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Problems with the Preparation of Anhydrous Single Crystal Sulphates II

The article deals with the problem of preparing single crystals of anhydrous sulphates of amphoteric metals lead and tin. It gives a comprehensive review on up to date recent knowledge on the chemical and physical properties of these sulphates and, in addition, it describes some methods of preparing their pure anhydrous form. It also informs about the experiments of single crystal growth. It draws attention to several possibilities of the solution of this problem, which is still not satisfactorily solved.

Keywords: single crystal growth, lead sulphate, tin sulphate, review, PbSO_4 , SnSO_4 , anhydrous sulphate

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1. Introduction

Lead and tin sulphates are simple compounds, but their preparation as single crystal is accompanied by many troubles, namely :

- a) both decompose at higher temperatures,
- b) their bivalent state is not steady and they undergo treats an oxidation to a more stable M^{4+} ion,
- c) both sulphates are hydrolysed already by air moisture,
- d) PbSO_4 shows a high-temperature polymorphic transition,
- e) according to literature data their solubility both in acidified aqueous solutions and in organic solvents is very low.

2. Preparation of pure sulphates

Because the chemical purity of substances influences physical and chemical properties of single crystals considerably, it is necessary to start from high-purity materials that we often need to prepare on our own.

2.1. PbSO_4

In the GMELINS guide book moreover in other chemical literature we can find many preparation methods for PbSO_4 . These are specially:

- a) reaction of SO_2 with metallic lead at $400\text{ }^\circ\text{C}$,
- b) reaction of PbO or $\text{Pb}(\text{OH})_2$ in boiling water solution with sulphur,
- c) oxidation of PbS at $700 - 800\text{ }^\circ\text{C}$ with oxygen in the presence of SO_2 ,
- d) melting of PbCl_2 with K_2SO_4 .

However, these techniques do not provide satisfactorily pure products. Much better results attained reaction of PbCl_2 with Na_2SO_4 at elevated temperatures in an acid medium (BLOUNT).

PbSO_4 of higher purity (99,8 %) may be prepared in such a way, that the raw material is mixed with aqueous solution of NH_3 that contains ammonium sulphate. The resulting basic lead sulphate is converted again by sulphuric acid or by NH_4HSO_4 to PbSO_4 , which precipitates from a solution (LAWAARREE). A different preparation method of high-purity PbSO_4 (by means of centrifugation) is described by GOLDSCHMIED. Accordingly, this problem is also a subject of a patent of the Japanese company DOWA MINING Co. They prepare high-purity PbSO_4 by means of impurity extraction. A aqueous solution of alkylamine in the presence of oxalic acid was used for the extraction.

2.2. SnSO_4

In the research literature we may find several procedures of SnSO_4 preparation. A well-known method is the method according to CARSON. Metallic tin converted to tin sulphate in boiling sulphuric acid solution under nitrogen. It is necessary to wash the prepared SnSO_4 in alcohol moreover in ether and next to dry it at 100 °C. A farther method of preparation is described by RICHTER. Finely grounded and wet tin converted to SnO at room temperature. This subsequently dissolved in diluted sulphuric acid. The solution must be warmed to 60-75 °C. Pure SnSO_4 precipitates from the solution. This method improved ROBOTYCKI et al.. They achieved perfect precipitation of SnSO_4 by methylalcohol. Of course, it is possible to prepare SnSO_4 by several different means. However, they are much more laborious and they do not provide adequate results. It would be interesting to test the reaction of dimethylsulphate with finely ground chlorides or carbonates or nitrates, lead or tin acetate, respectively (LAUTIE).

3. Chemical and physical properties

For working out a technological procedure of growing single crystals it is first necessary to have enough knowledge of chemical and physical nature of original materials.

3.1. PbSO_4

PbSO_4 decomposes at high temperatures (above 880 °C) to PbSO_4 , PbO and finally it oxidises to PbO_2 (KOLTA, ASKAR). The decay at a higher temperature accelerated also by the presence of some salts, i.e. NaCl , Na_2CO_3 . PbSO_4 forms double salts with many compounds, for example with K_2SO_4 , Na_2SO_4 . Hydrogen reduces lead sulphate to lead already at 500 °C and carbon reduces it at 550 °C. Silica reacts with PbSO_4 at temperatures under 750 °C forming lead silicate (GMELIN). In aqueous solutions lead sulphate is hydrolysed. The solubility of PbSO_4 in low acidic solutions of H_2SO_4 is small - 6.68 mg dm^{-3} . Higher concentrations of sulphuric acid, or additions of sulphates of alkali metals increase its solubility. The solubility in common organic solvents is negligible (GMELIN; LAPTEV et al.).

Majority of physical measurements have been carried out on powder samples. The measurements show that this material is paramagnetic. Its magnetic susceptibility has a value $\chi = -69,7 \cdot 10^{-6} \text{ cm}^3 \text{ g}^{-1}$. Different dielectric constants in the direction of its crystallographic axis have been measured on a natural crystalline sample - anglesite. Difference in their values indicates, that this material is anisotropy (ERRER, BRASSEUR). Because the specific conductivity of this substance increases linearly with temperature, it could show semiconductor properties (JAGITSCH). According to GMELIN lead sulphate shows

birefringence ($n = 1,8$). It is vigorously luminescent in the UV range from 2652 to 3650 Å. Of course, intensity of the green-yellow fluorescence depends on frequency (SMITH, PARSON). In 1958 RESHAUER alluded that lead sulphate could be used in a mixture with alkaline earth metal sulphates as a fluorescent material for X-ray emission. This attribute verifies the work of MOSES et al.. They suggest that PbSO_4 could be applied as a detector for high energy photons, especially for monitoring γ -ray emission. It might replace the still used bismuth germanate (BGO).

3.2 SnSO_4

Tin sulphate begins to decompose by heat already at a relatively low temperature (350 °C) and SnO_2 is formatted. At dynamic vacuum the temperature of decomposition decreases to 320 °C (HOSCHEK). This compound is hygroscopic at a room temperature and it rapidly absorbs air moisture. The incorporation of water molecules into the crystal lattice can be observed already after a few days. Additional reflections by powder diffraction demonstrate this effect (RENTZEPERIS). Tin sulphate is easily soluble in water, but hydrolysis occurs and basic salts are generated (DONALDSON, MOSER). Hydrochloric acid oxidises SnSO_4 at higher temperatures. The oxidation of Sn^{2+} to Sn^{4+} is supported by the presence of some anions as F^- , I^- , Br^- , moreover by the presence of some cations as As^{5+} , Sb^{5+} , Bi^{3+} , Hg^{2+} , Tl^{3+} , Fe^{3+} , Ag^+ (GMELIN). Therefore, it is necessary to pay attention to purity of SnSO_4 .

Unfortunately, only limited information is available about physical properties of SnSO_4 . All measurements have been performed only on powder samples. The density of SnSO_4 is $\rho = 4,21 \text{ g cm}^{-3}$ (GMELIN). Owing to low specific magnetic susceptibility of this compound ($\chi = -0,461 \cdot 10^{-6} \text{ cm}^3 \text{ g}^{-1}$) good electric conductivity can be expected. we have not found any closer information in the literature. Unfortunately, the above values of susceptibility date back to the end of the last century (MAYER). The optical properties (UV and IR spectra) have been studied on powder samples only (KIMURA, TAKEWAKI; STEGER, SCHMIDT). The powder of SnSO_4 is snow white. It shows direct extinction and it is optical active and shows birefringence $n=1,84$ (DONALDSON, MOSER; HOSCHEK).

4. Structure

Lead sulphate shows two modifications. Its low-temperature modification is orthorhombic and pertains to barite type. The latest structural measurements have been made on powder sample by HILL. SPIES and GRUEHN have detected a high-temperature modification above 600 °C. This modification is cubic and pertains to NaClO_4 type.

| Compound | Modification | Structural parameters | | | Symmetry group |
|-----------------|--------------|-----------------------|-------|-------|----------------|
| | | a | b | c | |
| PbSO_4 | orthorhombic | 6.96 | 8.48 | 5.40 | Pnma |
| | cubic | 7.23 | | | ? |
| SnSO_4 | orthorhombic | 8.799 | 5.319 | 7.115 | Pnma |

Table I: Structural parameters of anhydrous PbSO_4 , SnSO_4

The crystal structure of SnSO_4 has been determined also from a powder sample. It is orthorhombic as the low-temperature modification of PbSO_4 . The sulphate groups in the structural unit of SnSO_4 are connected with each other through bridges O-Sn-O. The Sn^{2+} atoms have a typically pyramidal trigonal co-ordination with bond distances Sn-O 2,27, 2,27 and 2,25 Å and bond angles O-Sn-O 77,0, 77,1 and 77,1° (DONALDSON, PUKSLEY). The pyramidal environment of the Sn atoms can be explained by covalent bonds in consequence

of the sp^3 hybridisation of the Sn^{II} orbital. As the ion radius of Sn^{2+} (1,27 Å) is similar as the ion radius of Ba^{2+} , $SnSO_4$ does not pertain to barite group. The structural parameters of these sulphates show table I.

5. Crystal growth

Although $SnSO_4$ seems to be a simple compound, we have not found any reference about preparation of its single crystals.

On the opposite, the single crystals of $PbSO_4$ have been prepared by several growth techniques, namely crystallisation from gels, hydrothermal growth and crystallisation from fluxes or solutions. The resulting crystals were of different size and were also of different quality. Decomposition of this compound at higher temperatures and its high-temperature modification that has larger crystal lattice volume avoided crystal growth by crystallisation from its melt. PATEL and BHAT (1970) have tried a method of crystal growth from gels. They applied silicagel as carrier in the medium of nitric acid. One from the reagents was sodium sulphate and the second lead nitrate. Plate-like crystals were growing. The authors have not given dimensions of the crystals. The hydrothermal growth method of $PbSO_4$ published LIEBERTZ. The crystals have been grown from an aqueous solution of sulphuric acid (70 - 90 wt. %). Needle crystals of about 5 mm length grew in the [010] direction on the cold part of the apparatus. The crystals did not have a good quality. Liquid medium of nitric acid chosed KIKUTA et al.. According to the introduction of their paper, the crystals were suitable for scintillation measurements. SOLC et al. applied NH_4Cl , $CaCl_2$ and $NaCl$, respectively as carrier medium for hydrothermal growth of $PbSO_4$.

Concerning decay of the lead sulphate at higher temperatures and to its high-temperature modification it is natural that the flux growth method found application in this case. The method of slow flux cooling modified ZHANG et al. They improved the well-known BRIDGMAN method by accelerated rotation of ampoule. They applied Na_2SO_4 as the flux with initial concentration of $PbSO_4$ - 54 mol. %. The starting temperature of the mixture was 800 °C. The authors placed the mixture into an alumina crucible. The drop speed of the crucible was 5 mm day^{-1} . Temperature gradient in the furnace was 15°C cm^{-1} . In this way they prepared crystals having dimensions of 5x6x8 mm. The authors tried a number of other fluxes, for example $PbCl_2$, Li_2SO_4 , KCl , $LiCl$ and K_2SO_4 , but Na_2SO_4 offered the best results. The method of flux evaporation tried PATEL and BHAT (1971). They applied Na_2SO_4 as flux again. However, the prepared crystals had only poorly definable forms.

The first experiment of preparing $PbSO_4$ crystals from solutions made DE SCHULTEN already in 1903. To a strongly diluted solution of H_2SO_4 he slowly dropped a hot solution of $PbCl_2$ diluted in hydrochloric acid. The method of slowly evaporation of solution applied O'CONNOR and BUCHANAN. During evaporation they added every day a defined quantity of K_2SO_4 solution to the solution of $PbNO_3$ in HNO_3 . The length of the resulting crystals was as high as 5 mm. By a similar method of solution evaporation BODE et al. prepared single crystals of $PbSO_4$ with Gd^{3+} as doping ion. The crystals prepared for EPR measurements. However, the authors have not mentioned the quality of crystals. Perfectly shaped crystals have been prepared by means of an interesting specific method of slow precipitation (BLOUNT). To a solution of HCl and $PbCl_2$ that was kept at 95 °C he dropped a diluted solution of Na_2SO_4 at the rate of 5 $cm^3 h^{-1}$. The dimensions of largest crystals were 2.3x1.3x1 mm. A further mentioned method is a method according to ZEKTZER. He grew the $PbSO_4$ crystals from a solution of perchloric acid. The crystals had the size of about 1x3x3 mm. This method is based on the solution transfer from a warmer zone to a colder area of the apparatus, where crystallisation of $PbSO_4$ take place. The author used an apparatus according to ROSTOCKY. Very interesting ways of preparation of $PbSO_4$ single crystals described

JOHNSTON and by FERNELIUS and DETLING, who prepared the PbSO_4 crystals by means of a diffusion method in solution. The diffusion between water solutions of lead nitrate and potassium sulphate took place in the first case. The solutions segregated a membrane. The prepared crystals had the form about 5 mm long needles. In the second case the authors applied solutions of lead acetate and sodium sulphate. They prepared plate crystals with an area of $3 \times 3 \text{ mm}^2$.

6. Discussion

Only sparse discussion about physical properties of these single crystals can be found in the literature, namely only about PbSO_4 . A simple reason for this fact is that there have not been prepared single crystals of sufficiently high quality and size up to now that could enable extensive investigation of their characteristics. As may be easily judged, hygroscopic properties of these sulphates will cause additional problems at their adjustment for the measurement, despite successfully mastering their crystal growth technology.

Owing to interesting amphoteric character of tin and lead and because of low dimensions of yet prepared crystals it will be desirable to seek a new technological procedure.

For mastering of the SnSO_4 crystal preparation it will be necessary to check out whatever technology of single crystal growth. The methods must respect the low temperature decomposition of this compound (350°C), its tendency to hydrolysis and the danger of metal oxidation to a higher oxidation degree. Consequently, it will be desirable to investigate its solubility in solutions of acids, where suppressed the hydrolysis or to determine its solubility in the presence of some salts. It must be verified the possibilities of crystallisation from these solutions. It will be necessary to search for appropriate fluxes having melting point lower than the decomposition temperature of SnSO_4 . The other chance is the verification of crystal growth in gels.

In the case of PbSO_4 the single crystals prepared by means of different growth techniques. However, in no case the edge length of the crystals exceeds of 10 mm. Accordingly, practicable exploitation of the crystals is considerably limited. To find a way of preparation of larger and perfect single crystals it will be necessary to test the solubility of PbSO_4 in acidified aqueous solutions moreover with addition of some salts that may improve the solubility of PbSO_4 . It would be desirable to check the solubility in some organic solvents too. Another successful way may be by application of some fluxes, that have already been used. Naturally the crystal growth technique must be improved. It is also a way of seeking such fluxes, that would extend the working area of concentrations and temperatures. The binary system $\text{PbSO}_4\text{-Li}_2\text{SO}_4$ and the ternary system $\text{PbSO}_4\text{-Cs}_2\text{SO}_4\text{-Li}_2\text{SO}_4$ appear to be very hopeful. The melting point of such systems, from which the low temperature modification of PbSO_4 segregates, is in these systems below 600°C (BELYAEV, TCHIKOVA). However, the use of some different fluxes can not be eliminated.

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