

tion présentes dans notre molécule: liaison hydrogène, peut-être attraction entre le groupe NO^2 et les carbones aromatiques de l'anneau voisin (cf. Briegleb & Kambeitz, 1936; Abrahams & Robertson, 1948), et les forces de nature électronique qui tendent à rapprocher le plus possible les angles des liaisons (angles de valence) de leur valeur 'théorique'.

Il existe, nous l'avons montré, une liaison hydrogène certaine (longueur 2,75 Å.) entre un seul oxygène des groupes NO^2 *ortho* et l'azote aminé. Cette liaison doit jouer un rôle important dans le comportement chimique de la molécule, et doit rendre compte de l'absence de basicité des picrylanilines. Elle expliquerait même, dans le cas de l'hexanitrodiphénylamine, le caractère acide de ce corps: la fonction amine a disparu, complètement masquée par les groupes NO^2 *ortho*, et la liaison hydrogène a pour effet de donner une fonction acide à un oxygène d'un groupe NO^2 , facilement accessible aux réactifs.

Enfin, puisque nous avons montré que la forme de la molécule était la même dans les trois structures, le polymorphisme est dû au fait que les mêmes molécules peuvent s'assembler en un réseau cristallin de trois manières différentes, correspondant toutes trois à un équilibre stable. La formation simultanée des trois variétés à partir de la même phase (vitreuse ou dissoute) et à la même température montre en outre que les différences d'énergie des trois réseaux doivent être très faibles.

Dans les variétés J_{II} et J_{III} , stables à la température ordinaire, la molécule a exactement la même forme.

Dans la variété J_I , stable à haute température, on relève de légères différences: la molécule est plus 'ramassée', l'angle de valence de l'azote aminé, plus faible. On ne peut néanmoins parler d'isomérisie par rapport aux autres variétés, car les différences entre les deux formes de molécules ne sont dues qu'à des rotations autour de liaisons simples (liaisons C-NH et C- NO^2), rotations qui sont plus ou moins libres (à l'empêchement

stérique près) à l'état liquide et qui 'se figent' à l'état cristallin dans des positions légèrement différentes, correspondant à des empilements différents des molécules. La légère contraction de l'angle de valence de l'azote aminé que nous avons constatée entre J_{II} et J_I peut vraisemblablement s'expliquer elle aussi par la rotation des radicaux qui, en modifiant les distances intramoléculaires, peut faire varier la valeur de certains angles de valence.

En ce qui concerne enfin le phénomène de la solidification vitreuse, nous avons constaté qu'on le rencontre non seulement dans notre dérivé mais dans toute une série de dérivés nitrés de la diphénylamine: il semble donc que ce soit simplement la forme assez compliquée de toutes ces molécules et le grand nombre de faibles interactions qui peuvent être mises en jeu (liaisons NO^2 -anneau benzénique par exemple) qui soit responsable d'une surfusion aussi prononcée: très enchevêtrées à l'état liquide, elles éprouvent quelques difficultés à prendre l'état cristallin ordonné.

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Short Communications

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Structure of BaTiO_3 at low temperatures. By R. G. RHODES, *Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England*

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Of the many papers concerned with the structure and properties of BaTiO_3 , very few refer to the changes which take place when this material is cooled below room temperature (Megaw, 1947; Harwood, 1949; Kay, Wellard & Vousden, 1949). In an attempt to elucidate the nature of these changes, single-domain crystals of BaTiO_3 have been investigated in the range from room temperature down to -150°C . The crystals used were plate-like, with

the uniaxial tetragonal axis perpendicular to the large face at room temperature.

The axial parameters were measured by X-ray diffraction methods with the results shown in Fig. 1. Large thermal hysteresis effects occurred at the two low-temperature transitions, i.e. near 0°C . and near -90°C . Although the actual transition temperatures varied to some extent from one crystal to another, depending on

the size and impurities, the range of hysteresis at each transition was about the same and agrees with that established by measurements on the dielectric constant (Merz, 1949). At both transitions, the axial parameters and the dielectric constant, measured perpendicular (ϵ_a) and parallel (ϵ_c) to the polar axis of the crystal at room

transition, as well as upon other factors such as the size and shape of the crystal and the impurities present. The X-ray reflexions observed in the pattern of a given specimen may be either single spots or double spots, or both kinds may occur together with relative intensities which differ from one specimen to another. These patterns

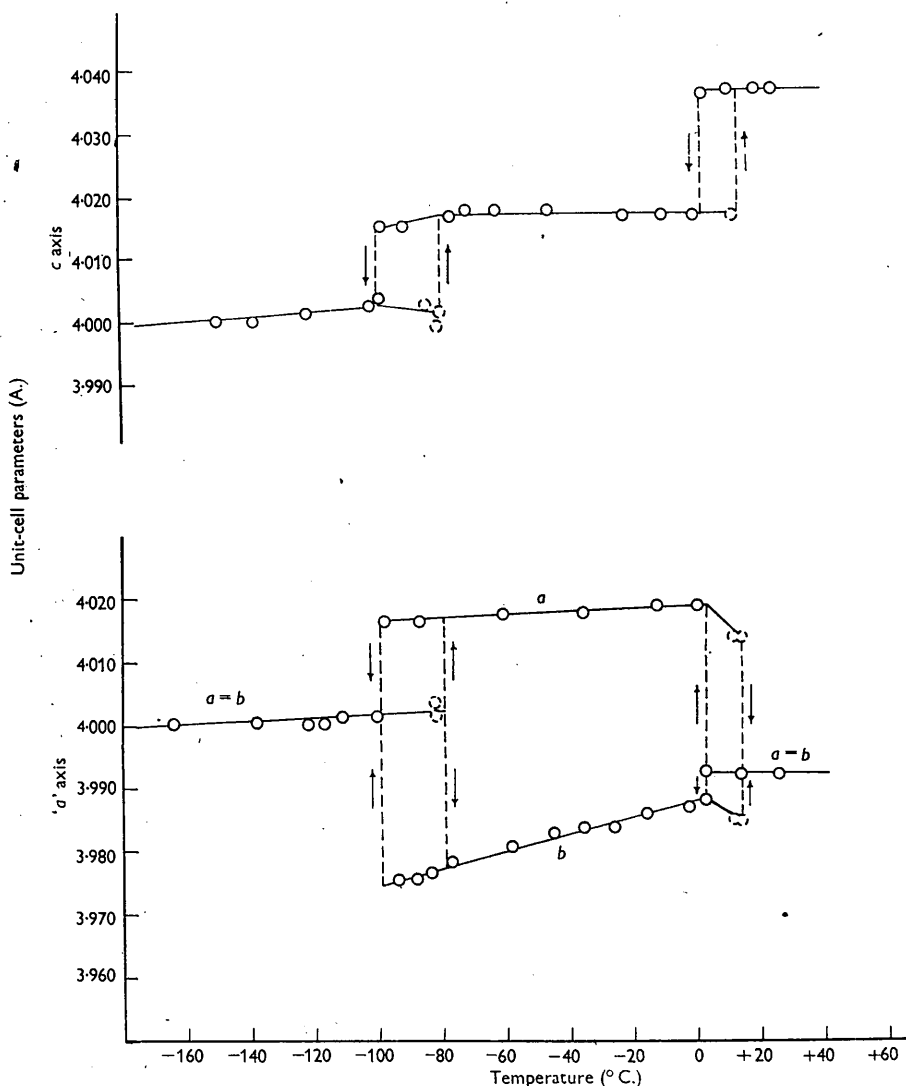


Fig. 1. Changes in the dimensions of the unit cell of BaTiO_3 over the temperature range $+20^\circ$ to -150° C. The arrows indicate the direction of cooling or heating of the crystal, and the points which show the hysteresis effect on heating have been represented as broken circles. The full circles represent the points which follow the same path on cooling and heating. The vertical scales for the two axial parameters are numbered separately. The c axis corresponds to the tetragonal c axis of the original crystal. The identical a and b axes of the original tetragonal cell change into axes of different lengths in the temperature range between 0 and -100° C.; they are labelled ' a ' axis in the diagram.

temperature, changed discontinuously from values characteristic of the high temperature to values characteristic of the low temperature (or vice versa).

Optical and X-ray tests show that, at room temperature, the crystal is tetragonal and consists of a single domain. At the first transition, at about 0° C., the crystal breaks up into several domains forming a highly twinned, mosaic structure.

The precise way in which the change occurs at the first transition seems to depend upon the previous history of the crystal, and upon the rate of cooling through the

are explicable in two different ways. First it may be assumed that two crystal phases occur at the first transition, one with a tetragonal cell ($a=b \approx 3.980$ Å., and $c=4.018$ Å.) and one with a monoclinic structure ($a=b=4.018$ Å., $c=4.018$ Å. and $\beta=90^\circ 12'$). A simpler alternative (Megaw, private communication) is to assume that a single monoclinic structure forms the observed mosaic, the axes being

$$a=c=4.018 \text{ \AA.}, \quad b \approx 3.980 \text{ \AA.}, \quad \text{with } \beta=90^\circ 12'.$$

The b axis is perpendicular to the ac plane and varies

from 3.986 Å. at 0° C. to 3.975 Å. at the lowest temperature reached before the second transition occurs in the neighbourhood of -90 to -100° C. (see Fig. 1). Geometrically, since $a=c$ and $\beta=90^\circ$, this lattice has orthorhombic symmetry, with the diagonals of the (010) face of the pseudo-monoclinic cell forming the new a and c axes (Megaw, 1946).

The individual subcrystallites of this low-temperature mosaic structure are inclined to one another at small angles of 25' with orientations in the orthogonal directions. Because of the breakdown into a mosaic structure dielectric measurements can only represent average values in the respective crystal directions.

At the second transition near -90° C., there is a further change in the axial parameters. In all cases investigated the crystal changes to a mosaic structure at this temperature with a unit cell having axes

$$a=b=c=3.999 \text{ \AA.}, \text{ with } \beta=90^\circ 14'.$$

The structure at this second transition is thus almost cubic with a slight distortion from true orthogonality.

Optical observations with the polarizing microscope showed that the transition from one phase to another, as the temperature was lowered gradually through either of

the transitions, occurred discontinuously. The new phase seemed either to creep across the crystal as a consequence of a series of very minute jumps, or to appear suddenly over large sections of the crystal. Microscope observations in polarized light show the low-temperature mosaic structure as consisting of sets of ill-defined dark lines, approximately parallel to the original a and b axes of the room-temperature tetragonal structure. Extinction was poor at approximately 45° to these axes. In all cases, the crystals returned to their original structure, or a similar one, when reheated to room temperature.

A full account of this work will be published later.

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Hydroxyl groups in awillite. BY HELEN D. MEGAW, *Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England*

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The mineral awillite (Parry & Wright, 1925) has the empirical formula $\text{Ca}_3\text{Si}_2\text{O}_{10}\text{H}_6$. An investigation of its structure, undertaken with the particular purpose of finding the part played in it by the hydrogen, has now been completed, though further work is needed to determine the atomic parameters exactly.

Experimental data were obtained from single-crystal oscillation and Weissenberg photographs, and used to construct Patterson projections and Patterson bounded projections. No *a priori* assumptions were made about the location of the hydrogen atoms. For this reason, the term 'oxygen atom' is used to include O^{2-} , and OH^- , H_2O groups; the distinction between them follows in the final stages of the determination of the structure.

The main features of the structure can be described by considering one formula-unit, $\text{Ca}_3\text{Si}_2\text{O}_{10}\text{H}_6$. The silicon atoms occur in SiO_4 groups, each sharing one edge and two corners with the oxygen polyhedra surrounding neighbouring calcium atoms. The two silicon atoms and two of the three calcium atoms are thus linked up in a densely packed belt continuous throughout the structure. The polyhedron surrounding the third calcium atom shares two opposite edges with neighbouring calcium polyhedra of two adjacent belts. Each silicon atom is at the centre of a fairly regular tetrahedron; each calcium atom has six close oxygen neighbours, and two others not quite so close.

The novel and most interesting feature of the structure is the environment of some of the oxygen atoms. Of the four oxygens of each silicon tetrahedron, each of the two which do not form part of the shared edge has only one other cation neighbour, a calcium atom. The sum of the Pauling bond strengths is $\frac{2}{2} + \frac{4}{4} = 1\frac{1}{2}$, as compared with the value 2 required by O^{2-} for electrical neutrality; it suggests that these atoms are OH^- . Further, the oxygen

atom has the two cation neighbours on the same side, and on its other side only oxygen neighbours—an arrangement which suggests the occurrence of hydroxyl bonds.

The two oxygen atoms not directly linked to silicon have one near calcium neighbour, and two rather more distant, again in a very one-sided arrangement with oxygens adjoining on the other side; they also seem to be OH groups. Detailed consideration of the system of hydroxyl bonds must wait till the refinement of the structure has been completed.

The remaining four oxygen atoms form the shared edges of the silicon tetrahedra and calcium polyhedra; they also partake in shared edges between two calcium polyhedra in the alternate layers. Thus they have each one silicon and three calcium neighbours, tetrahedrally arranged, and the sum of the bond strengths is

$$\frac{4}{4} + \frac{3 \times 2}{8} = 1\frac{3}{4};$$

they may reasonably be identified as O^{2-} .

There is another argument proving that at least some of the atoms directly linked to silicon are OH. This follows inevitably from the empirical formula $\text{Ca}_3\text{Si}_2\text{O}_{10}\text{H}_6$, once the existence of the SiO_4 groups is established. There are only two oxygen atoms not required for the SiO_4 groups, and they cannot accommodate more than four hydrogen atoms, unless, as seems very improbable, OH_2^+ ions should be present. This argument is quite independent of the details of the environment of the oxygen atoms considered in the previous paragraphs.

This direct linkage of silicon to OH is a new observation, which has not, to the best of the author's knowledge, been established in any published work on silicate structure. It may very well throw light on other problems of hydroxyl-containing silicates.