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The temperature dependence of the crystal structure of berlinite, a quartz-type form of AlPO_4

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Abstract The temperature dependence of atomic positions, mean-square displacements and probability density functions in a synthetic specimen of berlinite was analyzed using X-ray single crystal data measured at fourteen values of temperature. The characteristic features and the temperature dependence of the structure of berlinite were found to be quite similar to those of quartz, in detail. With increasing temperature, the equilibrium position of an atom, if expressed in fractional coordinates, appears to move steadily toward its β -position along a straight line, and finally attain the β -phase positions after abrupt displacements in a narrow temperature range around 583 °C. The temperature dependence of the displacements of atoms from the corresponding high-symmetry β -positions, in α -berlinite, is well fitted with a classical Landau type expression of first-order phase transitions.

The highly anisotropic mean square displacements, $\langle u^2 \rangle$, of O atoms increase with increasing temperature, especially in a narrow range just below the α - β transition, in the directions nearly perpendicular to the librating Al-O-P bonds, attaining a local maximum of 0.115–0.117 Å² just above the transition point. With varying temperature, the principal axes for the O atoms change their directions smoothly toward those of the high temperature phase, while the axis with the largest $\langle u^2 \rangle$ of the Al or P thermal ellipsoid remains in $\langle 100 \rangle$. These diffraction results are interpreted in terms of displacive structure transition involving both the ordered α - and β -forms. The Al-O and P-O bond distances are nearly constant around 1.73 and 1.53 Å, respectively, through the experimental range of temperature.

Introduction

The orthophosphates of some trivalent atoms such as Al, Ga and Fe crystallize in the structures homeotypic to one or more of the crystalline forms of SiO_2 , where the trivalent atoms and P atoms form tetrahedral units with O atoms. The structures are three-dimensional frameworks, in which the tetrahedral units link to one another by shared corner-oxygen atoms, and their formulae are designated as $\text{T}(1)\text{T}(2)\text{O}_4$, where T(1) represents the trivalent atom and T(2) is P. Of these, only AlPO_4 crystallizes as isostructured analogs to the silica polymorphs, quartz, tridymite and cristobalite (Kosten and Arnold 1980). The structure of the mineral berlinite, AlPO_4 , is derived from the structure of quartz by replacing the Si atoms alternately with P and Al atoms, resulting in a doubling of the c-axis length. The structure at room temperature is trigonal with space group P3_221 or P3_121 , and has been well established at room temperature (Schwarzenbach 1966). Both Al and P atoms lie on two-fold axes along $\langle 100 \rangle$, and two kinds of symmetrically independent O atoms, O(1) and O(2), occupy general positions. Figure 1 is a schematic drawing of the c-axis projection of berlinite in space group P3_221 . This structure changes to a high temperature polymorph with space group P6_222 (or P6_422) at about 580 °C (Kosten and Arnold 1980). A phase with an incommensurately modulated structure (abbreviated as inc) also has been found in a narrow range of temperature between the low (α) and high (β) forms of berlinite (Durand et al. 1983; Bachheimer et al. 1984; Saint-Grégoire et al. 1984), as in quartz. A unit-cell in either β or α AlPO_4 contains three formula units.

The thermal vibrations of atoms are highly anisotropic in the quartz structure (Young 1962; Ng and Calvo 1976; Baumgartner et al. 1984; Kihara 1990; Nakae et al. 1995). In the present study, the principal axes of the ellipsoids of thermal vibrations are represented by the numbers from 1 to 3 in the decreasing order of mean square displacements (abbreviated as m.s.d.), $\langle u^2 \rangle$.

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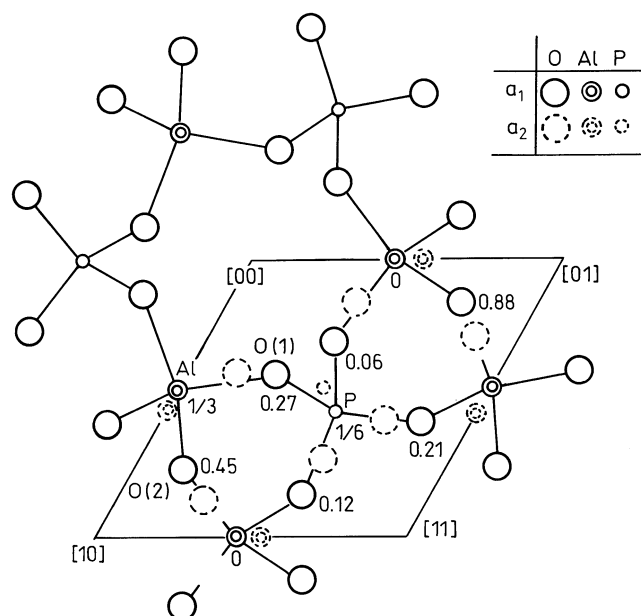


Fig. 1 C-axis projection of atoms in berlinite at room temperature. Two sets of configurations, α_1 and α_2 , related by Dauphiné twinning are indicated. A turn of linked TO_4 units around a channel along $[001]$ passing the origin of the cell, $[000]$, is $\dots\text{Al}(1/3)\text{--O}(1)\text{--P}(1/6)\text{--O}(1)\text{--Al}(0)\text{--O}(2)\text{--P}(-1/6)\text{--O}(2)\text{--Al}(-1/3)\text{--O}(1)\text{--P}(-1/2)\text{--O}(1)\text{--Al}(-2/3)\text{--}\dots$, where some selected atoms are shown with z -coordinates in fractions

In α -berlinite, Dauphiné twin positions of atoms can be defined as in α -quartz. The two configurations are related to each other by a rotation of 180° around $[001]$ and are designated as α_1 and α_2 (Fig. 1). A line connecting corresponding sites for an atom in the α_1 and α_2 configurations is denoted as $[\alpha_1\text{--}\alpha_2]$, and its length as $|\alpha_1\text{--}\alpha_2|$. Line $[\alpha_1\text{--}\alpha_2]$ for an O atom is parallel with one of the $\{100\}$ planes. In quartz, an atomic equilibrium position, as far as the fractional coordinates are concerned, appears to move along its $[\alpha_1\text{--}\alpha_2]$ at room temperature toward the corresponding position of the idealized β -phase structure (β -position) with increasing temperature. The length, $|\alpha_1\text{--}\alpha_2|$, for the O atoms at the transition temperature is estimated to be in the range 0.36 to 0.38 Å for quartz (Young 1962; Kihara 1993), and shorter than 0.1 Å for berlinite (Ng and Calvo 1976). Hence, only small displacements are required for an atom to switch from its site in α_1 to that in α_2 and *vice versa*. It also has been shown that a probability density function (p.d.f.) of a modeled disorder for the O atom in β -quartz is unimodal (Kihara 1990). It is thus very difficult to identify the real structure of the β -phase, not only for quartz but also for berlinite, in a conventional structural study.

Ng and Calvo (1976) attempted to determine directly the atomic mechanism of the transition of berlinite by examining diffraction intensities at just below and above the transition, following Young's (1962) study of quartz. They considered three structural models for the β -phase of berlinite:

(1) All atoms move to the average positions of α_1 and α_2 so that the Al and P atoms are on special positions with symmetry 222, and O(1) and O(2) become symmetrically equivalent and occupy a general position, in the new space group, P6_222 (or P6_422). The potential energy curve has a single minimum for the higher symmetry configuration of the β -phase.

(2) The potential energy curve has a double minimum corresponding to the α_1 and α_2 configurations, and each atom occupies either an α_1 or an α_2 position such that the volume ratio of twinned domains is 1:1.

(3) All the atoms are statistically distributed among the α_1 and α_2 positions, but have sufficient thermal energy to jump from one to the other.

The atom positions in the first model, i.e., the β -positions, may correspond to the mean positions obtained in a usual structure refinement. From above, Ng and Calvo (1976) favored an ordered arrangement of atoms in β -berlinite, as in model (1).

Van Tendeloo et al. (1976) have observed triangular columnar domains parallel to the c -axis at the α - β transition of both quartz and berlinite in a transmission electron microscope, and they concluded that the β -phase is a time-average of the α_1 and α_2 orientations. Lang et al. (1977) in an EPR study of Fe^{3+} -doped AlPO_4 have reported that at the transition temperature of 581°C , the spin Hamiltonian acquires the D_2 (222) symmetry of the β -phase. Kihara (1990), in an X-ray study of quartz, has shown systematic changes of the mean positions, p.d.f.'s, m.s.d.'s and the orientation of thermal-motion ellipsoids of the atoms with varying temperature, and then interpreted these results as support for the ordered model of the β -phase. Tezuka et al. (1991) have indicated on the basis of their hyper-Raman scattering measurement of the silent soft phonon in β -quartz that the α - β transition is well described by a simple displacive-type phase transition and that the β -quartz structure is not disordered. The displaciveness in the transition of quartz also has been affirmed by Salje et al. (1992) in their hard-mode spectroscopy study. On the other hand, Heaney and Vehlen (1991), in their electron diffraction study, have observed diffuse satellite peaks along c^* arising from the inc phase that persist well above the temperature of the inc $\leftrightarrow\beta$ transition, and they concluded that disordering over the two configurations with transient short range order is responsible for such behavior. Finally, Spearing et al. (1992) favored dynamical disorder in β -quartz based on their ^{29}Si NMR observations.

Ng and Calvo (1976), who also examined the temperature dependence of the structural parameters of berlinite using X-ray diffraction intensities measured at seven different temperatures ranging from 25 to 600°C , used only $hk0$ and $hh\ell$ reflections for the refinement of α -berlinite, because of Dauphiné twinning in their specimen. In comparing the X-ray studies for quartz and berlinite, we found remarkable differences in the temperature dependence of the atomic parameters. For instance, all the atomic positions in α -quartz approach linearly the high symmetry β -positions with increasing

temperature, but the approach is non-linear for the O atoms in berlinite. The use of the data from a limited part of the asymmetric unit of reciprocal space might lead to some biased results, as noted by the authors themselves.

As reviewed above, the β -phase structures are still controversial, and need to be reviewed to provide firm structural grounds to the studies of the α - β phase transition. Our present purpose is to examine the structural problem of the β -berlinite, using a technique of X-ray single-crystal structure-analysis. We believe that the β -phase structure involved is most effectively studied by measuring the temperature dependence of the structural data, along with those of its α -phase structure. In this study, hence, the structure of berlinite was refined at fourteen different temperatures, by employing initially the usual structure factor expression in the harmonic approximation and then a generalized structure factor expression involving coefficients from the first- to the fourth-order terms (mean, dispersion, skewness and kurtosis) in the Gram-Charlie expansion of a p.d.f. (Johnson and Levy 1974). Intensity measurement for the inc phase was not attempted in this study.

Experimental

The specimens of berlinite AlPO_4 used in this study are single crystals grown hydrothermally by Toyo Communications Apparatus & Co. The crystals are colorless and transparent, and they show remarkable growth of conical surfaces, lacking prism planes. A crystal was crushed into fragments with irregular shapes. Some fragments were examined with the X-ray Weissenberg and precession methods, and some were ground into spheres by the Bond method for the experiments with a four-circle automatic diffractometer PW1100. The observed X-ray reflections on Weissenberg and precession photographs were consistent with trigonal space group $P3_121$ or $P3_221$. X-ray diffraction data were obtained using graphite-monochromated $\text{Mo } K_\alpha$ radiation. The same heating system and calibration method as used by Kihara (1990) were employed. During the measurements, temperature at a thermocouple placed at approximately 1 mm from the specimen was controlled to within $\pm 1^\circ\text{C}$ of the given values. At the position of the specimen, however, temperature was a little but systematically different at the different χ -positions: it was approximately 2°C lower at $\chi = \pm 60^\circ$ than at $\chi = 0^\circ$. All intensity measurements were carried out within the range from $\chi = -60^\circ$ to $+60^\circ$. With experimental difficulties, mainly originated from heating, we needed two specimens to complete the present measurements of intensities and cell constants at the 14 points of temperature, one with diameter of 0.34 and the other 0.22 mm. No impurities in the single crystals were detected by energy dispersive spectroscopy in a scanning electron microscope.

The X-ray integrated intensities of reflections were first measured at 9 values of temperature below the transition using one of the specimens in its first heating run. The transition temperature was then examined with the change of the a -axis length in repeated heating and cooling experiments between 570 and 585°C : the values were determined in least-squares of d^* -values of $\pm h00$ reflections measured from the centroids of line profiles along a^* (Fig. 2). (In these runs, the inc phase could be involved, but the data used for Fig. 2 are only from main reflections corresponding to the unit cell of the α - (or β) phase.) In the first heating run, the cell dimension rapidly increased with increasing temperature up to $5.038 \text{ \AA}$ at 583°C , and remained virtually constant in further heating. In the succeeding cooling run, the cell dimension persist-

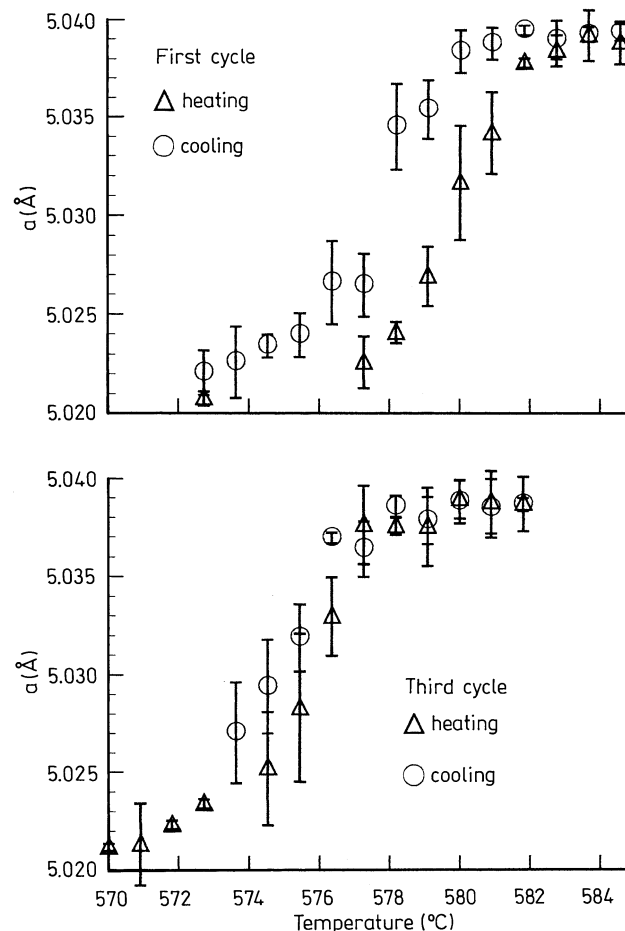


Fig. 2 Variation of a -axis length in repeated heating and cooling cycles in the vicinity of the α - β transition in berlinite: upper for the first cycle and lower for the third cycle. Each error bar indicates two-e.s.d

ed until 580°C . In the third cycle, the hysteresis became smaller. We concluded that the β -structure was already attained at 583°C for the present specimen. After these heating and cooling experiments, the intensity measurements were resumed for the β -phase, but only for 584°C . The specimen was accidentally lost, and further measurements for the β -phase were carried out using the second specimen. Listed in Table 1 are the cell dimensions, a and c , determined by least-squares fitting of the d^* -values of about 22 reflections after completion of the intensity measurements at each temperature. All the structural parameters given here are those obtained from the measurements during the first heating runs of the specimens, except the case for 584°C .

The ω - 2θ scan mode was employed using scan widths of $(2+0.3\tan\theta)^\circ$ for the intensity measurements. The reflections were omitted for $I_{\text{top}} - 2\sqrt{I_{\text{top}} I_{\text{bck}}} < I_{\text{bck}}$, where I_{top} was peak intensity and I_{bck} was background. For the α -phase, about 2000 reflections within the hemisphere of reciprocal space ($-8 \leq h \leq 8$, $0 \leq k \leq 8$ and $-18 \leq l \leq 18$) were measured at each temperature, whereas, for the β -phase, about 750 reflections in the quarter of the sphere ($-8 \leq h \leq 8$, $0 \leq k \leq 8$ and $0 \leq l \leq 18$) were measured. The intensities were converted to structure amplitudes after correcting for Lorentz and polarization factors and absorption ($\mu \approx 10 \text{ cm}^{-1}$ for $\text{Mo } K_\alpha$). The standard deviations were estimated from counting statistics, and the structure amplitudes were averaged for equivalent reflections. Intensity data at room temperature were also measured with $\text{Cu } K_\alpha$ radiation to determine the correct space group.

Table 1 Cell dimensions and volume of berlinite at different temperatures

Temperature (°C)	a (Å)	c (Å)	V _{cell} (Å ³)
25	4.9438(3)	10.9498(8)	231.78(4)
92	4.949(1)	10.955(3)	232.4(1)
183	4.9580(4)	10.967(2)	233.48(5)
275	4.9688(5)	10.979(3)	234.75(7)
366	4.9799(9)	10.992(3)	236.1(1)
458	4.9939(9)	11.010(3)	237.8(1)
486	5.000(2)	11.016(4)	238.5(2)
523	5.0017(5)	11.019(2)	238.72(6)
568	5.017(5)	11.038(2)	240.61(6)
585	5.0387(7)	11.061(2)	243.2(2)
589	5.040(1)	11.063(2)	243.3(1)
598	5.040(2)	11.061(3)	243.3(2)
612	5.0401(7)	11.063(2)	243.40(8)
631	5.0402(9)	11.063(2)	243.4(1)
640	5.040(1)	11.063(2)	243.4(1)

Refinements

The least-squares program LSGC (Kihara et al. 1986) was used to estimate coefficients from the first to the fourth order terms in the Gram-Charlier expansion (Johnson and Levy 1974). Spherical atomic scattering factors for neutral atoms, and real and imaginary components of the anomalous dispersion were taken from Cromer and Waber (1974) and Cromer (1974), respectively. The initial values of the positional parameters for

the room temperature refinement were taken from Ng and Calvo (1976), who undertook the refinements in P₃21. Positional parameters were also prepared for P₃21 by transforming their values. The least-squares refinements of the structural parameters were performed by using reflections with amplitudes larger than twice the e.s.d.'s. In berlinite, the intensities of reflections with ℓ odd, which are absent in quartz, are mainly contributed by difference of the scattering factors between Al and P, and therefore such reflections have much weaker intensities than others. However, most of the superstructure reflections were included in the present refinements. The refinement was first carried out with a conventional structure factor expression (represented as a 2G refinement), involving the positional parameters (first-order) and anisotropic temperature factors (second-order) in assuming harmonic p.d.f.'s. A more generalized expression including coefficients up to the fourth-order terms (4G refinement) was then applied to estimate the deviation from the Gaussian p.d.f..

In the 2G refinements, 28 and 15 atomic parameters for the α - and β -forms, respectively, were refined together with a scale factor and an extinction factor. The space group was determined to be P₃21 from a comparison of observed (with Cu K α radiation) and calculated structure amplitudes of five Bijvoet pairs. The following calculations were all undertaken in P₃21. The data obtained with the Mo K α radiation were used in the final stages of the calculations. The quantity minimized was $\Sigma w(F_o - k|F_c|)^2$ with $w = 1/\sigma^2$, where k was a scale factor.

Table 2 Numbers of reflections and parameters, and R-factors, R and Rw, in final cycles of harmonic and anharmonic refinements

α -berlinite									
Temperature (°C)	25	92	183	275	366	458	486	523	568
N _r	906	645	618	640	630	623	627	494	481
Harmonic refinements									
N _p	30	30	30	30	30	30	30	30	30
R	0.021	0.019	0.02	0.027	0.025	0.028	0.033	0.04	0.045
R _w	0.032	0.027	0.028	0.038	0.033	0.038	0.044	0.034	0.036
Anharmonic refinements									
N _p	75	67	75	65	66	76	72	65	65
R	0.02	0.018	0.018	0.025	0.022	0.024	0.027	0.032	0.033
R _w	0.029	0.024	0.024	0.033	0.026	0.029	0.033	0.026	0.024
β -berlinite									
Temperature (°C)	585	589	598	612	631				
N _r	241	227	238	180	237				
Harmonic refinements									
N _p	17	17	17	17	17				
R	0.056	0.049	0.049	0.049	0.052				
R _w	0.041	0.039	0.039	0.038	0.039				
Anharmonic refinements									
N _p	39	46	41	46	42				
R	0.037	0.033	0.036	0.031	0.035				
R _w	0.025	0.023	0.026	0.02	0.025				

N_p: Number of parameters varied in refinements
N_r: Number of reflections used in refinements
R: $\sum ||F_o| - |F_c|| / \sum |F_o|$
R_w: $\{\sum w(F_o - |F_c|)^2 / \sum w F_o^2\}^{1/2}$

Refinements involving third- and fourth-order terms were initiated with the 2G parameters from the preceding harmonic refinements and null values of 76 and 39 higher-order coefficients for the α - and β -structures, respectively. Some of the third- and fourth-order coefficients converged to magnitudes smaller than the corresponding e.s.d.'s, and were set as null in the final stage of the refinements. The degree of parameter correlation was not serious.

In Dauphiné twinning, an $hk\ell$ reflection of the α_1 -configuration is superimposed on an $\bar{h}k\ell$ reflection of the α_2 -configuration. Assuming a volume fraction x in the α_2 -configuration, the observed intensities were corrected for such twinning, using the following relations:

$$I_{hk\ell} = I'_{hk\ell} + y(I'_{hk\ell} - I'_{k\bar{h}\ell}),$$

$$I_{k\bar{h}\ell} = I'_{k\bar{h}\ell} - y(I'_{hk\ell} - I'_{k\bar{h}\ell}),$$

where I' and I are, respectively, the observed and corrected intensities and $y = x/(1-2x)$. Dauphiné twinning was tested in the least-squares refinements and the best fit was obtained with $x = 0.005$ for the data at 25–523 °C, and with 0.03 at 568 °C. This result is almost exactly the same as that for the quartz specimen used by Kihara (1990) and we believe that the specimens used in both studies are originally free from Dauphiné twinning. Grinding may cause the small volume fractions at the surfaces to switch their atoms to the α_2 positions and subsequent heating to increase the twin fraction. The final stage of the least-squares refinements was performed with the twin-corrected F_o data. Data relevant to the refinements are shown in Table 2.

Results and discussions

The transition to the β -phase in the present specimen takes place around 583 °C, which falls in the range of 3° from two previous measurements: 580 °C in the measurements of the cell dimensions with X-rays (Kosten and Arnold 1980), and 583 °C, which is the temperature of the α -inc transformation in calorimetric and neutron intensity measurements of satellite reflections (Bachheimer et al. 1984). A birefringence measurement by Saint-Grégoire et al. (1984) has shown a much higher transition temperature of 596 °C.

Positional and thermal parameters, and atomic distances and angles, obtained from the 2G refinements, for all the fourteen temperatures are given in Tables 3 and 4, respectively. The tables of the structural data obtained in the 4G refinements, the anisotropic temperature factors in the 2G refinements and the observed and calculated structure factors for both the 2G and 4G refinements are not given here, but are available from KK on request. The room temperature values of the atomic coordinates are in good agreement with those of Schwarzenbach (1966). The x coordinates of Al and P, and the y and z coordinates of O(1) and O(2) are plotted against temperature in Fig. 3.

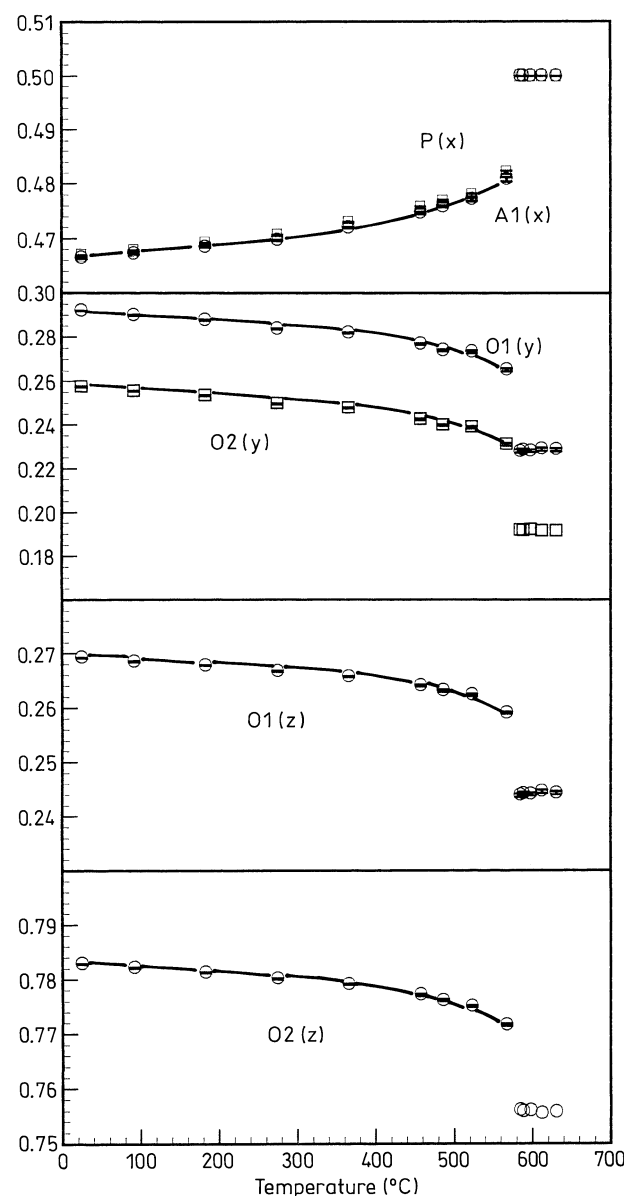


Fig. 3 Temperature dependence of x -coordinates of P and Al atoms, and y and z for both O(1) and O(2) atoms. Two-e.s.d.'s are indicated but confined within symbols. Lines are just for guide for eyes

Thermal expansions in AlPO_4 and the related quartz structures of GaPO_4 and SiO_2

The thermal expansion behavior of berlinite appears to be rather similar to that of quartz, but not GaPO_4 . The volume expansion coefficient of berlinite rapidly increases from $3.97 \times 10^{-5} \text{ (deg}^{-1}\text{)}$ at 25 °C to 18.5×10^{-5} at 577 °C, which are comparable with those of quartz, 3.7×10^{-5} at 25 °C and 23×10^{-5} at 565 °C, calculated from the table of Kihara (1990). The thermal expansion coefficient of isostructural GaPO_4 is always smaller than that of berlinite or quartz in the present experimental range: the values for GaPO_4 are calculated from Nakae et al. (1995) as 3.0×10^{-5} at 20 °C and 4.7×10^{-5} at 580 °C.

The thermal expansion of these structures is mostly due to the rotations of the TO_4 units around the two-fold symmetry axes. In GaPO_4 , such tetrahedral rotations are also systematic with varying temperature, but very small in comparison with berlinite and quartz, resulting in much smaller thermal expansion coefficients.

Positions and mean square displacements of atoms and their temperature dependence

The change in the x -coordinates of O(1) and O(2) with temperature is insignificant both in the α - and β -phases. In α -berlinite, the equilibrium position of an O atom, if it is expressed in fractional coordinates, appears to be displaced with increasing temperature toward the β -position along its $[\alpha_1-\alpha_2]$ line at room temperature (Fig. 4). In other words, $[\alpha_1-\alpha_2]$ lines for atoms appear not to change their orientations at every temperature. According to Ng and Calvo (1976), the separation between the α_1 (or α_2) and the β position for the O atoms decreases to values smaller than $0.05 \text{ \AA}$ just below the α - β transition. Our data apparently show much larger values, as seen in Fig. 5.

The displacements of atoms along $[\alpha_1-\alpha_2]$'s in α -quartz can be interpreted to be resulted from rotations and translations of the TO_4 tetrahedra around and along $\langle 100 \rangle$, respectively. The temperature dependence of the rotation angle, ϕ , from the β -orientation or of second-harmonic-generation coefficient were well fitted with an analytical equation derived from a classical Landau type expression for first order transitions (Grimm and Dorner 1975; Bachheimer and Dolino 1975). Saint-Grégoire et al. (1984) was also successful to fit the relation between their birefringence data of α -berlinite and temperature with the same expression. We found that the change of atomic displacements from their β -positions with temperature in α -berlinite were also well fitted with the same expression. The best fitted curve, shown in Fig. 5,

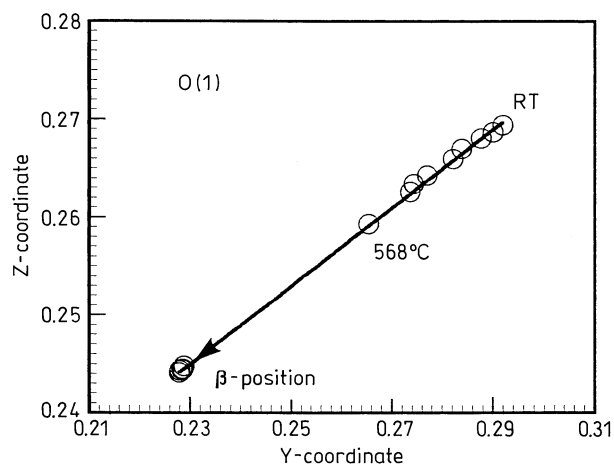


Fig. 4 Projections of O(1) at different temperatures in α -berlinite along $[210]$. The mean positions in the β -phase at different temperatures are also indicated

was obtained from the variables, $T_0 = 584.6 \text{ }^\circ\text{C}$, $|\alpha_1-\alpha_2|/2 = 0.232 \text{ \AA}$ at T_0 and a correlation factor of 0.995, where T_0 is the temperature, at which the α - and β -phases have the same free energy. The present value for T_0 is rather in good agreement with the reported temperatures from 580 to $583 \text{ }^\circ\text{C}$, above which the β -phase is stable, whereas the inc phase, which may exist in a narrow temperature range between the α - and β -phases, is ignored.

The characteristic features observed in the m.s.d.'s and the directions of their principal axes appear to be identical with those for quartz. The thermal vibrations might arise largely from the librational motions of the Al-O-P bonds around the Al-P axes and from correlated translational motions of both the Al and P atoms along $\langle 100 \rangle$. The librational thermal vibrations for the O atoms are illustrated in p.d.f. contour maps (Fig. 6), which are all unimodal. The values of $\langle u^2 \rangle$ for axes 1, 2 and 3 of the thermal ellipsoid of O(1) are shown in Fig. 7 to demonstrate the strong temperature dependence. The values in axis 1 for the O atoms steeply rise when temperature approaches the transition point from below, but do not change above it. Although the measured points in the present study are limited to rather low temperatures in the β -phase, this temperature dependence appears to be similar to that of quartz, which shows a cusp-shaped curve near the transition temperature (Kihara 1990).

Systematic changes in ellipsoid orientations with increasing temperature also are observed. The thermal ellipsoids for Al and P are oriented with their axes 1 parallel to the two-fold axes along $\langle 100 \rangle$ at all temperatures. On the other hand, axes 1 and 2 of the O ellipsoids rotate around axis 3, which stays within a small angular range from room temperature to above the transition point. Figure 8 shows the stereographic projections of the principal axes of the thermal ellipsoid and $[\alpha_1-\alpha_2]$ for O(1). We note three points as follows: (1) the principal axes for the

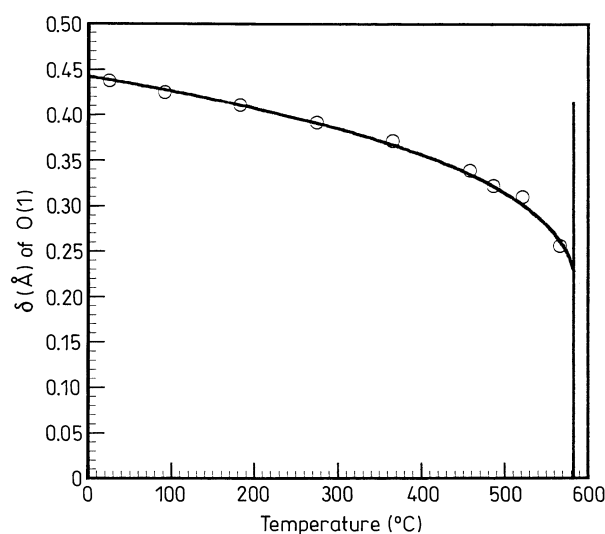


Fig. 5 Temperature dependence of $|\alpha_1-\alpha_2|/2 \text{ (\AA)}$, half of the separation between α_1 and α_2 sites, for O(1). A curve is a fitted one with a classical Landau expression for first-order phase transitions

Fig. 6a-c Contour maps of probability density functions for O(1). Sections perpendicular to axis 3 of thermal ellipsoids in 4G refinements are indicated. X and Y axes are in axes 1 and 2, respectively, and their directions are given by angles from [210], [010] and [001]. Contour values are multiplied by 10. **a** 366 °C. Angles from the three directions: X (37°, 69°, 61°) and Y (126°, 51°, 60°). **b** 568 °C. X (74°, 54°, 40°) and Y (164°, 83°, 76°). **c** 585 °C. X (89°, 47°, 44°) and Y (171°, 96°, 97°)

β -phase ellipsoid remain in virtually the same orientation at all five temperatures; (2) as α -berlinite is heated to the transition point, all of the principal axes move toward the corresponding β -orientations on smooth curves; and (3) the $[\alpha_1-\alpha_2]$ line is fixed at 49° from **c** in the a_2 - c plane at all the experimental temperatures for the α -phase, as a single point in Fig. 8. The axes of the O(2) ellipsoid (not shown) also progress toward the β -orientations with increasing temperature. In Fig. 8, the directions of three vectors **q**, **p** and **r** defining the orientation of an Al-O-P plane are also projected. As in quartz, axes 1 and 2 are not parallel with **q** and **p**, respectively; that is to say, the corresponding two directions separately move along different curves toward the respective β -orientations. These points indicate that the discussions given for quartz (Young 1962; Kihara 1990, 1993) are also applicable for berlinite. The characteristic features of $\langle u^2 \rangle$ in the α - and β -phases of both the minerals are identical, indicating that no extra factor other than the abrupt rise of vibrational amplitude in axis 1 is gained by the β -form

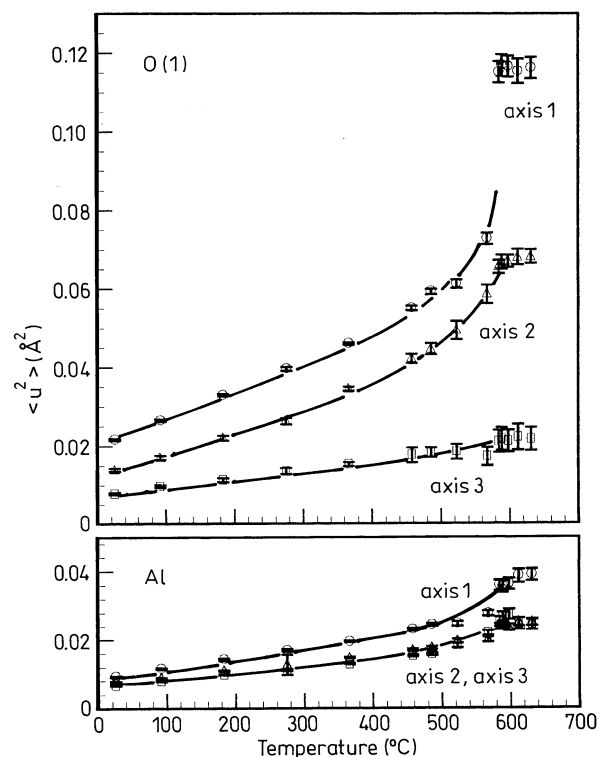
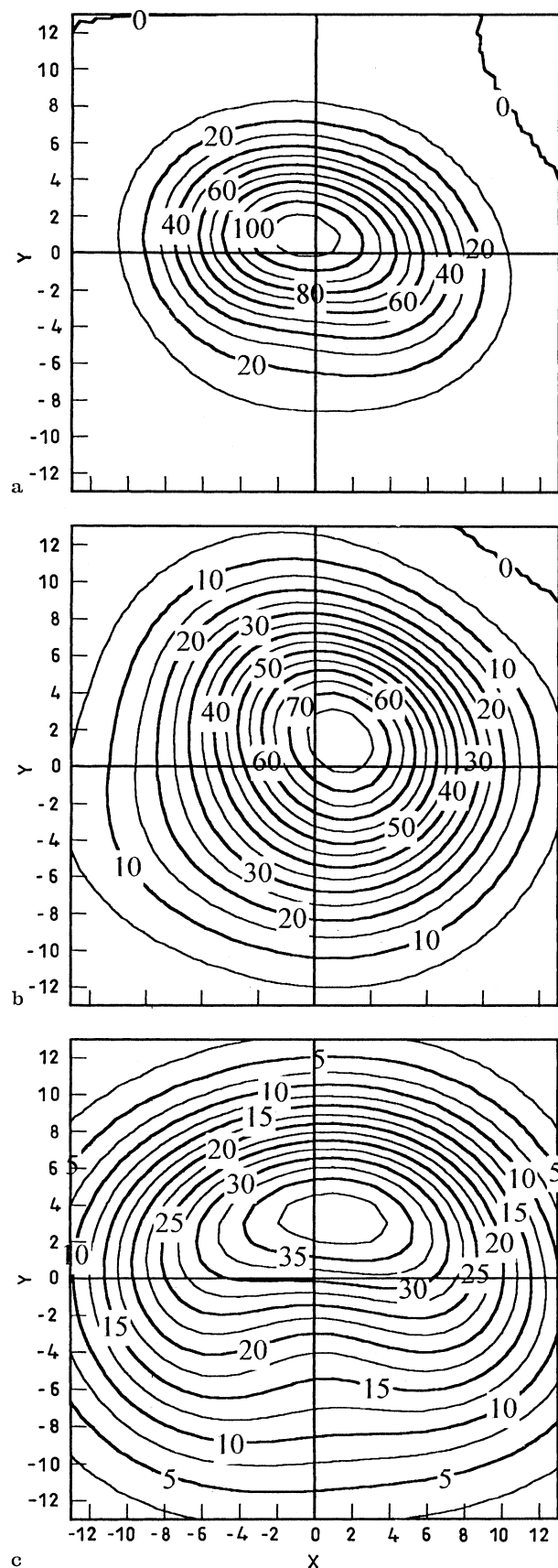


Fig. 7 Temperature dependence of mean square displacements ($\text{\AA}^2$) of selected atoms, O(1) and Al, in their principal axes of thermal ellipsoids. Two e.s.d.'s are indicated. Lines are just for guide for eyes



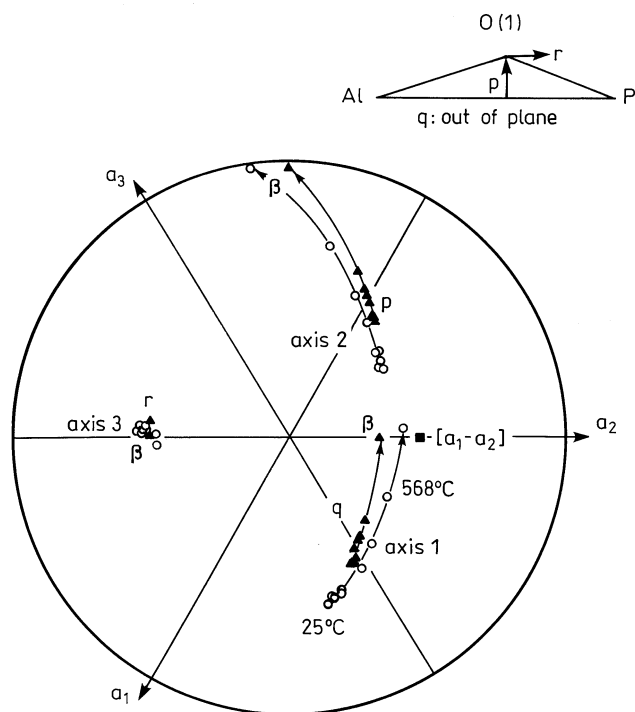


Fig. 8 Stereographic projections of the principal axes of the thermal ellipsoid and the directions of the lines joining α_1 and α_2 sites for O(1) at different temperatures from room temperature to β -berlinite. Three vectors $\mathbf{q}$, $\mathbf{p}$ and $\mathbf{r}$ are also projected; their relation to the Al–O(1)–P bonding plane is shown at the upper right corner. $\circ$: Principal axes 1, 2 and 3; $\blacksquare$: $[\alpha_1 - \alpha_2]$, and $\blacktriangle$: $\mathbf{q}$, $\mathbf{p}$ and $\mathbf{r}$

at the transition. In addition, in β -berlinite, axes 1 of the oxygen thermal ellipsoids are closely oriented with the corresponding $[\alpha_1 - \alpha_2]$'s, but their differences, ca. 6° for quartz and 7° for berlinite, are clearly fall outside experimental errors (Fig. 8). In this regard, we may refer to the case for β -quartz that such differences are almost exactly reproduced in lattice dynamical calculations of the idealized hexagonal symmetry configuration, i.e. model (1) using the force constants prepared in fitting the normal mode frequencies to the observed ones (Kihara 1993). The calculated directions of the principal axes agreed with the X-ray results to within 1° .

If the β -phase is a disordered form of the α -phase, axis 1 for an O atom, in the β -phase, at either α_1 - or α_2 -site might be oriented close to the corresponding $[\alpha_1 - \alpha_2]$ line, as observed at the highest experimental temperature in the α -phase, and its m.s.d. in axis 1, $\langle u^2 \rangle_1$, might be approximated as:

$$\langle u^2 \rangle_1 \approx \langle u_{\alpha}^2 \rangle_1 + \left(\frac{|\alpha_1 - \alpha_2|}{2} \right)^2,$$

where $\langle u_{\alpha}^2 \rangle_1$ is the m.s.d. in axis 1 of thermal vibrations at the α_1 - (or α_2 -) site. In this expression, we have used a nature of ellipsoids that the m.s.d. of an atom along a radius of its ellipsoid changes smoothly with changing directions. The above relation suggests that the stereographic projections of $\langle u^2 \rangle_1$ of O atoms, if they are disor-

dered, might be oriented much closer to $[\alpha_1 - \alpha_2]$'s than the observed directions on the ends of the smooth curves from room temperature (Fig. 8). In other words, the observed continuity of the changing orientations of axis 1 from room temperature to the β -phase is compatible with the interpretation that $|\alpha_1 - \alpha_2| \approx 0$ in the β -phase.

The thermal vibrational amplitudes for the tetrahedral Al and P atoms are practically equal each other at every temperature (Table 3). It may also be noted that, in the quartz form of GaPO_4 , Ga and P show nearly equal m.s.d.'s (Baumgartner et al. 1984; Nakae et al. 1995). This may arise from strong T–O bonding in the two kinds of tetrahedra, that makes the effects of the different masses less important in the librations.

Bond distances

The atomic distances of Al–O and P–O, and the angle Al–O–P calculated from the positional parameters in the 2G-refinements, decrease and increase, respectively, while temperature is elevated, as in quartz (Table 4). There are small but clear changes in such distances and angles at the transition from α to β berlinite. Grimm and Dorner (1975) have suggested for quartz that the decrease of the Si–O bond length in association with the increase of the Si–O–Si angle is attributed to increasing π -bond order. However, we can point out that strong librational motions, if they are approximated by harmonic p.d.f.'s, may cause underestimation of the T–O bond lengths and accordingly overestimation of the T–O–T angles, because the apparent mean positions of the atoms, represented by the centroids of the p.d.f.'s, are shifted inwards towards the centers of librations (Willis and Pryor 1975). Such distances might be corrected for the thermal vibrations. In the present case, the modes and means of p.d.f.'s for the O atoms are differently located, and the former is expected to be better in evaluation of the bond lengths than the latter. In the study of applying a generalized structure factor expression for analyzing anharmonic thermal vibrations of atoms, Johnson (1970) has shown that intermode separations tend to give more reasonable bond lengths than intermean distances when large thermal libration effects are present. Figure 9 shows the temperature dependence of the two kinds of distances for Al–O and P–O. The intermode separations were obtained from the coordinates of the mode positions indicated by the p.d.f. maps. The intermode distances are seen to be longer than the corresponding intermean distances at the most temperatures, especially at higher temperatures. The intermode distances, however, show peculiar changes for both Al–O and P–O: Al–O steeply rises in the β -phase and P–O increases in the α -phase, but decreases in the β -phases. The changes are apparently too large for temperature dependence of such bond distances. It is our present opinion that our higher order coefficients are accurately determined for establishing the essential feature of the p.d.f. contours of the librational motions, but not enough for obtaining the

Table 3 Positional and thermal parameters in harmonic refinements of berlinite at different temperatures

(a) α -berlinite												
Atom	Parameter	25 (°C)	92 (°C)	183 (°C)	275 (°C)	366 (°C)	458 (°C)	486 (°C)	523 (°C)	568 (°C)		
Al	x	0.46646(7)	0.46723(8)	0.46847(9)	0.46968(13)	0.47197(9)	0.4747(2)	0.4759(2)	0.4772(3)	0.4809(4)		
	$\langle u^2 \rangle_{\text{all}} (\text{\AA}^2)$	0.0079(2)	0.0095(2)	0.0117(2)	0.0136(2)	0.0157(2)	0.0184(2)	0.0193(3)	0.0209(4)	0.0233(5)		
P	x	0.46690(6)	0.46778(7)	0.46921(8)	0.47062(11)	0.47297(8)	0.4757(2)	0.4769(2)	0.4780(3)	0.4822(3)		
	$\langle u^2 \rangle_{\text{all}} (\text{\AA}^2)$	0.0079(1)	0.0095(2)	0.0117(2)	0.0139(2)	0.0160(2)	0.0189(2)	0.0199(2)	0.0213(4)	0.0240(4)		
O(1)	x	0.4164(2)	0.4164(2)	0.4167(3)	0.4151(3)	0.4181(2)	0.4185(4)	0.4184(5)	0.4188(7)	0.4193(9)		
	y	0.2919(2)	0.2900(2)	0.2877(2)	0.2838(3)	0.2821(2)	0.2769(4)	0.2742(4)	0.2735(6)	0.2654(6)		
	z	0.26921(6)	0.26852(7)	0.26786(8)	0.2668(1)	0.2658(1)	0.2641(2)	0.2632(2)	0.2624(2)	0.2591(2)		
	$\langle u^2 \rangle_{\text{all}} (\text{\AA}^2)$	0.0145(2)	0.0177(3)	0.0221(3)	0.0265(4)	0.0319(3)	0.0383(8)	0.0407(7)	0.043(1)	0.050(1)		
O(2)	x	0.4155(2)	0.4158(2)	0.4164(3)	0.4152(3)	0.4188(2)	0.4191(4)	0.4192(5)	0.4202(7)	0.4205(8)		
	y	0.2574(2)	0.2554(2)	0.2535(3)	0.2497(3)	0.2478(2)	0.2425(4)	0.2399(4)	0.2389(6)	0.2311(7)		
	z	0.78285(7)	0.78216(7)	0.78127(8)	0.7801(1)	0.7791(1)	0.7771(2)	0.7761(2)	0.7750(2)	0.7716(2)		
	$\langle u^2 \rangle_{\text{all}} (\text{\AA}^2)$	0.0143(2)	0.0175(3)	0.0221(3)	0.0263(5)	0.0318(3)	0.0384(6)	0.0408(7)	0.0422(1)	0.051(1)		
(b) β -berlinite												
Atom	Parameter	585 (°C)	589 (°C)	598 (°C)	612 (°C)	631 (°C)						
Al	$\langle u^2 \rangle_{\text{all}} (\text{\AA}^2)$	0.028(1)	0.029(1)	0.029(1)	0.030(1)	0.030(1)						
P	$\langle u^2 \rangle_{\text{all}} (\text{\AA}^2)$	0.029(1)	0.029(1)	0.029(1)	0.030(1)	0.030(1)						
O	x	0.4200(1)	0.4201(8)	0.4200(8)	0.4203(8)	0.4201(8)						
	y	0.2279(7)	0.2284(7)	0.2280(7)	0.2288(8)	0.2286(7)						
	z	0.2439(3)	0.2442(32)	0.2441(3)	0.2446(3)	0.2443(3)						
	$\langle u^2 \rangle_{\text{all}} (\text{\AA}^2)$	0.067(2)	0.069(2)	0.068(2)	0.068(2)	0.069(2)						

$\langle u^2 \rangle_{\text{all}} (\text{\AA}^2) = 1/3 (\langle u^2 \rangle_1 + \langle u^2 \rangle_2 + \langle u^2 \rangle_3)$, where $\langle u^2 \rangle_i$ is mean square displacement of an atom in principal axis i of a thermal ellipsoid

$\langle u^2 \rangle_{\text{all}} (\text{\AA}^2) = 1/3 (\langle u^2 \rangle_1 + \langle u^2 \rangle_2 + \langle u^2 \rangle_3)$, where $\langle u^2 \rangle_i$ is mean square displacement of an atom in principal axis i of a thermal ellipsoid

Table 4 Intermean distances and angles in berlinite at different temperatures

(a) α -berlinite									
Temp. (°C)	25	92	183	275	366	458	486	523	568
Distance (Å)									
Al–O(1) 1×2	1.7302(9)	1.729(1)	1.727(2)	1.726(2)	1.724(1)	1.720(2)	1.719(3)	1.722(4)	1.718(4)
Al–O(2) 2×2	1.7395(7)	1.739(1)	1.737(2)	1.739(2)	1.735(1)	1.733(3)	1.733(2)	1.725(3)	1.721(3)
Average	1.7349	1.734	1.732	1.733	1.73	1.727	1.726	1.724	1.72
P–O(1) 1×2	1.526(2)	1.524(2)	1.524(3)	1.526(2)	1.519(1)	1.518(2)	1.517(2)	1.510(3)	1.504(3)
P–O(2) 3×2	1.521(3)	1.518(3)	1.518(4)	1.516(2)	1.511(1)	1.507(7)	1.505(3)	1.507(49)	1.504(5)
Average (Å)	1.523	1.521	1.521	1.521	1.515	1.513	1.511	1.509	1.504
O(1) 1–O(1) 6	2.867(4)	2.863(4)	2.857(5)	2.846(2)	2.850(5)	2.839(8)	2.833(10)	2.839(12)	2.833(5)
O(1) 1–O(2) 2×2	2.829(1)	2.827(2)	2.823(2)	2.829(3)	2.812(2)	2.807(10)	2.805(4)	2.799(5)	2.794(6)
O(1) 1–O(2) 5×2	2.795(2)	2.796(2)	2.795(3)	2.801(3)	2.798(2)	2.798(4)	2.798(4)	2.797(6)	2.793(7)
O(2) 2–O(2) 5	2.882(1)	2.880(1)	2.877(2)	2.870(2)	2.878(2)	2.871(10)	2.869(3)	2.857(4)	2.842(5)
Average (Å)	2.833	2.832	2.828	2.829	2.825	2.82	2.818	2.815	2.808
O(1) 1–O(1) 4	2.486(2)	2.481(1)	2.481(2)	2.473(2)	2.475(2)	2.470(3)	2.466(3)	2.456(4)	2.439(5)
O(1) 1–O(2) 3×2	2.507(1)	2.504(1)	2.503(2)	2.510(2)	2.490(2)	2.487(5)	2.486(3)	2.483(4)	2.477(4)
O(1) 1–O(2) 5'×2	2.480(1)	2.478(2)	2.478(3)	2.481(2)	2.471(2)	2.470(3)	2.468(3)	2.462(5)	2.458(6)
O(2) 3–O(2) 5'	2.466(2)	2.460(2)	2.458(3)	2.446(3)	2.448(2)	2.436(16)	2.430(4)	2.437(6)	2.426(7)
Average (Å)	2.488	2.484	2.484	2.484	2.474	2.47	2.467	2.464	2.456
Angle (deg.)									
O(1)–Al–O(1) 6	111.9(1)	111.8(1)	111.7(2)	111.1(1)	111.5(1)	111.2(2)	111.0(3)	111.0(3)	114.7(3)
O(1) 1–Al–O(2) 5×2	107.3(1)	107.5(1)	107.6(6)	107.9(1)	107.9(1)	108.2(1)	108.3(1)	108.4(2)	108.6(2)
O(1) 1–Al–O(2) 2×2	109.2(1)	109.2(1)	109.2(1)	109.4(1)	108.7(1)	108.7(7)	108.7(1)	108.6(2)	108.7(2)
O(2) 2–Al–O(2) 5	111.9(1)	111.8(1)	111.8(1)	111.2(1)	112.1(1)	111.8(5)	111.7(2)	111.8(2)	111.4(3)
O(1) 1–P–O(1) 4	109.1(2)	108.9(2)	109.0(2)	108.3(1)	109.1(5)	109.0(1)	108.7(1)	108.8(2)	108.4(2)
O(1) 1–P–O(2) 3×2	110.7(3)	110.8(1)	110.7(3)	111.2(1)	110.5(7)	110.6(7)	110.7(2)	110.7(3)	110.9(3)
O(1) 1–P–O(2) 5'×2	109.0(1)	109.1(1)	109.1(2)	109.3(1)	109.3(6)	109.4(1)	109.5(1)	109.4(2)	109.6(2)
O(2) 3–P–O(2) 5'	108.3(2)	108.3(1)	108.2(2)	107.6(1)	108.2(5)	107.8(7)	107.7(2)	107.9(2)	107.5(2)
Al–O(1)–P	142.6(2)	143.1(2)	143.7(2)	144.2(2)	145.5(1)	146.9(2)	147.4(2)	147.9(3)	149.9(3)
P–O(2)–Al	142.3(1)	142.9(2)	143.6(2)	144.2(2)	145.7(1)	147.0(2)	147.7(2)	148.4(3)	150.3(3)
(b) β -berlinite									
Temp. (°C)	585	589	598	612	631				
Distance (Å)									
Al–O(1)×2	1.710(4)	1.710(5)	1.709(4)	1.709(5)	1.710(4)				
P–O(1)×2	1.490(3)	1.490(4)	1.491(4)	1.491(4)	1.490(4)				
O(1) 1–O(1) 6×2	2.805(4)	2.804(5)	2.804(4)	2.801(5)	2.804(5)				
O(1) 1–O(2) 2×2	2.781(5)	2.778(6)	2.779(5)	2.773(6)	2.778(6)				
O(1) 1–O(2) 5×2	2.790(2)	2.794(7)	2.790(7)	2.797(7)	2.795(7)				
Average (Å)	2.792	2.792	2.791	2.79	2.792				
O(1) 1–O(1) 4×2	2.394(5)	2.397(6)	2.396(5)	2.401(6)	2.397(6)				
O(1) 1–O(2) 3×2	2.464(4)	2.466(5)	2.466(4)	2.470(5)	2.467(5)				
O(1) 1–O(2) 5'×2	2.440(6)	2.436(6)	2.441(6)	2.433(6)	2.435(6)				
Average (Å)	2.433	2.433	2.434	2.435	2.433				
Angle (deg.)									
O(1)–Al–O(1) 6×2	110.2(2)	110.2(2)	110.2(2)	110.1(2)	110.2(2)				
O(1) 1–Al–O(2) 5×2	109.3(2)	109.6(2)	109.4(2)	109.9(2)	109.7(2)				
O(1) 1–Al–O(2) 2×2	108.9(2)	108.7(2)	108.8(2)	108.5(2)	108.6(2)				
O(1) 1–P–O(1) 4×2	106.9(2)	107.1(2)	107.0(2)	107.2(2)	107.1(2)				
O(1) 1–P–O(2) 3×2	111.6(3)	111.7(3)	111.6(3)	111.8(3)	111.8(3)				
O(1) 1–P–O(2) 5'×2	110.0(2)	109.7(2)	109.9(2)	109.4(2)	109.6(2)				
Al–O(1)–P	154.6(3)	154.7(4)	154.7(4)	154.7(4)	154.8(4)				

accurate mode positions. In this case, therefore, we only note that the sum of the intermode distances for both the Al–O and P–O bonds is seen to be independent of temperature or increase slightly with increasing temperature.

Concluding remarks

The temperature dependence of the positional and thermal vibration parameters of each atom, studied by using X-ray single crystal data, are strikingly similar to those

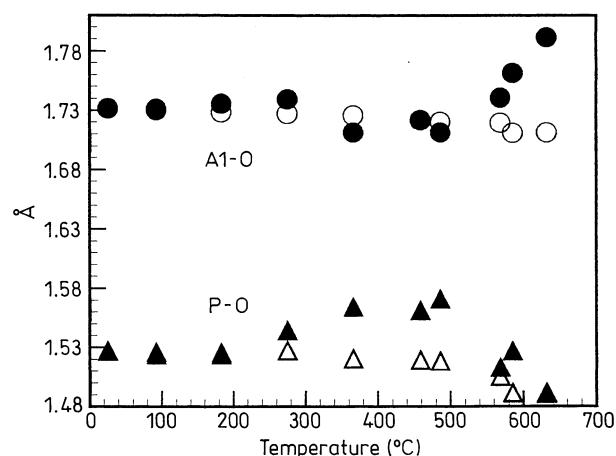


Fig. 9 Temperature dependence of intermean and intermode distances for Al-O and P-O. ○: intermean Al-O, ●: intermode Al-O; △: intermean P-O; ▲: intermode P-O

of the corresponding atoms in quartz. The structural change at the transition is much larger than given previously. The two kinds of tetrahedral atoms, Al and P, behave identically in terms of their thermal vibrations. The Al-O and P-O bonds are both rigid, and the sum of their lengths is independent of temperature or tend to increase slightly with increasing temperature. The diffraction results obtained in the present study are well interpreted in terms of displacive structure transition.

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