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Optical Properties of Synthetic and Mineral Chlorapatites

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Abstract

The birefringence and orientation of the indicatrix for acicular and prismatic habits of monoclinic flux-grown chlorapatite (ClAp), $Ca_5(PO_4)_3Cl$, have been measured. There are slight differences in birefringence between the habits due to compositional changes, which, because the indicatrix is very nearly spherical, cause the optic axial plane (OAP) to change its orientation by 90°, although the direction of the axes of the indicatrix do not change. The acicular crystals are the purer and are biaxial (−), $\gamma - \beta = 2{\cdot}9 \times 10^{-5}$, $\beta - \alpha = 8{\cdot}2 \times 10^{-5}$, mean refractive index $(n) = 1{\cdot}6672$ and have the unique c axis normal to the OAP. ClAp is uniaxial (+) above its monoclinic-to-hexagonal transition. Hydrothermally grown monoclinic ClAp has optical properties that can be understood from the results for the flux-grown crystals. Synthetic monoclinic F,ClAp and monoclinic ClAp from Bob's Lake, Ontario, is biaxial (+) with the unique axis lying in the OAP and $n = 1{\cdot}6635$.

Introduction

Stoichiometric ClAp is monoclinic (pseudohexagonal) with space group $P2_1/b$ (Mackie, Elliott & Young, 1972). The lattice constants are : $a = 9{\cdot}628$, $b = 2a$, $c = 6{\cdot}764$ Å and $\gamma = 120°$. The principal difference from the hexagonal structure is an ordered arrangement of Cl, which results in a doubling of **b**.

Some optical properties of 2–3 mm monoclinic crystals grown from a flux of $CaCl_2$ have been determined (Prener, 1967). He reported that the OAP was perpendicular (⊥) to (001), X parallel (‖) to **c**, $Z \wedge \mathbf{b} = 5°$ in obtuse γ and $\gamma - \beta \simeq 0{\cdot}0002$. The optic sign, $\beta - \alpha$ and $2V$ were not given. The crystals often showed three interpenetrating twins oriented at 120° to each other about **c**. A reversible transition from monoclinic to hexagonal between 458 and 483 K for different ClAp crystals was described. Above the transition, the crystals were uniaxial (optic sign not reported) and the doubling of **b** was lost. The twinning pattern on cooling was different from the original pattern. Loss of $CaCl_2$ on heating in a vacuum lowered the transition temperature (minimum 416 K) and partial replacement of Cl by F raised it (maximum 583 K with 16% Cl replaced by F). Further loss of $CaCl_2$ or substitution by F prevented the formation of a monoclinic structure.

Argiolas, Baumer & Lapraz (1979) described hydrothermally grown monoclinic ClAp. The crystals were up to $\frac{1}{4}$ mm and formed squat or acicular hexagonal prisms, each in a fairly well defined region of temperature and pressure. The mean n was 1·663–1·664 and the squat crystals were (+) and the acicular ones (−). Presumably the optic sign was determined with respect to the morphological hexagonal axis, as biaxial properties were not mentioned. The change in optic sign was ascribed to changes in Cl position. The crystals changed from (+) to (−) after heating at 973 K.

Mineral ClAp is usually hexagonal. Hounslow & Chao (1970) reported, for Na light, $n_o = 1{\cdot}665(2)$ and $n_e = 1{\cdot}662(2)$ for a hexagonal apatite from Norway with a deficiency of 18% Cl. Other measurements for mineral or synthetic hexagonal ClAp in the literature are similar, although slightly smaller values of birefringence (0·001) have been reported (Borgström, 1931). Hounslow & Chao (1970) described monoclinic ClAp with a 9% Cl deficiency from Bob's Lake, Ontario, which was biaxial (−) with $2V \simeq 10°$, $\alpha = 1{\cdot}665(2)$, $\beta = 1{\cdot}667(2)$ and $\gamma \simeq \beta$ for Na light, but the orientation of the indicatrix with respect to the unit cell was not given. These authors deduced from their work on hexagonal mineral ClAp and Prener's data that a deficiency of 16% Cl was very close to the transitional composition between the hexagonal and monoclinic structures.

Materials and methods

Samples of ClAp (some with small amounts of F) were available that had been grown at the Georgia Institute of Technology from flux after Prener (1967). These consisted of 3–5 mm hexagonal prisms, usually accompanied by needles of ClAp 2–5 mm long and about 0·1 mm thick and often by fine needles of chlorspodiosite. One crystal of ClAp grown from flux by Prener, several samples grown hydrothermally by Argiolas *et al.* (1979) and mineral ClAp from Bob's

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Lake were also examined. The hydrothermal samples (0·1–0·3 mm in size) were provided by Dr A. Baumer and grown under various conditions of temperature and pressure and described by him as (+) or (−) (details given in *Results* section). The mineral ClAp was an 8 mm pinkish-white hexagonal prism with a pale-yellow transparent core.

The needles of synthetic ClAp could be cleaved on (001) and the other crystals cut into sections. The birefringence was determined from the path difference for Na light for a known thickness of crystals with a Sénarmont compensator (for example, Hartshorne & Stuart, 1970). The optic sign was found in many cases from the direction of the acute bisectrix determined from the behaviour on rotation of biaxial obtuse optic figures seen down **c**. The refractive indices (estimated error ±0·0005) for Na light were determined with immersion liquids of mixtures of diiodomethane and 1-bromonaphthalene, whose refractive indices were measured at the time of use with an Abbé refractometer calibrated against a glass standard.

The optical properties of some crystals were investigated between 298 and 573 K with a Mettler FP6 hot stage whose temperature calibration was checked with pure tin (m.p. 505 K).

The orientation of the indicatrix with respect to the monoclinic cell was determined from polarized light observations and X-ray precession photographs. $h,k,2$ sections were used because they contain the strongest $h,2k+1,l$ reflections, and it is these that show the direction of **b***. The direction of **a*** was determined from a consideration of the intensities of pairs of reflections of the type $h,2k,2$ and $k,2h,2$ with the same reflections calculated for the hexagonal form of Cl-deficient ClAp, so that the unit cell would be consistent with that used to describe the structure of apatites.

Results

Flux-grown acicular chlorapatite

These crystals were only very occasionally twinned. OAP ∥ (001), $Y \parallel \mathbf{c}$, $\gamma - \alpha = 9{\cdot}5 \times 10^{5}$, $\gamma - \beta = 2{\cdot}9 \times 10^{-5}$, $\beta - \alpha = 8{\cdot}2 \times 10^{-5}$ and mean $n = 1{\cdot}6672$. The indicatrix is (−) and $2V_\alpha$ calculated from $\gamma - \beta$ and $\beta - \alpha$ is 38°. **b** = 65° in obtuse γ determined from X-ray diffraction.

The biaxial-to-uniaxial transition temperatures for two crystals were 488 and 489 K. $\gamma - \alpha$ decreased gradually on heating without detectable rotation of the extinction direction. On heating a length fast crystal through 10–20 K, the birefringence ⊥ to **c** decreased to zero, and then the crystal became length slow. The birefringence increased with temperature with an increasing rate of change without discontinuity at the transition. At 469 K, the birefringence was 50×10^{-5} and at 509 K 95×10^{-5} (compared with $2{\cdot}9 \times 10^{-5}$ of the opposite sign at 298 K). Uniaxial (+) above the transition.

Flux-grown chlorapatite prisms

The prisms were usually twinned. OAP ⊥ (001) and $X \parallel \mathbf{c}$. One prism had a small region for which the OAP was ∥ to (001). $\gamma - \beta = 1{\cdot}6 \times 10^{-4}$, $\gamma - \alpha = 1{\cdot}9 \times 10^{-4}$ and mean $n = 1{\cdot}6672$. The indicatrix is (+) with calculated $2V_\alpha = 134°$. $Z \wedge \mathbf{b}$ determined by X-ray diffraction was $66 \pm \frac{1}{4}°$ in obtuse γ.

The transition temperatures for three prisms were 488, 484 and 486 K. No rotation of Z was detectable on heating to the transition temperature. The rate of decrease of $\gamma - \beta$ increased towards the transition temperature. For the first prism $\gamma - \beta = 11 \times 10^{-5}$ at 459 K, 6×10^{-5} at 479 K and not detectable at 488 K. Uniaxial (+) above the transition.

Flux-grown fluor-chlorapatite

Flux composition of F/(F + Cl) = 1/24. Hexagonal plate biaxial (+), $2V_\alpha > 90°$, OAP ⊥ (001), $X \parallel \mathbf{c}$, $Z \wedge$ hexagonal edge = 70°. ½ mm stumpy prism, uniaxial (−) at 293 and 573 K. Acicular crystal uniaxial (−) at 293 K, isotropic at 523 K and uniaxial (+) at 563 K. Mean $n = 1{\cdot}6670$ but often less for parts of ½ mm stumpy prism with $n = 1{\cdot}6628$.

Flux composition of F/(F + Cl) = 1/12. One prism as for hexagonal plate. Acicular crystal uniaxial (−) at 293 K and much reduced (−) birefringence at 533 K. Another acicular crystal uniaxial (−), $n_o - n_e = 0{\cdot}0010$ and mean $n = 1{\cdot}6622$ at 293 K.

Hydrothermally grown chlorapatite

Sample *A*. 893 K, 150 MPa, 6 h (+). Needles with a few squat prisms. The needles were always heavily twinned and length slow irrespective of orientation about **c**. One crystal was heated to 523 K and cooled slowly, after which small regions were length fast. Some of the squat prisms without thermal treatment had small regions that were length fast. Mean $n = 1{\cdot}6672$.

Sample *B*. Prepared at 823 K, 0·1 GPa, reheated at 993 K for 15 h (−). The *c* axis of a squat prism was the fast direction except for a small region, which was slow. Mean $n = 1{\cdot}6690$.

Sample *C*. 1023(10)K, 100(10)MPa (−), generally squat, but sometimes acicular. The squat prisms were friable, not very clear optically and uniaxial (−) with $n = 1{\cdot}663$–$1{\cdot}664$.

Mineral chlorapatite from Bob's Lake

Untwinned biaxial (+), $2V_\alpha > 90°$, OAP ⊥ (001) and $X \parallel \mathbf{c}$. $Z \wedge$ hexagonal edge = 67°. Mean $n = 1{\cdot}6635$.

Discussion

The changes in refractive indices of ClAp with departure from stoichiometry are shown in Fig. 1. Following Hounslow & Chao (1970), ClAp is shown biaxial below a 16% replacement of Cl by F. The increase in birefringence from nearly zero and decrease in mean *n* as Cl is replaced by F is consistent with $n_e = 1{\cdot}629$ and $n_o = 1{\cdot}633$ for FAp (Lehr, Brown, Frazier, Smith & Thrasher, 1967). In Fig. 1, it has been assumed that $n \parallel \mathbf{c}$ changes linearly with Cl with the same slope either side of the transition. On the other hand, $n \perp \mathbf{c}$ shows a loss of degeneracy by splitting fairly abruptly into two when the Cl becomes ordered. In the monoclinic region, the mean of $n \parallel \mathbf{c}$ and $n \perp \mathbf{c}$ is made equal to the extrapolated value of n_o (dotted in Fig. 1) that would have been observed had the Cl not become ordered.

Fig. 1 is consistent with the observation that there is a wide compositional range from the synthetic stumpy prisms of ClAp at the high Cl end to Bob's Lake ClAp (this work) at the low end and including most of the synthetic F,ClAps, which all have the same shape of indicatrix and a mean *n* that decreases with a decrease in Cl content.

The acicular and prismatic flux-grown ClAp have different optical properties (*e.g.* different orientation of the OAP), which must be due to differences in stoichiometry. These must be very small because the transition temperatures, which Prener (1967) found to be quite sensitive to changes in stoichiometry, are insignificantly different, and also the mean *n* are indistinguishable. The optical differences can be explained, if the two lower refractive indices in Fig. 1 cross over near the maximum Cl content and the prisms have slightly less Cl than the needles. This fits the observation that the prisms, rather than the needles, are similar to F,ClAp, and the fact that a sample from a prism of flux-grown ClAp has been found to be 3–5% deficient in Cl by single-crystal X-ray diffraction (Mackie *et al.*, 1972). The optical properties of stoichiometric ClAp are thus best represented by those of the flux-grown needles.

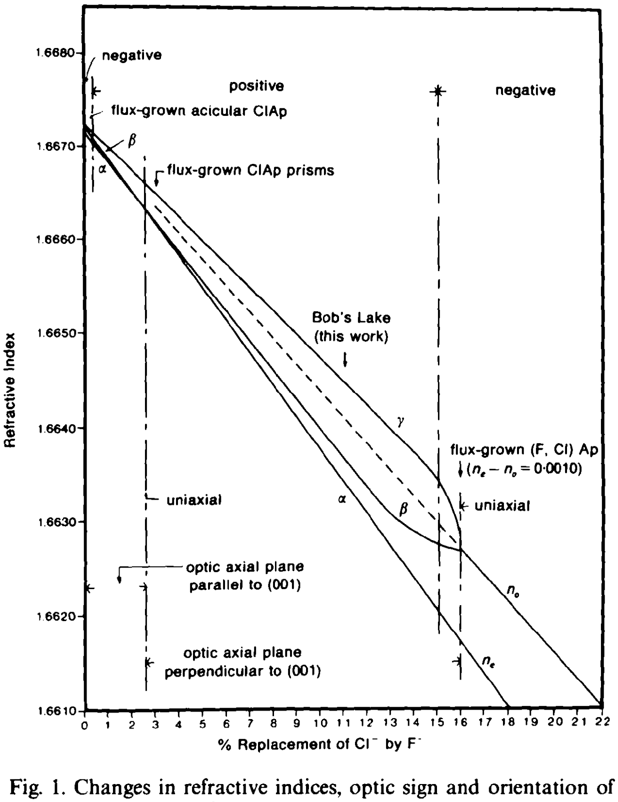

Fig. 1. Changes in refractive indices, optic sign and orientation of optic axial plane in fluor-chlorapatite as a function of percentage replacement of chlorine by fluorine.

The X-ray diffraction and polarized light studies of synthetic ClAp, F,ClAp and monoclinic mineral ClAp show that there is little change in the orientation of the indicatrix about **c** with changes in composition or on heating. This can be explained if the changes predominantly involve only the Cl *z* parameter, so that the electron density projected onto (001) remains the same. It might be expected that the orientation of the indicatrix about **c** would have a simple relation to some significant feature in the structure, but this has not been found. By contrast, the increased disorder in the Cl induced by heat or by the replacement of Cl by F does change to birefringence ⊥ to **c**, although the changes are of opposite sign.

The results for the ClAp prisms are in agreement with Prener (1967), except for the orientation of the OAP about **c**. $Z \wedge \mathbf{b}$ in obtuse γ found here is 60° greater. The discrepancy could occur if the morphology of the crystals alone was considered, but not from an error from reversal of *h* and *k* in the indexing of the diffraction patterns.

The observations on the hydrothermally grown crystals can be understood from Fig. 1. Sample *A* is the purest and has optical properties similar to the flux-grown needles. The *c* axis will be the slow direction for most of the orientations of the crystal about this axis so the heavily twinned needles will appear uniaxial (+), in agreement with Baumer. *B* is slightly less pure than *A*, so that the major part of the crystal is similar to the flux-grown prisms. Thus, **c** will always be the fast direction and a twinned crystal will appear uniaxial (−) in agreement with Baumer. The observation of Argiolas *et al.* (1979) of a change in sign from (+) to (−), after heating ClAp at 973 K, is probably due to an increased non-stoichiometry from the exchange of Cl in the crystal for OH derived from atmospheric water or the loss of $CaCl_2$ from the crystal. The actual change is from biaxial (−) to (+), accompanied by a change in the orientation of the OAP from ∥ to ⊥ to (001). More extensive heating would make the crystal uniaxial (−) with an increased birefringence (Prener, 1971). The refractive index of *C* indicates a significant departure from stoichiometry. The uniaxial (−) appearance suggests this is sufficient to make the structure hexagonal, but it could be monoclinic and twinned on a sub-microscopic scale.

Argiolas *et al.* (1979) ascribed the difference between the 'negative' and 'positive' crystals to the Cl positions. It would seem that Cl in the 'positive' crystals (and the flux-grown needles) would nearly all occupy normal Cl sites (Mackie *et al.*, 1972), with few at Cl′ sites. In the less-stoichiometric 'negative' crystals, the greater Cl disorder would cause a significant number of Cl′ sites to be occupied.

Hounslow & Chao (1970) reported that Bob's Lake ClAp was biaxial (−) with $2V \simeq 10°$, whereas here the one specimen studied was (+) with a much larger $2V_\alpha$. Hounslow & Chao's sample may have contained more F so that it was almost, but not quite, hexagonal. The optical properties would then be given in Fig. 1 from the curves immediately to the left of the transition, which would result in a (−) sign with small $2V_\alpha$.

This study has demonstrated the sensitivity of polarized-light microscopy for characterizing ClAps. Hydroxyapatite, often studied as a model compound for the inorganic phase of bones and teeth, is also monoclinic when pure, but more usually hexagonal because of impurities. It would seem that polarized-light microscopy could also be usefully used to characterize the more crystalline preparations of this compound.

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