

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.

This work was supported by funds of the BMFT under 03-102A04.

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

phlogopite-tetraferriphlogopite series it also leads to the displacement of tetrahedral cation from the apical oxygen in direction of the geometrical centre of tetrahedron. The decreasing of tetrahedron length along  $c^*$  and approaching its form to the ideal one in the structure of end tetraferriphlogopite are observed. The tetrahedral rotation angle  $\alpha$  changes from  $8.97^\circ$  in phlogopite to  $11.75^\circ$  in end tetraferriphlogopite. In the structure of tetraferriphlogopite the distortion of individual tetrahedron along with tetrahedral sheet ( $\alpha=8.96^\circ$ ) is similar to that observed in phlogopite structure.

**Interlayer cation.** In all the structures due to the large ditrigonal distortion the coordination of interlayer cation approaches to an octahedral group. In the tetraferriphlogopite the inner oxygens ( $K-O_{in}=2.932 \text{ \AA}$ ) are closer than in phlogopite ( $2.969 \text{ \AA}$ ). The height of interlayer space increases from  $3.446 \text{ \AA}$  (phlogopite) to  $3.461 \text{ \AA}$  (tetraferriphlogopite). In tetraferriphlogopite structure K-O bond length with inner oxygens is  $2.974 \text{ \AA}$ .

**Octahedral sheet.** The larger is the substitution of Al on Fe in tetrahedra the larger are the degree of flattening of octahedral sheet ( $h_o=2.164 \text{ \AA}$ ,  $\psi=58.6^\circ$ ;  $h_o=2.146 \text{ \AA}$ ,  $\psi=59.0^\circ$  in phlogopite and tetraferriphlogopite respectively) and its ensharing edges from  $3.074 \text{ \AA}$  in phlogopite to  $3.097 \text{ \AA}$  in tetraferriphlogopite. The distortion of octahedral sheet in tetraferriphlogopite is similar to that in phlogopite structure. The positional parameters of H atom were obtained from difference Fourier map. In all structures the O-H axis is normal to (001).

tings of 25 reflections with high  $\theta$ -angle:

	Thulite	Piemontite
a [ $\text{\AA}$ ]	16.2051(37)	8.8739(11)
b [ $\text{\AA}$ ]	5.5488(12)	5.6156(8)
c [ $\text{\AA}$ ]	10.0329(18)	10.1484(13)
$\beta$ [ $^\circ$ ]	90.0	115.488
S.G.	Pnma	$P2_1/m$

For thulite (corresponding piemontite values in parentheses) a total of 2142 (3027) reflections were collected, for the idiomorphic thulite crystal an absorption correction gave minimum and maximum transmission factors of 0.858 and 0.908, the piemontite data were not corrected for absorption because of the irregular shape of the crystal fragment. The programs SHELX (Sheldrick, University of Cambridge, 1976) and RFINTE (Finger and Prince, Natl. Bur. Stand. (U.S.) Tech. Note 854, 1975) were used for the refinement which included the variation of anisotropic temperature factors and of occupancy factors of possible  $M^{3+}$ -sites and resulted in residuals of 0.037 (0.029) for 1456 (2462) observed reflections. The chemical compositions obtained from EMP-analyses were used as a constraint for the site occupancy refinement, which in the case of thulite led to an Al-content of 7.96(3) atoms in the 8-fold M(1,2) position and of 3.47 in the 4-fold M(3) position. Al-distribution in piemontite is 3.80(2), 3.91(2) and 2.00 atoms in the three 4-fold positions M(1), M(2) and M(3). As expected for the piemontite structure most  $M^{3+}$  atoms are situated in the M(3) position but significant amounts are also present in M(1) and M(2), a result which confirms the interpretation of the  $\nu_{OH}$ -bands in synthetic piemontites with  $p>1.0$  Langer et al., Z. Krist. (1976) 144, 334).

08.4-42 CRYSTAL STRUCTURE REFINEMENTS OF COEXISTING THULITE AND PIEMONTITE,  $Ca_2Al_3-pM^{3+}[OH/O/SiO_4/Si_2O_7]$  ( $M^{3+}=Mn^{3+}+Fe^{3+}$ ).

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Coexisting thulite ( $Mn^{3+}$  orthozoisite) and piemontite from Lom/Norge have been analysed by microprobe (EMP) and structurally refined with the following aims:

(i) evaluation of the inter- and intra-crystalline partitioning of  $M^{3+}=(Mn^{3+}+Fe^{3+})$ , and (ii) solution of the discrepancy between the spectroscopic results of Burns and Strens (Mineral. Mag. (1967) 36, 204), i.e.  $M(3) \gg M(2) \gg M(1)$  in piemontites and structural results of Dollase (Am. Min. (1968) 53, 1882) who found  $M(3) \gg M(1) \gg M(2)$ .

Optically clear, inclusion-free crystals with homogeneous and sharp optical extinction were selected for data collection. EMP-results on these crystals (Cameca Camebax, Program MISO) yielded the crystallochemical formulae:

Thulite (TUPILA 19-Thu2)

$(Ca_{1.970}Mg_{0.002}Zn_{0.010})^{[7-8]}(Al_{2.857}Mn^{3+}_{0.030}Fe^{3+}_{0.096}Cu^{2+}_{0.009})^{[6]}[OH/O/SiO_4/Si_{2.018}O_7]$

Piemontite (TUPILA 19-Pie 1)

$(Ca_{1.975}Mg_{0.012}Zn_{0.008})^{[7-8]}(Al_{2.428}Mn^{3+}_{0.143}Fe^{3+}_{0.432}Cu_{0.014})^{[6]}[OH/O(SiO_4/Si_{1.994}O_7)]$

Lattice constants were refined from the set-

08.4-43 THE CRYSTAL STRUCTURE OF NEW MINERAL FROM DELCHAEILITE FAMILY AND THE CRYSTAL CHEMISTRY FEATURES OF TR-SILICATES. By K.G.Ragimov, M.I.Chiragov. The Institute of Inorganic and Physical Chemistry Academy of Sciences of the Azerbaijan SSR and The Azerbaijan State University, Baku, USSR.

The structure of K-delchaelite discovered in the Khibina massif of the USSR has been determined by single-crystal X-ray analysis. K-delchaelite- $K_4Na_2[Ca_2(Si_6Al_2O_{19})(F,Cl)_2]H_2O$  is orthorhombic with  $a=6.598(2)$ ,  $b=24.655(2)$ ,  $c=7.080(2) \text{ \AA}$ , space group  $Pn2_1m$ ,  $z=2$ . The structure was refined up to  $R=0.07$ . The structure is similar to that of delchaelite- $K_3Na_2[Ca_2(Si,Al)_8O_{19}(F,Cl)_2]$ . The crystal structure consists of layers formed by the Ca- and Na-polyhedra parallel to (010), which is held together by the doubled sheets of tetrahedra with the formula  $(Si_6Al_2)O_{19}$ . The formation of these doubled sheets may be considered as a condensation of the wollastonite chains and additional  $Al_2O_7$  groups. Atoms K and molecules  $H_2O$  are localized in the mixed framework cavities.

The crystal structure of monteredgianite -  $K_2Na_4Y_2Si_{16}O_{38} \cdot 10H_2O$  is closely related to that of delchaelite. Monteredgianite is orthorhombic with  $a=2x7.02$ ,  $b=23.91$ ,  $c=2x6.598 \text{ \AA}$ , space group  $Bmab$ . This structure is very probably based on a mixed framework made up of delchaelite ( $Si_8O_{19}$ ) sheet and octahedrally coordinated Y and Na. It is supposed that iso-