JOURNAL OF SOLID STATE CHEMISTRY 6, 430-432 (1973)

Crystal Growth and Properties of Lead Pyrophosphate, $Pb_2P_2O_7$

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Received June 26, 1972

Single crystals of $Pb_2P_2O_7$ have been grown by the Czochralski technique. They have the triclinic space group $P\bar{1}$ with cell dimensions $a = 6.9627$ Å, $b = 6.9754$ Å, $c = 12.764$ Å, $\alpha = 96.78°$, $\beta = 91.16°$, $\gamma = 89.68°$. There are four molecules per unit cell. Dielectric properties for this compound have been measured and are discussed.

Introduction

Argyle and Hummel (*1*) established by X-ray diffractometer studies that in the PbO–P_2O_3 binary system there exist at least seven compounds, representing seven different structures and having $PbO:P_2O_5$ ratios from 1:1 to 8:1. At least one other lead phosphate of formula $Pb_3(PO_4)_2$ has been reported (*2*) which gives the unusually high total of eight compounds in the simple PbO/P_2O_5 binary. Only one of these compositions, $Pb_3(PO_4)_2$, has been completely characterized structurally by Keppler (*3*). In examining the stability and melt characteristics of these lead phosphates, we started at the P_2O_5-rich side and found the first compound to melt congruently and yield a single crystal from the melt is $Pb_2P_2O_7$. It is the purpose of this paper to describe the growth procedure and the properties of this compound.

Experimental

Feed Preparation and Crystal Growth

$Pb_2P_2O_7$ feed material was prepared by interacting $PbCO_3$ (Fisher Scientific Co. certified) and $(NH_4)H_2PO_4$ (BDH Chemicals, Ltd., England, analytical grade) according to

$$2PbCO_3 + 2(NH_4)H_2PO_4 \rightarrow Pb_2P_2O_7 + 2NH_3 + 3H_2O + 2CO_2,$$

first at 300°C for 10–14 hr and after homogenization in a second firing step at 700°C for another 2–3 hr. About 200 g of this product was melted into a pure Pt-crucible by means of rf heating, using an Ecco 20 KVA generator. The melting point, determined with an optical pyrometer was 850°C. A platinum wire rotated at 40 rpm was inserted into the melt and a single crystal was grown at .5–1 cm/hr pulling speed.

TABLE I

LATTICE PARAMETERS AND SPACE GROUP OF $Pb_2P_2O_7$

Space group	a (Å)	b (Å)	c (Å)	α (deg.)	β (deg.)	γ (deg.)	Cell volume (Å^3)
$P\bar{1}$	6.9627 ± 9	6.9754 ± 9	12.764 ± 1	96.78 ± 1	91.16 ± 1	89.68 ± 1	615.4 ± 1

X-Ray Study

Single crystal photographs were taken with a precession camera and Mo radiation. X-Ray powder patterns were obtained with a Guinier–Hägg camera at 25°C with Cu$K\alpha_1$ radiation and an internal standard of KCl ($a = 6.2931$ Å). Refined cell dimensions were obtained by a least-squares treatment of the Guinier data.

Dielectric Measurements

Dielectric properties were measured as a function of temperature from −196 to 400°C at a frequency of 10^5 Hz. Polycrystalline pellets were formed by pressing 1/2 in. diameter disks at 10,000 psi and sintering at 800°C for 8 hr. After sintering gold electrodes were sputtered onto the major faces of the disks. Guarded two-terminal capacitance and dissipation factor ($\tan\delta$) measurements were made with a H.P. Model 4270A Automatic Capacitance Bridge. The digital output signals of this bridge were converted to analog information and displayed on x–y recorders. The x-axis of the recorders displayed the sample temperature as monitored by a chromel–alumel thermocouple.

Results and Discussion

The lattice parameters determined by least-squares refinement are summarized in Table I. The experimentally determined density of 6.52 g·ml^{-1} gave the number of molecules per unit cell Z as 4.[1]

Table II gives a comparison with the earlier data by Argyle and Hummel (*1*). As the space group determination could not distinguish between centric and noncentric triclinic symmetry, efforts were made to establish evidence for either of these possibilities. First, a piezoelectric test using the transmission technique of Blume (*4*) was negative. Second, a second harmonic generation test in equipment similar to that described by Perry and Kurtz (*5*) was also negative. These results strongly suggest that $P\bar{1}$ is the proper space group for $Pb_2P_2O_7$. No exothermic or endothermic peaks suggestive of phase transformation were found by DTA between room temperature and the melting point, 831°C. Similar to the experience of Keppler (*3*) with $Pb_3(PO_4)_2$, the present lead phosphate is micaceous and has a strong tendency to cleave.

[1] The calculated X-ray density is 6.85 g·ml^{-1}.

TABLE II

OBSERVED AND CALCULATED D-VALUES FOR $Pb_2P_2O_7$

I	h k l	D(obs)	D(calc)	D (Argyle and Hummel)
10	1 0 0	6.9481	6.9612	
15	0 1 −1	6.3992	6.4043	
20	0 0 2	6.3422	6.3360	6.37
20	1 0 −1	6.1547	6.1527	
15	1 0 1	6.0518	6.0509	
35	0 1 1	5.7977	5.7966	5.79
40	−1 1 0	4.9061	4.9023	4.90
50	1 1 −1	4.7421	4.7436	4.75
10	−1 1 −1	4.6811	4.6831	
10	1 0 2	4.6422	4.6402	
65	−1 1 1	4.4697	4.4686	4.46
45	1 1 1	4.4429	4.4404	
60	1 1 −2	4.0829	4.0830	4.10
10	−1 1 −2	4.0141	4.0149	
10	0 1 −3	3.8113	3.8119	
20	−1 1 2	3.7520	3.7528	
60	1 1 2	3.7130	3.7130	3.72
5	1 0 −3	3.6409	3.6432	
25	1 0 3	3.5803	3.5799	
80	2 0 0	3.4773	3.4806	
95	0 2 0	3.4631	3.4632	3.47
85	0 2 −1	3.4462	3.4457	
90	1 1 −3	3.3709	3.3713	3.38
100	2 0 1	3.3399	3.3394	3.35
80	−1 1 −3	3.3164	3.3162	
10	0 2 1	3.2434	3.2447	
90	0 2 −2	3.2019	3.2021	
100	0 0 4	3.1686	3.1680	3.18
95	1 2 −1	3.0983	3.0986	3.10
55	2 1 −1	3.0741	3.0748	3.07
60	1 1 3	3.0598	3.0598	
60	−2 1 −1	3.0419	3.0417	
30	2 0 2	3.0258	3.0254	
65	2 1 1	2.9752	2.9755	2.98
30	1 2 1	2.9404	2.9385	
10	1 2 −2	2.9237	2.9234	
60	0 2 2	2.8967	2.8983	2.90
5	2 1 −2	2.8766	2.8763	
10	1 0 4	2.8619	2.8622	
45	−2 1 −2	2.8289	2.8287	
45	1 1 −4	2.7899	2.7903	
30	−2 1 2	2.7510	2.7509	
60	2 0 −3	2.7131	2.7126	2.71
35	−1 2 2	2.6822	2.6818	
10	1 2 −3	2.6511	2.6508	
15	−1 2 −3	2.6213	2.6214	
15	2 1 −3	2.5959	2.5957	
15	1 1 4	2.5515	2.5520	
20	0 2 3	2.5356	2.5354	2.54

The results of the dielectric measurements show that polycrystalline $Pb_2P_2O_7$ has a K' of 17 and $\tan\delta$ of .0004 at room temperature. The K' of this specimen varied less than $\pm 5\%$ over the range −196–300°C.

Acknowledgment

The authors thank Dr. J. D. Bierlein for running the second harmonic generation test.

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