

The possibility that the optical second-harmonic generation in lead phosphate,  $\text{Pb}_3(\text{PO}_4)_2$ , is related to structural imperfections

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1994 J. Phys.: Condens. Matter 6 2093

(<http://iopscience.iop.org/0953-8984/6/10/027>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.147

The article was downloaded on 12/05/2010 at 17:54

Please note that [terms and conditions apply](#).

# The possibility that the optical second-harmonic generation in lead phosphate, $\text{Pb}_3(\text{PO}_4)_2$ , is related to structural imperfections

T Bleser†, B Berge‡, U Bismayer§ and E K H Salje†

† Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK

‡ Université Joseph Fourier, Laboratoire Spectrométrie Physique, BP 87, F38402 St Martin D'Heres Cédex, France

§ Institut für Mineralogie und SFB 173, Universität Hannover, Welfengarten 1, D30060 Hannover, Germany

Received 26 November 1993, in final form 10 January 1994

**Abstract.** The second-harmonic generation (SHG) of nominally pure lead phosphate  $\text{Pb}_3(\text{PO}_4)_2$ , was reinvestigated. SHG is confirmed at room temperature albeit with a large spatial variation within each sample. The signal did not disappear when the crystal was heated well above the ferroelastic transition temperature of 453 K. Chemical analysis using x-ray microprobe techniques showed a weak oxygen deficit for all samples. It is suggested that SHG is not necessarily indicative of an intrinsic symmetry breaking process in  $\text{Pb}_3(\text{PO}_4)_2$  but may be related to structural imperfections.

## 1. Introduction

Lead phosphate,  $\text{Pb}_3(\text{PO}_4)_2$ , was first observed to be ferroelastic by Brixner *et al* (1973), its potential for applications as an optical switch was pointed out by Salje (1976) and its ferroelastic hysteresis was first measured by Salje and Hoppman (1976). During the last two decades, this material and the related compounds  $\text{Pb}_3(\text{P}_x\text{As}_{1-x}\text{O}_4)_2$ ,  $\text{Pb}_3(\text{P}_x\text{V}_{1-x}\text{O}_4)_2$ , were considered prototypes of ferroelastics and much research concentrated on the elucidation of the physical origin of its ferroelasticity (see the references contained in the book by Salje (1993); Salje *et al* 1993, Darlington 1983, Dudnik and Nepochatenko 1980, Smirnov *et al* 1979, Vagin *et al* 1970, Kiat *et al* 1987).

The phase transition in  $\text{Pb}_3(\text{PO}_4)_2$  and related compounds is unusual, compared with other ferroelastics, because of two observations. Firstly, the ferroelastic strain  $e_1 \simeq 2\%$ ,  $2e_3 \simeq 0.7\%$  is large compared with other phase transitions with zone boundary instabilities (i.e. improper ferroelasticity with critical L-point behaviour  $R\bar{3}m-C2/c$ ). As a consequence, the domain structure contains straight ferroelastic twin walls and no curved anti-phase boundaries (Bismayer and Salje 1981) although local wiggles in the walls seem to exist (Wruck *et al* 1993). Secondly, two additional singularities connected with the phase transition at 453 K occur near 550 K and 433 K (Salje *et al* 1993, Bismayer *et al* 1982, Salje and Wruck 1983, Salje *et al* 1983). These additional transitions were analysed in terms of dynamical excitation of domain boundaries and coupling between three L-point instabilities (Salje and Devarajan 1981). Similarities with first-order martensitic phase transitions were pointed out by Kiat *et al* (1987) although the same behaviour was found in the case of

continuous transitions  $(\text{Ba}_x\text{Pb}_{1-x})_3(\text{PO}_4)_2$  (Bismayer *et al* 1993) and in samples with As or V replacing P (Bismayer *et al* 1986).

Although the various structural instabilities can be explained self-consistently within the model of Salje and Devarajan (1981), it appears possible that additional symmetry breaking transitions with comparatively subtle structural effects exist in  $\text{Pb}_3(\text{PO}_4)_2$ . Some evidence may be drawn also from the anomalous volume contraction with respect to the high-symmetry phase (Salje *et al* 1993). In fact, Wernecke (1985) tried to refine the crystal structures in  $\text{Pb}_3(\text{PO}_4)_2$  both in the commonly accepted space groups  $R\bar{3}m$  (at  $T = 580$  K) and  $C2/c$  (at room temperature) and in the reduced symmetries  $R3c$  and  $C2$ . No significant differences were found, however, largely due to uncertainties of absorption corrections and the appearance of weak forbidden reflections, which could not be identified as intrinsic. In view of this failed attempt to test additional weak symmetry breaking in the bulk of the crystal (and not only in domain boundaries or in regions close to lattice imperfections) a recent paper by Kiat *et al* (1992) is highly significant. These authors report diffraction signals seen in neutron scattering experiments not compatible with  $C2/c$  symmetry. They subsequently refined the crystal structure in  $C2$  and found weak distortions of the  $\text{PO}_4$  tetrahedra. Most importantly, these reflections fully disappear at  $T > 453$  K, in contrast to earlier experiments by Wernecke. Furthermore, the appearance of SHG at  $T < 453$  K but *not* at  $T > 453$  K was reported. This clearly indicates that the crystal has no global inversion centre and, thus the space group  $C2/c$  is inappropriate.

The question arises now of whether or not these important observations are related to intrinsic properties of  $\text{Pb}_3(\text{PO}_4)_2$  or, alternatively, to lattice imperfections. The importance of lattice imperfections for the optical and dielectric properties has already been established by Wruck *et al* (1981) who showed that the electronic band structure and the dielectric relaxations change dramatically if  $\text{Pb}_3(\text{PO}_4)_2$  is heated in air, although the phase transition is hardly affected. These authors failed, however, to identify the defects.

It is the aim of this paper to communicate the results of microprobe analyses and new SHG investigations, which show that *all* crystals investigated were non-stoichiometric with small oxygen deficit compared with the nominal composition. Our result on SHG essentially confirms the observation of Kiat *et al* (1992). It will also be shown, however, that the SHG signal is non-uniform in the crystal and that SHG intensity persists at  $T > 453$  K under heating in all crystals investigated.

## 2. Experimental details

### 2.1. Electron microprobe

Several samples were analysed by standard wavelength-dispersive techniques (Reed 1993) using a Cameca SX50 electron microprobe. An accelerating voltage of 13 kV and a stabilized and monitored beam current of 60 nA were used. The beam was defocused to 5  $\mu\text{m}$  diameter. In order to minimize chemical shift and matrix correction problems, one  $\text{Pb}_3(\text{PO}_4)_2$  crystal was used as the standard for P and O, while a synthetic Pb-Si glass (NBS K 456) served as the Pb standard. Analytical conditions are summarized in table 1. The counting time was 100 s on the peak, and 50 s at high and low background positions for each element. 201 points were analysed in total. Prior to quantitative analysis the whole wavelength range was scanned qualitatively at one location to confirm the absence of elements other than Pb, P and O. Samples were polished and carbon coated to provide

**Table 1.** Conditions used for the determination of the O, P and Pb content of the single crystals. The instrument was a Cameca SX50; the order of the reflection (Ord) was unity; the analyser crystals (Anal. xtal) are given. TAP and PET refer to standard crystals. PCI is a evaporated multilayer system with  $2d$  spacing of 60 Å. The spectrometer position (Spec. position) is given for the peak and two background conditions. The intensity of the peak is given in counts  $s^{-1} nA^{-1}$ . The acceleration voltage is 13 kV.

Element	x-ray line	Ord	Anal. xtal	Spec. position ( $\sin \theta$ )			Counts $s^{-1} nA^{-1}$	$2\sigma$ rel. error (%)	
				Peak	BG-	BG+			Standard
O	$K\alpha$	1	PCI	0.391 06	0.360 00	0.420 00	$Pb_3(PO_4)_2$	51	0.63
P	$K\alpha$	1	TAP	0.239 52	0.233 00	0.244 50	$Pb_3(PO_4)_2$	124	0.26
Pb	$M\alpha$	1	PET	0.604 18	0.595 00	0.611 00	NBS K 456	45	0.34

a flat conducting surface. Proprietary Cameca software was used for data acquisition and matrix corrections (PAP method; Pouchou and Pichoir 1987).

The absolute accuracy of the data is restricted by the lack of a homogeneous, independently analysed suitable standard for O and P. The  $Pb_3(PO_4)_2$  crystal used as a standard and reference, although grown in a closed Pt crucible, showed a variation of the Pb/P ratio of about six times the analytical uncertainty ( $2\sigma$ ). However, the data obtained still provide a reliable measure for the compositional variability of the samples, which in each case exceeds the analytical error (mainly due to counting statistics).

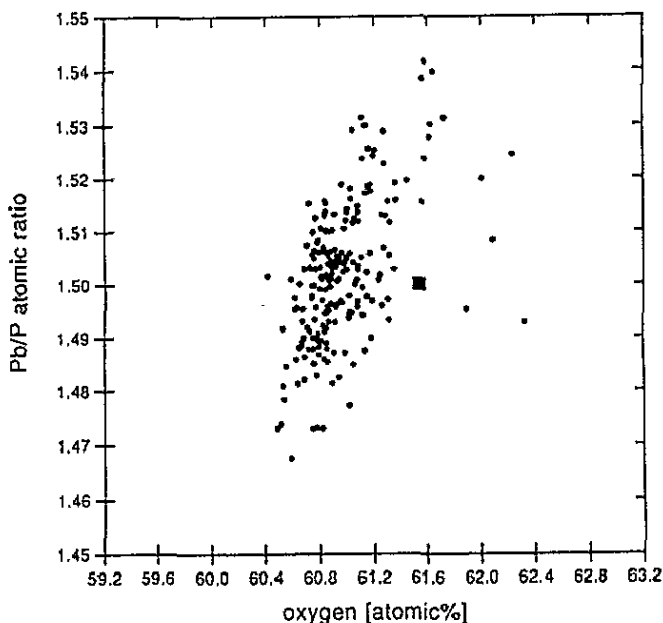
## 2.2. Second-harmonic generation (SHG)

The second harmonic was generated by Nd-YAG excitation at  $\lambda = 1.06 \mu m$ . The laser beam was pulsed at 1 kHz with a pulse length of 200 ns, filtered to avoid unwanted visible light and split into two beams, each of which was focused to a focal diameter of  $\sim 15 \mu m$ . The laser intensity was varied between the threshold of the laser action and  $\sim 0.2$  W at the sample. The sample and a quartz standard were then mounted at each of the two focal points. The sample was mounted in a heating chamber ( $\Delta T < 1$  K) which was translated in the plane perpendicular to the beam. Several points (up to 10 000) in any sample were illuminated and tested for SHG. The emitted light was again filtered, focused and measured using a photon multiplier and a subsequent lock in amplifier. The SHG signal of the quartz sample served as reference. The signal from  $Pb_3(PO_4)_2$  was several orders of magnitude smaller than that of quartz and no attempt was made to calibrate the SHG efficiency.

## 3. Results

### 3.1. Chemical composition

The variation of O, Pb and P over a small section of a crystal ( $2 \times 2$  mm) is shown in figure 1 for several samples. These results were then normalized with respects to the standards. In figure 2 the relevant parts of the triangular compositional diagram, Pb (top), P (bottom left) and O (bottom right), are shown. The ideal composition is  $Pb_3(PO_4)_2$ , indicated by the black square. The results from four different samples are shown. The spread of the data points is  $\sim 2\%$  for Pb/P and O with a tendency for O substoichiometry.

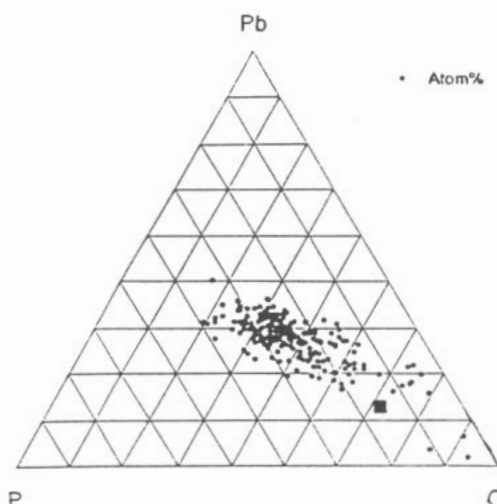


**Figure 1.** The variation of the atomic Pb/P ratio versus O (at.%): an accumulative plot of 201 electron microprobe analyses on four different  $\text{Pb}_3(\text{PO}_4)_2$  crystals. The large square represents the nominal stoichiometric composition. The analytical errors ( $2\sigma$ ) are Pb 0.08 (0.34%), P 0.04 (0.26%), Pb/P 0.01 (0.6%), O 0.04 (0.63%). Most analyses show a systematic offset to low oxygen values due to inhomogeneity (and hence partial non-stoichiometry) of the  $\text{Pb}_3(\text{PO}_4)_2$  crystal used as a standard. This does not affect the wide relative scatter within this set of samples, which is significantly larger than the analytical uncertainties. The compositional variation for the Pb/P ratio and O is within eight and 4.4 times their analytical uncertainties ( $2\sigma$ ), respectively.

### 3.2. SHG

The spatial distribution of the SHG signal is shown in figure 3. For better comparison of the background signal, this map shows the results of a scan that covers the crystal at the upper part of the figure and no sample at the lower end. Clearly, no signal exists outside the crystal plate. The lower edge of the crystal is very SHG active and appears as a dark stripe. Some parts of the crystal show very little SHG whereas other parts are equally as active as the edge. The variation between the strongest and the weakest SHG signals was between 1500 cps and 4 cps. For a further check of the reproducibility of the pattern, the top right quarter of the pattern was remeasured. No significant changes were found.

In a second experiment we tested the dependence of the 'SHG' signal on the laser power. For this purpose the ratio of the signal emitted from the  $\text{Pb}_3(\text{PO}_4)_2$  sample and the quartz standard were compared. For proper SHG, linearity between the two signals is required. In fact, all areas with strong signals in  $\text{Pb}_3(\text{PO}_4)_2$  showed a highly non-linear and non-reproducible behaviour for large laser intensities, which cannot be analysed as proper SHG. Only those parts of the crystal that show the weakest signals appear to respond linearly to changes of the laser intensity. In all cases, where the laser intensity exceeded a certain threshold, strong non-linear signals occur. In no case was recovery to the weak, linear signal found. Optical inspection showed pin-holes as a result of radiation damage for the strongest beam intensities. It appears very likely that the strong signals are due to beam damage or other structural imperfections.



**Figure 2.** The triangular composition diagram (at.%) for Pb, P, O (same data set as in figure 1). Data ranges are Pb, 22.75–25.00, P, 15–17.25 and O, 60.00–62.25. The grid spacing is 0.25. The compositional variation for Pb, P and O is within bands corresponding to 12.5, 25 and 4.4 times their analytical uncertainties ( $2\sigma$ ), respectively.



**Figure 3.** The SHG map of a typical crystal. Superimposed on a weak background signal, stronger SHG signals were found in various parts of the crystal. Scale, 2 mm horizontal diameter.

Heating the sample did not lead to significant changes of the 'SHG' map at  $T < 453$  K. As only the weak signals can be considered as possible SHG signals (i.e. linear response) these signals were followed first with increasing temperature. The temperature dependence

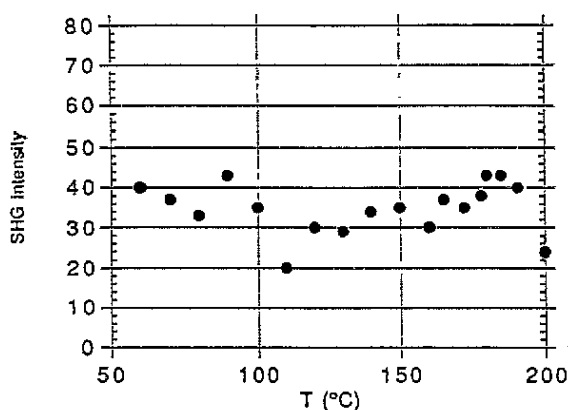


Figure 4. A plot of SHG signal versus temperature for the weak, linear SHG signal. The signal is practically independent of temperature and show no anomaly at  $T_c = 181.1$  °C.

of such a signal is shown in figure 4; it shows no singularity at  $T_c$ . Signals from areas with strong and non-linear response show a much more pronounced temperature dependence, similar to the results of Kiat *et al* (1992, their figure 2). In general, an almost exponential decrease of the signal was observed with increasing temperature. Even in these cases, weak signals were found at  $T > T_c$ .

#### 4. Discussion

Our results confirm those of Kiat *et al* (1992) who first found a frequency doubled signal in  $\text{Pb}_3(\text{PO}_4)_2$ . Great care has been taken, however, to qualify signals as SHG as pointed out already by Guggenheim *et al* (1983). In fact, we do observe laser radiation damage in several cases. Furthermore, strong signals show a non-linear relation with the quartz standard. This observation suggests that this type of signal may be due to defects and prevents the effect from being described as SHG. The weak signals, on the other hand, may qualify for SHG of the bulk of the surface of the crystal. These signals do not show any signature of a coupling with the ferroelastic order parameter. They are, in fact, almost independent of temperature and remain observable at  $T > T_c$ . Integrating all signals we find a temperature dependence that decays exponentially with increasing temperature. This observation is similar to that of Kiat *et al* (1992). Let us now consider the structural origin of the weak signals under the assumption that they are true bulk SHG. Firstly, we find that the intensity does not disappear at  $T > T_c$ , so it is not possible to relate the effect to further symmetry breaking in the ferroelastic phase only. If the signal is intrinsic, it means that no inversion centre exists in either the monoclinic or the trigonal phase. In view of the observed variation of the chemical composition of nominally pure  $\text{Pb}_3(\text{PO}_4)_2$ , the possibility of a defect related origin of the SHG must be considered, however. Lattice imperfections related to loss of O (e.g. via evaporation of PbO or other phases during the growth process) may also be the reason why weak structural distortions of  $\text{PO}_4$  tetrahedra were observed by Kiat *et al* (1992), although the physical nature of these defects is still not clear. It is remarkable, however, that these defects seem to show little influence on the ferroelastic phase transition. They appear to break the symmetry of the crystal in a manner unrelated to the symmetry of the macroscopic order parameters in  $\text{Pb}_3(\text{PO}_4)_2$  and  $\text{Pb}_3(\text{AsO}_4)_2$  although piezoelectric phases are known in  $\text{Pb}_3(\text{PO}_4)_2$ - $\text{Pb}_3(\text{VO}_4)_2$  with high V content.

## 5. Conclusion

There is an indication that the SHG and related loss of inversion symmetry in  $Pb_3(PO_4)_2$  is correlated with lattice imperfections. All crystals investigated showed a non-stoichiometric O content with substantial spatial variations. Further work on samples grown with higher degrees of non-stoichiometry or some degree of replacement of Pb (by Ba, say) would help to elucidate the nature or defect formation in  $Pb_3(PO_4)_2$ .

## References

- Bismayer U, Hensler J, Salje E and Güttler B 1993 *Phase Transitions* at press  
Bismayer U and Salje E 1981 *Acta Crystallogr. A* **37** 145  
Bismayer U, Salje E, Glazer A M and Cosier J 1986 *Phase Transitions* **6** 126  
Bismayer Y, Salje E and Joffrin C 1983 *J. Physique* **43** 1379  
Brixner L H, Bierstedt P E, Jaep W F and Barkley J R 1973 *Mater. Res. Bull.* **8** 497  
Darlington C N W 1983 *Phase Transitions* **3** 283  
Dudnik E F and Nepochatenko V A 1980 *Sov. Phys.-Crystallogr.* **25** 984  
Guggenheim S, Schulze W A, Harris G A and Lin J-C 1983 *Clays Clay Minerals* **31** 251  
Kiat J M, Calvarin G, Gregoire D and Garnier P 1987 *J. Physique* **48** 253  
Kiat J M, Yamada Y, Chevri er G, Uesu U, Boutroulle P and Calvarin G 1992 *J. Phys.: Condens. Matter* **4** 4915  
Pouchou J L and Pichoir F 1987 *ICXOM* **11** 249  
Reed S J B 1993 *Electron Microprobe Analysis* (Cambridge: Cambridge University Press)  
Salje E 1976 *Phys. Status Solidi a* **33** K165  
Salje E 1990 *Phase Transitions in Ferroelastic and Co-elastic Crystals* (Cambridge: Cambridge University Press)  
Salje E 1993 *Phase Transitions in Ferroelastic and Co-elastic Crystals* 2nd edn (Cambridge: Cambridge University Press)  
Salje E and Devarajan V 1981 *J. Phys. C: Solid State Phys.* **14** L1029  
Salje E, Graeme-Barber A and Carpenter M A 1993 *Acta Crystallogr. B* **49** 387  
Salje E and Hoppman G 1976 *Mater. Res. Bull.* **11** 1545  
Salje E and Wruck B 1983 *Phys. Rev.* **28** 6510  
Smirnov P S, Strukov B A, Gorelik V S and Dudnik E F 1979 *Bull. Acad. Sci. USSR Phys. Ser.* **43** 1670  
Vagin S V, Dudnik E F and Sinyakov E V 1979 *Bull. Acad. Sci. USSR Phys. Ser.* **43** 1735  
Wernecke Ch 1985 personal communication  
Wruck B, Bismayer U and Salje E 1981 *Mater. Res. Bull.* **16** 251