[Registered at the General Post Office, Perth, for transmission by post as a Periodical.]

JOURNAL

OF

THE ROYAL SOCIETY

OF

WESTERN AUSTRALIA, INC.

Founded 1913 :: :: Incorporated 1937

Vol. XXV
1938-1939

The Authors of Papers are alone responsible for the statements
and
the opinions expressed therein.

Printed for the Society by
FRED. WM. SIMPSON, Government Printer, Perth.

1939

g 6221/40

3.—X-RAY STUDIES OF SIMPSONITE.

By

L. E. R. TAYLOR, B.Sc. (Hons.).

Read, 9th August, 1938; Published, 26th June, 1939.

With three figures.

Simpsonite is a sodium-calcium-aluminium tantalate which occurs naturally in such poor crystal form that a determination of its crystalline symmetry cannot be carried out macroscopically. It forms natural crystals which appear to conform approximately to the shape of a short hexagonal prism but in no cases have crystals been found which show more than two good basal faces and four vertical faces. When this number of vertical faces does occur, the fourth is generally only a fragment. It is more usual to find one or two basal, and two vertical faces. Various optical methods were devised for the determination of the angle between the faces but the unevenness of the faces and their exceedingly low optical reflecting power rendered measurements inexact. The mineral is very hard and totally resists cleavage.

X-ray methods were adopted for the determination of the crystalline symmetry and crystallographic form. Preliminary measurements were obtained of spacings parallel to the natural faces of the crystal.

Simpsonite and its alteration product meta-simpsonite occur together in the same crystal, the former being recognised by its more transparent nature. If the two species occurred together in the thin sections used in the investigation, the crystalline form must have been similar, as photographs of different parts of the section yielded similar symmetry. The chemical constitution of both simpsonite and meta-simpsonite have been investigated by Mr. H. Bowley.

The most profitable method of X-ray analysis would have been that involving the use of a small single crystal of the mineral, of a size suitable for rotation photographs. An attempt was therefore made to obtain a small fragment of the mineral containing two recognisable natural faces—a basal and a vertical. This was successfully carried out but the first attempts to obtain Laue photographs of it oriented in a known direction proved unsuccessful. It was, therefore, decided that an easier line of approach lay in the investigation of thin sections of the mineral ground from basal and vertical faces, taken from the same specimen and with their relation to one another carefully noted. This method did not enable one to determine the angles between the faces as the former method would have done.

A crystal was chosen which showed three fairly good prism faces and two basal faces. From this crystal a section parallel to one of the basal faces and three sections parallel to each of the vertical faces were obtained in the following manner.

The faces of the crystal were ground to render them smooth and to remove surface material. It was then divided in halves by a cut parallel to the basal faces. The cutting was done with a hack saw, the teeth of which were filled with emery. Two cuts parallel to the first and third vertical

prism faces divided one of these halves into three sections each containing a prism face. Each of these four pieces of crystal were ground parallel to its contained natural face, *i.e.*, four sections were obtained, one parallel to the basal face and one parallel to each of three adjacent prism faces. The order of the vertical sections and their relation to the basal section were carefully noted. The three vertical sections will be designated as *a*, *b* and *c*. The thickness of the specimens varied from 0.24 to 0.34 mm. Even with a thinness of this order the Laue exposures were long, owing to the presence of the highly absorbing element, tantalum, which formed about 58% of the crystal's composition. The basal section and section *b* contained quite good transparent material. Section *c* consisted of very poor opaque material while section *a* was only fair.

A Hilger-Müller Improved X-ray goniometer spectrograph was used in the course of this work. For the Laue photographs radiation from a Coolidge XP-1 water-cooled X-ray tube was used. A Hilger all-steel gas X-ray tube with a copper target supplied monochromatic radiation as required. The high tension was supplied from a Victor Induction coil with mercury make-and-break. In all exposures the films were backed with a sheet of Levy-West Fluorazure Intensifying screen. With this screen and with 5 m.a. tube current and about 80 K.V.P., satisfactory intensity was obtained with Laue photographs in two hours.

A Laue photograph was taken with the X-ray beam normal to a section and the section adjusted until the symmetry that appeared was made exact. The section was then turned through 90° and reflections of Cu K radiations from the crystal face were obtained by the Bragg method. From the last pictures it was hoped to obtain the spacings of atomic planes parallel to the natural crystal faces.

The basal section was investigated first and proved to give all that was essential to the determination of the X-ray point group of the mineral. The vertical sections verified the conclusions drawn from this section.

Laue photographs of the basal section gave what is undoubtedly a hexagonal symmetry. The symmetry of the photograph is such that six rotations of 60° each about an axis normal to the plane of the film bring similar spots into coincidence. No lines of symmetry exist in the film, *i.e.*, no planes of symmetry exist in the crystal normal to the plane of the basal section and no twofold axes parallel to the basal section. A centre of symmetry in the film is present. The character of the spots varies. They are simple along a line in the film and composite along a line perpendicular to the first. This may be attributed to twinning.

From the point of view of X-rays, the hexagonal system contains only four distinguishable point groups—two in the rhombo-hedral division (3Di and 3Ci*) and two in the hexagonal division (6Di and 6Ci*). The symmetry elements of these four point groups with the resulting symmetry of the Laue photographs taken with the X-ray beam parallel to a threefold or sixfold axis is given in Table 1.

The Laue photograph obtained belongs to the point group 6Ci.

Laue photographs taken with the vertical section normal to the X-ray beam, *i.e.*, with the sixfold axis normal to beam, reveal a line of symmetry across the film. This confirms the conclusions deduced from the pictures of the basal section. Only photographs of vertical section *a* and *b* are shown

* Notation due to Wyckoff.

(Figs. 2 and 3). Section *c* which consisted of poor opaque material gave only very faint reflections but the few reflections obtained conformed with the pattern of the previous vertical sections.

TABLE I.

HEXAGONAL SYSTEM.

Division.	Point Group.	Symmetry Elements.	Resulting Symmetry in Laue Diagrams.
1. Rhombohedral	3Ci (Rhombohedral*)	Threefold axis. A centre of symmetry	Threefold rotational symmetry. No lines of symmetry.
	3Di (Ditrigonal scalenohedral*)	Threefold axis. Three co-planar twofold axes at right angles to threefold axis. Three planes intersecting along threefold axis. A centre of symmetry	Threefold rotational symmetry. Three lines of symmetry.
2. Hexagonal ...	6Ci (Hexagonal bipyramidal*)	Sixfold axis. Plane at right angles to sixfold axis	Sixfold rotational symmetry. No lines of symmetry.
	6Di (Dihexagonal bipyramidal*)	Sixfold axis. Six co-planar twofold axes at right angles to sixfold axis. Plane coincident with plane of twofold axes. Six planes each containing one twofold axis and the sixfold axis. A centre of symmetry	Sixfold rotational symmetry. Six lines of symmetry.

* Nomenclature due to Groth.

This was the limit to which the symmetry of the crystal could be determined by Laue diagrams. The classification is as follows:—the crystal belongs to the hexagonal division of the hexagonal system. It lies in the X-ray point group 6Ci which has the following symmetry elements:—a sixfold axis, a plane of symmetry at right angles to that axis, and a centre of symmetry. This X-ray point group contains the crystallographic point groups 6c, 6C and 6Ci. The form of each of these groups and the symmetry elements defining them are given below.

6c—Trigonal bi-pyramidal*; a threefold axis and a plane of symmetry perpendicular to the axis.

6C—Hexagonal pyramidal*; a sixfold axis.

6Ci—Hexagonal bipyramidal*; sixfold axis, plane of symmetry perpendicular to this axis, a centre of symmetry.

It is possible that the crystal may belong to any of these three but it is impossible, at present, to limit its symmetry elements further.

* Supra.

Reflections of Cu K radiation were obtained by the Bragg method, from the basal section and from the two vertical sections *a* and *b*. Preliminary results only are available.

From measurements on these spectrum photographs of the basal plane it can be concluded that the spacing of planes parallel to the natural basal face is approximately 4.5 A.* From measurement on the spectrum photographs of vertical section *b*, the spacing of planes parallel to the prism face is approximately 6.3 A. From measurements on that of vertical section *a* it is approximately 3.05 A. This would be in approximate agreement with the result from section *b* if the first order spectrum from section *a* was considered to be missing for the spacing deduced from section *a* would become 6.1 A. This assumption is justifiable as the reflections from section *a* are extremely faint and it was observed on the spectrum photograph of section *b* that the first order reflection was weaker than the second order. It is conceivable that the first order reflection from section *a* was too weak to appear.

SUMMARY.

Simpsonite was found to belong to the hexagonal division of the hexagonal system. It possesses no higher symmetry than that given to it by the possession of a sixfold axis, a plane of symmetry at right angles to that axis and a centre of symmetry.

A preliminary value for the spacing of planes of atoms parallel to the basal face was found to be approximately 4.5 A. A preliminary value for planes parallel to a prism face is approximately 6.2 A.

ACKNOWLEDGMENTS.

These investigations were carried out in the Physics Department of the University of Western Australia during the tenure of a Commonwealth research grant for which the author wishes to express her thanks to the Council for Scientific and Industrial Research. From a separate grant from the same source the X-ray goniometer spectrograph and X-ray tubes used in the work were provided. The author wishes to express her thanks for the use of this apparatus and for the facilities provided by the Physics Department.

Specimens of simpsonite were kindly provided by the Government Mineralogist and Analyst, Dr. E. S. Simpson.

The work was carried out under the supervision of Mr. J. Shearer, of the Physics Department, to whom the author's thanks are due for valuable advice and criticism.

DESCRIPTION OF PLATE.

Reproductions of X-ray photographs in original size.

Fig. 1. Laue picture taken with X-ray beam perpendicular to the basal plane. Crystal to film distance = 4.1 cms.

Fig. 2 Laue picture taken with X-ray beam perpendicular to prism face *a* Crystal to film distance about 5 cms.

Fig. 3. Laue picture taken with X-ray beam perpendicular to prism face *b* (adjacent face to *a*). Crystal to film distance = 4.0 cms.

*A = Angstrom unit = 10^{-8} cm.

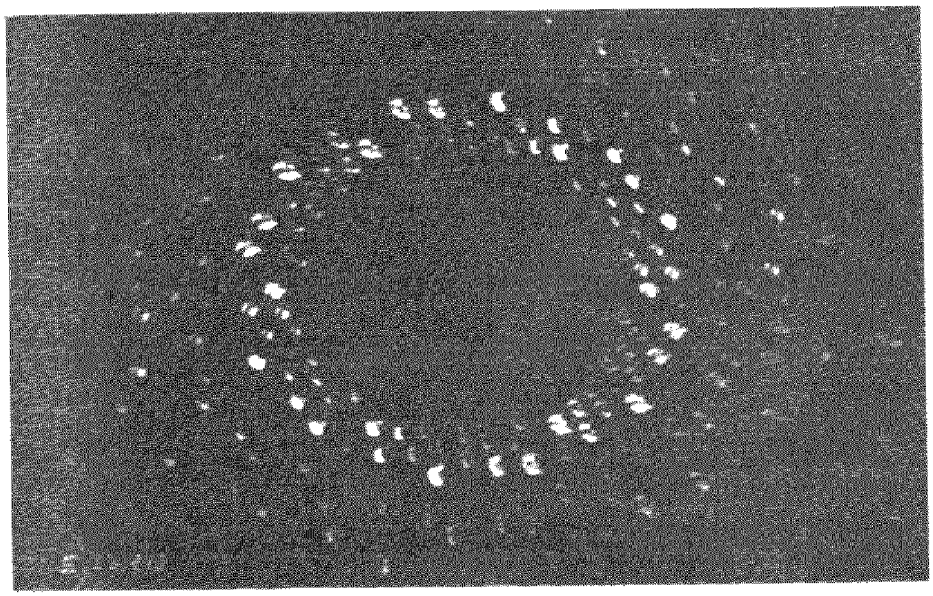

Fig. 1.

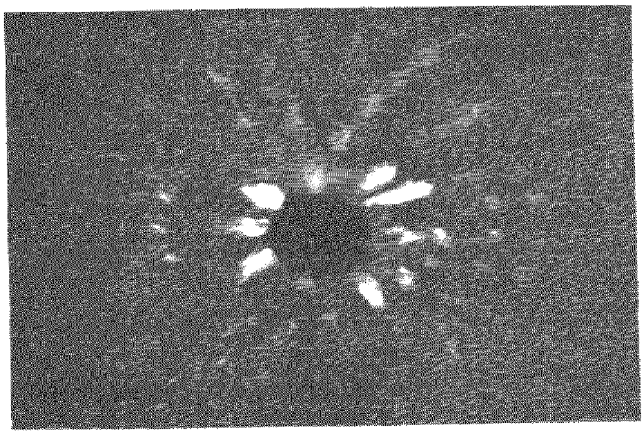

Fig. 2.

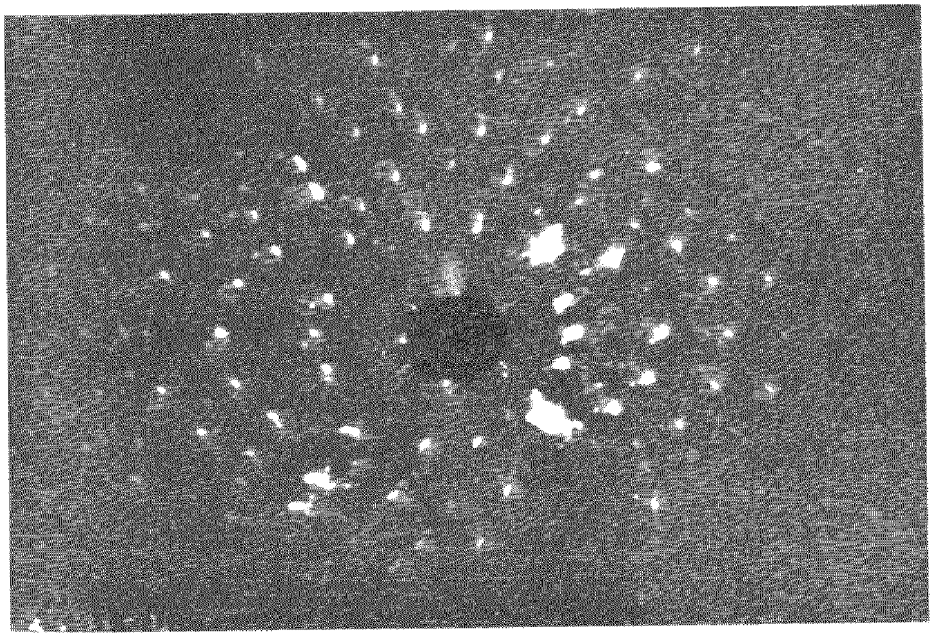

Fig. 3.