

05.1-14 THE STRUCTURAL PHASE TRANSITION OF THALLIUMSELENATE AT 72 K. By P. Seidel and W. Hoffmann, Institut für Mineralogie, Universität Münster, Germany.

The phase transition of thallium selenate (Tl_2SeO_4) at 72 K discovered by Eller (Diplomarbeit, Saárbrücken 1978, unpublished) and Unruh (H. G. Unruh, Ferroelectrics, 1980, 25, 507) has also been studied by optical and x-ray diffraction measurements (Th. Grunwald, W. Hoffmann and P. Seidel, Ferroelectrics, 1984, 56, 91-94 and 55, 35-38). The results of the crystal structure determination of thallium selenate at room temperature are presented. To determine the crystal structure of the low temperature phase, a low temperature Weissenberg camera developed at our Institute (P. Seidel, Ferroelectrics, 1984, 55, 309-312) is being used. So far, the crystals have always been heavily destroyed during transition, and the transition is incomplete, so that the diffraction patterns both of the room temperature phase and the low temperature phase appear in the same photograph. Using a new temperature controller in connection with the low temperature camera which allows cooling rates less than 0.6 K per hour, the destruction of the crystals can be prevented.

05.1-15 DEGREE OF ORDER IN "HIGH-TEMPERATURE" MODIFICATIONS OF SILICA FRAMEWORK STRUCTURES: RELATIONSHIPS TO "LOW-TEMPERATURE" FRAMEWORKS. By Daniel E. Appleman, Department of Mineral Sciences, NHB 119, Smithsonian Institution, Washington, D.C. 20560, U.S.A.

Crystal structures of high-temperature modifications of silica polymorphs universally exhibit anomalous Si-O distances, Si-O-Si angles and temperature factors. Several studies (e.g. Wright and Leadbetter, Phil. Mag., 1975, 31, 1391-1401 for cristobalite; Dolino et al., Bull. Mineral., 1983, 106, 267-285 for quartz) have suggested that these materials are in fact disordered, and that the average structures reported for them may represent several superimposed orientations of ordered domains with atomic arrangements similar to those of the corresponding low-temperature forms. It is proposed here that all so-called high-temperature silica framework structures consist of such short-range ordered domains, and that these domains are disordered with respect to each other. Furthermore, in every case the structure within a domain is very close to that of the corresponding low-temperature form, and the relative orientations of domains are predicted by twin laws observed in the low-temperature form. These disordered structures occur not only in the polymorphic forms of silica but also in the pure silica framework portions of clathrasils like melanophlogite (Gies, Z. Krist., 1983, 164, 247-257). The key to recognizing them is threefold: (a) short average Si-O distances, less than 1.58 Å; (b) large Si-O-Si angles, approaching a 180° average; and (c) anomalously large thermal parameters compared to those found for ordered polymorphs. New structural studies of naturally-occurring cristobalite, tridymite and melanophlogite strongly support the above interpretation. Similar high-low relationships may occur in aluminosilicate frameworks, but the evidence is largely masked by Al-Si order disorder effects.

05.1-16 A HIGH TEMPERATURE NEUTRON DIFFRACTION STUDY OF THE ANHARMONICITY AND STRUCTURAL INSTABILITY BELOW THE ORTHO-PROTO PHASE TRANSITION IN ENSTATITE, $\text{Mg}_2\text{Si}_2\text{O}_6$. By N. Haga and Subrata Ghose, Mineral Physics Group, Department of Geological Sciences, University of Washington, Seattle, WA 98195, U.S.A. and R. K. McMullan, Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, U.S.A.

The first order phase transition from ortho enstatite (Pbca) to proto enstatite (Pbcn) occurs at approximately 1320 K. High temperature single crystal neutron diffraction experiments were carried out using an electrical resistance furnace with a temperature stability of ± 1 K at 296, 730, 1000, 1200, 1245 and 1300 K. Structure refinements using harmonic and anharmonic thermal vibration parameters up to 4th rank tensors indicate pronounced anharmonic thermal vibrations of the Mg(2), followed by O3B, O3A, O2A, O2B, O1A, O1B and Mg(1) atoms, whereas those of SiA and SiB atoms are not significant. The structural changes at high temperatures are effected principally by the straightening out of the A- and B-silicate chains and the resulting increase in the Mg(2)-O3A and Mg(2)-O3B bond lengths from 2.288 and 2.444 Å at 296 K to 2.376 and 2.683 Å at 1300 K respectively (Fig. 1). The thermal expansion of the Mg-O and Si-O bond lengths are non-linear above 700 K and show anomalous behavior in the 1200-1300 K range indicating an impending phase transition.

The anharmonic thermal vibrations associated with the Mg(2) atom as represented by the probability density function (pdf) at 1300 K shows a trefoil pattern, with the strongest positive lobe directed towards an O3B atom (Fig. 2). The pdf for O3A and O3B on the Si-O-Si plane show double positive maxima, which occur on either side of the Mg(2)-O3A and Mg(2)-O3B bond directions, indicating a tendency of the ortho phase to adopt both proto and twinned high clino (C2/c) configurations just below T_C .

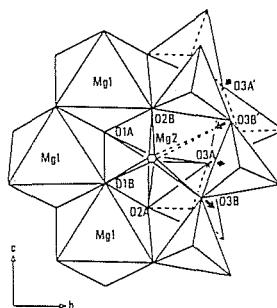


Fig. 1

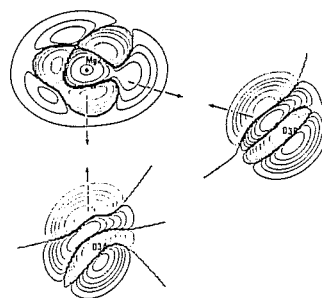


Fig. 2