Determination of the High-Low Inversion in Berlinite (AlPO₄) to 6 kbar

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Abstract

The high-low inversion in berlinite has been determined to 6 kbar by differential thermal analysis in hydrostatic apparatus. From near 584°C at 1 bar, the transition temperature rises linearly with pressure at the rate of 26.0 ± 0.5 deg kbar⁻¹.

Introduction

Because berlinite is structurally so closely related to quartz, data on AlPO₄ polymorphism might be useful for models for the much more important SiO₂ isotype. In particular, the high-low quartz inversion has been extensively investigated and much of the relevant thermodynamic and other data near that transition have been interrelated (Cohen and Klement, 1967; Klement and Cohen, 1968). For the high-low berlinite inversion, there has been no investigation of the variation of transition temperature with pressure; the thermodynamic data available for predicting the trajectory of this transition are also insufficient. Thus this investigation was undertaken.

Experiments and Results

AIPO₄ of 99.5 percent purity, obtained from Research Organic/Inorganic Chemical Company, was moistened with ~ 4M H₃PO₄ and then converted to the berlinite structure by hydrothermal treatment for ~1 day at ~400 bars, ~280°C in a sealed gold capsule. The resulting crystals, of ~0.2 mm maximum dimensions, were verified to be berlinite by comparison with the X-ray diffraction data of Swanson et al (1960). In experiments under pressure, the possibility that grain-to-grain contact might result in unsymmetric stresses on the crystals which could smear out the transition is reduced by admixing a soft, chemically inert material of high thermal conductivity, but without phase transition in the p-T range of interest. Boron nitride powder (~325 mesh) from Atlantic Equipment Engineers was chosen. A mixture of calcined BN powder and the berlinite crystals, in equal portions by weight, were mixed at least 30 minutes without grinding in a WIG-L-BUG. Some of this mixture was then packed to ~5 mm length in a 1.59 mm O.D. platinum tube of 0.13 mm wall thickness, which was then sealed in an oxyacetylene flame. The arrangement of sample capsule and chromel-alumel thermocouples and the hydrostatic pressure apparatus using argon will be described elsewhere (Cohen et al, in preparation).

In the differential thermal analysis (dta) runs, temperature was varied at 0.3 to 0.8 deg sec⁻¹ and the maximum temperature difference between the measuring and reference thermocouples was always less than 2°. The temperature corresponding to the peak of the differential signal was observed on heating and cooling, and two or more cycles were made at each pressure. In the runs, data were obtained on increasing pressure and then corroborated by data taken on decreasing pressure. Pressures were read to ±5 bar on a Heise bourdon pressure gauge. The temperatures plotted in Figure 1 represent the average of the temperatures obtained on heating and on cooling, the temperature on heating always being less than 2° higher than that obtained on cooling. This “hysteresis” in temperature did not vary with pressure, within the present precision. The reproducibility in average temperature at any point was within 1°; the data from the different runs appear to agree within 1°.

Standard chromel-alumel thermocouple tables were used, and the manufacturer’s calibration corrections for the reels of wire used in this investigation were applied. An in situ calibration of the
thermocouple used in one run was made using the Curie temperature of iron as a standard. Mallinckrodt reagent grade iron wire gave a Curie temperature, on both heating and cooling, of 767 to 768°C, which compares favorably with the widely-quoted (Boulanger, 1955) value of 769°C.

The data from the runs are plotted in Figure 1. At 1 bar, the transition temperature is 584°C, with a precision of ±1°C. The data in Figure 1 may be fitted by a straight line of slope 26.0 ± 0.5 deg kbar⁻¹ and no curvature is indicated, within the experimental precision.

Discussion

The transition temperatures obtained here at 1 bar are consistent with the values obtained by other workers, e.g., 586 ± 2°C (Beck, 1949), 581 ± 1°C (Troccaz et al, 1967), and 580°C (Flörke and Lachenmayr, 1962), although some workers report significant hystereses. However, Lang et al (1969), in establishing that the transition is first order, report no hysteresis for the transition temperature at 579°C. Troccaz et al (1967) also indicate high and low berlinito coexisting over a range of temperature near the inversion, which is not corroborated by other investigators.

Shafer and Roy (1957) were unable to detect any indication of the transition by dta. Assuming that the transitions were first order in both quartz and berlinito, they estimated an upper limit for ΔH in berlinito to be less than 1/50 that of low-high quartz. Troccaz et al (1967) gave estimates for values of ΔV and ΔH at the transition. Substituted into the Clausius-Clapeyron equation, \( dT/\Delta p = \Delta V/\Delta S \), a slope of 35 ± 7 deg kbar⁻¹ is obtained. This is beyond agreement with the present results, which is not surprising, since Troccaz et al did not distinguish between the rapid variations near the transition temperature and the actual discontinuities (first order component).

By analogy with low-high quartz (Coe and Patserson, 1969), it is likely that thermal effects of a lambda transition are superimposed on the first-order inversion in berlinito and that very careful and closely-spaced measurements are necessary to establish the discontinuity in thermophysical properties.

The similarities between the high-low berlinito and high-low quartz inversions have been well emphasized (e.g., Beck, 1949; Flörke, 1967). Small differences, such as the ~10° difference in transition temperatures and small differences in molar volumes at 1 bar, have been recognized although the properties of berlinito are not that firmly established near the inversion, and it is very probable that other small differences would appear upon careful measurement. On the other hand, the present measurements emphasize only the similarities between the berlinito and quartz inversions, since the slopes of the two phase boundaries are identical (Cohen and Klement, 1967).

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References


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