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Detection of Non-Hexagonal Symmetry in an Apatite-Structure-Related Mineral (Nasonite)

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Abstract

An analysis of nasonite by high-resolution electron microscopy (HREM) has shown: (a) a loss of the twofold screw axis in the structure, and (b) a deviation from hexagonal symmetry. These results have been checked with a series of computer calculations which show the absence of artefacts in the imaging process. An X-ray structure determination of the same specimen has been carried out resulting in space group $P6_3/m$ which is in contradiction with the HREM findings. It is suggested that the differences in results between the HREM and the X-ray diffraction techniques arise from the presence of phase microdomains inside the original crystal, although no crystal domain showing a hexagonal structure was observed using HREM.

Introduction

Apatite minerals are of fundamental importance in several areas, especially for the chemistry of human calcified tissues (bones, teeth and cartilage). Hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] has a hexagonal structure (space group $P6_3/m$) which is preserved by a random positioning of the OH^- groups in two sites situated above and below the mirror planes at $z = \frac{1}{4}$ and $z = \frac{3}{4}$. The Ca^{2+} ions occupy two non-equivalent positions in the hydroxyapatite structure: $\text{Ca}^{2+}(1)$ ions are on the fourfold sites at $(\frac{1}{3}, \frac{2}{3}, 0.001)$ and $\text{Ca}^{2+}(2)$ ions are on the sixfold sites at $(0.2464, 0.9938, \frac{1}{4})$ (Kay, Young & Posner, 1964).

A step towards understanding the mechanisms of substitution of Pb for Ca in biological apatites is the

determination of the detailed structural location of the substituted Pb^{2+} ions in the simpler systems provided by synthetic and mineral apatites. In the biological as well as in the mineral context, it is the partial rather than the complete substitution that is of direct interest. Often, the mixed-crystal structural details and properties cannot be obtained from end-member properties [an example is the interactions of F^- , Cl^- and OH^- reported by Sudarsanan & Young (1978)]. Engel, Krieg & Reif (1975), Verbeeck, Lassuyt, Heijligers, Driessens & Vrolijk (1981) and Andres-Verges, Hijes-Rolando, Valenzuela-Calahorra & Gonzalez-Diaz (1983) have shown from X-ray powder diffraction patterns that the Pb^{2+} ions in (Ca,Pb) solid solutions occupy mainly the $\text{Ca}^{2+}(2)$ sites and that the crystallinity of the solid decreases for the highest values of substitution.

Nasonite [$\text{Pb}_6\text{Ca}_4(\text{Si}_2\text{O}_7)_3\text{Cl}_2$] is a mixed (Ca,Pb) mineral showing 60% lead substitution and with strong structural and chemical relations with pyromorphite and the apatite group. Furthermore, a structure determination carried out by Giuseppetti, Rossi & Tadini (1971) ($R = 0.054$) has shown that like all members of the apatite group nasonite crystallizes in the hexagonal structure characterized by space group $P6_3/m$. The six PO_4^{3-} groups of the apatite structure are replaced in the nasonite structure by three $\text{Si}_2\text{O}_7^{6-}$ groups with an equal number of Cl^- and (Pb^{2+} , Ca^{2+}) ions.

In order to study the local substitution of Pb^{2+} in either of the apatite Ca^{2+} sites in the apatite structure as well as possible structure variations due to the substitution process, an analysis of a nasonite sample

has been carried out by high-resolution electron microscopy (HREM). HREM has been outstandingly successful in revealing a variety of crystalline defects and phase domains which are very difficult to detect by X-ray structure analysis (Fryer, 1979). It has been used with success to determine the local stoichiometry of germanium niobate oxide crystals (Skarnulis, Iijima & Cowley, 1976) and titanium monoxide crystals (Shen, Bursill, Yoshida, Yamada & Ota, 1984).

High-resolution electron micrographs of synthetic and tooth-enamel apatite crystals showing the Ca, P and OH atomic sites have been obtained recently by Brès, Barry & Hutchison (1985), Ichijo & Yamashita (1983), Kanaya, Baba, Shinohara & Ichijo (1984) and McLean & Nelson (1982, 1983). These micrographs were matched for several directions, defocus values and crystal thicknesses to images computed for the hydroxyapatite atomic positions and microscope parameters. Furthermore, the feasibility of detecting the preferential substitution of lead ions in the $\text{Ca}^{2+}(2)$ sites of the hydroxyapatite structure $[\text{Pb}_{6(2)}\text{Ca}_{4(1)}(\text{PO}_4)_6(\text{OH})_2]$ over the statistical distribution of Pb^{2+} in both $\text{Ca}^{2+}(1)$ and $\text{Ca}^{2+}(2)$ sites $[\text{Pb}_{3.6(2)}\text{Ca}_{2.4(1)}\text{Pb}_{2.4(1)}\text{Ca}_{1.6(1)}(\text{PO}_4)_6(\text{OH})_2]$ has been shown by Brès, Voegel, Barry, Waddington & Frank (1986).

Experimental

A nasonite mineral sample was cut into 2–3 mm blocks and embedded in Epon 812. The blocks were subsequently sectioned with a Sorvall-Porter ultramicrotome equipped with a diamond knife.

The specimens were examined with a JEOL 200CX electron microscope fitted with a high-resolution pole piece at a voltage of 200 kV. The 200CX microscope has an information limit of 1.7 Å and a structure resolution limit of 2.5 Å. An objective aperture of diameter sufficient to select all beams up to 2.0 Å resolution was employed and a tilting stage was used to orient the specimens along the crystallographic directions desired. The spherical aberration constant of the lens was 1.2 mm and the beam divergence 0.8 mrad. An anticontamination stage was used.

The image calculations were performed on an ICL 2988 digital computer using a computer program developed by M. A. O'Keefe (O'Keefe & Buseck, 1979; O'Keefe, 1973; Lynch, Moodie & O'Keefe, 1975). The atomic positions determined by Giuseppetti, Rossi & Tadini (1971) were used. For the multislice calculations the crystal slice thickness employed was 4.365 Å, the number of beams was 1069 and the sum of their intensities at the 36th slice was 0.99133. The illuminating beam was successively tilted by 0.0, 0.9, 1.7 and 3.5 mrad towards the c^* direction.

Single-crystal X-ray diffraction analysis of a nasonite crystal was carried out with an Enraf-Nonius CAD-4 automatic single-crystal diffrac-

tometer. $\text{Mo K}\alpha$ ($\lambda = 0.71069$ Å) radiation was used. Well defined sharp peaks were obtained, the breadth of the peaks at half maximum intensity was 0.2° (2θ). Refinement of the structure was based on 513 observed reflections and was carried out to obtain a value of the shift/e.s.d. of 0.001–0.003 and a goodness of fit of 0.85. An absorption correction was applied.

Results and discussion

Observations of the specimen indicated the presence of a strong (001) lattice plane in high-resolution images and the corresponding reflection in electron diffractograms of crystals oriented along the [220] zone axis (Fig. 1a). This lattice plane corresponds to the presence of the 001 reflexion in reciprocal space (Fig. 1b). 001 reflexions (l being odd) are kinematically and dynamically forbidden in the case of the $P6_3/m$ apatite space group because of the presence of the screw axis (Gjønnes & Moodie, 1965; Tanaka, Sekii & Nagasawa, 1983), so the presence of such reflexions on diffractograms of our specimen shows the absence of screw axes.

High-resolution images show extreme sensitivity to local imaging conditions, especially when imaging structures with space-group extinction conditions (Smith, Saxton, O'Keefe, Wood & Stobbs, 1983; Smith, Bursill & Wood, 1985). It has been shown that the intensity of a forbidden reflexion can increase when the incident beam is tilted from the zone axis and can even become comparable with the normal reflexion intensity (Nagakura, Nakamura & Suzuki, 1982). A series of computer calculations have been carried out in order to show that this was not the case for the structure determined by Giuseppetti, Rossi &

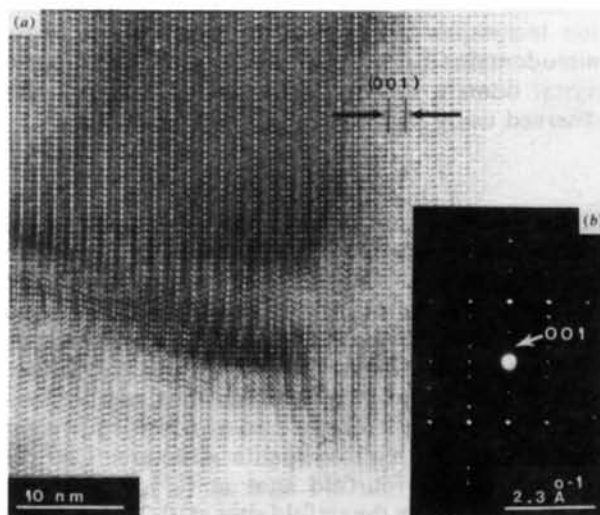


Fig. 1. (a) High-resolution electron micrograph of a nasonite crystal viewed down the [120] zone axis, and (b) the corresponding diffraction pattern.

Tadini (1971). This shows that tilting the specimen towards the c^* direction does not favour the 001 reflexion preferentially (Fig. 2 and Table 1).

High-resolution electron micrographs of nasonite crystals oriented along [001] (Figs. 3*a* and 3*b*) show angles of 58, 57 and 65° between the 100, $\bar{1}\bar{1}0$, 010 and $\bar{1}00$ reflexions; this deviation of the lattice angles indicates a loss of hexagonal symmetry in the structure examined.

The single-crystal X-ray diffraction analysis of the sample examined by HREM has revealed that nasonite crystallizes in a hexagonal unit cell with

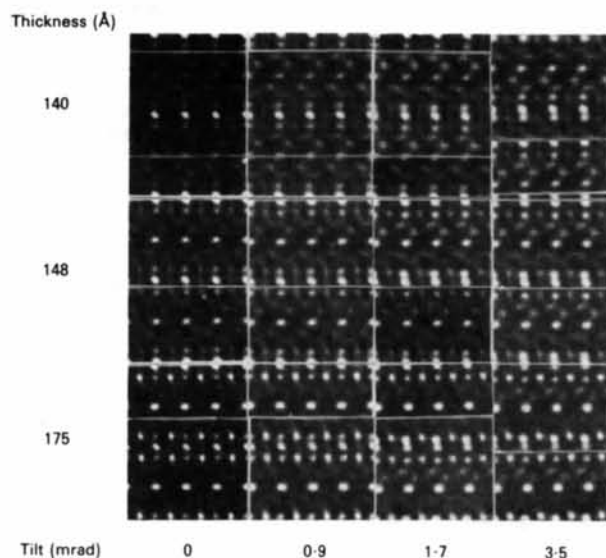


Fig. 2. Calculated images corresponding to the nasonite structure as determined by Giuseppetti, Rossi & Tadini (1971) for several values of tilt towards the c^* direction; the defocus value is -200 and the c lattice parameter corresponds to the vertical direction.

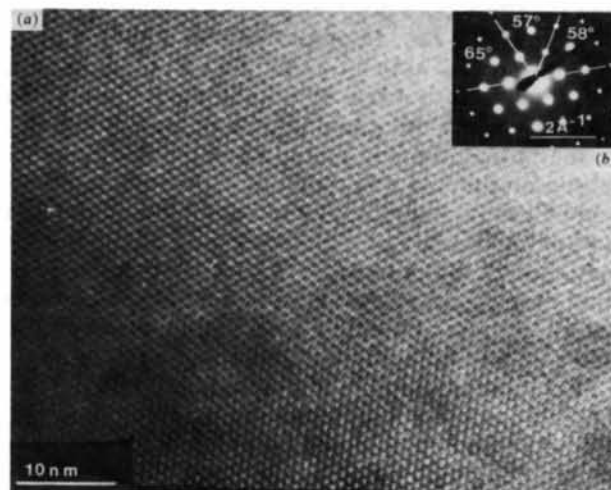


Fig. 3. (a) High-resolution electron micrograph of a nasonite crystal viewed down the [001] zone axis, and (b) the corresponding diffraction pattern.

Table 1. Intensities of a selection of reflexions for various angles of tilt towards the c^* direction

Tilt angle (mrad)	0.0	0.9	1.7	3.5
000	0.254	0.257	0.267	0.310
001	0.037	0.038	0.038	0.031
00 $\bar{1}$	0.037	0.035	0.030	0.018
002	0.063	0.068	0.069	0.065
00 $\bar{2}$	0.063	0.056	0.047	0.024

lattice constants $a = 10.064$ Å and $b = 13.228$ Å; the space group is $P6_3/m$. The structure refinement gave an R factor of 0.0496. The detailed structure is in excellent agreement with that reported by Giuseppetti, Rossi & Tadini (1971).

Both the loss of the screw axis and the disparity of the α and β lattice angles show that the nasonite structure examined by HREM clearly does not possess space group $P6_3/m$. A possible reason why the specimen shows space group $P6_3/m$ when examined by X-ray diffraction and strong deviations from this space group when examined by HREM might be the presence of phase microdomains too large to be distinguished by HREM but which would be globally sampled by the X-ray beam. This would explain why these domains were not observed in Figs. 1(*a*) and 3(*a*). No domains with space group $P6_3/m$ have been observed by HREM; this, however, does not necessarily mean that such domains do not exist. We hope that in the near future a localized space-group determination as well as the study of the atomic structure of nasonite will be made possible by the use of a microscope with a higher resolution than the JEOL 200CX. This would facilitate the direct determination of atomic

the use of a technique such as the convergent-beam electron diffraction (Steeds, 1979).

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On the Structure of $[\text{Fe}(\text{9}]\text{aneN}_3)_2]\text{Cl}_3 \cdot 5\text{H}_2\text{O}$: Some Caveats

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Abstract

The crystal structure of (1,4,7-triazacyclononane)-iron(III) chloride pentahydrate, $\text{Fe}(\text{C}_6\text{H}_{15}\text{N}_3)_2\text{Cl}_3 \cdot 5\text{H}_2\text{O}$, has been reinvestigated, and the space group is shown to be $R32$ [$a = 8.076(2)$, $c = 31.363(6)$ Å, $Z = 3$] rather than $P3$. The new data comprised 3640 intensity measurements which, when averaged according to 32 symmetry, led to 1154 independent reflections; the final goodness-of-fit was 2.10 for 74 parameters and R was 0.0213 for 1140 reflections with $F^2 > 0$. The dimensions of the $[\text{Fe}(\text{9}]\text{aneN}_3)_2\text{Cl}_2]^+$ grouping are little changed from the earlier, $P3$ description [Boeyens, Forbes, Hancock & Wieghardt (1985). *Inorg. Chem.* **24**, 2926-2931]; however, the arrangement in the layer of water molecules (and one Cl^- ion) is quite different and entails considerable disorder. Possible reasons for the incorrect assignments of lattice type and Laue symmetry in the earlier investigation are examined, and some recommendations are made for avoiding such errors in the future.

Introduction

For several years I have been concerned with the problem of describing a crystal structure in the most appropriate space group, and in particular of reducing the chances of describing it in an incorrect space group (see, for example, Marsh, 1981, 1986; Schomaker & Marsh, 1979; Marsh & Herbstein, 1983). I recently came across, in the literature, an example where three components of the space group - the lattice, the Laue group and the presence or absence of a center of symmetry - seemed questionable. I have re-examined this structure and found that two of the three components were, indeed, incorrectly assigned. It is the purpose of this paper not only to describe the corrected structure but also to examine possible causes for the incorrect assignments in the hope of preventing similar problems in the future.

The crystal structure of $\text{Fe}(\text{C}_6\text{H}_{15}\text{N}_3)_2\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ - an Fe^{III} complex with triazacyclononane (Boeyens, Forbes, Hancock & Wieghardt, 1985; BFHW) - was described in the trigonal space group $P3$, with three independent complexes in the hexagonal unit cell. The reported structure raised three questions in my mind: (1) Is the hexagonal lattice rhombohedrally

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