

# Synthesis of Galena (PbS) in Silica Gel Composite Particles by Sulphidisation and Hydrothermal Reaction

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**Abstract**—This paper reports the synthesis and characterisation of lead sulphide (PbS) in silica gel (amorphous quartz) as a binary composite particle, in an attempt of mimicking real ores. Silica gel was synthesised via an economic route sol-gel method using sodium metasilicate as a precursor. Lead sulphide particles in the gel were synthesised by using lead acetate and sulphide ion donor thioacetamide, via a hydrothermal reaction method. Lead sulphide particles were grown at hydrothermal temperature of 220°C, where thioacetamide breaks down to release sulphur (S<sup>2-</sup>) ions to sulphidised lead from the acetate. The products were obtained in lumps which were ground and characterised by quantitative X-ray diffraction (QXRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). QXRD results showed that the silica gel is of low quartz, partially crystalline and predominantly amorphous. The XRD pattern for the PbS showed crystals of galena and a quantified grade of 1%. SEM image confirms that the shape of PbS synthesised were of perfect cleavage with striated form, multifacets of agglomerated composite particles with regular shapes and few cubic crystals of few nanometres to microns (about 10 µm). The EDX spectrum indicates that PbS was synthesised in amorphous quartz.

**Keywords**- Lead sulphide, silica gel, synthesis, composite particles

## I. INTRODUCTION

Naturally occurring sulphide composite particles are generated in grinding of ores where the valuable sulphide mineral, such as galena (PbS), chalcopyrite (CuFeS<sub>2</sub>) or sphalerite (ZnS), is locked up in host gangue (unwanted) mineral such as silicate, quartz or carbonate. Several efforts have been made to produce an ideal binary composite particles from natural rock sources with two mineral phases, but there are difficulties in finding two phase particles whose phases are

free from other mineral impurities or associations [1]. The use of naturally occurring composites is limited because it is difficult controlling the locking texture. When synthetic or artificial composite particles are prepared, the locking texture can be controlled [2, 3]. The general procedure to synthesise artificial composite particles is to put monosize grains of the required mineral into a plastic or resin matrix which acts as the host gangue mineral. For example, [4] fabricated composites using defined size grains of pyrite (FeS<sub>2</sub>) and polystyrene as the matrix, [3] put lead oxide powder into polystyrene matrix to form a composite, [2] created their composite particles by embedding grains of silica in a matrix of epoxy resin and composite particles of silica in lead borate were also synthesised by [1].

Sulphide mineral are often found crystallised in bands in nature. Large, nearly perfect composites are occasionally found in silicate rocks or quartz band. To produce synthetic mineral composite particles close to the natural occurring composite, silica gel can be used as supporting matrix to represent the silicate or quartz band. The synthesis is carried out at high temperature and high vapour pressure to mimic the natural rock composite instead of using resins or plastics which are far from minerals. Crystals of the needed sulphide mineral may be allowed to grow in the gel by introducing solutions of compounds of the mineral into it for diffusion and precipitation of the desired sulphide in the gel [5-9]. Growing single crystals of mineral in gel involves a step reaction of two ions at some advantageous rate to form mineral crystal nuclei, a number of which is limited by diffusion in the gel [5]. The use of an organic sulphur compound thioacetamide, as a precursor for the sulphur ion donor, overcomes the difficulty of excessive nucleation mostly exhibited by inorganic sulphide donor (Na<sub>2</sub>S/H<sub>2</sub>S), by using its slow and controllable rate of hydrolysis, which makes available a limited number of sulphide ions at a time [10].

This paper reports the synthesis of lead sulphide (galena) in quartz (silica gel) composite particles hydrothermal and sulphidisation precipitation approach, using thioacetamide as

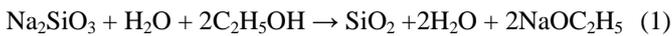
sulphide ion donor at a controlled pressure to represent the natural occurring sulphide composite.

## II. EXPERIMENTALS

### A. Synthesis

An autoclave with a thick-walled steel cylinder, hermetically sealed in order to withstand high temperatures and pressures for a very long period of time, was used for the hydrothermal method [11]. A Teflon beaker was inserted in the internal cavity of the autoclave to prevent corrosion, as shown in Fig. 2. The beaker has an inner diameter of 30 mm and a volume of about 15ml. The autoclave and the Teflon beaker used were from South Australia Museum (SAM, mineral science dept.)

Silica gel was prepared by mixing 20 g of sodium metasilicate ( $\text{Na}_2\text{SiO}_3$ ) solution and 10 g of ethanol under constant stirring with drop wise mixing of 1M hydrochloric acid (HCl) and water as a catalyst in 50 ml beaker for 20 minutes to initiate the reaction. The process is shown in Figure 1. The mixture was stirred for 2 hours until a clear solution with a solid soft gel was formed at the bottom of the beaker. The clear solution was decanted and the solid soft gel was washed in water for 72 hours to remove the associated impurities before using it for the reaction process. The reaction for the gel formation is shown in (1) as follows:



To embed galena (PbS) in the gel, 5 g of solid soft gel was put into 15 ml Teflon vessel, 0.01 g of lead acetate ( $(\text{CH}_3\text{COO})_2\text{Pb} \cdot 3\text{H}_2\text{O}$ ), 0.001 g of thioacetamide ( $\text{C}_2\text{H}_5\text{NS}$ ) and pH 4 buffer solution (about 10 ml) were added to the gel in the Teflon beaker to control the reaction. The Teflon beaker and its content then goes into the stainless steel autoclave, sealed and placed inside an electrical muffle furnace (SAM) at a temperature of  $220^\circ\text{C}$  for 7 days for the hydrothermal reaction to take place (Figure 2). The process was set for 6 autoclaves and the product obtained at the end of the reaction synthesis was removed and characterised after cooling the autoclave to room temperature or by quenching with water to control the texture. The reaction process for forming lead sulphide (galena) in the gel is as follows:

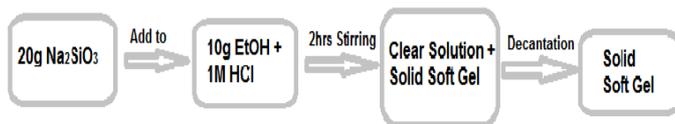


Figure 1: Schematic diagram for the preparation of  $\text{SiO}_2$  by the sol-gel process

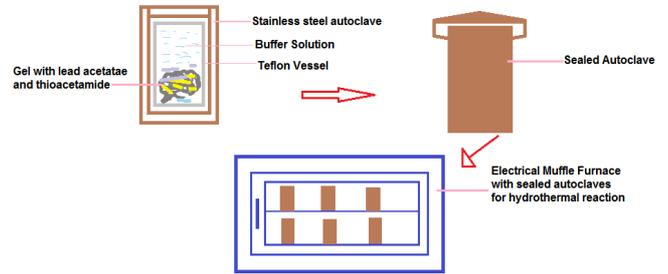


Figure 2: Schematic diagram of sulphidisation and hydrothermal synthesis of galena doped in silica gel

### B. Characterisation

Quantitative X-ray diffraction (QXRD) analysis was carried out on the synthesised ground product. Before measurement, the sample was piked with about 10% (8.3 w %) of ZnO to allow calculation of amorphous content of the sample. Due to limited quantity of sample, it was placed onto silicon 'zero plate' rather than the traditional method of using a sample cup insuring that it is packed, flat and is level with the top of the cup. The sample was analysed using Scintag ARL X'tra diffractometer and  $\text{CuK}\alpha$  radiation ( $\lambda=1.5406 \text{ \AA}$ ). XRD traces were collected between  $2^\circ$  and  $90^\circ 2\theta$  at 0.02 intervals at the rate of  $0.24^\circ$  per minute. The minerals were identified using X Powder software and then quantified using SIROQUANT V3 software. All peaks were identified and quantified. The results are provided in table 1. The synthesised sample morphology was studied by an environmental scanning electron microscope at Adelaide microscopy, Australia (SEM, FEG Quanta 450) with accelerating voltage of 200V to 30Kv, continuous adjustable probe current  $\leq 200\text{nA}$  and magnification of 6 to 1000000 (x). The SEM has an in built energy dispersive spectroscopy detector (EDAX) with EDS take-off angle of  $35^\circ$ . This was used to determine the semi quantitative chemical composition of synthesised products.

## III. RESULTS AND DISCUSSIONS

At a temperature above  $100^\circ\text{C}$ , the thioacetamide, gradually breaks down, releasing sulphide ions which sulphidised the lead (Pb) from the acetate salt by precipitation reaction to form PbS, as shown in (2) and (3).

Figure 3 shows BSE-SEM images of the PbS synthesised in the silica gel. The brighter colour represents the PbS and the dark ones represent the silica gel (amorphous quartz). The images A and A' in Figure 4 show the products obtained after quenching the autoclave and its content immediately in a bucket of water. The images B and B' were the products obtained after allowing the autoclave and its content to cool slowly to room temperature. The quenching and the slow cooling of the autoclaves were carried out to look at the

different morphologies and the locking textures of the PbS in the gel matrix. It can be seen from these figures that the shape of the PbS synthesised was of imperfect cleavage with strati form, multi-facets of agglomerated composite particles with regular shapes of perfect cleavage and few cubic crystals as shown in A, A', B and B' respectively. The crystals of PbS are embedded or bonded to the gel as sulphide in quartz mineral composite as shown in images A and A/. The crystals of PbS in images B and B/ look more like liberated particles in quartz. This may be due to the perfect cleavage of the lead sulphide which becomes difficult to bond well with gel as compare to an imperfect cleavage of PbS with irregular shape. The amorphous silica gel consists mainly of agglomerates and aggregate of few nanometres to micron particle size with partial crystalline shapes as shown by the XRD patterns (Fig.4) due to strong sharp peaks but more low and blunt peaks. The lead sulphide particles were almost of regular shape and also display length of few nanometres to microns (about 10  $\mu\text{m}$ ) from the SEM analysis.

Figure 4 shows the XRD patterns of PbS crystals in low quartz (silica gel) composite. The peaks of the low quartz overshadow that of the PbS. The spectrum shows weak and low diffraction peaks for PbS at  $2\theta$  values of  $25.9^\circ$ ,  $30.1^\circ$ ,  $43.0^\circ$ ,  $51.0^\circ$ ,  $53.4^\circ$ ,  $62.5^\circ$ ,  $68.9^\circ$ ,  $70.9^\circ$ ,  $79.0^\circ$  and  $84.8^\circ$  corresponding to the diffraction planes (111), (200), (220), (311), (222), (400), (331), (420), (422) and (511) respectively. This is similar to cubic zinc blend phase of PbS. The cell lattice constant of the PbS crystallites was determined from the XRD pattern and  $5.95 \text{ \AA}$  was obtained as the lattice constant. This result is almost the same as standard phase PbS ( $5.94 \text{ \AA}$ ). The average crystallite size  $L$  was determined by measuring the full width at half of the (111), (200) and (331) peaks by using the Scherer formula as shown in equation (4). The average crystallite size obtained was  $533\text{nm}$ . The  $\beta$  in the equation is the full width at half maximum (FWHM) of the diffraction peaks and  $\lambda$  is the wave length of X-ray used which is the Cuka radiation ( $\lambda=1.5406 \text{ \AA}$ ).

$$L = \frac{0.9\lambda}{\beta \cos \theta}$$

Again from Figure 4, the spectrum showed peaks for quartz (silica gel), ten of them were selected at  $2\theta$  values of  $20.9^\circ$ ,  $26.7^\circ$ ,  $36.5^\circ$ ,  $39.4^\circ$ ,  $40.3^\circ$ ,  $42.5^\circ$ ,  $45.9^\circ$ ,  $50.1^\circ$ ,  $50.6^\circ$  and  $54.8^\circ$  corresponding to a diffraction (100), (101), (110), (102), (111), (200), (201), (112), (003) and (202) respectively. The cell lattice constant for the low quartz was obtained as  $4.78\text{\AA}$  from the XRD and this is slightly less than the standard low quartz phase ( $4.91\text{\AA}$ ). The quantified grade of the PbS and low quartz (silica gel) has been given in Table I. The amorphous content might be overestimated due to lack of identification of the following peaks  $2\theta$  value of  $13.2^\circ$  ( $6.70\text{\AA}$ ),  $24.2^\circ$  ( $3.67\text{\AA}$ ) and  $34.2^\circ$  ( $2.62\text{\AA}$ ).

TABLE I. QUANTITATIVE XRD RESULTS

Minerals	Mass %
Quartz	85.5
Galena	1.1
Amorphous Content	13.4

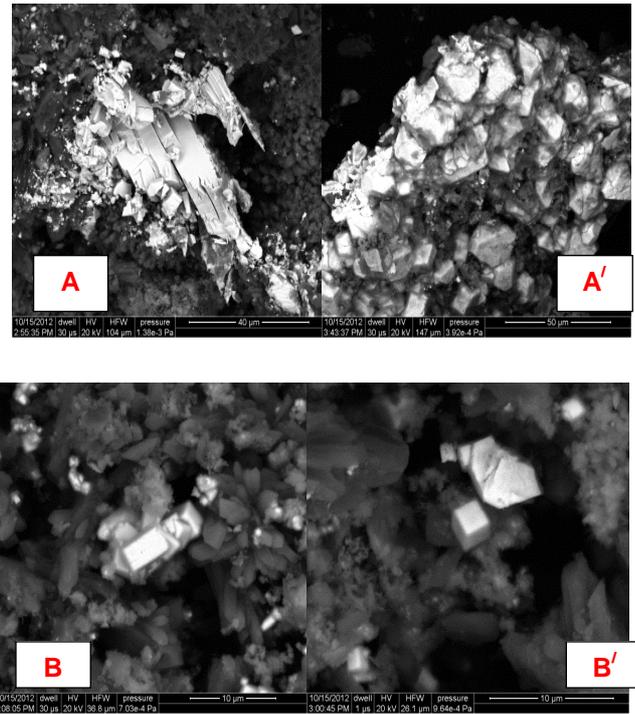


Figure 3: BSE-SEM morphologies of PbS in silica gel (amorphous quartz) after synthesis

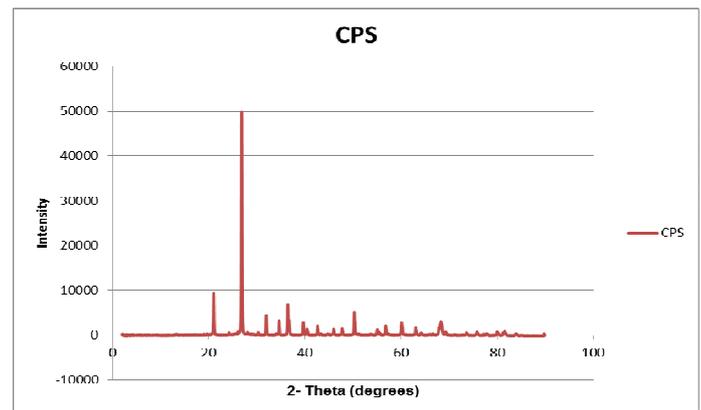


Figure 4: The X-ray powder patterns of the analysed sample showing measured data of PbS in silica gel composite (PbS and quartz peaks inclusive)

A typical EDAX spectrum of lead sulphide in gel (images A and B) is shown in Fig.5 and 6. The EDAX analysis (using the standard less quantification ZAF) was done on the composite specifically image A and B, the composition of lead sulphide in silica gel was shown indicating that lead sulphide was synthesised in the amorphous quartz. The elemental composition obtained from the analysis is shown in Tables II

and III. The high quartz content of PbS in image A is due to the fact that the PbS is more bonded or associated with the silica gel (low quartz) as compared to the PbS from B which looks almost liberated the host matrix. The presence of sodium in the PbS in A is coming from the precursor, and its presence is as a result of improper washing of the gel and for that matter sodium depositing in association with the PbS.

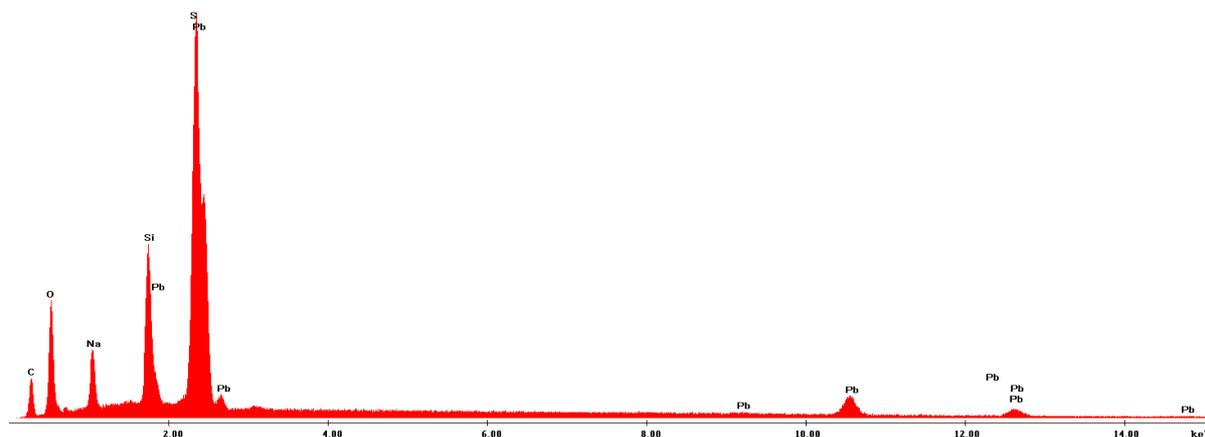


Figure 5: EDAX spectrum of the lead sulphide in gel synthesised (A)

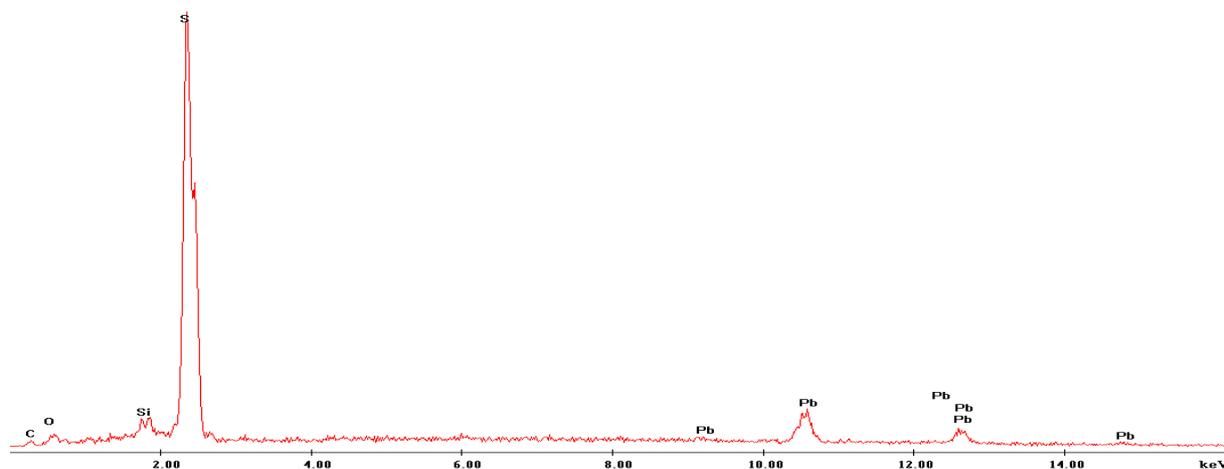


Figure 6: EDAX spectrum of the lead sulphide in gel synthesised (B)

Table 2: EDAX elemental composition of PbS in silica gel from image A

Image A		
Element	Weight %	Atomic %
Oxygen (O)	17.5	48.5
Sodium (Na)	5.50	10.6
Silicon (Si)	9.53	15.1
Sulphur (S)	9.80	13.5
Lead (Pb)	57.8	12.4
<b>Total</b>	100	100

Table 2: EDAX elemental composition of PbS in silica gel from image B

Image B		
Element	Weight %	Atomic %
Oxygen (O)	0.93	5.97
Silicon (Si)	0.73	2.70
Sulphur (S)	15.6	50.2
Lead (Pb)	82.7	41.2
<b>Total</b>	100	100

The problem associated with this method of synthesis is that bonding between the phases in the composites produced are not strong and there is also very small amount of composite particles produced since the growth of the sulphide mineral does not spread throughout the matrix. The synthesised product was to be used for the fundamental studies of mineral flotation of composite particles with only two phases, hydrophobic (PbS) and hydrophilic (quartz) fraction. In mineral flotation, composite particles with hydrophobic and hydrophilic phases generally occur in coarse size fractions. The floatability of these composite particles depends on the proportion of these hydrophobic and hydrophilic phases which stay together as a compact aggregate. The aggregates of this composite particles produced are not strong and easily undergoes crushing and grinding in a typical mechanical flotation cell producing very fine particles with no distinguishable phases. This makes the synthesis of composite particles by this methodology undesirable for study of mineral composite flotation.

## CONCLUSIONS

Galena (PbS) in quartz composite has been synthesised by hydrothermal and sulphidisation reaction method using an economic sol-gel route method. Quenching the autoclave immediately in water gave PbS particles which embedded or bonded well to the low quartz as compare to the slow cooling of the autoclave to room temperature.

The SEM images showed PbS particles (about 10  $\mu\text{m}$ ) of agglomerated composite and cubic structure which compared well with the standard galena structure. The XRD showed PbS crystals with an average grain size of more than 500nm with cubic structure.

The ZAF quantification from the EDS showed the elemental composition of the composite which indicated that PbS has been synthesised in quartz (silica gel). The challenge associated with this method of synthesis is producing larger mass of material with large crystals. There is also an issue with the mechanical properties of the composite aggregates, which impedes the application of this methodology in the synthesis of sulphide composite particles for mineral flotation.

## ACKNOWLEDGMENT

The financial support for this work from AMIRA international and Australian Research Council (ARC) is gratefully acknowledged.

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