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; LeVeen et al., American Mineral. (1980) 65, 920). An improved version of this cell is presented at this meeting by Dietrich et al.

X-ray intensities were collected on a Philips PM1100 at 1 at 40, 72, and 102 kbar. Experimental conditions chosen were: MoKα-radiation, sin(θ/2) = 0.9 Å⁻¹, stepscans. Half a sphere of reciprocal space with -12h ≤ k ≤ 12, 1 ≤ l ≤ 10 was collected. The number of measured reflections lies 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 equal. 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 0-0 distances decrease from 3.419(2) Å and from 3.425(2) Å to 3.409(2) Å and 3.405(2) Å. Because of (2) the small but significant decrease in the average Si-O bond length observed by LeVeen et al. at pressures up to 61.4 kbar is again open for discussion.

To test a new type of high-pressure 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; LeVeen et al., American Mineral. (1980) 65, 920). An improved version of this cell is presented at this meeting by Dietrich et al.

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Centimeter

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.

The illianite structure (3PbS·Bi2S3) is well known as being composed of polyhedral cell twinning, across (311) of the galena structure, of galena slabs (Takēuchi and Takagi, Proc. Japan Acad. 12 (1936), 843). The cell parameters and the space group are: a = 13.535(3), b = 20.451(5), c = 6.104(1) Å and P2₁/a. The unit cell contains four formula units (Takagi and Takuchi, Acta Cryst. B32 (1976), 649). According to the structure already determined based on film intensity data (MoKα), 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 illianite by selecting suitable X-ray wave length.

The specimen employed for the present study was almost cubic in form with dimension of approximately 0.09 mm 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 0.06 Å. The value of wave length was selected just longer than both L-III-absorption edges of Pb(λ = 0.9529 Å) and Bi (λ = 0.8923 Å) atoms. It results in the fact that a linear absorption coefficient (μ) can be made into small value of 338 cm⁻¹ (cf. 866 cm⁻¹ for MoKα). Under the condition, the anomalous dispersion terms of both Pb and Bi atoms were estimated as f(Pb) = 1.49 and f(Bi) = 0.82 respectively, but imaginary terms(μ) were neglected at this stage of analysis compared with large values of real term(μ). The difference between

Sursassite, the mineral was obtained starting from the sursassite-pumpellyte case, a different analogy to the sursassite-pumpellyte case, a different
scattering factor of Pb and Bi atom at sinθ/λ = 0.0 is enlarged to 3.2. A set of 237 intensity of 44 reflections (including 37 standard reflections) was collected with the 0.2θ step scan mode, using a four-circle diffractometer set up at the BL10A 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-squares 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

0.87E/A-3

0

1/2

M(1)

M(2)

M(3)

1/2

α

8.4-37 FORMATION OF α-Al₂O₃ BY DEHYDRATION OF DIASPORE. By M. Ohmaka¹, T. Ryuta¹, K. Terada², H. Namada³, S. Sueno², N. Nakasawa², K. Tsukimura⁴ and S. Sasaki², University of Osaka, Japan, and Sasaki⁸, Japan. Inorganic Materials, 3; Geol. Survey, 4; Nat. Lab. for High Energy Physics, Japan.

Diaspore (α-Al₂O₃H₂O) transforms to α-Al₂O₃ at about 500°C and the change is expressed as follows: 2α-Al₂O₃H₂O → α-Al₂O₃ + H₂O. Lime-de-Parìa (Z. Kristallog. 1963) 115, 176) studied the dehydration and found that a topoatomic relation exists between diaspore and α-Al₂O₃ 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 (Yasari, J. Sol. Stat. Chem. 1976 23, 117). 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 diaspore is orthorhombic, with dimensions a = 4.425, b = 9.286, c = 2.844Å and that of α-Al₂O₃ is rhombohedral R3c with a = 4.781 and c = 13.032Å. Topotaxy was confirmed between diaspore and α-Al₂O₃: (100)α/001p and (001)α/(110)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-axis of α-Al₂O₃ 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 of powders, 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-Al₂O₃.