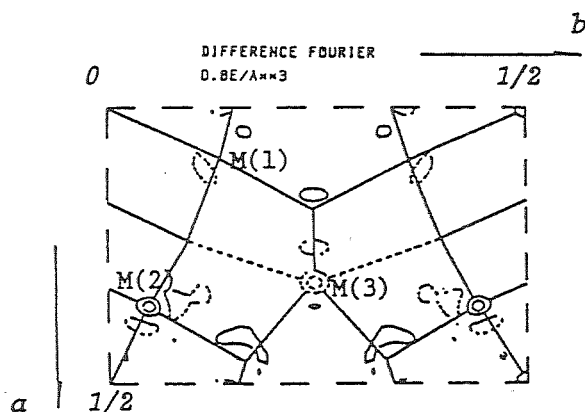


scattering factor of Pb and Bi atom at  $\sin\theta/\lambda = 0.0$  is enlarged to 3.2. A set of 237 intensity of  $hk0$  reflections (including 37 standard reflections) was collected with the  $\omega$ - $2\theta$  step scan mode, using a four-circle diffractometer set up at the BL-10A station. After correction of dead time of detector system, Lorentz factor and absorption, all the intensities were normalized by those of standard reflections measured every ten reflections during data collection.

Several cycles of least-square refinement gave R-factor 0.06 under the condition of referring to the already determined structure as the starting model and employing the averaged scattering factors of Pb and Bi for both metal atoms. The difference among weights of metal sites in d-Fourier map seems to reveal features on the site occupancy of each metal site. A more quantitative study of the site occupancy is now in progress.



**08.4-37 FORMATION OF  $\alpha$ - $\text{Al}_2\text{O}_3$  BY DEHYDRATION OF DIASPORE.** By M. Ohmura<sup>1</sup>, J. Ryuta<sup>1</sup>, K. Terada<sup>1</sup>, N. Yamada<sup>1</sup>, S. Sueno<sup>1</sup>, H. Nakazawa<sup>2</sup>, K. Tsukimura<sup>3</sup> and S. Sasaki<sup>4</sup>, 1: Univ. of Tsukuba, 2: Nat. Inst. for Research in Inorganic Materials, 3: Geol. Survey, 4: Nat. Lab. for High Energy Physics, Japan.

Diaspore ( $\alpha$ - $\text{AlOOH}$ ) transforms to  $\alpha$ - $\text{Al}_2\text{O}_3$  at about 500°C and the change is expressed as follows:  $2\alpha$ - $\text{AlOOH} \rightarrow \alpha$ - $\text{Al}_2\text{O}_3 + \text{H}_2\text{O}$ . Lima-de-Faria

(Z. Kristallogr. (1963) 119, 176) studied the dehydration and found that a topotactic relation exists between diaspora and  $\alpha$ - $\text{Al}_2\text{O}_3$  and reflections of the latter are accompanied by satellites. He concluded that the satellites could be ascribed to a modulation of amplitude, but recently his conclusion was opposed (Watari, J. Sol. Stat. Chem. (1979) 29, 417). The present studies have been undertaken to check the validity of both results and to clarify the mechanism of the dehydration.

Good single crystals from Shokozan, Hiroshima, Japan were selected for experiments. The process of the dehydration was observed by two different methods. One of them was a quenching method; that is, the specimen were heated at definite temperatures for various periods and then quenched in air. The specimens were tested by X-ray diffraction. The temperatures selected were 450°C, 500°C and 550°C, and the period ranged from 15 minutes to 24 hours. The second was a direct observation of the change at elevated temperatures by X-ray diffraction with SR beam in Nat. Lab. for High

Energy Physics.

The unit cell of diaspora is orthorhombic Pbnm with dimensions  $a=4.425$ ,  $b=9.380$ ,  $c=2.844\text{Å}$  and that of  $\alpha$ - $\text{Al}_2\text{O}_3$  is rhombohedral  $R\bar{3}c$  with  $a=4.781$  and  $c=13.032\text{Å}$ . Topotaxy was confirmed between diaspora and  $\alpha$ - $\text{Al}_2\text{O}_3$ :  $[100]_s // [100]_p$  and  $[001]_s // [1\bar{1}0]_p$  where  $s$  and  $p$  indicate the starting material and the product, respectively. The transformation progresses gradually. The satellites come up in the early stage and their feature changes slightly when the samples are heated at different temperatures. Streaks are observed between satellites and main reflections. Their intensity is affected by the temperature and the period of heating. The following features are also noted: (1) the satellites are observed along the  $c^*$  of  $\alpha$ - $\text{Al}_2\text{O}_3$  and the period of modulation derived is about three times of the  $c$ , and (2) satellites of higher order are not observed and the intensity of outer satellites are slightly stronger than the inner one. Since satellites were also noticed by direct observation with SR beam, the modulation should not be formed by quenching. The above features ascribe the modulation to a periodic distribution of Al-deficient layers along the  $c$ . The spots of the products, being broad, become sharper when the specimens are heated longer and with higher temperature. This suggests that nucleation and growth play important roles in the formation of  $\alpha$ - $\text{Al}_2\text{O}_3$ .

**08.4-38 PHASE TRANSITION AND ORDERING IN LEUCITE.** By T. Grögel, H. Boysen and F. Frey, Institut f. Kristallographie d. Universität, München, FRG.

Leucite ( $\text{KAlSi}_2\text{O}_6$ ) is known to undergo a phase transition from a cubic high temperature form ( $Ia\bar{3}d$ ) to a tetragonal low temperature form ( $I4_1/a$ ). Quoted transition temperatures  $T_c$  range from  $\sim 870$  K to  $\sim 950$  K, where single crystal X-ray investigations revealed only one transition point (Peacor, Z. Krist. (1967) 127, 213), while DTA measurements seem to indicate an additional intermediate phase (Faust, Schweiz. Min. Pet. Mit. (1963) 43, 165). The transition is mainly connected with a rearrangement of the  $(\text{Si,Al})\text{O}_4$ -tetrahedra, whereas a

suggested Si-Al ordering on crystallographical different positions could not be detected with X-rays (Mazzi, Galli, Gottardi, Am. Mineral. (1967) 61, 108). To clarify this latter point a neutron powder study (taking advantage of the larger Si/Al-scattering lengths ratio for neutrons and the absence of any twinning problems being serious in single crystals) on natural leucite has been performed at 5 different temperatures between room temperature and 1073 K together with supporting single crystal X-ray measurements. Using the Rietveld refinement program (final structural parameters will be given) the neutron data clearly revealed a partial Si-Al ordering of the starting material at r.t., which becomes complete after heat treatment at higher temperatures and totally disordered again in the cubic phase (requested by symmetry). Moreover, the results indicate

an intermediate phase of space group  $I4_1/acd$  between  $T_{c1} \sim 910$  K and  $T_{c2} \sim 960$  K. This was further confirmed by a measurement in narrower temperature intervals of the  $c/a$ -ratio (using the (400)-reflexion) showing an abrupt change of the slope at  $T_{c1}$ , as well as by the intensity variation of a superstructure reflexion (503) (extinct in  $Ia3d$ ), which becomes diffuse approaching  $T_{c2}$  from below. These latter reflexions are also visible on X-ray photographs using longer exposure times. Together with these changes there appears a strong increase of the diffuse background in the powder diagrams showing a characteristic modulation, which can be connected with overdamped soft modes at the  $\Gamma$ -point and in  $(\xi\xi 0)$ -directions observed by inelastic neutron scattering (Boysen, Eckold, Symp. on Neutron Scattering, Berlin, 1984). In conclusion the transition is characterized by a rotational rearrangement of (nearly) rigid  $(Si, Al)O_4$ -tetrahedra combined with an ordering of Si and Al, the extent of which is probably due to the rate of cooling and the formation of twins separated by (110)-interfaces.

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08.4-39 COEXISTENCE OF TRIDYMITE POLYMORPHS AND CRISTOBALITE IN TRIDYMITE CRYSTALS. By A. Nukui and O.W. Flörke\*, National Institute for Research in Inorganic Materials, Namiki 1-1, Sakura-mura, Ibaraki, 305 Japan. \*Institut für Mineralogie, Ruhr-Universität Bochum, D-4630 Bochum 1, Germany-B.R.D..

Tridymite is known to have 6 modifications at room temperature. Through the experimental studies under high temperatures and pressures, MC (monoclinic Cc;  $a=17.21$ ,  $b=4.991$ ,  $c=25.83A$  and  $\beta=117.75^\circ$ ), PO-10 (triclinic F1;  $a=17.21$ ,  $b=9.93$  and  $c=81.86A$ ) and MX-2 (monoclinic;  $a=8.6$ ,  $b=15.026$ ,  $c=16.434A$  and  $\beta=91.496^\circ$ ) modifications are suggested to be low-temperature phases (e.g. Nukui et al., J. Mineral. Soc. Japan (1980) 14, 364).

A variety of diffraction patterns of tridymite crystals were obtained by the X-ray precession method in this study, which can be explained by some combinations of the three modifications (MC, PO-10 and MX-2) and cristobalite. For these four, 15 combinations are possible; single (4), two (6), three (4) and four phases (1). 13 of them have so far been observed in crystals with different formation conditions. The patterns of MX + cristobalite and MX + PO + cristobalite phases are not observed. Because the three tridymite modifications are superstructures with a common fundamental cell, their stacking direction is parallel to the  $c$ -direction of the high-temperature form of tridymite (Gibbs, Proc. Roy. Soc. London (1927) A113, 351) as well as [111] of cristobalite. These facts can be used to understand: a) the stability relationships between tridymites and cristobalite, b) the polymorphic relationships among them, and c) their coexistence mechanism.

08.4-40 THE CRYSTAL STRUCTURES OF ALKALINE CARBONATES: BARENTSITE, BONSHTEDTITE AND DONNAYITE. By Trinh Thi Le Thi, E.A. Pobedimskaja, T.N. Nadezhina, A.P. Khomjakov. Geological Faculty, Moscow State University, Moscow, USSR.

The structure of barentsite  $Na_7Al(CO_3)(HCO_3)_2F_4$  ( $a=8.806$ ,  $b=6.735$ ,  $c=6.472A$ ,  $\alpha=119.32$ ,  $\beta=97.33$ ,  $\gamma=92.50^\circ$ ,  $Z=1$ ,  $P\bar{1}$ ) is based on brucite-like layers alternating with distorted ones of double columns of Na-octahedra. The hydrogen atom makes connection between neighbouring  $CO_3$ -groups. The structure of bonshtedtite  $Na_3F(PO_4)(CO_3)$  ( $a=8.955$ ,  $b=6.029$ ,  $c=5.149A$ ,  $\beta=89.55^\circ$ ,  $Z=1$ ,  $P2_1/m$ ) consists of complex sheets of Fe-octahedra,  $(PO_4)$ -tetrahedra and Na-polyhedra. The  $CO_3$ -groups connect polyhedra of cations. In the structure of donnayite-like carbonate  $(Na, Y, TR)Sr(CO_3)_2 \cdot H_2O$  ( $a=8.535$ ,  $b=6.818$ ,  $c=5.212A$ ,  $\gamma=109.29^\circ$ ,  $Z=2$ ,  $Pn$ ) Sr has coordination 10, and Na and TR are seven-coordinated. The layers consisting of Sr-polyhedra are alternating with ones of Na, TR-polyhedra and connected with ones other by  $CO_3$ -groups.

08.4-41 THE STRUCTURAL CHARACTERISTICS OF MICAS WITH TETRAHEDRAL IRON CONTENT REGARDING ISOMORPHOUS SUBSTITUTIONS. By T.F. Semenova (a), I.V. Rozhdestvenskaya (b) and V.A. Frank-Kamenetskii (a), Faculty of Geology, Leningrad State University, University Embankment 7/9, Leningrad, USSR (a), NPO "Burevestnik", Stahanovtsev 1, Leningrad, USSR (b).

The structures of three members of isomorphous series of phlogopite-tetraferriphlogopite

$(K_{0.9}Na_{0.1})(Mg_{2.85}Fe_{0.15}^{2+})[Al_{1-x}Fe_x^{3+}Si_3O_{10}(OH)_2]$  (samples 1-3) and tetraferriphlogopite  $(K_{0.9}Na_{0.1})(Mg_{1.64}Fe_{1.37}^{2+})[Al_{0.03}Fe_{0.87}^{3+}Si_3O_{10}(OH)_2]$  (sample 4) have been refined:

	x	a (Å)	b (Å)	c (Å)	$\beta$ (°)	R
1.	0	5.319	9.220	10.288	99.93	0.031
2.	0.45	5.341	9.259	10.297	99.95	0.057
3.	0.85	5.358	9.297	10.318	100.02	0.042
4.	0.87	5.373	9.311	10.306	100.10	0.079

Single crystal investigations were carried out using a X-ray four-circle diffractometer with  $Mo K\alpha$ -radiation. The refinement of the structures was carried out in sp.gr. C 2/m in anisotropic approach. It was determined that  $Al \leftarrow Fe^{3+}$  substitution in tetrahedral sheets significantly influenced upon all the structural parameters of micas. Tetrahedral sheet. The incorporation of large  $Fe^{3+}$  cations leads to the linear increasing of the tetrahedral bond lengths from  $d_t=1.660$  Å in phlogopite structure up to 1.665, 1.680 and 1.676 Å in intermediate, end tetraferriphlogopites and tetraferriphlogopite respectively. In