

A neutron diffraction study of ferroelectric PbHAsO_4 at room temperature

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Abstract. A single-crystal neutron-diffraction structural study of PbHAsO_4 in its ferroelectric phase at room temperature (24°C) is presented as part of an investigation of a family of monetites. The crystal structure of PbHAsO_4 , and its phase transition mechanism are discussed. Comparison of the crystal structures of PbHPO_4 and PbHAsO_4 reveals that these two ferroelectrics are isomorphous. The role of protons in structural phase transition of PbHAsO_4 is also discussed.

Keywords. Neutron diffraction; ferroelectric properties; Structural phase transition; least-squares refinement; disordered hydrogen; isomorphous.

1. Introduction

Lead monohydrogen arsenate, PbHAsO_4 (LHA)-which has recently been shown to be ferroelectrics (Blinic *et al* 1976) belongs to a family of monetites of the general formula MHXO_4 ($M = \text{Ba, Sr, Ca or Pb}$; $X = \text{P or As}$). From the preliminary studies of crystal structures (Schulten 1904; Bengtsson 1941; Claringbull 1950) and physical properties of LHA and LHP (PbHPO_4) using various experimental techniques (Blinic *et al* 1976; Kroupa *et al* 1978; Lavrenčič *et al* 1978), it has been shown that both compounds are similar. The transition temperatures (T_c) for LHA and LHP were found to be 313.5 K and 310 K respectively (Blinic *et al* 1976; Negran *et al* 1974). From the large isotope effect on T_c (≈ 142 K) and other evidence (Smutny and Fousek 1978) it has been suggested that the protons of the H-bonds in these compounds play an important role in the phase transition phenomenologically similar to that observed in tetragonal KH_2PO_4 (KDP) and monoclinic CsH_2PO_4 and TiH_2PO_4 (Nelmes and Choudhary 1978a, 1981). Although the extensive structural studies of some phosphate monetites, namely, CaHPO_4 (Denne and Jones 1971; Dicken *et al* 1972; Catti *et al* 1980), BaHPO_4 (Burley 1958) and SrHPO_4 (Berndt and Lamberg 1971) have already been reported, no complete crystal structures of LHA, LHP and other monetites were available. The structural studies of LHA and LHP are particularly interesting because of (a) the transitions involving ordering of the disordered hydrogen bonds, (b) the small unit cell and one-dimensional chain of H-bonds, (c) the second order transition and saturation of spontaneous polarization slowly over the temperature range T_c-80 K (Smutny and Fousek 1978) and (d) centrosymmetric structure in the paraelectric phase. In order to examine these interesting features,

and for the better understanding of the transition mechanism in these materials, we have carried out the extensive structural studies of LHP (Nelmes and Choudhary 1978b; Nelmes *et al* 1982) and LHA using x-rays and neutron-diffraction techniques. In this paper, a neutron-diffraction structural study of LHA at room temperature only is reported.

2. Experimental

The experiment was performed (sample size of LHA $\approx 1.6 \times 1.5 \times 1.5$ mm³) on the MK VI four-circle diffractometer of the DĪDO reactor at AERE, Harwell (UK). The *b*-axis of the crystal was mounted approximately along the ϕ -axis of the diffractometer. The cell dimensions were measured with a calibrated wavelength of 1.1802 (2) Å and found to be: $a = 4.855(1)$ Å, $b = 6.750(1)$ Å and $c = 5.837(1)$ Å and $\beta = 95.41(1)^\circ$ [cell dimensions of LHP: $a = 4.688(4)$ Å, $b = 6.649(5)$ Å, $c = 5.781(5)$ Å, $\beta = 97.11(2)^\circ$]. From careful examination of the systematic absences, the space group of the crystal was found to be *Pc* or *P2/c*. A total of 1000 reflections (two equivalents, in general) were measured for the hemisphere ($\pm h, +k, \pm l$) out to $\sin \theta/\lambda = 0.6 \text{ \AA}^{-1}$ ($1 \leq 2\theta \leq 90^\circ$) using $\theta/2\theta$ step scan method. The stability of the experiment was checked by measuring a standard reflection after every 15 reflections. As the intensities of the symmetry-related reflections agreed within two standard deviations, no absorption corrections were applied to the data. All the measured reflections were lorentz corrected. After averaging over the symmetry-related reflections, a total of 490 independent reflections were found. The reflections with $I_0 \leq 2 \sigma(I_0)$ were removed, the remaining 359 reflections were used in the final structural analysis.

3. Structural analysis

The positional and thermal parameters of all the non-hydrogen atoms (Pb, As and O), determined by the author in a preliminary x-ray experiment, were again refined using a computer program. The neutron scattering amplitudes: $b(\text{Pb}) = 0.94$, $b(\text{P}) = 0.51$, $b(\text{O}) = 0.58$ and $b(\text{H}) = -0.374$ (all $\times 10^{-12}$ cm) (Bacon 1972) were used for all calculations. From the refined parameters, 3-dimensional Fourier difference-syntheses were computed to locate the hydrogen atoms. An independent hydrogen atom (H_1) was located between two oxygens, O_1 and $\text{O}_{3'}$ (figure 1); this was consistent with forming of an asymmetric H-bond for a small O...O distance (table 2). Finally positional and anisotropic thermal parameters of all the atoms (including H_1), were refined, together with a scale factor and an isotropic extinction parameter (Cooper *et al* 1968). In the last cycle of refinements the conventional R ($= \sum (|F_0| - |k F_c|) / \sum |F_0|$; F_0 and F_c are the moduli of the observed and calculated structure factors respectively, and k is the scale factor) and weighted R_w ($= \sum w (|F_0| - |k F_c|)^2 / \sum w |F_0|^2$)^{1/2} = $|\sum w \Delta^2 / w |F_0|^2$)^{1/2} factors were found to be 5.2 and 7% respectively. The empirical weighting scheme $w = [\sigma(F_0) + 0.055 F_0]^{-1}$ was used to get approximately constant $\sum w \Delta^2$ as a function of small ranges of F_0 and $\sin \theta$. The final positional parameters of LHA are given in table 1.

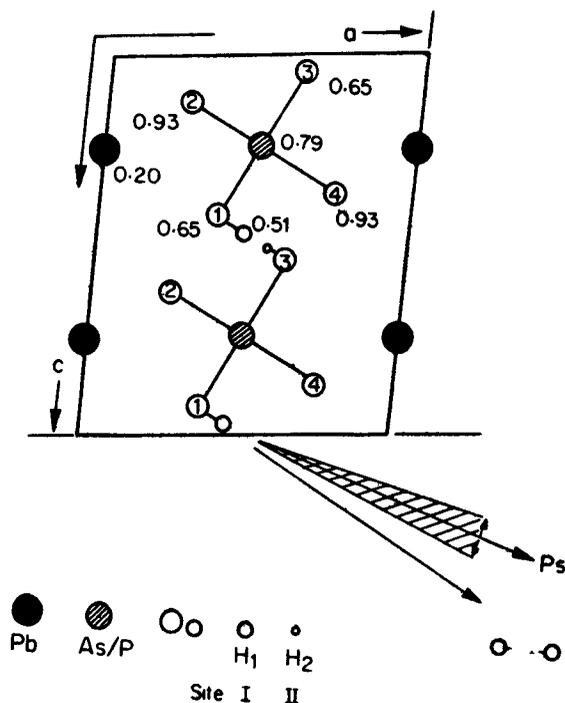


Figure 1. A projection of the crystal structure of $\text{PbHAsO}_4/\text{PbHPO}_4$ looking down the b -axis on the a - c plane. Approximate heights (in fractional coordinates) are given beside the atoms. The direction of the spontaneous polarisation, P_s , (determined by Negran *et al* 1974) and the $\text{O}\dots\text{O}$ bond are shown. The estimated errors in the angles between P_s and a -axis have been shown in the figure. The two sites I and II of the disordered hydrogen atom are also shown.

Table 1. Comparison of positional parameters (in fractional coordinates) of PbHAsO_4 (a) and PbHPO_4 (b) at room temperature. The estimated standard deviations are given in parentheses.

Atoms		x	y	z
Pb	a	0.00	0.2032 (1)	0.25
	b	0.00	0.1999 (1)	0.25
As/P	a	0.5076 (8)	0.7957 (3)	0.2359 (3)
	b	0.5053 (6)	0.7939 (2)	0.2379 (3)
O_1	a	0.3641 (6)	0.6472 (4)	0.4309 (3)
	b	0.3800 (8)	0.6569 (5)	0.4217 (5)
O_2	a	0.2499 (6)	0.9305 (4)	0.1047 (3)
	b	0.2579 (8)	0.9236 (5)	0.1215 (3)
O_3	a	0.6459 (6)	0.6500 (4)	0.0429 (3)
	b	0.6225 (8)	0.6610 (5)	0.0538 (5)
O_4	a	0.7548 (6)	0.9321 (4)	0.3831 (3)
	b	0.7457 (8)	0.9218 (3)	0.3659 (3)
H_1	a	0.4837 (10)	0.5136 (6)	0.4758 (7)
	b	0.4852 (8)	0.5209 (5)	0.4698 (5)

Table 2. Comparison of Bond lengths (in Å) and bond angles (in degrees) of PbHAsO_4 and PbHPO_4 at room temperature. The estimated standard deviations are given in parentheses.

Bonded atoms	PbHAsO_4	PbHPO_4
(i) As/P—O distances		
As/P — O ₁	1·713 (4)	1·568 (4)
As/P — O ₂	1·673 (4)	1·533 (4)
As/P — O ₃	1·682 (4)	1·534 (4)
As/P — O ₄	1·683 (4)	1·524 (4)
(ii) O...O distances		
O ₁ — O ₃	2·718 (3)	2·496 (4)
O ₁ — O ₂	2·754 (3)	2·531 (5)
O ₁ — O ₄	2·734 (5)	2·503 (5)
O ₂ — O ₃	2·746 (4)	2·505 (5)
O ₂ — O ₄	2·810 (4)	2·532 (4)
O ₃ — O ₄	2·766 (3)	2·515 (4)
(iii) Angles		
O ₁ — As/P — O ₂	106·8 (2)	107·2 (2)
O ₁ — As/P — O ₃	108·4 (2)	109·4 (3)
O ₁ — As/P — O ₄	107·2 (2)	108·1 (2)
O ₂ — As/P — O ₃	109·9 (2)	109·5 (2)
O ₂ — As/P — O ₄	113·8 (2)	111·9 (2)
O ₃ — As/P — O ₄	110·6 (3)	110·7 (2)
(iv) Hydrogen bond geometry		
H ₁ — O ₁	1·091 (5)	1·050 (5)
H ₁ — O ₃	1·391 (5)	1·425 (5)
$\angle \text{O}_1 - \text{H}_1 - \text{O}_3'$	176·5 (4)	175·4 (4)
O ₁ — H ₁ — O _{3'}	2·481 (4)	2·473 (5)

4. Results and discussion

The crystal structure of LHA is very simple with two formula units in the primitive cell. The structure can be described in terms of H-bonded one-dimensional chains of AsO_4 groups along the *c*-axis. The AsO_4 groups are linked by the hydrogen atoms (figure 1). The hydrogen atom is found near one of the oxygen, O₁ of O₁...O_{3'} bond at a distance of 1·091(5) Å. The Pb atoms are surrounded by the six nearest oxygen atoms. One of the six Pb-O distances has a considerably larger value, 2·869(3) Å, than the average distance, 2·557 (3) Å. The minimum and maximum Pb-O distances are 2·355 (3) Å and 2·869 (3) Å respectively.

There is only one independent AsO_4 group in the unit cell. The AsO_4 group is fairly regular (table 2), and shows a general and definite relationship between the bond distances and angles. That is, the O-As-O angle usually decreases with the increase of the two corresponding distances. The average As-O distances of AsO_4 group is 1·688 (4) Å. The longest and smallest As-O distances are 1·713 (4) Å and 1·673 (4) Å respectively (table 2). The smallest and largest O-As-O angles are 106·8(2)° and 115·8(2)° respectively. Thus it is found that $\text{As-O}_1 > \text{As-O}_3 \approx \text{As-O}_2 \approx \text{As-O}_4$.

The small distortion of the AsO_4 group can be characterised by Δ (As-O), the difference in the length of As-O₁ and As-O₃. Like many other compounds (Olovsson *et al* 1976; Kvik *et al* 1974), the donor distance (O-H₁) of the O₁-H₁...O₃' bond was found to be significantly greater than that of the normal value ($\approx 1 \text{ \AA}$). The off-centred locations of the hydrogen atom in LHA at room temperature was also supported from infrared spectra (Kroupa *et al* 1978; Blinc *et al* 1976).

The crystal data and positional parameters (table 1) of all the atoms of LHA and LHP are remarkably similar. In both materials PO_4/AsO_4 groups are linked by short asymmetric hydrogen bond (in the ferroelectric phase) across the *c*-glide plane to form an infinite one-dimensional chain along *c*-axis (figure 1). Both structures have fairly regular PO_4/AsO_4 groups (table 2). At room temperature, Pb and P/As are in general positions. In the high temperature phase these atoms are found in a special position (2-fold axis) of centrosymmetric space group $P2/c$. Then, as has been observed in LHA, the H-atom can be found on both sides of the mid-point of O₁...O₃' with 50% occupancy which has been suggested by a large shift in T_c on deuteration. In the low temperature phase, change in magnitude of spontaneous polarisation in LHP was found to be mainly dependent on the onset of order of the hydrogen atoms (Nelmes *et al* 1982). To examine this effect (H-distribution) in LHA, a disordered model was tried. The position at which the hydrogen atom was found near to O₁ was defined as site I (figure 1). The partial occupancy of the H-atom at site I-remainder being at site II found by inverting site I in the mid-point O₁...O₃' was refined with the same weighting scheme and same data set as before. No improvement in $\Sigma w\Delta^2$, and other agreement factors, were observed. This is because of the low resolution of the data. The minimum value of $\Sigma w\Delta^2$, however, was observed when the occupancy of H₁ (at site I) was fixed 0.74(5) which was the value obtained in LHP at room temperature. At room temperature, 74% and 26% occupancy of the hydrogen atom on the two sides of the pseudo-centre of symmetry is supported by the other experimental results (Smultny and Fousek 1978). As we have found in LHP, at 200 K H-atom will also be completely ordered. So ordering of the disordered hydrogen atom play an important role in phase transition. As have been done in LHP, it will be now worthwhile to investigate the partial occupancy of H₁ in LHA at site I with high resolution data collected at various temperature in the low temperature phase.

5. Conclusion

From the detailed comparison of the crystal structures and some physical properties of LHA and LHP, it is concluded that these two ferroelectric materials are very similar. Like LHP, LHA undergoes a structural phase transition of the second order, and ordering of the disordered hydrogen atom plays an important role in the phase transition mechanism.

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