

CHANGES IN CRYSTAL LATTICE PARAMETERS OF PENTAERYTHRITOL AT PRESSURES UP TO 10,000 kg/cm²

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An x-ray study has been made of the change in the crystal lattice parameters a and c of pentaerythritol $C(CH_2OH)_4$, which has a tetragonal structure with $a = 6.10$ Å and $c = 8.73$ Å, resulting from direct action of quasihydrostatic pressures up to 10,000 kg/cm² at room temperature. The lattice parameters had the following values at 9000 kg/cm²: $a = 5.99$ Å and $c = 8.46$ Å. A phase transformation of pentaerythritol was observed in the pressure range 4200-5600 kg/cm² from a jump in the parameters a and c and in the volume ($\sim 2.6\%$), the crystal structure remaining the same both below and above the transition pressure.

A good description of the behavior of pentaerythritol under pressure is given by two empirical equations of state of third degree in the pressure having the form:

$$\begin{aligned} \text{before transition} \quad -\frac{\Delta V}{V_0} &= 1.584 \cdot 10^{-5}P - 2.380 \cdot 10^{-9}P^2 + 0.330 \cdot 10^{-13}P^3, \\ \text{after transition} \quad -\frac{\Delta V}{V_0} &= 2.404 \cdot 10^{-5}P - 3.848 \cdot 10^{-9}P^2 + 2.202 \cdot 10^{-13}P^3, \end{aligned}$$

Above the transition pressure, pentaerythritol shows an anomalous compressibility, in that the compressibility increases with increase in pressure.

1. The apparatus described in [1] for making x-ray studies at high pressures up to 18,000 kg/cm² has been used in the present work to investigate the changes in the crystal lattice parameters of pentaerythritol occurring under pressure. The high pressure chamber used in the apparatus was a beryllium vessel of new and original form, which could be supported in a reliable way. A special system for adjusting and testing the x-ray chamber was provided. The construction of the apparatus is also such as to make it possible to rotate the sample under pressure.

The apparatus is comparatively simple in construction the pressure inside the chamber can be measured within relatively narrow limits, it is portable, and the film can be changed without losing pressure. The accuracy of the pressure measurements in the apparatus has been found from a considerable number of calibrating experiments and is 2% of the measured pressure (up to 10,000 kg/cm²). A diagram of the experimental apparatus is shown in Fig. 1.

Pentaerythritol was chosen for the study because, like many organic crystals [2], a considerable change in volume was to be expected at high pressures.

Pentaerythritol $C(CH_2OH)_4$ belongs to the tetragonal system and has an elementary cell with $a = 6.10$ Å and $c = 8.73$ Å. Z (the number of molecules in the cell) = 2, the Fedorov group is $S_4^2(I\bar{4})$, and the symmetry of the molecule, both inherent and in the crystal, is $\bar{4}$ [3]. Very pure pentaerythritol was used in the present experiments. The samples were made from coarse crystalline pentaerythritol powder by selecting perfectly transparent crystals with dimensions from 0.5 to 3 mm and grinding them fine enough to give continuous x-ray lines without rotating the sample. The pentaerythritol samples were pressed into small cylinders 0.8 mm in diameter and 4 mm high.

2. The present experiments were made with a beryllium chamber (used repeatedly under pressure) having an internal cylindrical channel with a diameter of 1.215 mm.

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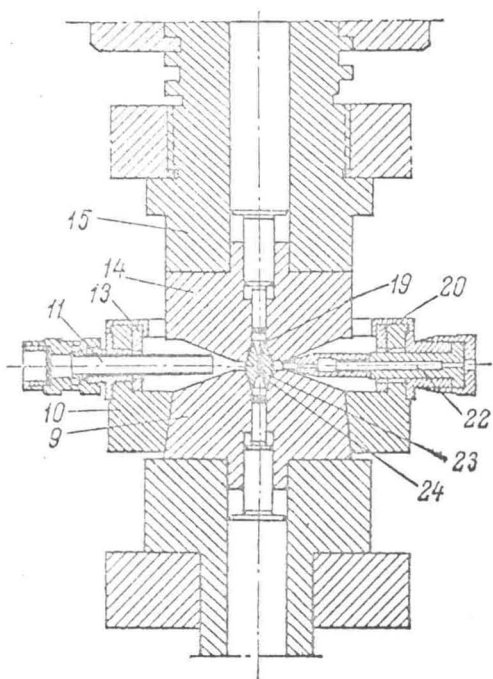


Fig. 1. The beryllium high pressure vessel 24 and part of the channels in the steel supports 9 and 14 are filled with lithium. The test sample 23 surrounded by lithium 19 is placed in a cylindrical opening in the beryllium vessel 24. The x-ray cassette (diameter 68.4 mm) 10 has the usual collimator 22 and catheter 11 for the Debye chamber. The x-ray film 13 is pressed onto the body of the cassette by the ring 20. The pressure is produced in the apparatus by means of the upper screw 15 and the lower nuts on the columns, not shown in the diagram.

Secondary rays were filtered out by putting a 0.016 mm thick aluminum foil in front of the film on the cassette ring. A nickel filter 0.01 mm thick was placed on the collimator cap to filter the copper radiation and reduce the background on the diffraction picture. Exposures were from 1.5 to 3 hours at 30 kv and 26 ma. A demountable tube [4] was used as the x-ray source.

Some pictures were taken in a 143.25 mm diameter VRS-3 chamber at atmospheric pressure to index the diagrams and calculate the lattice parameters of pentaerythritol. A diagram had already been taken in this chamber on a 0.23 mm diameter aluminum sample with asymmetric location of the film. The calculated effective diameter of the chamber was 143.44 mm. The pentaerythritol was used in the form of a 0.5 mm diameter cylinder in a zapon mantle. The results gave the following values for the lattice parameters of pentaerythritol: $a_0 = 6.10 \pm 0.01$ A and $c_0 = 8.73 \pm 0.015$ A.

The pictures were taken under pressure in our apparatus using the asymmetric method, calculating the ef-

fective radius of the chamber for each picture, and using the corresponding x-ray diagram to check the displacement of the sample in the beryllium vessel. Within the limits of experimental error, no displacement of the sample was observed from raising and lowering the pressure.

It was found experimentally that the spread in the value of the parameters a and c became less as the length of time the sample was kept under pressure was increased, varying from 12 hours to 18 days. With samples kept under pressure for 18 days, the mean-square error in the parameters a and c (calculated from measurements on different lines in the x-ray diagram) was less than 0.01 A. All the pictures were taken at room temperature, $18^\circ \pm 1^\circ$ C. The films were measured independently on the comparator by two observers to avoid subjective errors.

Pictures were taken with both increasing and decreasing pressure, as well as with repeated increase in pressure. The x-ray patterns taken with increase in pressure (in both the first and in repeated cycles) gave very nearly the same results. However, the diagrams taken with decreasing pressure showed hysteresis. The reason for the hysteresis is apparently that there is friction in the system, and the pressure measurements are not right when the pressure is being lowered.

Two to four diagrams were taken at each pressure, giving 46 pressure diagrams in all. The results of the calculations made on the x-ray data are given in the table.

3. A least-squares treatment of the results up to cubic terms in the pressure gave the following expressions for the change in the crystal lattice parameters of pentaerythritol along the a and c axes, respectively:

1) For pressures up to 4200 kg/cm^2

$$-\frac{\Delta a}{a_0} = 0.563 \cdot 10^{-5} P$$

$$- 1.984 \cdot 10^{-9} P^2 + 2.204 \cdot 10^{-13} P^3,$$

$$-\frac{\Delta c}{c_0} = 0.457 \cdot 10^{-5} P$$

$$+ 1.587 \cdot 10^{-9} P^2 - 4.078 \cdot 10^{-13} P^3;$$

2) For the pressure range $5600\text{--}9000 \text{ kg/cm}^2$

$$-\frac{\Delta a}{a_0} = 0.804 \cdot 10^{-5} P$$

$$- 1.431 \cdot 10^{-9} P^2 + 0.845 \cdot 10^{-13} P^3,$$

$$-\frac{\Delta c}{c_0} = 1.060 \cdot 10^{-5} P$$

$$- 1.690 \cdot 10^{-9} P^2 + 0.994 \cdot 10^{-13} P^3.$$

The calculated values of $\Delta a/a_0$ and $\Delta c/c_0$ agree with the measured values to the fourth decimal place. Figures

Change in the Parameters \underline{a} and \underline{c} of pentaerythritol under pressure*

Pressure, P, kg/cm ²	Lattice parameters, A	
	\underline{a}	\underline{c}
1800	6.07	8.63
3000	6.07	8.58
4200	6.07	8.58
5600	6.01	8.52
6000	6.01	8.52
7200	6.01	8.50
7800	6.00	8.49
9000	5.99	8.46

*Here \underline{a} is found with an accuracy of ± 0.02 A, for \underline{c} , ± 0.03 A.

2 and 3 show graphs of the above polynomials and the experimental points.

It may be seen from the graphs that the compressibility is greatest in the direction in which the intermolecular distances are greatest and hence the binding forces are weaker.

At a pressure of 9000 kg/cm², the total change in the parameter \underline{c} is 2.5 times greater than the corresponding change in the parameter \underline{a} , and the ratio $\underline{c}/\underline{a}$ changed at the same time from the value 1.43 at atmospheric pressure to the value of 1.41.

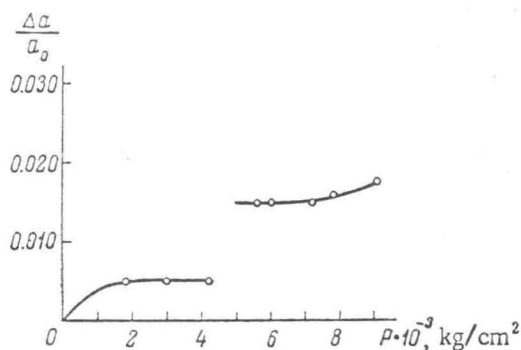


Fig. 2. Linear compressibility, $\Delta a/a_0$, of $C(CH_2OH)_4$ as a function of pressure.

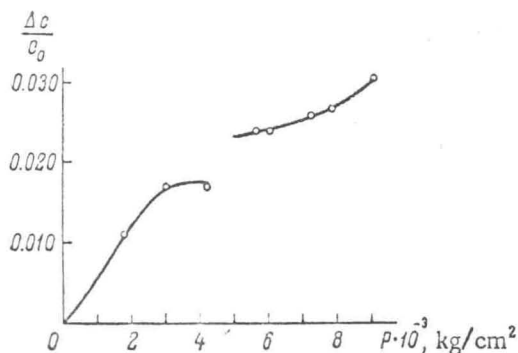


Fig. 3. Linear compressibility, $\Delta c/c_0$, of $C(CH_2OH)_4$ as a function of pressure.

The equations for $\Delta V/V_0$ as a function of P in the pressure ranges given are:

$$-\frac{\Delta V}{V_0} = 1.584 \cdot 10^{-5} P$$

$$-2.380 \cdot 10^{-9} P^2 + 0.330 \cdot 10^{-13} P^3,$$

$$-\frac{\Delta V}{V_0} = 2.404 \cdot 10^{-5} P$$

$$-3.848 \cdot 10^{-9} P^2 + 2.202 \cdot 10^{-13} P^3.$$

It may be seen from the data that in the pressure range 4200-5600 kg/cm² there is a jump in the lattice parameters \underline{a} and \underline{c} and in the volume ($\sim 2.6\%$) which is greater than the error of the measurements. When calibrating the apparatus with a pentaerythritol sample as well as when taking the x-ray diagrams, a jump in volume was observed from the dynamometer readings at a pressure close to 5000 kg/cm².

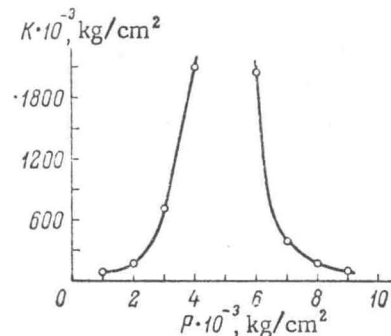


Fig. 4. Bulk modulus of $C(CH_2OH)_4$ as a function of pressure.

Analysis of the x-ray patterns showed that the crystal structure of pentaerythritol stays the same below and above the transition pressure, and the volume jump is probably to be explained by an increase in packing density of the pentaerythritol molecules in the crystal lattice.

Analysis of the equations giving $\Delta a/a_0$ and $\Delta c/c_0$ as a function of pressures shows that the change in compressibility along the \underline{a} and \underline{c} axes is of a different nature below and above the transition pressure. Below the transition pressure (4200 kg/cm²) the compressibility drops off in a normal way as the pressure is increased, while above the transition pressure the compressibility increases with increasing pressure. This peculiarity in the behavior of pentaerythritol we have shown in Fig. 4 for the bulk modulus K, which is the reciprocal of the compressibility. It turned out that in contrast to the bulk moduli of metals and some ionic crystals [5, 6] the change in the K modulus of pentaerythritol with pressure is nonlinear and is discontinuous in the transition region.

The experimental data obtained in this work on the pressure dependence of the volume V and the bulk modu-

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Fig. 5. X-ray patterns of pentaerythritol taken under pressure (lower picture) and without pressure.

where Θ_p and Θ_1 , K_p , K_1 , V_p , and V_1 are the Debye temperatures, the bulk modulus, and the unit cell volumes at pressure P and 1000 kg/cm^2 , respectively. Calculating Θ_p/Θ_{1000} as a function of pressure from this formula has shown that it is qualitatively the same as that of the modulus K as a function of pressure.

4. After the pressure was completely removed from a pentaerythritol sample that had been in the apparatus for ten days, a series of x-ray patterns was taken which showed that there are residual changes in the lattice parameters (exceeding the error of measurement) which decrease with time.

To verify this data a pattern was taken in the VRS-3 chamber (diameter 143.25 mm) on a pentaerythritol sample which had been subjected to the same pressure. The pattern showed that the changes in the lattice parameters actually occur, and even persist for 30 days after the pressure has been removed.

It was shown in [8, 9] that hydrostatic and quasihydrostatic pressures can have different effects on the structure of the samples being tested. To verify this, we took a series of patterns of pentaerythritol under pressure under the same conditions but with the cylindrical channel in the beryllium chamber filled with pentaerythritol powder without any lithium envelope. It is obvious that these conditions differ more from hydrostatic pressure than the conditions under which the previous series of measurements had been made, and represent essentially compression from two sides.

Analyzing the x-ray patterns and working up the results showed that the way $\Delta a/a_0$ and $\Delta c/c_0$ varied with pressure remained the same and was still expressible as a polynomial of third degree in the pressure. However, the absolute values of the changes in the parameters a and c became less than at the corresponding pressures in the first series of experiments.

Another interesting result of this investigation was the demonstration that the (002) line becomes more intense under pressure. Figure 5 shows x-ray patterns taken in our apparatus at atmospheric pressure (upper picture) and under high pressure. It is easily seen from the diagrams that the intensity of the reflection from the 002 plane (the second line from the small hole in the diagram) becomes considerably greater under pressure. This change in intensity of the (002) line persisted for ten days after removing the pressure.

In conclusion, the authors consider it their duty to thank V. P. Goryachev for aid in carrying out the experiments and in working up the results.

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lus K enable us to find the change with pressure of the Debye temperature of pentaerythritol from the formula given in [7]:

$$\frac{\Theta_p}{\Theta_1} \cong \left(\frac{K_p}{K_1} \right)^{1/2} \left(\frac{V_p}{V_1} \right)^{1/6}$$

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

The dielectric constant of the solid dielectric material used in the present work is of great importance for the study of the temperature dependence of the permittivity of the perovskite-type materials of the type CaTiO_3 and barium titanate, strontium titanate, etc. Measurements were made at frequencies up to 1 kc; in some cases up to 10 kc.

To carry out the measurements a holder was used which was simple and practical. Figure 1 shows a schematic diagram of the tube support. The sample is held between contacts 2 and 3 and is electrically insulated by soldered to the contacts. The electrical connections are made at points 5 and 6. The current was measured at points 5 and 6 since the sample is not heated by the temperature of the contacts. The springs 6 are used to hold the sample. The sample 7 is a ceramic dielectric material. The asbesto-thermometer casing which was heated