrive from different cubane packings [5]. We have reinvestigated precisely NaGe ($\text{P}2/c$, $a=12.373(4)$, $b=6.668(3)$, $c=11.498(3)$ Å, $\beta=120.21(2)^\circ$); KGe ($\text{P}\bar{4}3n$, $a=12.734(1)$ Å); RbGe ($\text{P}\bar{4}3n$, $a=13.198(3)$ Å) and CsGe ($\text{P}\bar{4}3n$, $a=13.654(5)$ Å) to discuss the cubane geometry in different structures [6]. Moreover new ternary germanides of alkaline metals with the composition $\text{M}_2\text{M}'_{1-x}\text{Ge}$ have been prepared and investigated. Two new structure types occur which contain new arrangements of cubanes and exhibit the special character of the Na- Ge_4 interaction.

The compounds M_7NaGe_8 crystallize cubic in $\text{Pa}\bar{3}$ (K_7NaGe_8 , $a=12.684(1)$ Å; Rb_7NaGe_8 , $a=13.165(1)$ Å; Cs_7NaGe_8 , $a=13.472(3)$ Å) with $Z=4$. They contain the linear $\text{M}_3\text{Ge}_4\text{-Na-Ge}_4\text{M}_3$ unit, which exhibits the geometry of a corner-shared double cubane M_3NaGe_4 . One of the large cations M stays without direct contact to Ge_4 , preserving the MX composition. The structure of such compounds is therefore represented by a quaternary aristotype $\text{M}'\text{M}''_6\text{NaX}_8$, which could be rationalized in $\text{CsK}_6\text{NaGe}_8$ ($\text{Pa}\bar{3}$, $a=12.879(3)$ Å).

The compound $\text{Cs}_2\text{Na}_2\text{Ge}_4$ crystallizes with a new structure type, which is related to the NaPb-