

X-Ray Powder Diffraction Data—Identification and Structure Elucidation of Unknown Stone—Rietveld Refinement Approach

Munusamy Baskar^{1*}, Anju Patania²

¹Central Forensic Science Laboratory, Directorate of Forensic Science Services, Bhopal, India

²Central Forensic Science Laboratory, Directorate of Forensic Science Services, Chandigarh, India

Email: *munubas@yahoo.com

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Abstract

A dark and lead to silver grey soft irregular-shaped with heavy weight stone has been analysed as a part of research work for determining the components of the stone thereby leading to identify curiously to pinpoint whether the stone is in a category of gemstone, radioactive elements, raw or ingredients for making a powerful bomb or otherwise. In addition to the physical and optical parameters measured such as specific gravity, hardness, luster, transparency, cleavage, streak and other associated minerals for identification of unknown stone, Powder X-ray diffraction (PXRD) is one of the primary techniques in identification of minerals to examine the physico-chemical make-up of unknown materials, and has also been employed using Philips, DY993 X-ray Powder Diffractometer. The diffraction spectrum has been measured with the proportional counter in the 2° to 100° range at room temperature 300 K. This study reveals that the stone is not a category of precious stone; instead it is a category of mineral deposition, PbS, Galena.

Keywords

Precious Stone, Galena (PbS), Polycrystalline, Mineral, Titanium, Copper Target

1. Introduction

Powder X-ray Diffraction (PXRD) is a decisive tool in identifying polycrystalline materials by their unique diffraction patterns and is one of the best common analytical methods for nondestructive technique which provides information on structures, phases, texture, and other structural parameters of grain size, crystal-

linity, strain for characterizing crystalline materials about the composition of the solid crystalline material and are especially significant for the analysis of solid materials in forensic science for the forensic identification of unknown solid [1]. High-resolution PXRD patterns provide good data to determine the phase composition of crystalline samples, yet morphology and particle shape/size can induce severe preferential orientation that can degrade the utility of XRD powder data. Indeed the morphology of a stone can even induce to adopt the X-ray diffraction technique in identification of unknown solid samples [2]. Very small changes in the X-ray powder diffraction pattern may appear as a new peak(s) or shoulders or shifts in the peak position due to impurity of the solid sample or some other well-defined crystalline material adhered with the very high percentage of the solid sample can imply the presence of a new form of crystal components [3] [4]. X-ray diffraction is the principle method of characterization and its simplicity and advantages of the powder diffraction technique can help to identify the unknown material after comparing with the diffraction spectrum of the specimen material provided by the Joint Committee for Powder Diffraction File (JCPDF) [5] inbuilt in the software and licensed.

In this article, a dark and lead to silver grey soft irregular-shaped stone has been studied and identified for forensic purpose in order to reveal whether the stone is a kind of gemstone category? If not, what kind of stone it is and its components.

At large, structure determination from X-ray powder data and single crystal data may not be the new approach. However, handling the X-ray powder data to identify the unknown stone by determining its molecular structure through Rietveld method [6] could be the beginning of the history of Forensic Science.

The structural determination and its refinement of poly-crystals are being routinely carried out using X-ray powder diffraction with crystallographic software based on the Rietveld method [6] [7].

2. Methods

2.1. Physical Properties

The stone has been broken into pieces among which representative stone particles have been selected for measuring various optical parameters such as cleavage, hardness, specific gravity etc. The stones were opaque and brittle in nature. The stone was even heavy in weight as compared to any other metallic materials and having deposited a bluish tint on it. Some meager quantity of small sized whitish patches as a streak in a round shape has been observed on the stone. This whitish patch may mislead the analyst as a rock crystal. In this study, the stone was first subjected to measure its specific gravity then morphological identification. The morphology of the stone is as depicted in **Figure 1**. The decomposition temperature has been accessed as greater than 400°C using a temperature controlled digital furnace. The stone is dissolved in analytically pure HNO₃ and hot concentrated HCl.

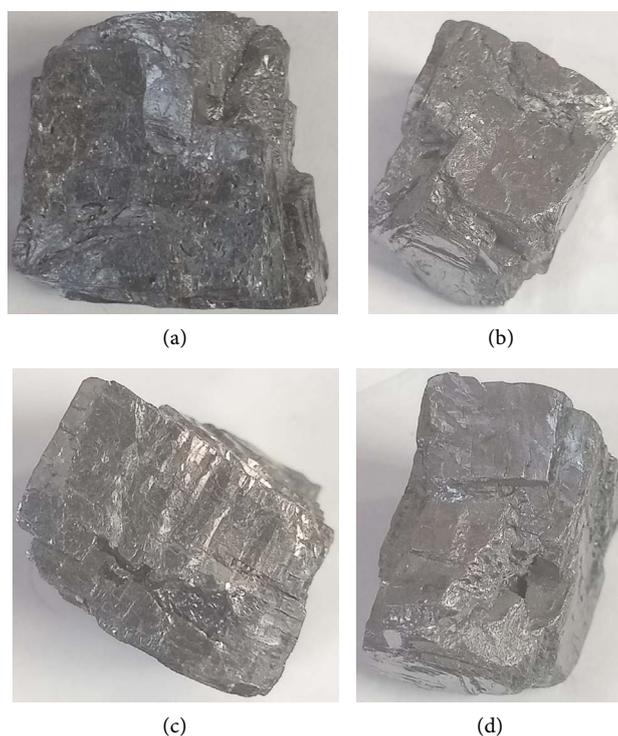


Figure 1. Morphology of various orientation of the unknown stone.

2.2. Physical Examination

The stone was cut into approximately equal size and its specific gravity was determined using the immersion method and averaged for five repeated values as 7.5 g/cm^3 . The preliminary study such as the specific gravity, luster, shape, colour and morphology etc., data of the stone made intuition to lead further examination in order to identify the unknown.

2.3. Data Collection

The stone has been broken gently into pieces from a solid lump of about 1 kg and then subjected to make a powder using the planetary ball mill, Retsch-PM100, for a grain size suitable for scanning under X-ray powder diffractometer. The ground powder sample was sieved with a sieve Mesh No.270 (0.053 mm or 0.0021 inches or 53 microns). The procedure was repeated till the particle size comes approximately equal to 1 - 5 μm in order to get the sharp and continuous X-ray diffraction peaks. Approximately, 0.2 g of powder particle passed through the sieve No. 270 was tightly packed into the titanium sample stub having a cavity of 13 mm diameter and 3 mm depth and then the sample was smoothed to make it to bring even surface around all over the sample with a glass slide. The sample loaded in a titanium sample stub has been carefully mounted on the sample chamber in X-ray diffractometer along the optical axis of the goniometer in the Bragg-Brentano geometry. The diffractometer parameters during the data collection were set at 45 kV and 30 mA with a Cu radiation ($\lambda = 1.54056 \text{ \AA}$). The diffractometer had a proportional counter. The goniometer position was fixed

and allowed for 2θ to move from 2° to 100° . The step size for moving the goniometer was set as 0.02° at a speed of 2° per minute. While scanning the sample, the goniometer moves through its range *i.e.* from 2° to 100° and stopping at each step by the allotted time. The raw scanning using the X-ray powder Diffractometer of the unknown stone powder is as shown in **Figure 2**. The X-ray counts at each step were saved in a file for further analysis for stripping out $K\alpha$ radiation and smoothing the X-ray spectrum with a weighted moving average and finally a diffractogram like the one shown in **Figure 3** is displayed. X-ray diffracted data were collected at a room temperature of 300 K using a Panalytical X-PERT PRO, DY993 X-ray Powder Diffractometer.

The analysis has been constrained to a total of 100% relative intensity which will be collected from each peak. The d spacing and the intensity data has been compared to similar data in the Joint Committee on Powder Diffraction Standards (JCDPS) provide with the software in the Philips (Panalytical) X-PERT PRO, Dy993 XRPD.

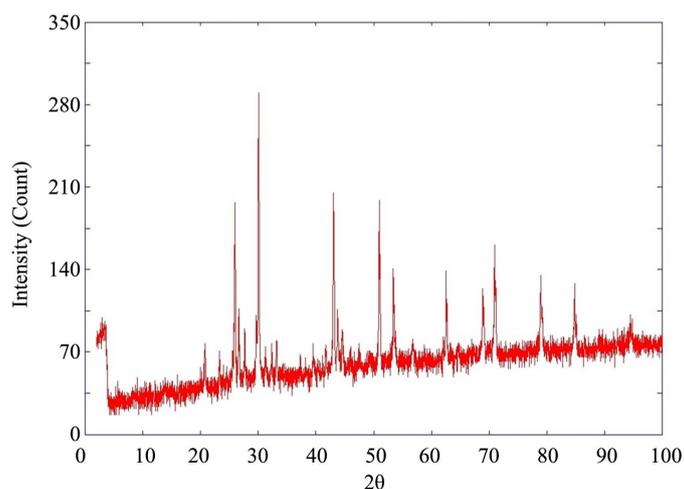


Figure 2. XRD pattern of unknown stone.

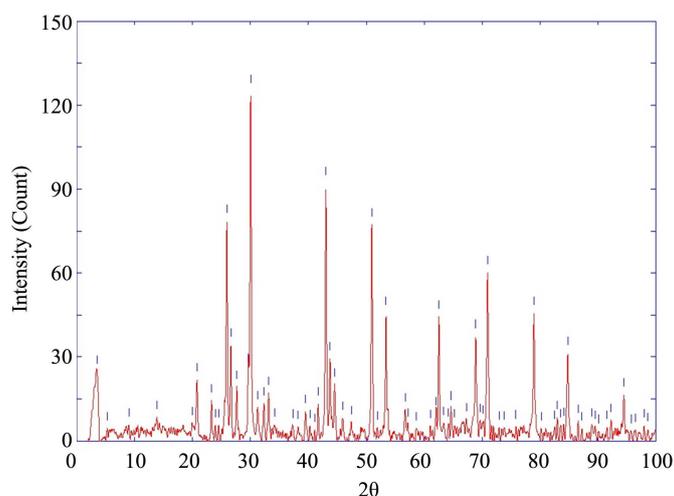


Figure 3. Powder spectrum after $K\alpha$ removal and indexation.

*The wavelengths (Å) for copper radiation are:

K-Alpha1 (Å)	:	1.54056
K-Alpha2 (Å)	:	1.54439
K-Alpha2/K-Alpha1 ratio	:	0.50000
K-Beta (Å)	:	1.39222
Used wavelength	:	K-Alpha1

3. Results and Discussion

X-ray diffraction patterns were obtained using a Philips DY993, X-PERT PRO X-ray Powder Diffractometer equipped with proportional detector. The sample was exposed with the X-rays produced under the copper target (1.5418 Å) and diffracted data was collected through the proportional counter. The 2θ , d , relative intensity etc. values have been obtained. Accordingly, the spectrum pattern obtained from the X-ray powder diffraction has been analysed eliminating the $k\alpha$ values and then the peak has been searched using the software X-PERT PRO ver 3.0. Phase identification was performed using the software, search Match ver 3.01, from Philips and the PDF database file version 2003 from ICDD.

On the basis of the JCPDS, the peaks were indexed and analysed for the identification of minerals the stone sample contains. The Hanawalt procedure, prevalently adapted to the diffractometric technique [8] [9] [10] [11] has been used in identification of mineral contents in the stone sample and then by searching the crystalline component phases of a mixture or unknown in its X-ray diffraction pattern using PCPDFWIN software which can retrieve/display for accessing records from the search from JCPDS having 60,000 compounds. Indexation of the powder pattern and calculation of the lattice constant(s) have been carried out manually by using the method of $\sin^2\theta$ and experimental d values respectively. Alpha-2 Stripping, Background subtraction and Indexation has also been carried out using the procedure Treor incorporated in the POWDER X [12] software for an intermediate check if the background subtraction and indexation do compromise with the Treor inbuilt with the Fullprof [13] suite of programs. The indexing of this pattern is shown in **Table 1**.

3.1. Rietveld Refinement

The data thus obtained from POWDER X has been subjected to Rietveld refinement using Fullprof Suit of Programs [13], General Structure Analysis System (GSAS) [14] software packages. The refinement was conducted based on the model for the crystal structure, peak profile, background intensities, lattice constants, atomic position etc. the refinement method based on the likelihood estimation of fluorapatite $\text{Ca}_3(\text{PO}_4)_3\text{F}$ [15] [16], anglesite PbSO_4 [17] and barite BaSO_4 [18] have been carried and demonstrated out using DBWS, Fullprof and RIETAN-FP software packages [19]. The structure of a novel layered aluminum methylphosphonate, $\text{Al}_2(\text{CH}_3\text{PO}_3)_3$, has been solved from X-ray powder diffraction data by simulated annealing of five independent structural sub-units, revealing a combination of four-and five-fold coordinated aluminums within the

Table 1. Measurement parameters X-PERT PRO, Dy993 XRPD.

Scan axis	:	Gonio; PW3050 (Theta/2Theta)
Incident beam radius (mm)	:	200
Take-off angle (°)	:	6.0
Scan mode	:	Continuous
Start angle (°)	:	5.0
End angle (°)	:	100.0
Step size (°)	:	0.020
Time per step (s)	:	0.25
Scan speed (°/s)	:	0.08
Number of steps	:	4750
Total time(h:m:s)	:	00:19:48
X-ray tube	:	PW3373/00 Cu LFF
Soller slit	:	Soller 0.04 rad. (MPD)
Sample stage	:	PW3072/00 Bracket
Focus	:	Line
Min. 2 Theta angle (°)	:	-2.754
Max. 2 Theta angle (°)	:	167
Min. Omega angle (°)	:	-3.262
Max. Omega angle (°)	:	180.0
Optic number	:	1
offset (°)	:	0.01
Radius (mm)	:	200
Detector	:	PW3011 Miniprop

inorganic lamellae that is unique for this kind of solid [20]. The X-ray powder diffraction pattern of Fe_2GeSe_4 , semi-conducting compound, has been recorded in room temperature and evaluated and the structure refinement was carried out using the Rietveld method [21]. Structure of Lead Chalcogenides PbX ($X = \text{S}, \text{Se}, \text{Te}$) was carried out with the single crystal X-ray diffraction data [22] using the full-matrix least-squares program RADIEL [23].

The crystallographic properties have been uniformly maintained in both the two software packages for getting the results from the refinement of the data. The structure, thus, obtained is as summarized below.

3.2. Fullprof Suit

The software, Fullprof-Suit of programs, was employed for refinement of the powder data thus obtained from the X-ray powder diffractometer as described. The matching .cif file as suspected was chosen from Crystallographic Open Data Base [24] along with input raw data in the .rd format obtained from the X-ray

diffractometer. The procedure as described in the Fullprof user manual was followed for refining the crystallographic parameters such as unit cell values, atomic coordinates, atomic displacements, background of the spectrum, the $K\alpha$ removed original powder data of the spectrum, asymmetric data sets etc.

The background information was refined using linear interpolation between a set background points with refinable heights. The pattern contribution information for phase and the peak shape were refined under X-ray and Pseudo-Voigt function respectively. The unit cell parameters were converged as, $a = b = c = 5.93557 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$.

3.3. General Structure Analysis Software (GSAS)

The refinement was also carried out using the software GSAS with the Raw XRD data and CIF file downloaded from open crystallographic database. The weighted R value is converged as 13.38% with R background 17.45%. The unit cell parameters were, $a = b = c = 5.97822 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$. The limit values refined is from 2° to 100° and the converged structure is placed in van der Waals model (VDW) model in **Figure 4** and **Figure 5**.

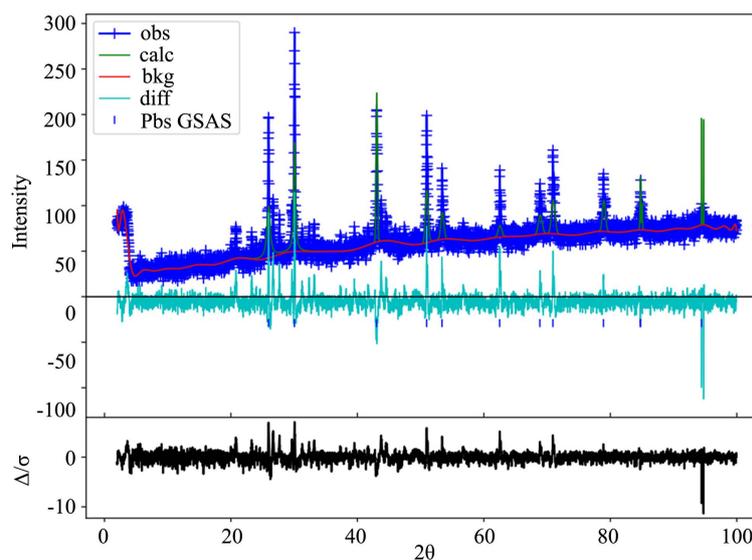


Figure 4. Results of Rietveld refinement using GSAS.

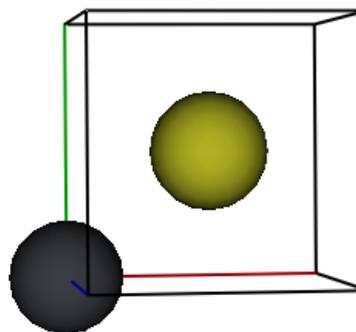


Figure 5. VDW model of PbS structure Rietveld refinement using GSAS.

The image of the stone is agglomerated composite particles with a cubic crystal and shapes of perfect cleavage in **Figure 1**. **Figure 3** shows the pattern of PbS crystal in composite with the space group Fm3m in face centered cubic crystal. The unit cell parameters of the unknown is $a = 5.935 \text{ \AA}$ and $\alpha = \beta = \gamma = 90^\circ$. The spectrum shows the diffraction peaks for PbS in **Figure 3**, **Figure 6** and **Figure 7** at 2θ values are given in **Table 2**.

The cell lattice constant of the PbS crystallites was determined from the XRD pattern as 5.935 which is the same as standard phase PbS (5.94 \AA) reported [25] as experimentally proved from the XRD results on the Galena synthesized. From the calculations of the indices [26] hkl presented in **Table 2** the unit cell is falling under cubic FCC lattices and the same values have been calculated by the PowderX Diffraction analysis software.

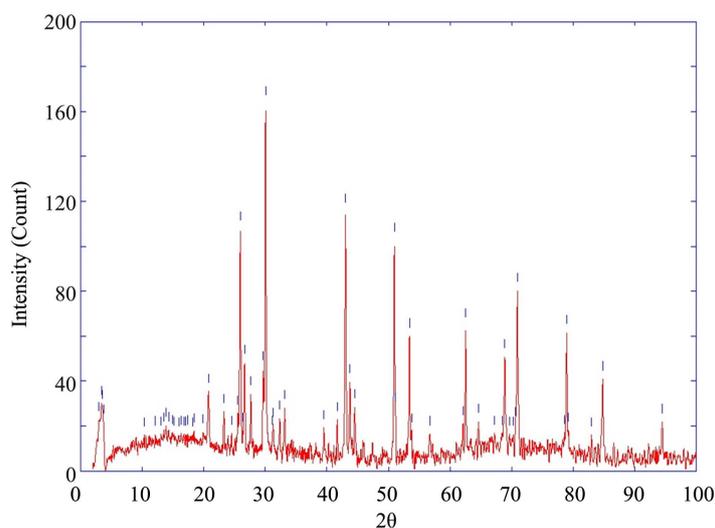


Figure 6. Powder spectrum after $K\alpha$ removal, background correction and indexation.

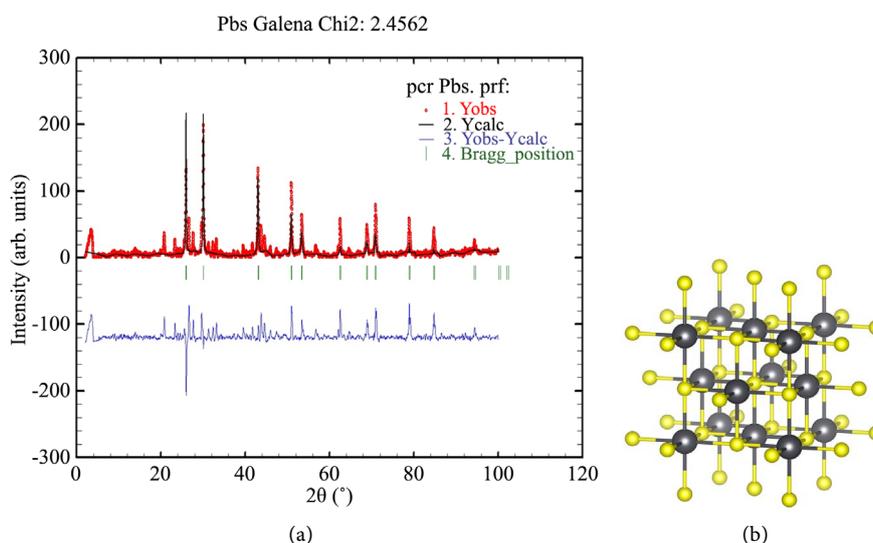


Figure 7. Results of Rietveld refinement using Fullprof suite determining the PbS structure. (a) Spectrum of completed Rietveld refinement; (b) Structure of the PbS.

Table 2. The prominent peaks selected from the original spectrum.

2 Theta	θ	Radians	$\sin \theta$	$\sin^2 \theta$	Ratio 1 * 3	d (Å)	hkl	Height	Area	FWHM
25.984	12.992	0.226638	0.224703	0.050491	3	3.42629	111	108.0	1478.4	0.2828
30.092	15.046	0.262469	0.259466	0.067323	4.000038	2.96725	311	45.3	3280.3	0.3304
43.076	21.538	0.375718	0.366941	0.134646	8.000109	2.09816	200	167.9	2335.1	0.2941
50.997	25.4985	0.444807	0.430284	0.185144	11.00053	1.78932	220	117.7	1880.1	0.3240
53.440	26.72	0.466116	0.44942	0.201978	12.00073	1.71314	311	96.5	1668.2	0.3505
62.556	31.278	0.545627	0.518954	0.269314	16.00155	1.48363	222	54.9	995.9	0.3723
68.912	34.456	0.601066	0.565522	0.319815	19.00213	1.36147	400	48.2	876.5	0.3559
70.867	35.4335	0.618118	0.579502	0.335823	19.95325	1.32699	331	41.8	983.4	0.4677
78.969	39.4845	0.688785	0.6356	0.403987	24.0033	1.14210	420	68.0	1534.3	0.4403
84.822	42.411	0.739836	0.674167	0.454501	27.00465	1.14210	422	48.9	1123.8	0.4745
94.487	47.2435	0.824137	0.733962	0.5387	32.00739	1.04908	440	35.4	863.7	0.5003

4. Conclusions

This study has been used to identify and confirm the unknown stone which was subjected to identify for the forensic purpose. The data collected using the powder X-ray diffraction was subjected to analysis with the Rietveld techniques with the help of two crystallographic software packages, in order to cross-check the results, such as Fullprof and GSAS both ended elucidating the similar molecular structure of the unknown stone as PbS, Galena by converging both the unit parameters of unknown stone $a = b = c = 5.93557$, $\alpha = \beta = \gamma = 90^\circ$ and $a = b = c = 5.97822$, $\alpha = \beta = \gamma = 90^\circ$ respectively and also their atomic positions with Vander Waals radii and temperature factors are:

Atoms	Coordinates			Uiso	VDW radii
	x	y	z		
Pb	0.00000	0.00000	0.00000	0.34677	2.02
S	0.50000	0.50000	0.50000	-0.16415	2.00

Hence, on the basis of the crystal unit cell parameters of the unknown stone, their coordinates and the peak positions at 2θ values and the structure of the molecule PbS elucidated by these two refinement software packages used in this study also in addition to the physical parameters, which are very essential to direct the study in this direction, the authors have concluded that this unknown stone could be only belonged to PbS, Galena and nothing otherwise.

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cal X-PERT PRO, DY993 X-ray Powder Diffractometer, in the laboratory at CFSL, Chandigarh.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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