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Preparation of Indian Reference Material for the calibration of Powder X-ray Diffractometer: α-Alumina

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ABSTRACT

The CSIR- National Physical Laboratory of India (NPLI) constantly prepares and disseminates Indian Reference Materials (Bharatiya Nirdeshak Dravya; BND®) in various areas. Recently, NPLI has prepared the Indian Reference Material (IRM) of α-Alumina to calibrate the Powder X-Ray Diffractometer (PXRD). In this report, the preparation and certification procedure of α-Alumina (BND 2001) has been examined as an Indian Reference Material that can be utilized as the primary standard for powder X-ray diffraction instruments. The developed IRM was utilized to calibrate PXRD for phase purity. The stability of the prepared α-alumina was studied by using powder X-ray diffractometer. The homogeneity and the particle size of the material were characterized by using scanning electron microscopy. The repeatability of the preparation and pertinent characterization were affirmed using different calibrated instruments. The phase purity of the material was verified by performing a round-robin test, and the related uncertainty estimations were reported in the paper.

1. Introduction

A powder X-ray diffractometer (PXRD) is an essential and primary tool for the numerous characterization analyses used to calculate the crystallographic parameters and crystallite size of all the organic and inorganic materials. Nowadays, PXRD assumes an imperative part in environmental, biological, and mineral fields [1]. It is a non-destructive technique, and it is available in almost all higher education institutions, industries, and pharmaceutical companies. Therefore, it is necessary to ensure the authenticity of the data recorded from the powder X-ray diffractometer. It has an incredible influence in the field of materials and solid-state chemistry, which potentially administer all the information regarding crystal structure and phase composition of the material under investigation as each compound has a different unit cell parameter, particle size, and structure which diffracts to show a different pattern of diffraction [2, 3]. Measurements play a crucial role in the establishment and authentication of theoretical concepts in all scientific areas. Hence, it is a responsibility to ensure accuracy and precision while operations and measurements are conducted by any instrument [4, 5]. Therefore, to obtain the actual value, which must be close to its true value, the instrument should be calibrated using some CRMs (Certified Reference Materials). By utilizing an appropriate standard, one can ensure the authenticity of the data recorded from the above-said instrument. Even though couples of Certified Reference Materials (CRMs) are additionally accessible in the market, they are unaffordable due to their high price by different educational institutions. Due to this, the measurements carried out from the un-calibrated instrument can rise to

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erroneous measurement data. The inaccurate data further lead to a wrong conclusion, and the endeavors put down by researchers for making synthesis into vain [6, 7].
. In return, industries are following the SOPs more sincerely and taking an interest in the traceability and accuracy of their outcomes. The Reference materials (RM) play an essential role in such developments and raise their support for screening the product's quality for the market [8, 9]. There are many RM's presently manufactured to an adequate system of quality control and assurance (QC/QA). RM with the suitable matrix is certified for mercury content that might be a reference for the study of animal tissue, bottom sediment, food samples collected from the affected areas by disaster, or the contaminated part of the environment struggling with the mercury [10]. The RM's for quantitative and qualitative analysis for PXRD has been classified in various ways for obtaining a pattern of diffraction by PXRD instrument [11, 12]. Owing to the fascinating Physico-chemical, thermal and mechanical properties of alumina, this ceramic material is promising for various industrial, medical, and electronic applications. During thermal treatment, the phase transition of alumina has been recorded, which ends with the thermodynamic stability of α-phase [13-15]. Hence, in this work, α-alumina is taken as a primary material for making RM (BND®) due to its abundancy, environmental stability, homogeneity, and non-toxic behavior. In the present report, we explain the preparation and certification procedure for the α-Alumina as an Indian Reference Material (BND®), and the different characterization with their analysis has been discussed in detail in the forthcoming sections.

2. Experimental details

2.1. Sample preparation

A high pure α-Alumina powder having a particle size of ≥2-5 µm was taken as the source material with a chemical purity of ≥99.99 %. A small feedstock material was taken out to reconfirm its purity and crystalline phase. After the preliminary confirmation, 150 g of α-Alumina was undergone for high-temperature annealing at 1308°C ± 20°C with a rated flow of 4.7°C /min in a well-calibrated tubular Carbolite furnace (figure 1(a)) with an Argon gas flow [16]. As per the chemical nature of the α-Alumina, a temperature profile diagram was followed strictly (figure 1(b)).

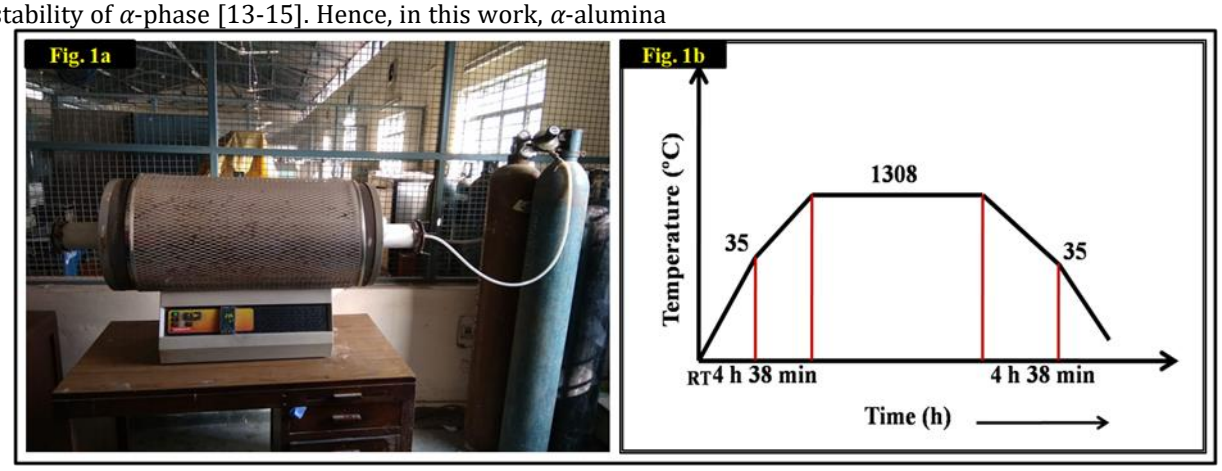

Fig. 1. (a) Picture of tubular heating furnace (b) Temperature profiling flow chart diagram.

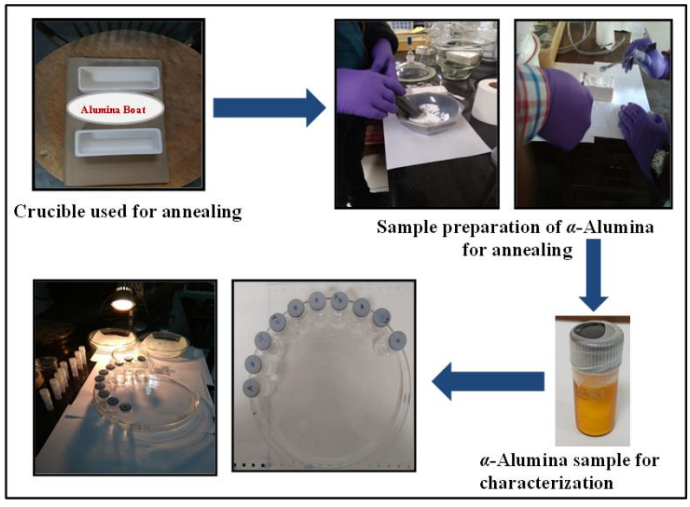

Fig. 2. Preparation process of α-Alumina.

The proper precautions were taken into account while preparing the material and the systematic procedure, as shown in figure 2. The material was first annealed by the above-said method, and then the sample was ground well with the help of agate mortar to get the desired particle size (≥ 2-5 μm). After grinding, the material was packed and sealed in amber color glass bottles. The annealed material has been characterized and analyzed via various spectrometric techniques like Scanning Electron Microscopy (SEM), High-Resolution Transmission Electron Microscopy (HRTEM), Particle Size Analyzer (PSA), and Powder-X-Ray Diffraction. A batch of 10 IRM bottles with proper labeling and serial numbers has been made from the annealed material. The repeatability of the results was confirmed by performing the same analysis over the randomly chosen sample bottle from the batch.

2.2. Standard Operating Procedure (SOP) for PXRD

The material has been finally prepared to be used as the IRM for the Powder X-ray diffractometer. The Powder X-ray diffraction experiment has been decided to conduct at least ten times by following the standard operating procedure. The same procedure has been mailed while performing the round-robin test with other National Measurements Institutes (NMIs). The said experiments have been performed on Rigaku ultima-IV multi-purpose X-ray diffractometer. The various parameters for the X-ray diffractometer have been set and used to perform the repetitive experiment. The source of CuK_α (40 kV/40 mA) has been used with the scanning speed of 1°/min over the angular 2θ range of 10 -150° with the rotation speed of 30 rpm having a slit width of 3 mm. In addition to that, the various slit system like anti scattering slit, divergence slit, and detector slit has been adjusted at 2/3°, 2/3°, and 0.03°, respectively, with the step size of 0.02°/sec. During the measurements, the room temperature was kept at 25°C ± 5°C, and humidity was kept in control at 45% ± 10%. The recorded data were analyzed by FullProf (Rietveld) analysis. The recorded data is in tune with the NIST SRM 676a. The Scherrer's formula calculated the crystallite size and agreed well with the recorded SEM images. The step-wise process is well explained in the following flow chart diagram (figure 3).

2.3. Homogeneity, repeatability, and Stability determination

The stability of *α*-Alumina has been examined by performing powder X-ray diffraction at different time periods for the same sample and found that there is no variation in the observed diffraction angle (2θ) over a period of time (figure 4). As mentioned earlier, the batch of 10 IRM bottles has been made from the annealed material. It is necessary to test the homogeneity of the samples in various bottles. Therefore, the homogeneity of the material has also been confirmed by performing the experiment with randomly collected samples from different packed bottles (figure 5). The six random samples from different bottles were taken and subjected to PXRD showing no variation in the peaks and in good agreement with the JCPDS data of *α*-Alumina.

2.4. Data collection through round-robin test (RRT)

As per the guidelines of uncertainty measurement (GUM) [17] protocol and ISO documents 17034 and ISO-13528, an round-robin test was carried out. The measurements have been performed with the same SOPs formulated and carried out at NPLI.

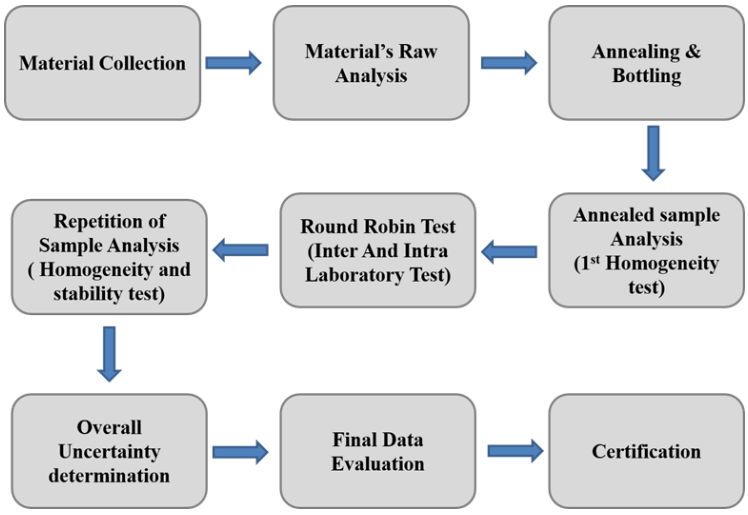

Fig. 3. Process followed for the production of Indian Reference Material.

3. Results and discussion

The recorded powder X-ray diffraction pattern for the present *α*-Alumina material was used for Rietveld refinement and shown in figure 6 [18-20]. The current analysis reveals that the titled powdered material crystallizes in the trigonal system with the space group of $R\bar{3}C$ (No.167). After carefully evaluating the pattern, it

shows the corundum structure, and no second phase has been observed.

The refinement showed that the lattice parameters are refined at the best fit with increased refinement cycles. It has also been shown that data is fully fitted by the observed and calculated spectra confirming the high phase purity of the compound. The enhancement in the intensity counts was also observed in the analysis, and the α-phase has been confirmed by the completely fitted peaks of the refinement. Lattice parameters of this refinement were found in good agreement with the reported literature, which also supports the *α*-phase of alumina powder. The refined and actual parameters have been summarized in table 1[25].

Scanning Electron Microscopy has been used for analyzing the surface morphology, i.e., the shape and size of the pre-treated alumina particles. The homogeneity and the particle size calculation have been the prime concern of the current study. The crystallite size was observed in the range of 5-10 μm, as shown in figure 7. The SEM micrograph also reveals the aggregates of the particles having relics of the sponge-like structure [21].

HRTEM is one of the essential characterizations to authenticate the 'd' spacing among the compound lattices. The annealed *α*-Alumina sample was analyzed via HRTEM to gather information about interplanar spacing present within the material. The TEM micrographs, as shown in figure 8, reveal that the material is highly crystalline, and the result obtained is completely matched with the result obtained from PXRD followed by JCPDS (No.461212).

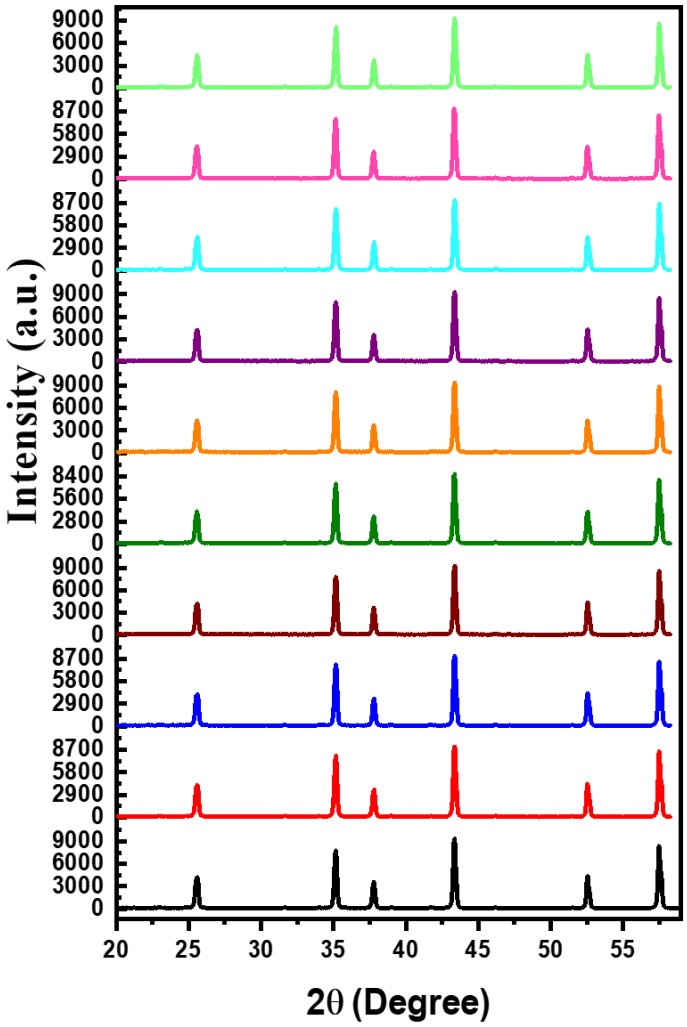

Fig. 4. Stability test for *α*-Alumina Powder over the same sample for 10 months.

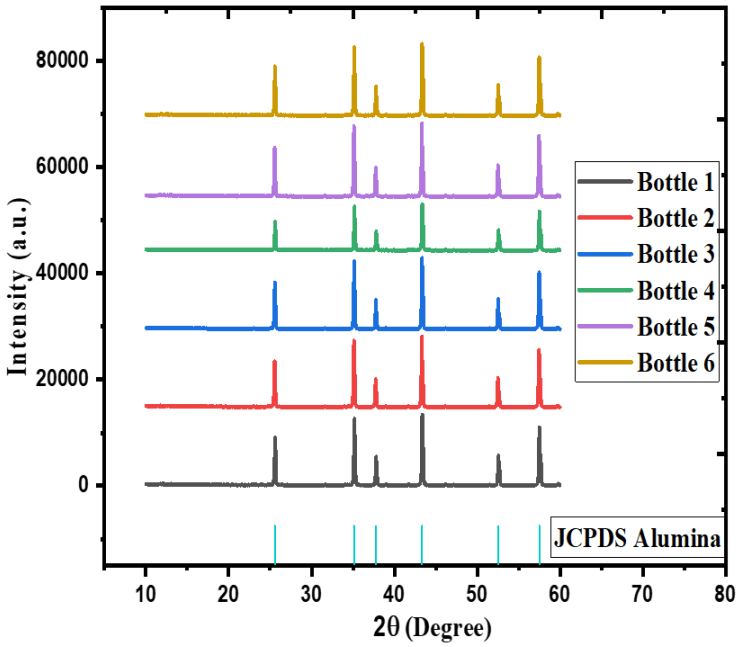

Fig. 5. Powder X-ray diffraction pattern of randomly chosen bottles for homogeneity test.

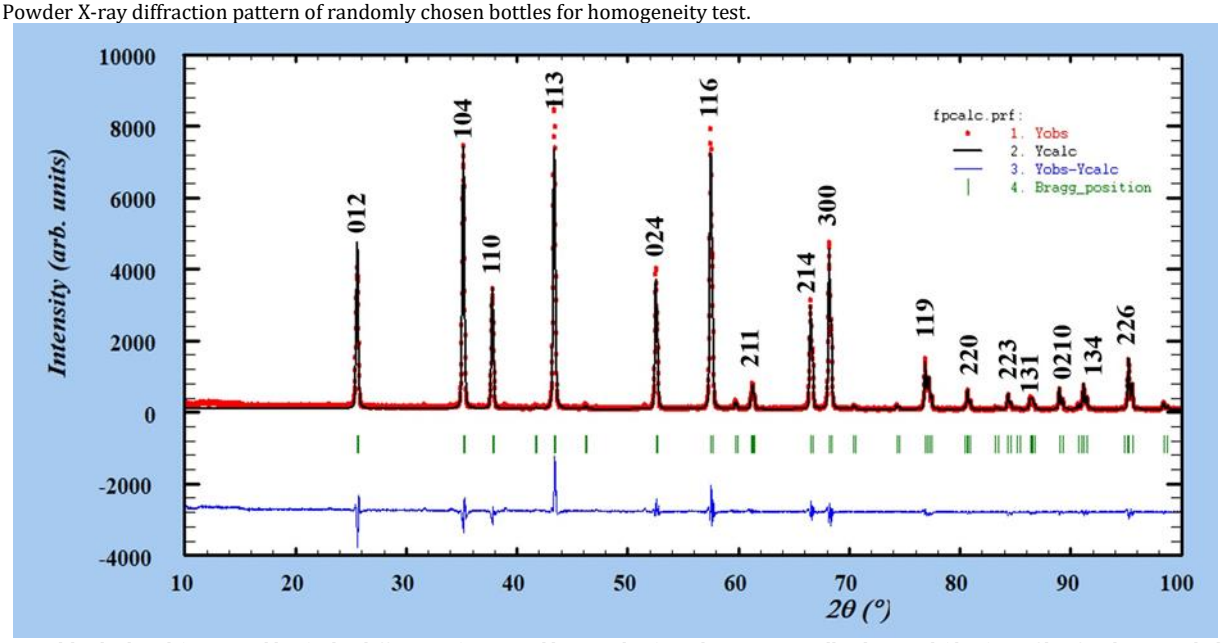

Fig. 6. Rietveld calculated (continual line), the difference (continual bottom line), and experimentally observed (dots) profiles for the annealed sample achieved after Rietveld analysis of PXRD data.

Table 1. Space group, Rietveld analysis (the integrity of fitness), lattice parameters of α- Alumina (annealed sample).

Sample	Space group	Crystal system	Rietveld data fitting (chi-2)	Actual lattice parameters (Å)	Refined lattice parameters (Å)
α-Alumina powder	$R\bar{3}C(167)$	Trigonal (hexagonal axis) a=b≠c α=β=γ	1.9	a=b=4.7591 c=12.9907	a=b=4.7591 c=12.9909

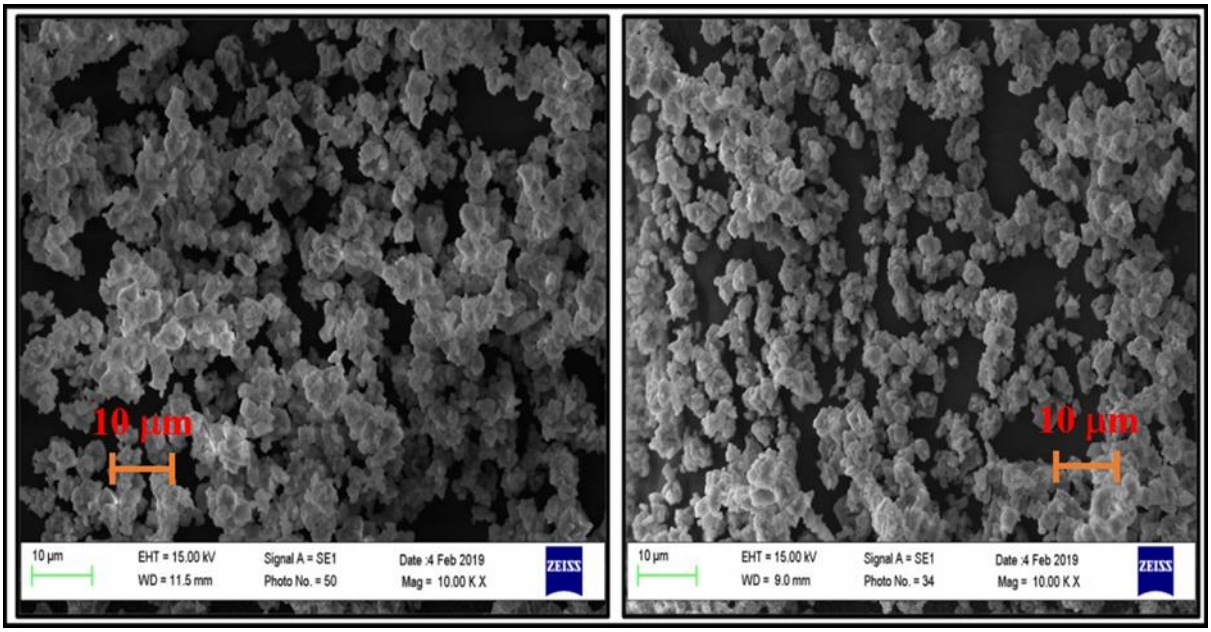

Fig. 7. Scanning Electron Microscopy micrograph of annealed α-Alumina.

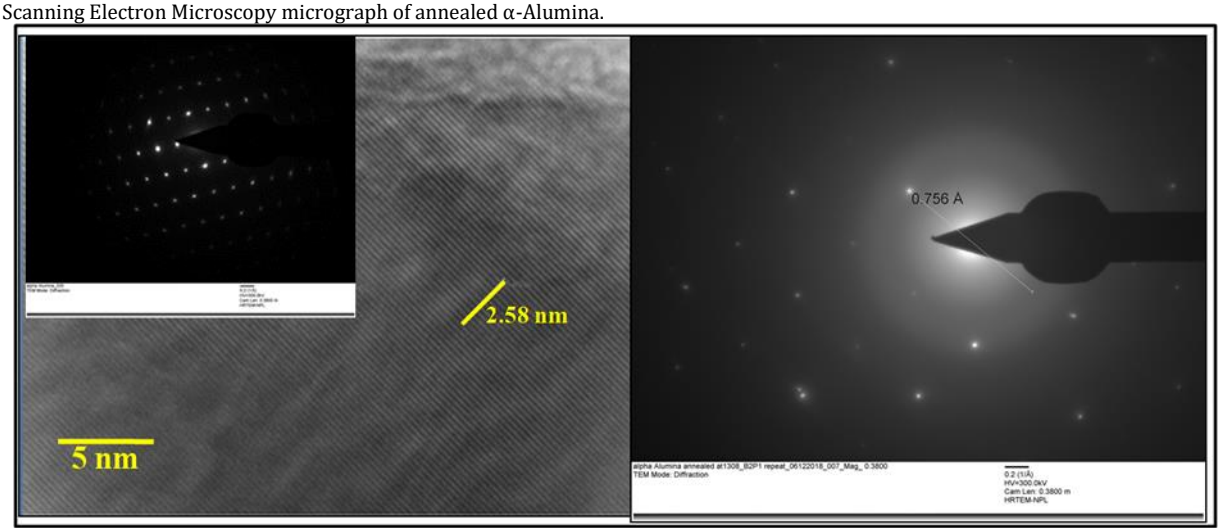

Fig. 8. High-Resolution Transmission Electron Microscopy micrograph of annealed *α*-Alumina.

4. Uncertainty Estimation

To estimate uncertainty in the measurement for further Certification, the values are certified in terms of crystalline alumina phase purity in terms of mass percentage and other information values, i.e. relative intensity percentage (RI %), and lattice parameters were also examined, which is [22-24] shown in figure 9. Uncertainty budget for both type-A and type-B Uncertainty was associated with the specific source of uncertainty in the measurement, have been summarized in table 2.

The results obtained in estimating uncertainty associated with the lattice parameters after the refined values with the Rietveld analysis were grouped in table 3. The certified phase purity of the material expressed as a mass fraction is:

Crystalline alumina = 97.06 ± 3.57 %. (*k*=2)

This phase purity is evaluated by the RIR (Reference Intensity Ratio) quantitative phase analysis method.

The uncertainties associated with BND®2001 have been combined with all the PXRD patterns, and finally, the developed *α*-Alumina (BND® 2001) material has been certified as the Indian Reference Material (IRM) for the quantitative analysis of powder X-ray diffraction. This material can be used as an internal standard for the calibration of the powder X-ray diffractometer instrument, and the packaged product is shown in figure 10. The results obtained for the uncertainty estimation of the relative intensity have been recently reported [25].

Table 2. Uncertainty Budget.

Source of Uncertainty	Limits Δx_i	Probability Distribution/ type-A & type- B	Sensitivity Coefficient	Degree of Freedom	Uncertainty Contribution (u_i)	Dispersion
Powder X-ray diffraction pattern	0.8882	Normal type-A	1	9	0.36261	0.13149
Environmental condition	0.8	Rectangular type- B	1	∞	0.46188	0.21333
Manual sample preparation	0.7	Rectangular type- B	1	∞	0.40414	0.16333
Instrumental error	0.8	Rectangular type-B	1	∞	0.46188	0.21333

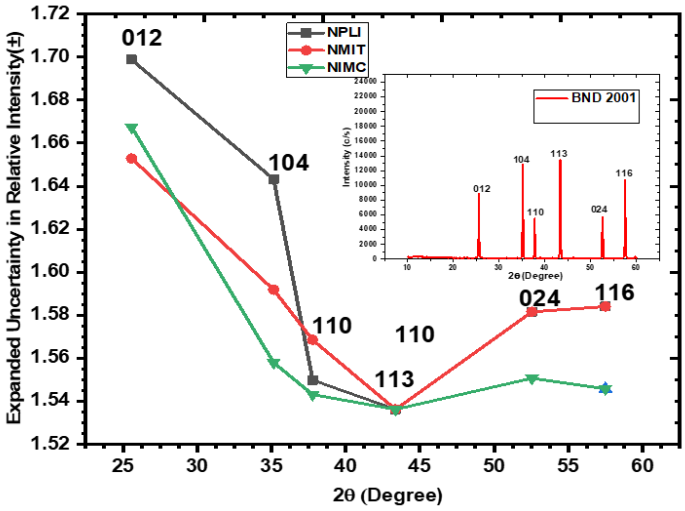

Fig. 9. Graphical representation of associated uncertainty in the results of NPLI, NIMC, and NIMT laboratories.

Table 3. Results obtained for the estimation of the lattice parameters.

Parameter	Estimate (Å)	Expanded uncertainty (*k*=2)
A	4.7584	± 0.0038
c	12.9914	± 0.0044

Fig. 10. *α*-Alumina: The Indian Reference Material for the calibration of PXRD.

5. Conclusion

We have successfully prepared the Indian reference material of α-Alumina for the calibration of PXRD in context to phase purity analysis. The phase purity of α-Alumina we found is 97.06 ± 3.57 %. *(k*=2). This value is calculated by considering both Type-A and Type-B uncertainty by conducting a round-robin test with NMIT and NIMC. To carry out precise measurements in atomic levels, one should ensure the instruments' calibration, which will reduce the chances of getting the wrong measurement data. Getting accurate data from the PXRD instrument is a challenging task for materials researchers. However, to record accurate data, reference materials are essential. As of now, reference materials are imported from various countries, and the currently prepared BNDs will act as the import substitution. In India, many colleges/universities may not be able to afford the cost of imported reference material. The reference material from CSIR-NPL will cost much less and can be used widely by the stakeholders. This reference material will give good visibility of our Indian research work to the international scientific community.

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