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X-Ray powder diffraction - structure prediction of unknown stone using FullProf and GSAS - Rietveld Refinement

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Abstract

A slightly violetish blue, cone shaped, hexagonally soft sheen, a soft lustre on a surface, and semi/nearly transparent with reasonable weight of a natural stone has been analysed as a part of investigation for determining the components of the stone thereby leading to identify as to whether the stone is in a category of gemstone, radioactive elements, or otherwise. Philips, X-pert Pro, DY993 X-ray Powder Diffractometer has been employed for collecting the powder diffraction data in the Bragg-Brentano geometry using proportional counter in the $5^\circ < 2\theta < 85^\circ$ range at room temperature 300 K. The data, thus, obtained from the XRPD has been used in FullProf and GSAS (General Structure Analysis Software) software with the Rietveld refinement technique for elucidating the possible molecular structure of the unknown stone. In addition to the XRPD technique, the physical and optical parameters such as specific gravity, hardness, luster, transparency, cleavage, streak and other associated minerals have also been measured. This study reveals that the stone is in a category of precious stone which is of mineral deposition Corundum, a blue sapphire. The structure has been determined from Rietveld analysis in space group R-3c, with $a = 4.7655 (2) \text{ \AA}$ and $c = 13.0132(3) \text{ \AA}$.

Keywords: Precious; Gem stone; Blue Sapphire; Corundum ($\alpha\text{-Al}_2\text{O}_3$); Polycrystalline; Violetish blue; Rietveld refinement

1. Introduction

The X-ray powder diffraction (XRPD), one of the primary technique in identification of minerals examining the physico-chemical make-up of the unknown materials and a decisive tool in identifying polycrystalline materials by their unique diffraction patterns which provides information on structures, phases, texture, and other structural parameters of grain size [1], crystallinity, strain for characterizing crystalline materials about the composition of the solid crystalline material especially significant for the analysis of unknown solid materials. High-resolution XRPD patterns provide good data to determine the phase composition of crystalline samples. The advantages of the powder diffraction technique can help to identify the unknown material after comparing qualitatively with the diffraction data of the specimen material provided in PCPDFWIN software inbuilt with Joint Committee for Powder Diffraction Data -International Centre for Diffraction Data (JCPDS-ICDD).

In this article, a violetish bluish regular cone (hexagonal) shaped stone has been studied and identified in order to reveal if the stone is a kind of gemstone category. At large, molecular 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 material by determining its molecular structure through Rietveld method for refinement [2], widely used for different kinds of analysis for the known molecular structure and its unit cell parameters of the material, could be the new

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approach to elucidate the structure of unknown material refining its diffraction data of high probability with reference to the known parameters of the similar material. Rietveld method has also been employed in determining the cell parameters and approximate chemical compositions in analyzing the phase of multicomponent mixture [3,4,5]. Number of research work has been published for the determination of molecular structure with the Rietveld refinement being routinely carried out on X-ray powder diffraction data of poly-crystals with the use of various crystallographic software also for determination of characterization, phase analysis, particle size etc. [6,7,8]. Rietveld method has also been used in quantifying the phases in cement contents contains polycrystalline materials and mineralogical contents [9] and phase composition and morphological characterization of human kidney stones [10]. It has been justified [11] that powder X-ray diffraction provides information about structure, phase, composition, shape size an important features of nanoscale materials and the confirmation of the complete formation of phase on synthesized α -Al₂O₃ at temperature 550° has been obtained [12]. The range and effect of various strategies of Rietveld refinement round robin was examined with the 18 and 20 refinement with X-ray and neutron data respectively of PbSO₄ [13] and indicated that results of possibly high precision but low accuracy are not uncommon in Rietveld analysis. With the Rietveld refinement approach the similar molecular structure, PbS, of an unknown material was elucidated using Fullprof and GSAS software [14].

Rietveld method was tested on synthetic mixture and ceramic-ware materials and was observed that the method can provide an accurate, fast and standard less method of analysis suitable for quality and research controls [15] and the molecular structure of the yellow pigment 2,5-Dihydroxy-benzo [de] benzo [4,5]-imidazo [2,1-1] isoquinolin-7-one (C₁₈H₁₀N₂O₃) [16] was determined with high accuracy. Results were presented for Rietveld refinements using diffraction data sets acquired with an α -Al₂O₃ powder, and also with mixtures made up with this material and a ZnO powder [17] and achieved site occupation of the nitrogen atoms in the tetragonal ThMn₁₂-type structure [18]. Structural characterization of the nanocrystals on different sizes of synthesized cobalt ferrite CoFe₂O₄ has been carried out using powder X-ray diffraction [19]. The structure information such as the layer charge density, iron content, and occupancies of *cis*-octahedral sites has been carried out directly from X-ray diffraction patterns by the Rietveld method [20] and proved that the raw sample led to good agreement with the observed data, structure of Binary tetrahydrofuran (3-OH THF) + O₂) was determined using the Rietveld method with the direct space method [21]. The Rietveld method has been used to refine the structure of boron doped diamonds synthesized [22] and shown that unit cell parameter of a diamond with boron has two discrete values around 3.570 and 3.578 for small and large concentrations respectively, thermal expansion coefficients were calculated [23] from the unit cell parameters obtained from variable temperature diffraction in the case of Methscopolamine Bromide. It has been observed that the Rietveld method is the most reliable and powerful tool for refining crystal structure when powder diffraction data are available along with the requirement of structure model to be adjusted is as when powder diffraction data are available [24]. A qualitative study has been conducted [25] using Powder XRD for identification and differentiation of natural gemstones of corundum (α -Al₂O₃) from synthetic stones and observed the shifting of XRD peaks of synthetic corundum considerably high and high strain on synthetic corundum that that of natural variety.

2. Material and Methods

2.1. Physical/Optical properties

The stone, bluish streaked, polished, hexagonal shaped with white patches on the bluish streak, has been selected as representative stone for measuring various optical parameters such as cleavage and fracture, hardness, specific gravity, and preparing the sample of slide of 0.03 mm thickness to identify the minerals. The stone with its smooth surface is transparent, hard to break in nature and is heavy in weight as compared to any other transparent like materials. Some meager quantity of small sized whitish patches as a line of streak has been observed on the stone. This whitish patch may mislead the analyst as a rock crystal or any other calcium like substances. In this study, the stone was first subjected to measure its specific gravity, refractive index, hardness, streak etc. The unknown stone is as depicted as in Figure 1. It has been found that using a temperature controlled digital furnace, the stone lose its color at 800° C and retaining its original color by cooling. When the temperature increased sufficiently high, the bluish color disappearing permanently and become as white crystal. The stone could not be dissolved in any mineral acid or analytical reagent. However, the white patches/substances adhered on the stone has been removed with care full scrapping the same with fine tip of metal needle so that the measurement of refractive index and density of the stone should not deviate or mislead from its original value of these two physical parameters.

2.2. Physical Examination

The physical parameters such as composition, hardness, toughness cleavage fracture, specific gravity and Refractive index and optical parameters, luster, transparency, Birefringence and optical character (uni/bi axial) respectively and making a slide of 0.03 mm thickness to identify the presence of minerals have been observed. The specific gravity of the stone has been found with the help of immersion method by measuring for measuring five repeated values. 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. The stone was crushed using the planetary ball mill, Retsch-PM100 for the purpose of data collection under the X-ray powder diffractometer and also for preparing the microscopic slide of 0.03 mm thickness and studied under the microscopic for luster, like polished surface, which depends upon the Refractive Index of the stone.

2.3. Data Collection

The white patches adhered on the stones was removed with the fine tip of the needle after immersing the stone in the water for at least two hours and has been broken gently in to pieces weighing maximum about 1 gm 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 (0.053mm or 0.0021 inches or 53microns). 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, 0.3g of powder particle passed through the sieve No.270 was tightly packed in to the titanium sample stub having a cavity of 13mm diameter and 3mm depth and then the sample was smoothed at its top side to make it to bring even and fine 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 85° . 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 85° and stopping at each step by the allotted time.

The analysis has been constrained to a total of 80% 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. The instrument parameters are as given in Table 1.

* The wavelengths (\AA) for copper radiation are:

K-Alpha1 (\AA): 1.54056

K-Alpha2 (\AA): 1.54439

K-Alpha2/K-Alpha1 ratio: 0.50000

K-Beta (\AA): 1.39222

Used wavelength: K-Alpha1

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

Scan axis	:	Gonio; PW3050 (Theta/2Theta)
Incident beam radius(mm)	:	200
Take-off angle ($^\circ$)	:	6.0
Scan mode	:	Continuous
Start angle ($^\circ$)	:	5.0
End angle ($^\circ$)	:	100.0
Step size ($^\circ$)	:	0.020

Time per step (s)	:	0.25
Scan speed ($^{\circ}$ /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 ($^{\circ}$)	:	-2.754
Max.2 Theta angle ($^{\circ}$)	:	167
Min. Omega angle ($^{\circ}$)	:	-3.262
Max. Omega angle ($^{\circ}$)	:	180.0
Optic number	:	1
offset($^{\circ}$)	:	0.01
Radius(mm)	:	200
Detector	:	PW3011 Miniprop

The XRPD spectrum of unknown stone and stripping of $K\alpha$ radiation and its index performed with zero convolution using the software Powder X is as shown in **Figures 2(a)** and **(b)**. Diffracted data were collected at a room temperature of 300 K using a Panalytical X-PERT PRO, DY993 X-ray Powder Diffractometer.

3. Results and Discussion

X-ray diffraction patterns are 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 copper target (1.5418 \AA) and 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 data base file version 2003 from International Crystallographic Diffraction Data (ICDD).

In the beginning while processing the diffraction data file in .rd format for conducting the Rietveld refinement with the help of Fullprof and GSAS software packages, indexation of the powder pattern has been carried out using POWDER X [26].

3.1. Rietveld Refinement

The Rietveld refinement has been conducted based on a number of various reference models, the crystal structure of barite, BaSO_4 , from was refined by means of the Rietveld method using X-ray powder diffraction data [27, 28] which confirm the basis barite structure. Structure of a novel layered aluminium methylphosphonate, $\text{Al}_2(\text{CH}_3\text{PO}_3)_3$ [29, 30], diffraction pattern of Fe_2GeSe_4 [31]. The synthesized polycrystalline powder samples of pure and Yb (5 mol %) doped $\text{Bi}_2\text{ZnOB}_2\text{O}_6$ (BZOB) in the ternary system $\text{Bi}_2\text{O}-\text{ZnO}-2\text{H}_3\text{BO}_3$. Powder samples were subjected to powder X-ray diffraction (XRD) analysis to confirm crystalline phase and study crystal structure [32].

The diffraction data in the .rd format of unknown material obtained from Philips, X-pert Pro, DY993 X-ray Powder Diffractometer and processed using by POWDER X using Fullprof Suit of Programs [33, 34] and General Structure Analysis System (GSAS) [35]. Quantitative X-ray diffraction analysis on the phase composition of Portland clinker an cement using GSAS Rietveld [36] software packages based on the model for the crystal structure, peak profile, background intensities, lattice constants, atomic position etc.

The crystallographic properties have been uniformly maintained in both the 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. Eight .cif files (Table 2) available and matching with the chemical formula, Al_2O_3 , were taken from Crystallographic Open Data (COD) Base [37] along with raw scan data of the unknown stone (Figure 2) in the .rd format obtained from the X-ray diffractometer. The spectrum of powder of unknown stone and corrected background, the $K\alpha$ removed and the peaks identified using the software, asymmetric data sets etc. Mainly the crystallographic parameter used to refine the structure is Gaussian, Linear interpolation between a set of background points and Thompson-Cox-Hastings Pseudo-Voigt Axial Divergence Asymmetry.

Table 2 Details of CIF file from COD taken for Rietveld refinement

S.No	COD CIF	Unit Cell Parameters						System	Vol.	Space group	δ g/cm ³	Formula
		a	b	c	α	β	Γ					
1	1000017	4.7619	4.7619	13.000	90	90	120	Hexa	255.303	R-3c	3.798	Al ₂ O ₃
2	1000032	4.7741	4.7741	13.032	90	90	120	Hexa	257.250	R-3c	3.880	Al ₂ O ₃
3	1000059	4.7743	4.7743	13.032	90	90	120	Hexa	257.251	R-3c	3.865	Al ₂ O ₃
4	1000442	4.9176	8.2504	8.6506	90	90	90	Ortho	350.976	Pna21	3.859	Al ₂ O ₃
5	1010914	5.1369	5.1369	5.1369	55	55	55	Cubic	85.344	R-3cr	4.059	Al ₂ O ₃
6	1010951	5.1321	5.1321	5.1321	55	55	55	Cubic	85.115	R-3cr	3.978	Al ₂ O ₃
7	1101168	7.9320	7.9320	7.9320	90	90	90	Cubic	499.055	Fd-3m	0.003	Al ₂ O ₃
8	1200005	11.783	2.9055	5.6361	90	104	90	Mono	187.249	C12/m1	3.617	Al ₂ O ₃

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 Thompson-Cox-Hastings Pseudo-Voigt Axial Divergence Asymmetry respectively. The spectrum as well as the final structure of Al_2O_3 obtained after refinement is as shown in Figures 3(a) and (b). The details of parameters of the unknown stone refined with all the eight COD CIF data was finally obtained using Fullprof-Suit of programs as detailed below given in the Table 3.

Table 3 Details of Refined Parameters using Fullprof Suit of Programs

S.No	COD CIF	Real Space-Unit Cell Parameters						Crystal System Converge	Fractional Coordinates			Mol. Formula	Brag Factor/ RF/Chi ²	δ g/cm ³
		a	b	c	α	β	γ		x	y	z			
									O/Al	O/Al	O/Al			
1	1000017	4.7655	4.7655	13.0132	90	90	120	Hexa	0.7071 0.0000	0.0000 0.0000	0.2500 0.3553	Al ₂ O ₃	13.1 9.37 0.831	3.969
2	1000032	4.7773	4.7773	13.0022	90	90	120	Hexa	0.2974 0.0000	0.0000 0.0000	0.2500 0.3536	Al ₂ O ₃	25.7 32.3 2.59	3.953
3	1000059	4.7743	4.7743	13.032	90	90	120	Hexa	0.2954 0.0000	0.0000 0.0000	0.2500 0.3546	Al ₂ O ₃	17.0 21.6 0.924	3.963

4	1000442	4.9741	8.0372	8.7662	90	90	90	Ortho	- 0.0984 0.6047	0.7720 0.7945	0.8194 0.0000	Al ₂ O ₃	90.0 53.5 3.65	3.866
5	1010914	5.1432	5.1432	5.1432	55	55	55	Rhombo	0.5477 0.3555	- 0.0478 0.3555	0.2500 0.3555	Al ₂ O ₃	30.8 37.9 2.60	3.975
6	1010951	4.4198	4.4198	4.4198	61.8	61.8	61.8	Rhombo	- 0.1656 0.3193	0.6656 0.3193	0.2500 0.3193	Al ₂ O ₃	53.1 31.6 4.05	5.119
7	1101168	7.9573	7.9573	7.9573	90	90	90	Cubic	2.7672 0.2500	2.7672 0.2500	2.7672 0.2500	Al ₂ O ₃	97.2 85.7 4.30	3.985
8	1200005	11.7084	2.8983	5.5609	90	104.4	90	Mono	0.2048 0.3731	0.0000 0.0000	0.0000 0.7590	Al ₂ O ₃	80.5 60.5 3.74	3.707

The cell lattice constants, a, b, c, α , β and γ , of the Al₂O₃ crystallites was determined from the XRPD pattern as 4.7655, 4.7655, 13.0132, 90°, 90° and 120° respectively which are much closer to the standard phase of Al₂O₃ (a=4.7619, b=4.7619, c=13.0000, α =90°, β =90° and γ =120°) as reported [38] as experimentally proved from the XRD results on the Al₂O₃. Moreover, the structure convergence was highly optimized under the Bragg Factor, RF and Chi² values respectively with 13.1, 9.37 and 0.831. Among 53 lines generated, only 16 indices (h k l) shown on the peak (Figure 3a) presented in the Table 4 consistent with the values of American Mineralogist Crystal Structure Database [38] data base the unit cell is falling under hexagonal lattice type Primitive system. The indices obtained are convincing the diffraction data The crystal structure of Al₂O₃ was visualized and presented in this article by the software Visualization for Electronic Structural Analysis (VESTA) [39] based on the results using the software, Rietveld Refinement using Fullprof and GSAS, on crystallographic data obtained by XRPD analysis.

Table 4 hkl indices using Fullprof

PatternNo.	2 Theta (θ)	Intensity	d _{hkl} (Å)	h k l	Multiplicity	Sigma	Iobs	Icalc	Sin ² (θ)	Vol. of Unit cell (Å ³)
1	25.5378	90.40	3.4851	0 1 2	6	0.683	15.2	15.1	0.048801	255.936
2	35.0940	123.40	2.5549	1 0 4	6	0.673	22.4	23.3	0.090806	
3	37.7215	108.90	2.3828	1 1 0	6	2.935	25.3	12.4	0.104401	
4	43.2872	147.70	2.0884	1 1 3	12	11.636	24.0	24.7	0.135906	
5	46.1085	14.10	1.9670	2 0 2	6	0.397	0.2	0.0	0.153206	
6	52.4681	111.90	1.7426	0 2 4	6	0.676	20.3	18.4	0.195214	
7	57.4034	155.60	1.6039	1 1 6	12	0.854	28.6	27.4	0.230426	
8	59.6480	15.70	1.5488	2 1 1	12	0.309	2.4	1.9	0.247117	
9	61.0341	27.80	1.5164	1 2 2	12	0.063	0.7	0.5	0.257619	
10	61.1941	25.00	1.5133	0 1 8	6	0.411	5.8	5.0	0.258841	
11	66.4095	116.50	1.4066	2 1 4	12	0.623	19.8	17.5	0.299632	
12	68.1004	106.30	1.3757	3 0 0	6	0.652	22.4	21.0	0.31323	
13	70.2979	14.20	1.3380	1 2 5	12	0.006	0.1	0.1	0.331142	
14	74.1668	17.20	1.2775	2 0 8	6	0.006	0.2	0.1	0.363265	

15	76.7282	72.20	1.2411	1 0 6	10	0.010	0.9	0.7	0.384884
16	77.0925	33.70	1.2361	1 1 9	12	0.012	0.9	0.4	0.387979

3.3. General Structure Analysis Software (GSAS)

The refinement was also carried out using the software GSAS with the Raw XRPD data and .cif file downloaded from open crystallographic data base used for Rietveld refinement in Fullprof suit of programs. The limit values refined is from 2 to 80° and the corresponding Rietveld spectrum and the converged structure is placed in van der walls model (vdw) model in shown in Figures 4(a) and (b).

The data obtained from the XRPD were refined under reference COD CIF Nos. detailed in the Table 3. However, the data is maximally consistent with the structure of COD CIF Nos.1000017, 1000032 and 1000059 and the Unknown structure are not consistent with structure of CIF Nos. 1000442, 1010914, 1010951 and the CIF No. 1101168 and 1200005 are not converges. The cell lattice constants, a, b, c, α , β and γ , of the Al₂O₃ crystallites was determined from the XRPD pattern as 4.7619, 4.7619, 13.0000, 90°, 90° and 120° respectively which are much closer to the standard phase of Al₂O₃ (a=4.7619, b=4.7619, c=13.0000, α =90°, β =90° and γ =120°) as reported as experimentally proved from the XRD results on the Al₂O₃. The indices (hkl) presented in the Table 6 and the unit cell is falling under Hexagonal lattice type Primitive system. Moreover, the structure convergence was highly optimized under the wR with 24.93 and the details of data of unknown stone powder consistent for each COD CIF is as given in Table 5.

Table 5 Details of Refined Parameters using GSAS

S.No	COD CIF	Real Space-Unit Cell Parameters in Å and degree						Crystal System	Fractional Coordinates			Mol. Formula	wR in %	δ g/cm ³
		a	b	c	α	β	γ		x	y	z			
									O/Al	O/Al	O/Al			
1	1000017	4.7619	4.7619	13.000	90	90	120	Hexa	0.7076 0.0000	0.0000 0.0000	0.2500 0.3549	Al ₂ O ₃	24.93	3.7988
2	1000032	4.7741	4.7741	13.032	90	90	120	Hexa	0.2983 0.0000	0.0000 0.0000	0.2500 0.3548	Al ₂ O ₃	24.54	3.8799
3	1000059	4.7743	4.7743	13.032	90	90	120	Hexa	0.2954 0.0000	0.0000 0.0000	0.2500 0.3546	Al ₂ O ₃	25.15	3.8649
4	1000442	4.9176	8.2504	8.6506	90	90	90	Ortho	0.3290 0.6787	0.8313 0.8416	0.8927 0.0000	Al ₄ O ₆	63.45	3.4228
5	1010914	5.1369	5.1369	5.1369	55	55	55	Cubic	0.5496 0.3545	-0.0496 0.3545	0.2500 0.3545	Al ₂ O ₃	29.85	4.0588
6	1010951	5.1321	5.1321	5.1321	55	55	55	Cubic	-0.0464 0.3558	0.5464 0.3558	0.2500 0.3558	Al ₂ O ₃	66.40	-
7	1101168	7.9320	7.9320	7.9320	90	90	90	Cubic	- -	- -	- -	Al ₂ O ₃	63.31	0.0033
8	1200005	11.783	2.9055	5.6361	90	104	90	Mono	- -	- -	- -	Al ₂ O ₃	63.27	3.6144

The raw scan data was used to refine with two software such as Fullprof and GSAS The results of both the software used for Rietveld refinement resulted almost similar molecular structures consistent with the structure of first three COD CIF Nos. except the two CIF data at the last in the table. However, the results of Rietveld refinement show that the molecular structure of the unknown stone sample is highly consistent with, in particular, the hexagonal crystal system for both the software. Moreover the next five and three respectively differing from their COD CIF file structure data refined with the Fullprof and GSAS with their crystal system, results of optimization, unit cell parameters, atomic position etc. The last two COD CIF data are not even converging with the unknown scanned powder data. It could be due to the structure of

the scanned powder data may not be consistent with the said COD CIF files. The structure converged, consistent with the COD CIF data of Al_2O_3 and refined powder pattern with Unknown stone is as given separately in Tables 6 and 7 respectively.

Table 6 Crystal Structure of the unknown stone obtained after Rietveld refinement using Fullprof and GSAS

S.No.	COD CIF	Molecular Formula	Crystal System	Rietveld Refinement-Structure of Unknown Stone along c axis	
				Fullprof	GSAS
1	1000017	Al_2O_3	Hexa		
2	1000032	Al_2O_3	Hexa		
3	1000059	Al_2O_3	Hexa		
4	1000442	Al_4O_6	Ortho		
5	1010914	Al_2O_3	Rhombo		

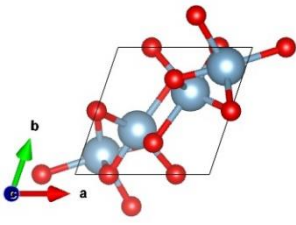
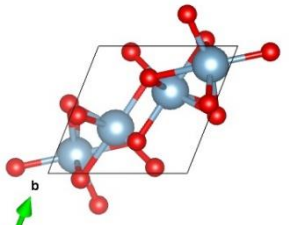
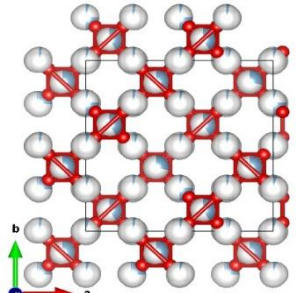
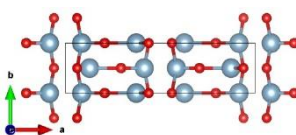
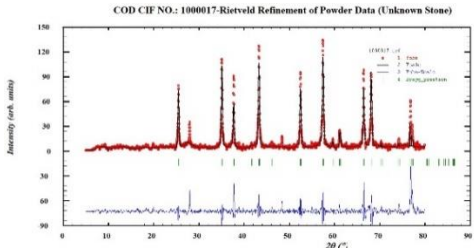
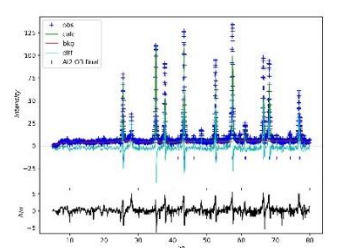
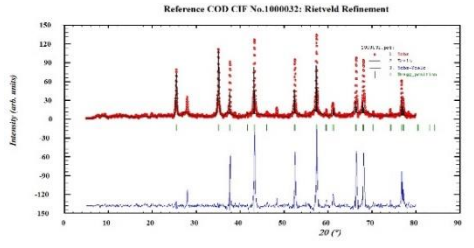
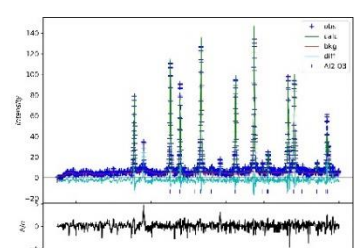
6	1010951	Al ₂ O ₃	Rhombo		
7	1101168	Al ₂ O ₃	Cubic		Not converged
8	1200005	Al ₂ O ₃	Mono		Not converged

Table 7 Powder pattern of the unknown stone obtained after Rietveld Refinement using Fullprof and GSAS

S.No.	COD CIF	Molecular Formula	Crystal System	Rietveld Refinement-Powder pattern of the Unknown Stone with CIF data	
				Fullprof	GSAS
1	1000017	Al ₂ O ₃	Hexa		
2	1000032	Al ₂ O ₃	Hexa		

3	1000059	Al ₂ O ₃	Hexa		
4	1000442	Al ₄ O ₆	Ortho		
5	1010914	Al ₂ O ₃	Cubic		
6	1010951	Al ₂ O ₃	Cubic		
7	1101168	Al ₂ O ₃	Cubic		
8	1200005	Al ₂ O ₃	Mono		

4. Conclusion

This study has been aimed to identify and confirm the molecular structure of unknown stone. On the basis of the Rietveld refinement of the unknown stone, data collected after scanned with the XRPD, which was refined with eight COD CIF

files as a reference as mentioned in the Table 3 and the raw scan data was used to refine with two software such as Fullprof and GSAS and final results of the crystallographic data, thus refined, has been presented in the tables and figures. Thus the study reveals that the crystalline hexagonal phase of α -Al₂O₃ could be obtained at room temperature and the lattice parameters calculated from the XRPD data were approximated as $a=b=4.7619 \text{ \AA}$, $c=13.000 \text{ \AA}$, $\alpha=\beta=90^\circ$, $\gamma=120^\circ$. With the refined values of the data it is found that the unknown crystal data scanned is only and highly consistent with the molecular structure and crystal system of hexagonal lattice type Primitive and belonging to space group R-3c and that too it is maximally compromised with COD CIF file No.1000017. Hence, it is concluded that the molecular structure of unknown scanned powder data is as determined and finalized as belonging to Al₂O₃ of Hexagonal crystal system.

Compliance with ethical standards

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Disclosure of conflict of interest

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

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