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Reinvestigation of the ferroelastic phase transition of lead phosphate ($Pb_3(PO_4)_2$)

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Abstract. The symmetry of the different phases of the 'textbook' pure ferroelastic compound lead phosphate ($Pb_3(PO_4)_2$) was reinvestigated. Neutron experiments were performed with a four-circle goniometer and a triple-axis spectrometer. A non-centrosymmetry test was carried out by the optical second-harmonic generation method. It is shown that the ferroelastic phase of this compound is non-centrosymmetric up to $T_c = 180\,°C$ (453 K) with $C2$ space group; above this temperature, lead phosphate transforms into an $R\bar{3}m$ paraelastic phase. Structural refinements in the $C2$ space group only show slight distortions of the PO_4 tetrahedra compared with the results obtained with the centrosymmetric $C2/c$ space group. The non-centrosymmetry of the monoclinic phase leads to the possibility of spontaneous polarization. This result shows that lead phosphate is not a pure ferroelastic compound as previously reported; the ferroelasticity of this material could be coupled to other physical properties.

1. Introduction

A great many studies have been initiated on lead phosphate ($Pb_3P_2O_8$ or $Pb_3(PO_4)_2$) because it was the first reported ferroelastic compound (Brixner *et al* 1973) for which the ferroelasticity was not coupled with any other properties such as ferroelectricity. It is now considered as one of the best textbook examples of a pure ferroelastic compound (Salje 1990).

$Pb_3P_2O_8$ undergoes a first-order ferroelastic phase transition at $T_c = 180\,°C$ (453 K) between a high-temperature (HT) rhombohedral $R\bar{3}m$ phase and a low-temperature (LT) monoclinic $C2/c$ phase (see the references contained in the book by Salje (1990)). In a previous paper (Kiat *et al* 1987) we have shown that the phase transition of this ionocovalent compound presents many typical features of the martensitic transformation of metals and alloys. As in these compounds, the phase transformation of lead phosphate is strongly first order with important shears and large phase coexistences; moreover it progresses through the crystal by moving a planar stress-free interface (habit plane). A structural interpretation founded on the existence of the electronic lone pairs of the lead atoms has been given by Kiat *et al* (1991).

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The critical regime of this phase transition was also intensively studied because it is particularly prominent. Inelastic neutron scattering studies revealed the existence of an acoustic mode which is already soft at 530 °C (803 K), i.e. $T_c + 350$ °C, and which gradually freezes as the temperature decreases (Benoit *et al* 1981). However, more recent experiments have shown that this mechanism was only an average picture; indeed from x-ray diffraction, neutron diffraction, Raman scattering and EPR measurements there is considerable evidence that small embryos of the LT phase persist well above T_c in the HT phase (see references contained in the book by Salje (1990)). On the other hand a pre-martensitic-like anomalous incommensurability was recently evidenced by x-ray and neutron experiments in the diffraction pattern of $Pb_3P_2O_8$ (Kiat *et al* 1992). This behaviour could be satisfactorily interpreted in the framework of a phenomenological model of first-order phase transitions (Fuchizaki and Yamada 1989).

In this paper we restrict our interest to the average symmetry of the HT and LT phases at room-temperature (RT). The diffraction experiments were performed with a neutron four-circle goniometer and a triple-axis spectrometer. Moreover a non-centrosymmetry test was carried out by an optical second-harmonic generation (SHG) method. The results show that the ferroelastic phase of $Pb_3P_2O_8$ is non-centrosymmetric; they are discussed in the framework of the Landau theory.

2. Sample preparation

Single crystals of $Pb_3P_2O_8$ were made by the Czochralski method in a platinum crucible, at the Centre National d'Etudes des Télécommunications, Bagneux. Silver, copper and tin impurities were detected on a parts-per-million level by emission spectroscopy in the starting material; in order to eliminate them the crystals were melted again and the final samples were obtained from a second growth. Disorientations of the monoclinic planes were examined by monochromatic convergent x-ray diffraction (Lambot method) and were found to be less than a minute. After chemical attack by soda the dislocation density was found to be about 10^5 cm^{-2} (Toledano *et al* 1975).

3. Experimental results

3.1. *Symmetry of the RT phase*

The reported monoclinic symmetry $C2/c$ was tested at RT by recording a data collection in the primitive cell $P2$. The data were collected using a single crystal of dimensions 12 mm × 10 mm × 7 mm on the neutron four-circle diffractometer 5C2 (P110) at the Orphée reactor (CEN-Saclay), with a wavelength of 0.0831 nm. Systematic extinctions were observed for the reflections hkl with $h + k = 2n + 1$, which agrees with the C-centred face symmetry. On the other hand, intensity was observed on $h0l$ positions with $l = 2n + 1$. The measured intensity was weak but the corresponding diffraction peaks were sharp; among the 295 measured $h0l$ reflections, 33 reflections have an I/σ between 2 and 6, 27 reflections an I/σ between 6 and 10, and 15 reflections in I/σ above 10. The systematic existence of these reflections forbidden by the $C2/c$ symmetry was also observed in five other crystals grown from different baths.

The existence of these 'forbidden' peaks observed by the neutron diffraction technique in large single crystals indicates a breakdown of the c-mirror symmetry on a long-range scale which excludes any local effects due to impurities or defects. This result shows that the real symmetry of $Pb_3P_2O_8$ is $C2$ or $C2/m$. As this result is in opposition to a previous x-ray study indicating $C2/c$ as space group (Ng and Calvo 1975), further careful tests were carried out. The absence of any double-diffraction effects was systematically checked for the forbidden reflections by rotating the sample around the diffraction vector ('ψ scan' method). The absence of intensity which could arise from the $\lambda/2$ effect was also checked; for instance, the measured ratios I_{001}/I_{002} and I_{005}/I_{0010} are respectively 11×10^{-3} and 16×10^{-3}, which is much stronger than the instrumental value of 0.7×10^{-3} (erbium filter).

In order to confirm the neutron results an optical SHG method was used, as this method is very sensitive to the existence of non-centrosymmetry in crystals. The specimen used for this experiment had a cleavage plane perpendicular to the threefold axis in the trigonal phase and was found to consist of a large area of a single ferroelastic domain under the polarizing microscope. Its thickness was 0.553 mm. The fundamental wave from a pulsed Nd^{3+}:YAG laser (wavelength, 1060 nm; pulse energy, 5.62 mJ) impinged on the specimen and the resultant second-harmonic wave was detected with a photomultiplier connected to a lock-in amplifier (Uesu *et al* 1989). Although the SHG signal was found to be very weak (i.e. the total intensity was approximately 10^{-2} times smaller than the intensity of the d_{36} component of KH_2PO_4), the SHG of $Pb_3P_2O_8$ was clearly detected in the LT phase. As this signal was weak, the SHG intensity was measured with the circularly polarized incident wave; under this condition, the d_{22}, d_{23} and d_{34} components of the SHG tensor of the $C2$ phase could contribute to the observed intensity.

3.2. *Structure of the RT phase*

As the intensity of the forbidden reflections as well as the SHG signal were found to be very weak, the real structure of $Pb_3P_2O_8$ cannot be very different from the structural model deduced from x-ray measurements. This consideration rules out the space group $C2/m$ which would imply a complete structural change.

Structural refinements were carried out in the two space groups $C2$ and $C2/c$ with the Prometheus program (Zucker *et al* 1983). The starting positions were those of the x-ray structural model. Integrated intensities were determined from resolution-adapted profile measurement of the peaks; 3363 reflections were measured and averaged to give 2591 unique reflections (internal R-factor, 0.018); 2568 of them had $|F_{hkl}| \geqslant 2.5\sigma$. The experimental intensities were corrected for absorption (evaluated coefficient $\mu = 0.053$ cm^{-1}) and for secondary isotropic extinction (Becker and Coppens 1975). The refinement converged to $R = 0.030$, $R_w = 0.036$ and $S = 4.86$ for 119 parameters and for 2568 reflections.

In table 1 the atomic positions are given in both $C2$ and $C2/c$ symmetries and compared with the x-ray results (Ng and Calvo 1975). The u_{ij} thermal parameters are given in table 2.

In the $C2/c$ space group the neutron and x-ray results are very similar. However, a better precision is obtained on the positions of the phosphorus and oxygen atoms by the neutron technique. The only slight differences observed between the two refinements concern the y coordinates of O(1) and O(3) atoms and the z coordinate of the O(2) atom. In addition the values obtained in the neutron refinements for u_{ij}

Table 1. Atomic coordinates of the RT monoclinic phase in the two space groups $C2/c$ and $C2$; the x-ray results are those of Ng and Calvo (1975).

		X-ray, $C2/c$	Neutron, $C2/c$	Neutron, $C2$	
Pb(1)	x	0	0	0	0
	y	0.2879(5)	0.2883(2)	0.2883(fixed)	−0.2880(2)
	z	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$-\frac{1}{4}$
Pb(2)	x	0.3183(1)	0.3183(1)	0.3189(1)	−0.3179(1)
	y	0.3092(3)	0.3102(2)	0.3088(3)	−0.3111(3)
	z	0.3517(2)	0.3515(1)	0.3515(1)	−0.3515(1)
P	x	0.3958(8)	0.3981(1)	0.3979(8)	−0.3981(8)
	y	0.244(3)	0.2491(2)	0.2499(5)	−0.2491(5)
	z	0.053(1)	0.0534(1)	0.535(1)	−0.0533(1)
O(1)	x	0.353(1)	0.3546(1)	0.3552(1)	−0.3542(1)
	y	0.0254(1)	0.0302(2)	0.0266(4)	−0.0334(4)
	z	0.108(2)	0.1114(1)	0.1119(2)	−0.1107(1)
O(2)	x	0.3634(5)	0.3659(1)	0.3660(1)	−0.3656(1)
	y	0.4659(3)	0.4696(2)	0.4701(4)	−0.4691(4)
	z	0.119(1)	0.1289(1)	0.1280(2)	−0.1292(2)
O(3)	x	0.1402(8)	0.1425(1)	0.1422(1)	−0.1425(1)
	y	0.232(4)	0.2212(2)	0.2185(4)	−0.2237(4)
	z	0.111(3)	0.1118(1)	0.1141(1)	−0.1099(1)
O(4)	x	0.5076(1)	0.5109(1)	0.5107(1)	−0.5144(1)
	y	0.223(2)	0.2290(3)	0.2323(4)	−0.2260(4)
	z	0.079(1)	0.0828(2)	0.0826(2)	−0.0804(2)
a (Å)		13.81(3)	13.74(5)	13.74(5)	
b (Å)		5.71(1)	5.66(1)	5.66(1)	
c (Å)		9.31(1)	9.39(3)	9.39(3)	
β (deg)		102.4(1)	102.4(3)	102.4(3)	

were normal whereas the values obtained in the x-ray refinements were abnormally high and could not be determined for all the atoms (table 2).

In the $C2$ space group the loss of the symmetry centre gives rise to a doubling of the number of independent atoms. The u_{ij}-parameters were not refined in this case. Compared with the results obtained with the $C2/c$ group the main differences concern the y coordinates of the two O(1) atoms and the z coordinates of the O(3) atoms. These results clearly indicate that the structural modifications in the $C2$ space group are weak.

3.3. Phase transition

The experiments described above revealed at RT a non-centrosymmetry whose signature is the existence of sharp forbidden reflections $h0l$ with $l = 2n + 1$ and the existence of an optical second-harmonic generation. The existence of a second phase transition towards a monoclinic centrosymmetric phase ($C2 \rightarrow C2/c$) has been tested. For this, the thermal evolutions of some forbidden reflections were recorded with another single-domain sample (4 mm × 4 mm × 7 mm), using the triple-axis spectrometer 4F2 on a neutron cold source with a wavelength of 0.24 nm. In figure 1

Table 2. Thermal parameters u_{ij} in the space group $C2/c$; the x-ray results are those of Ng and Calvo (1975).

		X-ray, $C2/c$	Neutron, $C2/c$
Pb(1)	U_{11}	0.032(1)	0.0058 4(5)
	U_{22}	0.037(5)	0.0108(5)
	U_{33}	0.037(1)	0.0128(5)
	U_{13}	0.0057(9)	0.0024(8)
Pb(2)	U_{11}	0.034(1)	0.055(4)
	U_{22}	0.037(5)	0.0092(4)
	U_{33}	0.043(1)	0.0136(4)
	U_{12}	−0.0003(7)	−0.0010(2)
	U_{13}	0.0051(7)	0.0023(3)
	U_{23}	−0.0001(7)	−0.0001(8)
P	U_{11}	$U_{iso} = 0.031(3)$	0.0029(5)
	U_{22}		0.0038(5)
	U_{33}		0.0017(5)
	U_{12}		0.0000(3)
	U_{13}		0.0003(4)
	U_{23}		0.0001(3)
O(1)	U_{11}	$U_{iso} = 0.046(8)$	0.0078(5)
	U_{22}		0.0072(5)
	U_{33}		0.0137(5)
	U_{12}		−0.0012(4)
	U_{13}		0.0028(4)
	U_{23}		0.0063(4)
O(2)	U_{11}	$U_{iso} = 0.050(8)$	0.0112(2)
	U_{22}		0.0066(5)
	U_{33}		0.0090(5)
	U_{12}		0.0010(3)
	U_{13}		0.0067(4)
	U_{23}		−0.0033(4)
O(3)	U_{11}	$U_{iso} = 0.032(6)$	0.0106(5)
	U_{22}		0.0099(5)
	U_{33}		0.0025(4)
	U_{12}		0.0012(4)
	U_{13}		0.0015(4)
	U_{23}		0.0003(3)
O(4)	U_{11}	$U_{iso} = 0.048(9)$	0.0025(6)
	U_{22}		0.0180(6)
	U_{33}		0.0194(7)
	U_{12}		−0.0013(4)
	U_{13}		0.0005(5)
	U_{23}		−0.0042(5)

the evolution versus temperature of the intensity of the 401 and 601 reflections is plotted. The intensity of the peaks vanishes only for $T > T_c$, showing that the space group of the crystal remains $C2$ in the whole temperature range of the ferroelastic phase. Moreover the thermal evolution of the SHG signal was measured (figure 2);

as the critical temperature was approached, this signal decreased gradually and almost vanished above T_c. The extremely weak signal detected above T_c could arise from the existence of the local breakdown of the rhombohedral symmetry due to the pre-martensitic-like critical regime (Kiat *et al* 1992). However, further precise examination seems necessary to extract the pre-martensitic behaviour of the crystal from the SHG data. In order to clarify this precursor behaviour above T_c, we are now investigating the hyper-Rayleigh and hyper-Raman scatterings of the crystal.

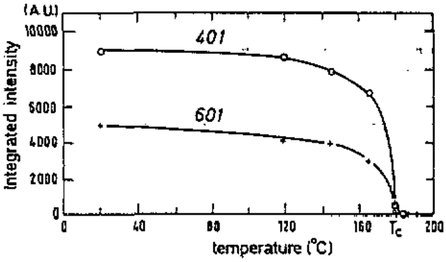

Figure 1. Thermal evolution of the integrated intensities of two 'forbidden' reflections 401 and 601 measured with a triple-axis neutron spectrometer.

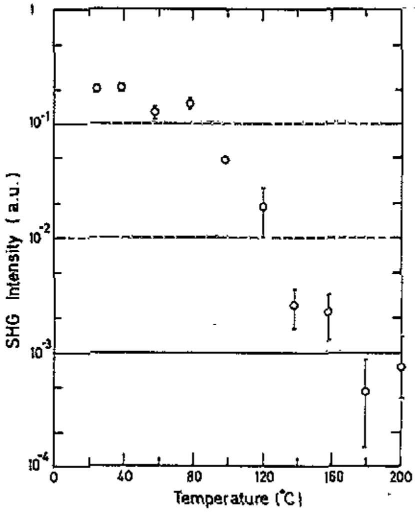

Figure 2. Thermal evolution of the optical SHG signal. The bars in the figure indicate the estimated experimental errors.

4. Discussion and conclusion

From the results of the experiments presented above, it can be concluded that the change in the average symmetry of lead phosphate at the ferroelastic transition is $C2 \rightarrow R\bar{3}m$ and not $C2/c \rightarrow R\bar{3}m$.

The primary order parameters of this phase transition are known to be amplitudes of the triply degenerate L-zone boundary phonon modes η_1, η_2 and η_3 (Torres 1975), whereas the strain components play the role of secondary order parameters. The free-energy expression has been given by Torres in terms of these order parameters. The standard treatment based on this free energy leads to the improper ferroelastic transition from $R\bar{3}m$ to $C2/c$.

The non-centrosymmetry of the monoclinic phase evidenced in the present study suggests the possibility of spontaneous polarization at $T < T_c$. From the phenomenological standpoint this is allowed if higher-order couplings between the order parameters and the polarization are taken into account.

The simplest symmetry-adapted coupling terms are (in the coordinate system with x along the twofold axis, y along the c axis and z along the HT threefold axis) as follows:

(i) $P_z^2(\eta_1^2 + \eta_2^2 + \eta_3^2)$;
(ii) $P_z^2 e_{zz}$;
(iii) $(P_x^2 + P_y^2)(\eta_1^2 + \eta_2^2 + \eta_3^2)$;
(iv) $(P_x^2 + P_y^2)(e_{xx} + e_{yy})$, etc.

For instance, let us consider the case of coupling (i). We add the following contributions to the free energy:

$$\Phi = \chi_1/2P_z^2 + \chi_1/4P_z^4 + (\gamma/2P_z^2)(\eta_1^2 + \eta_2^2 + \eta_3^2).$$

The stability condition with respect to the polarization P_z leads to

$$P_z^2 = [(-\chi_1 - \gamma\langle\eta\rangle^2)/\chi_2]^{1/2}$$

below T_c. If the condition $\chi_1 < -\gamma\langle\eta\rangle^2$ is satisfied, the spontaneous polarization as given above should appear below T_c.

The existence of a SHG intensity indicates the appearance below T_c of a spontaneous polarization P. However, the thermal dependence of the SHG intensity does not correspond generally to the change in the spontaneous polarization with temperature; the expression for the SHG intensity contains not only the square of the SHG constant d (which reflects the behaviour of P), but also an interference term which can vary sensitively with the change in the coherence length of the crystal. This is why the thermal variations in the diffraction 'forbidden' intensities, which reflect the temperature dependence of the spontaneous polarization, do not scale with the variation in the SHG signal.

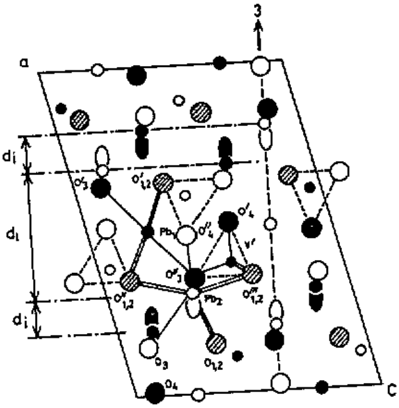

Figure 3. Projection of the structure of the rhombohedral phase of the mixed compounds $Pb_3P_{2x}V_{2(1-x)}O_8$ described in the monoclinic a–c plane. The small, medium and large circles represent, respectively, the phosphorus or vanadium, the lead and the oxygen atoms. The lobes represent the electron lone pairs. The open circles are located at $y = \frac{1}{4}$, the full circles at $y = \frac{3}{4}$ and the shaded circles at $y \simeq 0$ and $y \simeq \frac{1}{2}$. The PO_4 or VO_4 tetrahedra are represented by broken lines. d_l and d_i are the layer thickness and interlayer distance, respectively, and are equal to 0.192 nm and 0.484 nm in the case of $Pb_3P_2O_8$. (From Kiat *et al* (1991).)

The structural refinement in the $C2$ space group shows that the origin of the non-centrosymmetry is due to small displacements of oxygen atoms, mainly in the PO_4 tetrahedra, that would be unobservable by x-ray measurements. In a preceding study (Kiat *et al* 1991) it has been shown that the structure of the rhombohedral phase and of all monoclinic phases of the compounds $Pb_3P_{2x}V_{2(1-x)}O_8$ (lead orthophosphovanadates) consists of a stacking of PO_4 (or VO_4 tetrahedra) layers (figure 3). The electronic lone pair of Pb(2) atoms, which is rejected by the proximate oxygen atoms along the threefold axis, occupy the large interlayer volume and connect weakly the layers of tetrahedra. The main atomic displacements taking place at the critical temperature are those of Pb(2) atoms, parallel to the layers. We have shown that the different monoclinic phases of lead orthophosphovanadates (including the monoclinic phase of lead phosphate) differ mainly in the direction of tilting of the lone pair at the critical temperatures. This explains the existence of strong shears occurring at the phase transitions, as in metals and alloys. The results of the refinements in the $C2$ space group only show some slight distortions of the PO_4 tetrahedra compared with the results obtained with the $C2/c$ group and thus do not modify the above mechanism based on lead atom displacements.

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