

Short Communication

New preparation methods and accurate X-ray powder diffraction data for tribasic lead sulfate hydrate, precursor of the active material in lead/acid batteries

F. Vallat-Joliveau^a, A. Delahaye-Vidal^{a,*}, M. Figlarz^a, A. de Guibert^b

^a *Université de Picardie Jules Verne, Laboratoire de Réactivité et de Chimie des Solides, URA CNRS 1211, 33 rue St. Leu, 80039 Amiens Cedex, France*

^b *CEAC, 18 quai de Clichy, 92111 Clichy Cedex, France*

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Abstract

Pure tribasic lead sulfate hydrate was prepared by two different methods and characterized by X-ray diffraction and scanning electron microscopy. One of these methods consisted of grinding the starting materials while the other involved the precipitation of the tribasic lead sulfate hydrate from a lead acetate solution in a buffered ammonia solution. The phases so prepared led to the same X-ray diagram. The results of the refinement of the lattice parameters are given.

Keywords: Lead sulfate; Lead/acid batteries; Crystal structure

1. Introduction

Tribasic lead sulfate hydrate $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ (3BS) is involved in the manufacturing process of lead/acid battery electrodes. The first step of this process is the preparation of a paste by mixing 'leady oxide' (particles of α - and β -PbO with free Pb) with water and sulfuric acid. The resulting paste is a mixture of 3BS with other compounds such as unreacted lead, lead monoxide with the two (α and β) modifications, and sometimes tetrabasic lead sulfate (4BS). After pasting on lead alloy grids, the plates are cured in a highly humid atmosphere at temperatures in the 60–100 °C range so that 3BS is transformed into 4BS, and/or recrystallizes. Curing also induces the oxidation of residual lead into PbO. For controlling and optimizing the mixing and curing stages, X-ray diffraction (XRD) is used as a method to analyse the paste. However, some inconsistencies appear in the 3BS XRD patterns given in the literature [1–3]. The more recent work is done by Küzel [3], the only one who succeeded in the preparation of single 3BS crystals. From Weissenberg photographs, he found a triclinic system and proposed an indexing ($P1$ or $P\bar{1}$ space group). The corresponding

PDF card (No. 29-0781) does not exhibit the reflection at 3.08 Å although this reflection was mentioned earlier by Bode and Voss [2]. It is important not to have any doubt concerning this reflection because it can be confused with the more intense 3.06 Å reflection of β -PbO which is another component of the paste. As the structure of 3BS remains unknown because much disorder characterizes this phase [4], the only way to verify the validity of the Küzel indexing is to prepare pure samples of 3BS in order to collect accurate XRD data. This is the aim of the present work.

For this purpose, several methods of synthesizing 3BS were investigated. By mixing PbO, H_2SO_4 and H_2O as in the industrial process, pure samples of 3BS will not be obtained [5]. We have studied the mechanism of the reaction:



The results lead to the conclusion that the lead oxide does not react completely due to kinetic factors; only a mixture of PbO and 3BS can be prepared by this method. Consequently, two other preparative procedures were developed. The first one is very similar to a synthesis first described by Bode and Voss [2]. It consists in precipitating the 3BS phase from a lead acetate solution in an ammoniacal buffer solution. The

* Corresponding author.

second method is completely different from the first one. The starting products are PbO and PbO·PbSO₄ (1BS). These solid precursors of the 3BS phase are ground in a mixer mill by means of a steel ball subjecting the powder particles to repeated impacts. Such a treatment increases the state of division of the ground phases rendering the reactivity very high. Hence, chemical reactions are allowed to take place by grinding at a relative low temperature [6]. Both methods lead to the same powder diagram of the 3BS phase.

2. Experimental

2.1. Preparation of tribasic lead sulfate

2.1.1. Grinding method

1BS and PbO were ground in stoichiometric amounts with 1 ml of water in a SPEX mixer mill Model 8000. One steel ball was used in a cylindrical stainless vial. The weight ratio steel ball to solid powder precursors was 15. The detailed description of the preparation is given in Ref. [7]. This preparation mode leads to small sticks ($0.5 \mu\text{m} \times 2 \mu\text{m}$) of pure 3BS as shown in Fig. 1.

2.1.2. Bode and Voss method [2]

A lead acetate aqueous solution is added to a solution of ammonium sulfate in a mixture of 32% ammonia and water. As soon as the two solutions are mixed a white precipitate appears and the suspension is stirred during about 10 min. In order to determine the best experimental conditions for preparing the pure 3BS phase the concerning parameters were varied in the following range: temperature (20–60 °C); PbO/SO₄²⁻ molar ratio (2.4–15), and volumic 32% NH₃/H₂O ratio (10/90–80/20).

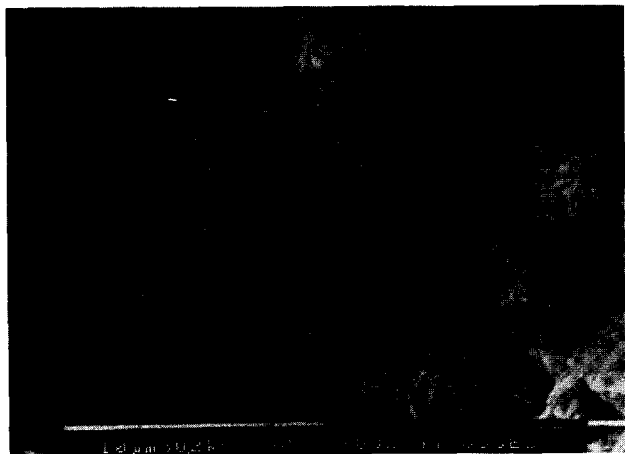


Fig. 1. Scanning electron micrography of tribasic lead sulfate prepared by the grinding method.

Table 1
pH stability range of the tribasic lead sulfate phase according to Bode and Voss [2]

SO ₄ ²⁻ (mol/l)	pH-stability range of 3BS
10 ⁻⁴	8.1–13.2
10 ⁻¹	9.0–14.2

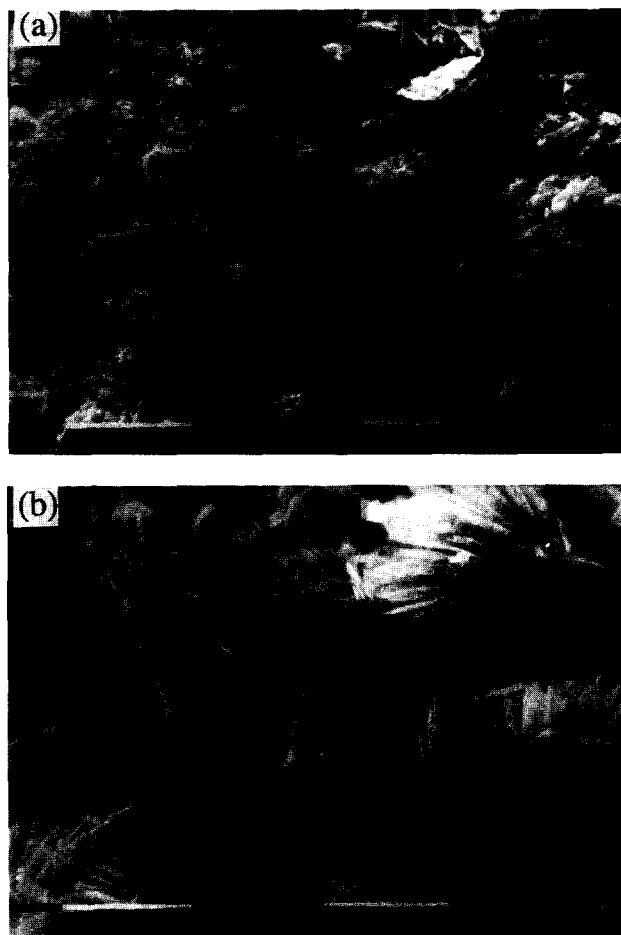


Fig. 2. Scanning electron micrographs of tribasic lead sulfate prepared by the Bode and Voss method: (a) at 20 °C, and (b) at 40 °C.

The pH, which depends on the 32% NH₃/H₂O ratio is a very important parameter. The 32% NH₃/H₂O ratio must be adjusted in the 50/50 to 80/20 range because these values correspond to the pH stability range of the 3BS phase reported by Bode and Voss (see Table 1). Below the 50/50 ratio, PbSO₄ is produced, while above an 80/20 ratio a mixture of 3BS and PbO is obtained.

The temperature plays also an important role. Above 40 °C, it is difficult to prepare the 3BS phase. 1BS or PbSO₄ are generally obtained unless a very large excess of lead acetate is used (PbO/SO₄²⁻ ratio ≥ 15). Moreover, the temperature strongly affects the morphology of the particles of the 3BS phase. At 20 °C, the 3BS

powder is composed of small particles without definite shape ($< 1 \mu\text{m}$) while needles ($1 \mu\text{m} \times 8 \mu\text{m}$) are formed at 40°C (Fig. 2).

Finally, the following experimental conditions were chosen for preparing 3BS samples that can be used as standards for the XRD study: 20°C ; $32\% \text{NH}_3/\text{H}_2\text{O} = 50/50$; $\text{pH} = 12.7$, and $2.4 < \text{PbO}/\text{SO}_4^{2-} < 7.2$.

3. Results

Fig. 3 shows the XRD diagram of pure 3BS prepared by the two methods described above. These crystallographic data were collected on a 1050 Philips powder diffractometer using monochromatic $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$). In these diagrams, the 3.08 \AA line can be seen,

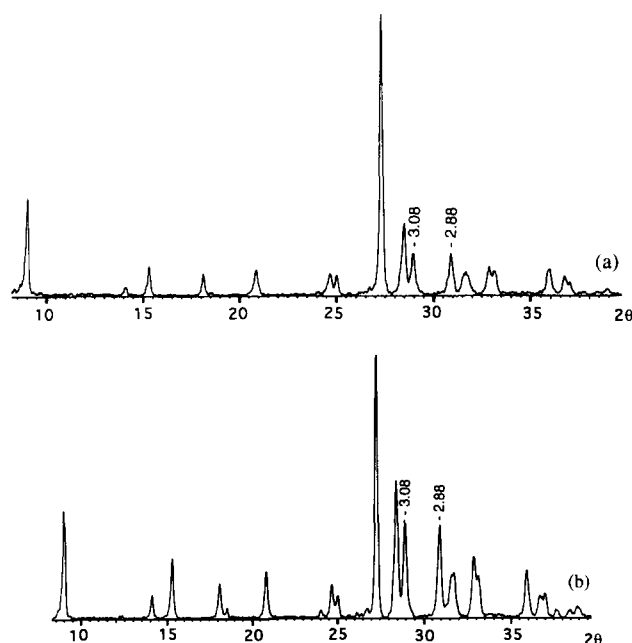


Fig. 3. X-ray powder diffraction diagram of pure tribasic lead sulfate: (a) prepared by the grinding method, and (b) prepared by the Bode and Voss method.

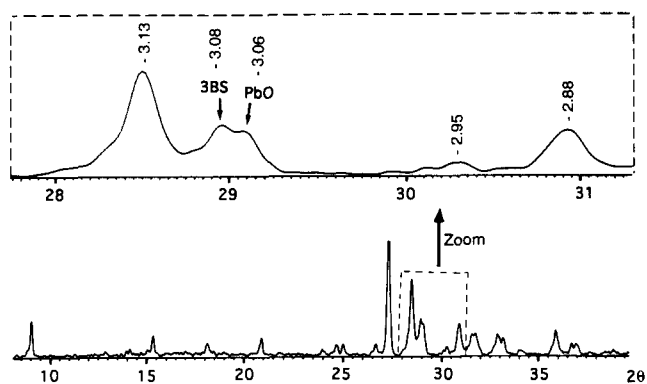


Fig. 4. X-ray powder diffraction diagram of a mixture of tribasic lead sulfate and $\beta\text{-PbO}$.

Table 2
X-ray powder diffraction data of tribasic lead sulfate

$h k l$	d (observed)	d (calculated)	I relative
1 0 0	9.779	9.788	45
0 1 0	6.253	6.259	11
1 1 0	5.769	5.772	26
-1 1 0	4.881	4.884	17
0 -1 1	4.760	4.762	3
2 1 0	4.249	4.250	19
1 0 2	3.695	3.695	3
0 0 2	3.600	3.600	6
-2 1 0	3.553	3.553	12
2 -1 1	3.461	3.462	2
2 0 2	3.328	3.329	4
3 0 0	3.263	3.263	100
0 2 0	3.128	3.129	51
2 1 2	3.080	3.081	27
2 2 0	2.886	2.886	24
-1 2 0	2.834	2.834	11
3 0 2	2.793	2.794	12
-1 1 2	2.724	2.723	17
-3 1 0	2.699	2.698	15
3 2 0	2.498	2.498	18
4 0 0	2.449	2.447	7
4 1 0	2.434	2.435	7
0 -2 2	2.381	2.381	3
0 2 2	2.343	2.343	3
4 0 2	2.313	2.313	4
-3 0 2	2.161	2.162	7
-4 1 0	2.151	2.150	3
0 3 0	2.086	2.086	4
-3 2 0	2.077	2.077	14
2 3 0	2.060	2.059	3
4 2 2	2.023	2.023	3

but at 2.95 \AA no line can be distinguished although both lines belong to the $\beta\text{-PbO}$ diffraction pattern. This indicates that the first one cannot be attributed to the lead oxide. Such an hypothesis is confirmed by the following fact. The XRD pattern of a mixture of tribasic lead sulfate with a great amount of PbO shows a splitting of the line at $3.06\text{--}3.08 \text{ \AA}$ (Fig. 4). These results enable us to think that the diffraction line at 3.08 \AA actually belongs to the 3BS diffraction diagram.

In order to validate the XRD diagram of the tribasic lead sulfate with the 3.08 \AA reflection, accurate crystallographic data have been collected with a D5000 Siemens XRD using Bragg–Brentano geometry with a curved germanium monochromator in order to obtain a monochromatized $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.540598 \text{ \AA}$). The powder diffraction has been scanned in steps of $0.02^\circ 2\theta$ with a fixed-time counting of 30 s. The peak positions were determined with a fitting program using the pseudo-Voigt function available in the PC software package Diffrac-At. The relative intensities were estimated by the Diffrac-At program. The powder diagram can be indexed in the triclinic system. A least-squares refinement of the lattice parameters by a NBS-AIDS

program leads to the following values: $a = 10.288(2) \text{ \AA}$; $b = 6.367(1) \text{ \AA}$; $c = 7.440(2) \text{ \AA}$; $\alpha = 87.22(3)^\circ$; $\beta = 75.34(3)^\circ$, and $\gamma = 79.37(2)^\circ$, with the figures-of-merit $M_{20} = 32.1$ and $F_{28} = 29.7$ (0.0081, 117). The observed and calculated reflections are listed in Table 2.

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