08.4—33   HIGH-PRESSURE CRYSTAL STRUCTURE OF QUARTZ UP TO 102 KBAR. By J. Glinnemann & H. Schulz, Max-Planck-Institut für Festkörperforschung, Stuttgart, FRG

To test a new type of high-pressure cell for single-crystal work on four-circle diffractometers (Malinowski et al., Z. Krist. (1982) 159, 93), quartz was chosen to allow a comparison with recent work (D'Amour et al., Acta Cryst. (1979) B35, 550; Levien et al., American Mineral. (1980) 65, 920). An improved version of this cell is presented at this meeting by Dieterich et al.
X-ray intensities were collected with a Philips PW1100 at 1 atm and 40, 72, and 102 kbar. Experimental conditions chosen were: MoK_α-radiation, $max(\sin\theta/\lambda)=0.9\text{Å}^{-1}$, stepscans. Half a sphere of reciprocal space with $-10\le h,k\le10, 1\le l\le10$ was collected. The number of measured reflections laid between 1100 and 1300, i.e. nearly 90% of all non-Friedel reflections. Averaging yielded 240-280 unique observations with about 20% of the I's$\le3\sigma I$. The structural changes observed with increasing pressure include:

(1) A decrease in the Si-O-Si angle from 143.8(1) to 130.3(1)°;
(2) One Si-O bond distance remains constant at 1.614(1)Å, whereas the other one decreases from 1.605(1) to 1.600(1)Å. This results in only a minor decrease of the mean Si-O length from 1.610(1) to 1.607(1)Å.
(3) The two inter-tetrahedral O-O distances decrease from 3.414(2) to 2.947(2)Å and from 3.345(2) to 2.793(2)Å.

Because of (2) the small but significant decrease in the average Si-O bond length observed by Levien et al. at pressures up to 61.4 kbar is again open for discussion.

08.4—34   AVERAGE STRUCTURE AND FAULTED SEQUENCES IN ORIENTITE. By M. Mellini, S. Merlino and M. Pasero, Dipartimento di Scienze della Terra, Università di Pisa, Pisa, Italy.

Orientite is a manganese silicate, closely related to ardennite (Moore et al., 1979). A structure model for the mineral was obtained starting from the sursassite-pumpellyite structural relationships (Mellini et al., 1983). Sursassite, $Mn_2Al_3[(OH)_3(SiO_4)(Si_2O_7)]$ and pumpellyite, $Ca_2Al_3[(OH)_3(SiO_4)(Si_2O_7)]$, apart from the chemical differences, are built up by identical structural layers, differently stacked. The distinctive feature in the two structures is that whereas in pumpellyite similar silicate groups (ortho-ortho and diortho-diortho) face each other, in sursassite different silicate groups face each other on both sides of the aluminum octahedral rows.

Similarly, ardennite, $Mn_4(Al,Mg)_6[(OH)_6AsO_4(SiO_4)_2 (Si_3O_{10})]$, is characterized by trisilicate and orthosilicate groups, with different groups facing each other. By analogy to the sursassite-pumpellyite case, a different modification can be envisaged, with similar groups facing each other. This model was now refined to R = 0.08 for orientite from Cuba (a=9.044, b=6.091, c=19.031 A, Pcmm) and resulted in the ideal crystal chemical formula $Ca_4Mn_6[(OH)_6(SiO_4)_3(Si_3O_{10})]$.

As for sursassite, disorder phenomena are now observed also in orientite, which is characterized by disordered alternation of orientite-like and ardennite-like domains. Such faults can explain the difficulties found during the X-ray structure analysis and also the previous assumption of a C-centered cell for orientite: the C-cell is due to the average structure, resulting from the two domains.

08.4—35   ISOTOPIC VARIATIONS IN DIAMOND IN RELATION TO CATHODOLUMINESCENCE

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Using a Q-switched neodymium-YAG laser delivering 1.3mJ focussed with a 25mm objective such as is used for the production of heat sinks, diamond plates approximately 5mm in diameter and 0.4mm thick have been dissected to provide specimens for carbon isotope analyses at known locations within a single stone (Nature; 303 (1983) 793).
This technique has now been further developed, and subsequent experiments have shown significant variations on a sub-millimetre scale, ranging from regular progressions compatible with isotope fractionation calculations to very erratic variations whose cause is unknown.
It has also been found that the complexity of these isotopic variations appears to correspond to the complexity of the observed cathodoluminescence patterns. Diamonds generally contain measurable quantities of nitrogen, and most cathodoluminescence is thought to be associated with nitrogen in various states of aggregation.
We have recently been able to make systematic measurements of nitrogen isotope ratios and nitrogen concentrations in addition to the carbon isotope determinations at selected locations within individual diamonds, and available results will be presented.
Isotopic variations associated with the two main types of diamond will also be illustrated.

08.4—36   REINVESTIGATION OF LILLIANITE STRUCTURE WITH SYNCHROTRON RADIATION

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The lillianite structure$(3PbS \cdot Bi_2S_3)$ is well known as being composed of polysynthetic cell twinning, across (311) of the galena structure, of galena slab (Takéuchi and Takagi,Proc.Japan Acad. 10(1974),843). The cell parameters and the space group are : a = 13.535(3), b = 20.451(5), c = 4.104(1)Å and Bbmm. The unit cell contains four formula units (Takagi and Takéuchi,Acta Cryst. B28(1972),649). According to the structure already determined based on film intensity data$(MoK\alpha)$, there are three kinds of metal sites named M(1), M(2) and M(3). Although the M(1) and M(2) sites were thought to be occupied by Pb and Bi at random, while M(3) by only Pb, the accurate occupancy in each metal site has been left unknown. Making use of the synchrotron radiation at Photon Factory, we may now directly study the atomic occupancy at each atomic site of lillianite by selecting suitable X-ray wave length.

The specimen employed for the present study was almost cubic in form with dimension of approximately 0.09mm in edge and contains a small amount of Ag detected by electron microprobe analysis. Synchrotron radiation was monochromated by pyrolytic graphite(002) to provide X-ray beam with the wave length of 0.96Å. The value of wave length was selected just longer than both L-III-absorption edges of Pb$(\lambda = 0.95029\text{Å})$ and Bi $(\lambda = 0.92336\text{Å})$ atoms. It results in the fact that a linear absorption coefficient(μ) can be made into small value of 339cm^{-1} (cf. 866cm^{-1} for Mo$k\alpha$). Under the condition, the anomalous dispersion terms of both Pb and Bi atoms were estimated as f'(Pb) = -14.5 and f'(Bi) = -12.3 respectively, but imaginary terms(f'') were neglected at this stage of analysis compared with large values of real term$(f^0 + f')$. The difference between

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 ω-2θ 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.

DIFFERENCE FOURIER

0.8E/A**3

Energy Physics.

The unit cell of diaspore is orthorhombic Pbnm with dimensions a=4.425, b=9.380, c=2.844Å and that of α-Al_2O_3 is rhombohedral R$\bar{3}$c with a= 4.781 and c=13.032Å. Topotaxy was confirmed between diaspore and α-Al_2O_3: [100]s//[001]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 α-Al_2O_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 α-Al_2O_3.

08.4—37　FORMATION OF α-Al_2O_3 BY DEHYDRATION OF DIASPORE. By M. Ohmasa[1], J. Ryuta[1], K. Terada[1], N. Yamada[1], S. Sueno[1], H. Nakazawa[2], K. Tsukimura[3] and S. Sasaki[4], 1: Univ. of Tsukuba, 2: Nat. Inst. for Research in Inorganic Materials, 3: Geol. Survey, 4: Nat. Lab. for High Energy Physics, Japan.

Diaspore(α-AlOOH) transforms to α-Al_2O_3 at about 500°C and the change is expressed as follows: 2α-AlOOH $\rightarrow$ α-Al_2O_3 + H_2O. Lima-de-Faria (Z. Kristallogr. (1963) 119, 176) studied the dehydration and found that a topotactic relation exists between diaspore and α-Al_2O_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

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 ($KAlSi_2O_6$) is known to undergo a phase transition from a cubic high temperature form (Ia3d) to a tetragonal low temperature form (I4$_1$/a). Quoted transition temperatures T_c range from ~870 K to ~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 (Si,Al)O_4-terahedra, 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