STRUCTURE OF DEUTERATED KDP CRYSTAL: DEUTERIUM CONCENTRATION DETERMINATION

B. Isherwood, J. James

To cite this version:


HAL Id: jpa-00214963
https://hal.archives-ouvertes.fr/jpa-00214963
Submitted on 1 Jan 1972

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
STRUCTURE OF DEUTERATED KDP CRYSTAL:
DEUTERIUM CONCENTRATION DETERMINATION

B. J. ISHERWOOD and J. A. JAMES
(The General Electric Company Limited, Central Research Laboratories,
Hirst Research Centre, Wembley, England)

Résumé. — Nous avons effectué les mesures des paramètres de la maille élémentaire et de la température de transition \( T_c \) de plusieurs cristaux de phosphate de potassium deutérés avec un pourcentage \( c \) variable de deutérium 76-96 \%. Il a été démontré que le paramètre \( a_0 \) (mesuré à 22 °C) et \( T_c \) ont une variation linéaire en fonction de la concentration en deutérium. Ces relations sont les suivantes:

\[
T_c = 123 + 106 x, \text{ K} \\
a_0 = 7,452.39 + 1.759 \times 10^{-2} x, \text{ Å} \quad \text{où} \quad x = D/(D + H).
\]

Abstract. — Measurements of the structure-cell parameters and ferroelectric Curie temperature, \( T_c \), of a number of tetragonal potassium dideuterium phosphate crystals, with deuterium contents covering range 76-96 \%, have been conducted. It has been demonstrated that both the \( a_0 \) structure-cell parameter (measured at 22 °C) and \( T_c \) exhibit a linear dependence with deuterium content. The relationship between these parameters being established as,

\[
T_c = 123 + 106 x, \text{ K} \\
a_0 = 7,452.39 + 1.759 \times 10^{-2} x, \text{ Å} \quad \text{where} \quad x = D/(D + H).
\]

Introduction. — Laser radiation is conventionally controlled by an electro-optic Pockels cell. The fundamental requirements of a material suitable for use in such a cell are that it exhibits a linear electro-optic effect, has high optical transmittance and an operationally low half-wave voltage. This latter parameter is related directly to the electro-optic coefficients of the material.

Crystals of the tetragonal form of potassium dideuterium phosphate, \( \text{KD}_2\text{PO}_4 \), have been shown to satisfy these requirements and furthermore to possess a high relevant electro-optic coefficient, twice that of \( \text{KH}_2\text{PO}_4 \) at room temperature [1]. Such crystals are conventionally grown from solutions of heavy water by the falling temperature technique. To exploit fully the large electro-optic coefficient it is desirable that highly deuterated crystals be grown. It is important in the assessment of the crystals to be able to determine with adequate precision, say \( \pm 2 \% \), their deuterium contents. Within our experience, fully deuterated crystals grow in the monoclinic form.

The similarity of \( \text{KH}_2\text{PO}_4 \) and \( \text{KD}_2\text{PO}_4 \) makes it impracticable to attempt to distinguish between these two materials by their chemical reactivity. A mass spectrometer analysis will provide a direct estimation of the composition of the crystals, but not with sufficient precision [2]. Certain physical properties of this structure are known to be dependent on deuterium content. For example, the ferroelectric Curie temperature, \( T_c \), increases from 123 °K for \( \text{KH}_2\text{PO}_4 \) to a value in excess of 220 °K for a highly deuterated crystal [3]. The results of a preliminary examination have also revealed that the \( a_0 \) tetragonal structure-cell parameter is dependent on the degree of deuteration.

The primary aim of this investigation was to establish whether there exists a correlation between \( a_0 \), \( T_c \) and the deuterium content of the crystals which could be exploited as an analytical facility.

Results. — The room temperature lattice parameters of the crystals were determined by the X-ray multiple diffraction method. For a description of this method the reader is referred to Isherwood and Wallace [4], Isherwood [5]. This technique was chosen for two main reasons, (i) the high available precision, and (ii) that measurements could be conducted non-destructively on single crystals. Attempts to use the more conventional powder X-ray diffraction methods proved impracticable because of the hydrogen-deuterium exchange with the atmosphere which occurs and which is accelerated when the surface area of the crystal is increased by grinding into the required fine powder.

To remove any damage induced by cutting and polishing and any surface layer which may have been subject to a hydrogen-deuterium exchange the crystals were all heavily etched in \( \text{D}_2\text{O} \). The effect of exchange at the surface was assessed by monitoring the lattice parameter of a crystal over a period of five days exposure to the atmosphere. Although an obvious surface reaction had occurred no change in lattice parameter was detected. It has been demonstrated that the hydrogen-deuterium exchange is accompanied by a degradation of the crystal structure. As has been previously stated the multiple diffraction method is applicable specifically to the study of single crystals and, therefore, the recorded diffraction patterns will contain information relating essentially to the undistorted crystal matrix. No attempt was made to isolate the crystal from the atmosphere during the period of examination.

The correlation obtained between the two parameters \( a_0 \) and \( T_c \) for the range of crystal studied is
displayed graphically in figure 1. To a good approximation there is a linear dependence between \( a_0 \) and \( T_c \). The corollary of this finding is that both \( a_0 \) and \( T_c \) exhibit the same functional dependence with deuterium content, expressed as the atomic ratio \( D/(D + H) \).

The results of Kaminow [2] would indicate a linear dependence between \( T_c \) and \( D/(D + H) \) concentration of the crystals. If \( T_c \) and \( D/(D + H) \) are so related, then it follows that \( a_0 \) is also related linearly with \( D/(D + H) \). In order to specify the dependence between \( a_0 \) and \( D/(D + H) \) two calibration points are necessary. In the first instance these were taken as the \( a_0 \) parameter of KH2PO4 i.e. \( D/(D + H) = 0 \), and that of a crystal reputedly of 95% deuteration. The estimate of deuterium contents of the crystal examined from measurements of their \( a_0 \) and \( T_c \) parameters are tabulated in Table I. Also contained in Table I are the \( D/(D + H) \) estimates evaluated from the \( H-O-D \) infra-red absorption band (3 370 cm\(^{-1}\)) recorded when the crystals were dissolved in D\(_2\)O. Details of these measurements will be published at a later date.

In the three methods of assessment adopted various assumptions were made regarding the dependence of the measured parameters with \( D/(D + H) \). These, and the chosen calibration standards, would now appear to be vindicated by the consistency of the \( D/(D + H) \) estimates made on the basis of these assumptions. It is concluded, therefore, that both the tetragonal \( a_0 \) structure-cell parameter (measured at room temperature, 22 °C) and the ferroelectric Curie temperature, \( T_c \), are linearly dependent on the deuterium content. The relationships between these parameters being established as,

\[
T_c = 123 + 106 \times x, \text{°K} \\
a_0 = 7.45239 + 1.759 \times 10^{-2} x, \text{Å}
\]

where \( x = D/(D + H) \). These results indicate that a fully deuterated crystal, KD\(_2\)PO\(_4\), would exhibit the following parameters,

\[ a_0 = 7.46998 \text{ Å} \quad \text{and} \quad T_c = 229 \text{°K}. \]

No correlation was established between deuterium content and the \( c_0 \) parameter of the tetragonal cell. It is significant, however, that all the deuterated crystals have \( c_0 \) parameters which are slightly greater than that of KH\(_2\)PO\(_4\), \( c_0 = 6.97656 \pm 0.00003 \text{ Å} \). Values ranging between 6.97875 Å and 6.97665 Å have been determined for these crystals. It would appear that any isotope effect on \( c_0 \) is not only very small, but is being masked by some other phenomenon, the most likely of which is a variation of the «crystal perfection». This may be as a result of, for example, impurity segregation on the c-face or faulting of the structure.

It has also been established that there is a partition of hydrogen between the solution and crystals of the tetragonal form of approximately 1.5 : 1, favouring the crystal. Crystals of the monoclinic species grow with a deuterium content closer to that of the solution.

Results of investigations conducted on the monoclinic form of KD\(_2\)PO\(_4\) will be reported in a future publication. These will include a precision determination of the parameters of the monoclinic structure-cell and observations on the transformation to the tetragonal phase on exposure to the atmosphere.

Acknowledgment. — This work was done under a CVD contract and is published by permission of the Ministry of Defence (Navy Department).

References