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Quantitative estimation of mullite in alumina based porcelain insulators samples

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Although porcelain insulators in power lines have been in use for decades, several undergo catastrophic failures while early in service. A study addressing the materials aspects has been conducted on alumina based porcelain insulators. Apart from their electro mechanical stability characteristics, material aspects like composition, phase and microstructure play a very important role in their performance. The qualitative phase analyses on the insulator samples give an idea about the different major and minor phases present. Attempts have already been made to estimate α alumina and α quartz content in porcelain body. Mullite is another important phase present in the porcelain body, which gets formed during firing of raw materials during insulator manufacture and which has not been estimated quantitatively. An attempt has been made here to assess the mullite content in the alumina based insulator samples by X-Ray diffraction quantitative analysis. Internal standard method of quantification has been adopted successfully for the analysis. This article describes the quantification of mullite phase by the internal standard method based on X-Ray diffraction principle.

Keywords *: Porcelain insulator, Mullite, Internal Standard, Titanium oxide*

1.0 INTRODUCTION

Quantitative analytical chemistry readily gives the elemental composition of a material, but usually has great difficulty in distinguishing the chemical identify of various phases in a mixture and in determining the precise amounts of each phase present. For crystalline mixture analysis, powder X-ray diffraction is seemingly the perfect technique, since each component of the mixture produces its characteristic patterns independently of the others. This makes it possible to identify the various phases by indexing their superposed patterns [1]. Moreover, the intensity of each component is proportional to the amount present so that a quantitative analysis for the various components may be performed.

Hull [2] in 1919 pointed out the unique feature of the powder pattern by saying that:

I. Powder diffraction pattern is characteristic of the substance.

II. Each substance in a mixture produces its pattern independently of the others.

III. It tells the state of chemical combination of the elements in the material.

IV. Only a minute amount of the development as a quantitative analysis.

The growth and development in instruments and techniques made x-ray diffraction applicable for analytical determinations such as quartz in the presence of mineral silicates, mixed alloy phases

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of different composition of different proportions of the same elements and the different amount of polymorphs in mixtures on a routine basis, alumina, mullite in the presence of alumina based porcelain insulators samples, but are difficult or impossible by chemical methods.

This paper describes quantitative analysis of mullite in alumina based porcelain insulators samples by internal standard method.

Mullite is commonly denoted as $3Al_2O_3 .2SiO_2$ (i.e. 60 mol% Al_2O_3). However it is actually a solid solution with the equilibrium composition limits of 60 – 63mol % Al_2O_3 below 1600° C. Mullite is the mineralogical name given to the only chemically stable intermediate phase in the SiO_2 - Al_2O_3 system. The natural mineral is rare, occurring on the Isle of Mull off the west coast of Scotland.

Mullite rarely occurs as a mineral in nature. In fact, the word mullite is derived from the Isle of Mull off the English coast, where the only naturally occurring deposits of mullite have ever been found. Naturally occurring mullite is so rare because it is the result of extremely high temperatures that have come into contact with aluminosilicate minerals of just the right type.

Despite the fact that mullite rarely occurs in nature it is an extremely valuable mineral to anyone involved in producing products that need to withstand high temperatures, corrosive environments, or other adverse conditions. Its use, therefore, as an industrial mineral, has to be supplied by synthetic alternatives. These methods generally involve high temperature reactions of aluminosilicate minerals such as kyanite, andalusite or sillimanite or alternatively bauxites and kaolins [3].

Mullite is a very important phase in high temperature, high hot strength, and thermally shock resistant products. It is virtually volume stable at very high temperatures. It has a low coefficient of thermal expansion. It is a good thermal and electrical insulator – even at very high temperatures. It has outstanding hot load-bearing properties, and it is resistant to many corrosive environments. It is, in short, the key ingredient in many refractory and ceramic products.

2.0 SYNTHETIC MULLITE

Various starting materials and preparation methods are used to make synthetic mullite ceramics. For example, a mixture of solids, a mixture of sols, or a mixture of sol and salt can each be used as the starting materials. Similarly, a variety of preparation methods exist, for example reaction sintering of mechanically mixed powders, hydrothermal treatment of mixtures of sols and chemical vapor deposition.

The starting materials and preparation method influence the properties of the mullite. Reaction sintered mullite made from mechanically mixed powders is usually characterized by low strength (<200 MPa) and low fracture toughness (1 – 2 MPa $m^{-1/2}$) due to amorphous grain boundary phases. In contrast gelation routes produce intimately mixed sub-micrometer particles that can be sintered or hot pressed to produce single phase materials with superior mechanical properties. Mechanical properties can be improved further by producing composites. Additions of Zr_2O and SiC have produced fracture toughness at room temperature close to 7 $MPam^{-1/2}$.

3.0 MULLITE IN PORCELAINS

Mullite is also one of the important constituents of porcelain. Clays with < 60% Al_2O_3 convert to mullite. The amount of mullite produced is directly related to the amount of Al_2O_3 and the calcining temperature. Typically, the composition of a good alumina based porcelain insulators consist of 35-40% α-alumina, 4-8% mullite and < 2 %α-Quartz, along with other Compounds. Mullite acts as reinforcement in the matrix, and the preferable morphology is needle shape. If the mullite content is reduced, the mechanical properties of the α-alumina matrix will be poor due to the lack of reinforcing effects induced by the needle shaped mullite. Vice versa, if

the mullite content in the matrix exceeds the optimum content, it will cause high brittleness in the composite, which results in the early failure of the insulators [6].

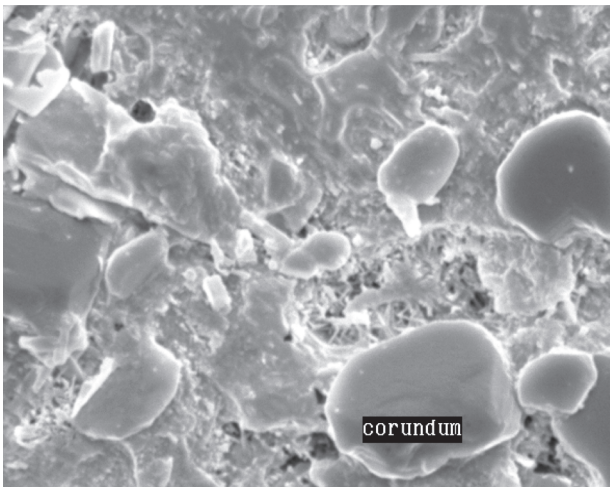

FIG. 1 ALUMINA BASED PORCELAIN INSULATOR WITH OPTIMUM MULLITE CONTENT

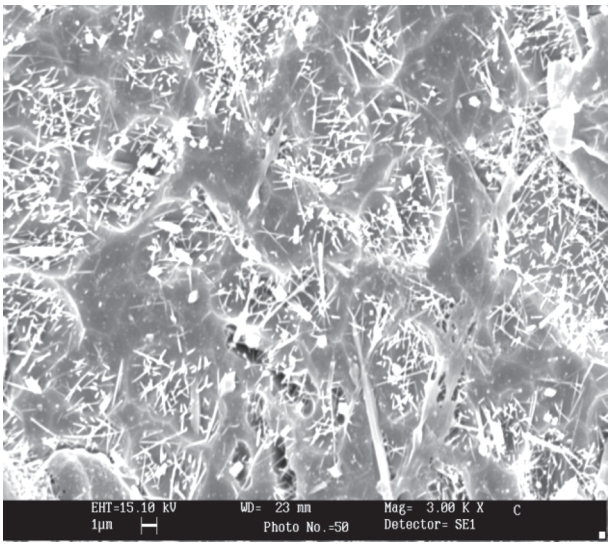

FIG. 2 ALUMINA BASED PORCELAIN INSULATOR WITH HIGH MULLITE CONTENT

4.0 PROPERTIES

Mullite has long been used as a refractory material. Its properties include:

- Good high temperature strength
- Good thermal shock resistance
- Excellent thermal stability
- Resistance to most chemical attack; it has excellent stability in acid metal slags and is insoluble in most acids
- Resistance to oxidation and attack by furnace atmospheres
- Resistance to abrasion
- Good electrical resistivity

The approximate limiting temperatures of use are 1800° C in air and 1600° C in vacuum.

Typical properties of mullite are given in Table 1.

TABLE 1

PROPERTIES OF MULLITE	
Density (g/cm^3)	3.03
Young's modulus (GPa)	130
Fracture toughness(MPa.m$^{-1/2}$)	2-4
Modulus of rupture(MPa)	160
Thermal Expansion Co-Efficient (x10^{-6} °C)	4.5-5.6
Thermal Conductivity (W/m.K)	4.0-6.0 (100-1400°C)
Maximum Operating Temperature (°C)	1725°C IN AIR
Density (g/cm^3)	3.03

5.0 APPLICATIONS

By far the largest use of mullite based products is in refractories. The glass and steel industries are two main markets. The steel industry is the largest user, where refractoriness, high creep resistance and thermal shock resistance are important. The main use of high-mullite based products is in hot blast stove checker bricks. Many refractories in use in the steel industry have varying amounts of mullite based aggregates in them. Steel ladles, lances, reheat furnaces and slide gates are examples of mullite aggregate based products with various alumina contents. The use of monolithic and precast shapes is increasing with the use of bricks declining [4].

The glass industry uses mullite based refractories in burner blocks, ports and in checker bricks as well as in the upper structure of the tanks where the glass is melted and in the drawing chambers. Thermal shock resistance, chemical attack resistance, high hot strength and creep resistance are the primary properties valued by the industry.

Mullite based products are also resistant to particulate carryover into the glass melt. This is particularly important in flat glass production, where contamination by low levels of Al_2O_3 is undesirable. The next largest user of mullite is the ceramic industry mostly in kiln furniture items such as kiln setter slabs and posts for supporting ceramic ware during firing. The aluminium and petrochemical industries also use mullite-based aggregates for applications requiring chemical attack resistance, thermal shock resistance and hot-load strength.

Other engineering applications include new mullite materials that have more controlled mechanical and physical properties and are providing opportunities for a wider use of the material. The good mechanical properties at high temperatures of high purity mullite have made them potential high temperature engineering ceramics, for example in turbine engine components. Mullite is also a leading candidate material for high-strength infrared transmitting windows. Other applications also include electronic substrates and protective coatings.

6.0 QUANTITATIVE SINGLE PHASE ANALYSIS

Mullite in alumina based porcelain insulators samples

Because of the seriousness of the aluminum and silicosis hazard to individuals who work in the presence of aluminum silicate (mullite), X-ray diffraction analysis for mullite has had a very large account of study. These analytical schemes in general are based on the internal standard technique with either photography or spectrometric diffraction methods.

For analysis of mullite in alumina based porcelain insulators samples, the internal standard method can be applied. In the present study titanium oxide is used as an internal standard for mullite determination in alumina based porcelain insulators samples.

7.0 THEORY OF INTERNAL STANDARD METHOD

The internal standard method has been applied in emission spectrographic analysis for some years. Alexander and Klug [5] demonstrated the applicability of the same technique in x-ray diffraction analysis of multi component system in which the absorption coefficient of unknown component is different from that of the matrix and the latter is not know. Alexander and Klug proved the validity of the technique in a brief theoretical treatment.

The sample is assumed to be an uniform mixture of 'n' components where n>2, with a particle size small enough such that the extinction and so called micro absorption effects are negligible and of such thickness as to give maximum diffracted intensities. With such a powder cake the total intensity of x-ray diffracted by the i^{th} component of the mixture by some selected plane is given by:

$$I_i = (k_i . f_i) / \mu \quad ....(1)$$

Where k_i depends on the nature of the components 'I' and geometry of the apparatus and fi is the volume fraction of the ith component and μ is the liner absorption coefficient of the powder mixture. If x_i is the weight fraction and ρ_i is the density of the ith component it may be shown that

$$F_i = (x_i/ \rho_i) / (n_1€ (x_i/ \rho_i)) \quad ….(2)$$

Suppose an internal standard component 's' is added to the sample in known amount and the volume fraction of unknown and internal standard components after such addition are f_{1i} and f_s the volume fraction of the component i in the original sample being f_i from equation 'a' it is seen that:

$I_i = (k_i . f_i') / \mu$ ….(3)

$I_s = (k_s . f_s) / \mu$ ….(4)

Dividing I_i and I_s and substituting f_i and f_s from equation (b) gives

$I_i/I_s = (k_i . x_i' . \rho_s) / (k_s . \rho_i . x_s)$ ....(5)

This on solving for x1 yields

$X_i' = ((k_s . \rho_i . x_s) / (k_i . \rho_s)) . (I_i / I_s)$

$= (k' . (I_i/I_s))$ ….(6)

Provided x_s is held constant. It is the weight fraction x_i in the original sample. Which is relates to x_i as follows

$X_i = x_i / (1 - x_s)$ ….(7)

When the equation (f) is combined with (e)

$X_i' = (k' / (1-x_s)) . (I_i/I_s)$ ….(8)

Thus, when the internal standard is added in a constant proportion xs, the concentration of component i is a linear function of the intensity ratio I_i/I_s.

The internal standard method can be applied to materials like alumina based porcelain insulators samples, which contain several mineral phases. However, this method calls for a construction of a calibration curve for each phase. The numbers of calibration curves required are as many phases to be analyzed in the mixture. Suppose, a mixture contains kyanite, andalusite or sillimanite or alternatively bauxites and kaolins all the components in the mixture can be analyzed by adopting the internal standard method. For mullite analysis, synthetic mixture containing 10, 20, 30, 40, 50, 100% mullite in a suitable diluent (Calcium Fluoride) is admixed with Titanium Oxide in a constant proportion x_s=1.0. The intensity ration of the 3.39A° mullite line and the 3.23A° Titanium Oxide is determined. A plot of intensity ratio versus % mullite gives a straight line passing through the origin. After obtaining the calibration curves, the sample (0.5g) has to be mixed with 0.25g of titanium oxide and the intensity rations for each phase have to be determined and the concentration of each phase has to be read from the respective calibration curves.

Important considerations in the choice of an internal standard and diluent are that they should be readily in good purity and of a suitable crystalline size to give sharp diffraction lines near the strong lines of the unknown substance to be determined and that these lines not be superposed by the unknown or by other materials commonly found mixed with the unknown.

8.0 EXPERIMENTAL

8.1 Apparatus

A Philips PANalytical™, X'pert PRO X-ray diffractometer having copper X-ray tube operated at 40KV and 30mA was used for obtaining the diffraction patterns. The optical system contained 1° divergence slit and 2° antiscatter slit in the primary side (incident beam) 0.11mm receiving slit in secondary side (diffracted beam). The diffraction patterns were recorded and the speed was 153.2854 sec / ° 2Θ.

FIG. 3 X RAY DIFFRACTOMETER

9.0 CALIBRATION CURVE FOR MULLITE ANALYSIS

The standard series of mixtures for the calibration curve were made from fine mullite and diluent calcium fluoride powders. The mixtures were prepared in 3.0 g proportions representing 10, 20, 30, 40, 50 and 100% mullite in them. To each of these mixtures an internal standard Titanium Oxide was added in a constant proportion of 1.0 g. To achieve the above proportion suitable quantity of fine diluent (calcium flouride) was added. These mixtures were then homogenized in a mortar and pestle by thoroughly mixing in acetone medium for about one hour. Each of these mixtures was scanned over the range 25 °2Θ to 28 °2Θ under the measurement conditions given in below. The XRD patterns of the mixtures were recorded. The intensities in counts per sec of mullite line at 3.39 A° and that of titanium oxide at 3.23 A° were measured and corrected to background. Intensity data for mullite and Titanium Oxide lines of the mixtures is given below.

The calibration curve is obtained by plotting I Mullite / I Ti O_2 against % Mullite Where I Mullite is the intensity of Mullite and I TiO_2 is that of Titanium Oxide. Calibration curve is shown in Figure 5.

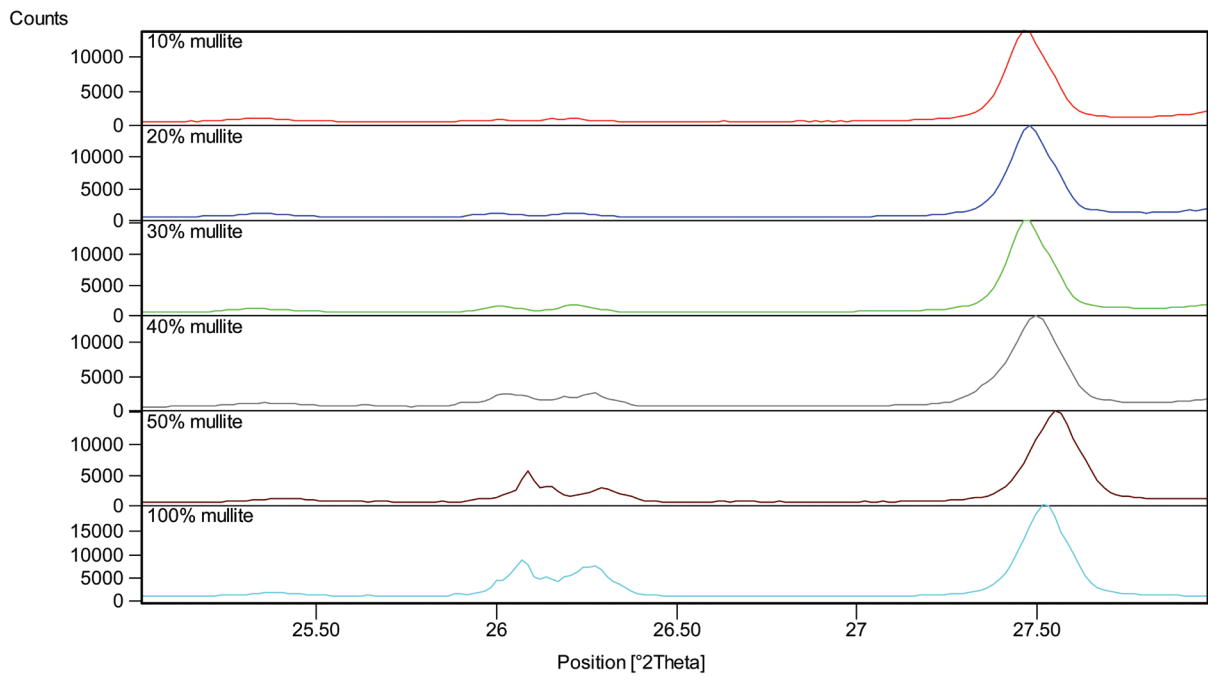

FIG. 4 X-RAY DIFFRACTION TRACES OF CALIBRATION RUNS FOR MULLITE ANALYSIS

TABLE 2

XRD DATA FOR CALIBRATION CURVE

Sl.No	Weight in g			Mullite %	I_O	$I_{Ti O2}$	Ratio $I_O / I_{Ti O2}$
	Mullite	$Ca F_2$	$Ti O_2$				
1	2.0	--	1.0	100	6178.28	19324.26	0.31976
2	1.0	1.0	1.0	50	2324.63	14526.64	0.16005
3	0.8	1.2	1.0	40	1328.35	14759.46	0.13559
4	0.6	1.4	1.0	30	1763.50	13005.22	0.08999
5	0.4	1.6	1.0	20	770.22	12837.03	0.05999
6	0.2	1.8	1.0	10	469.52	13155.15	0.03569

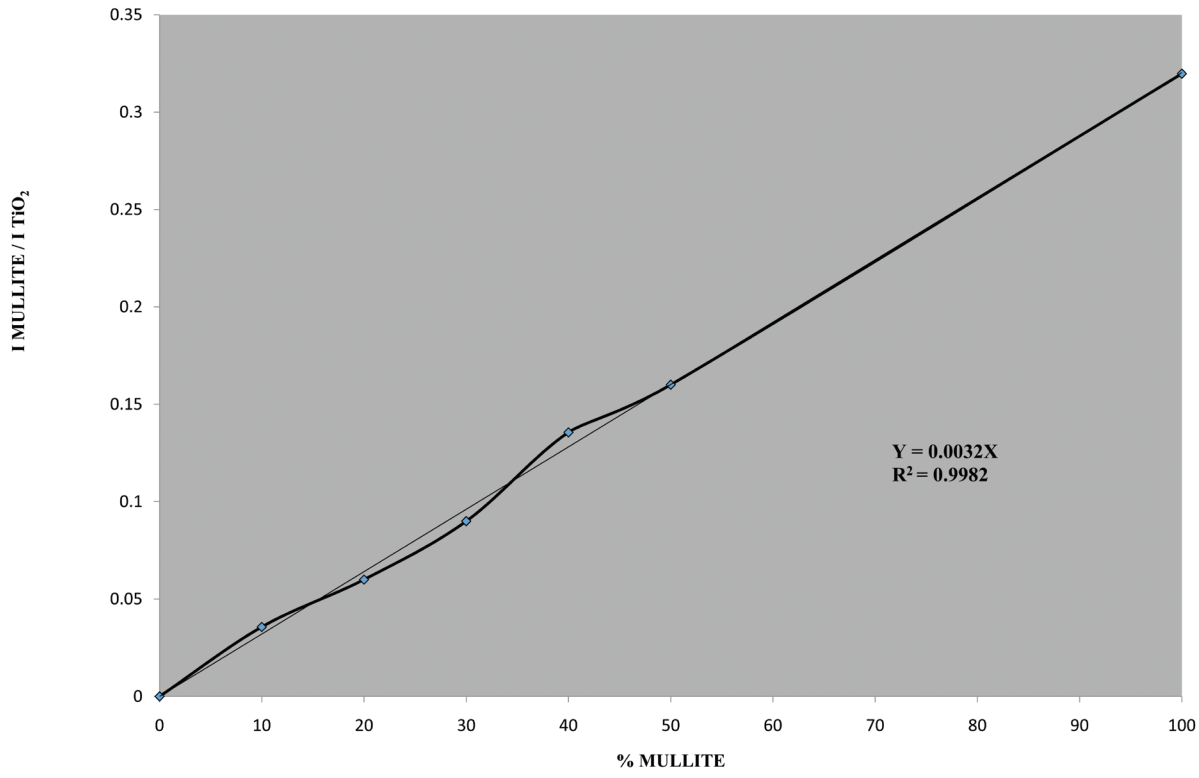

FIG. 5 MULLITE CALIBRATION CURVE

10.0 ANALYSIS OF MULLITE IN ALUMINA BASED PORCELAIN INSULATORS SAMPLES

10.1 Insulator sample preparation

Sample cut from the central part of the sample provided (without glaze) was thoroughly cleaned in acetone medium in an ultrasonic cleaning chamber and crushed into fine powder in a pestle mortar and used for quantitative phase analysis.

10.2 Mullite determination

0.50g of finely ground insulator sample was taken in a mortar pestle. 0.25 g titanium oxide was added to the insulator sample and mixed. The mixture was ground for about 60 min in acetone medium. The well homogenized dry mixture was loaded onto a sample holder. The sample was scanned over the range 25 to 28°2Θ under the instrument measurement conditions given and the diffraction patterns were recorded. The intensity of mullite line 3.39 A° and Titanium Oxide 3.23 A° were measured. The corrected intensities in counts per sec were used for calibration of % mullite. The % mullite can be read from the calibration curve using the intensity ratio of mullite to titanium oxide lines. It can also be computed by the calibration equation,

$$\% \text{ Mullite} = (I_{O} / I_{Ti O2}) / 0.0032 \quad \ldots.(9)$$

Where I_O stands for the intensity of mullite line and $I_{Ti O2}$ stands for the intensity of titanium oxide.

The variation of mullite content in alumina based iorcelaininsulators samples are depicted in Figure 6. Table 3 also gives the calculated % mullite in alumina based porcelain insulators.

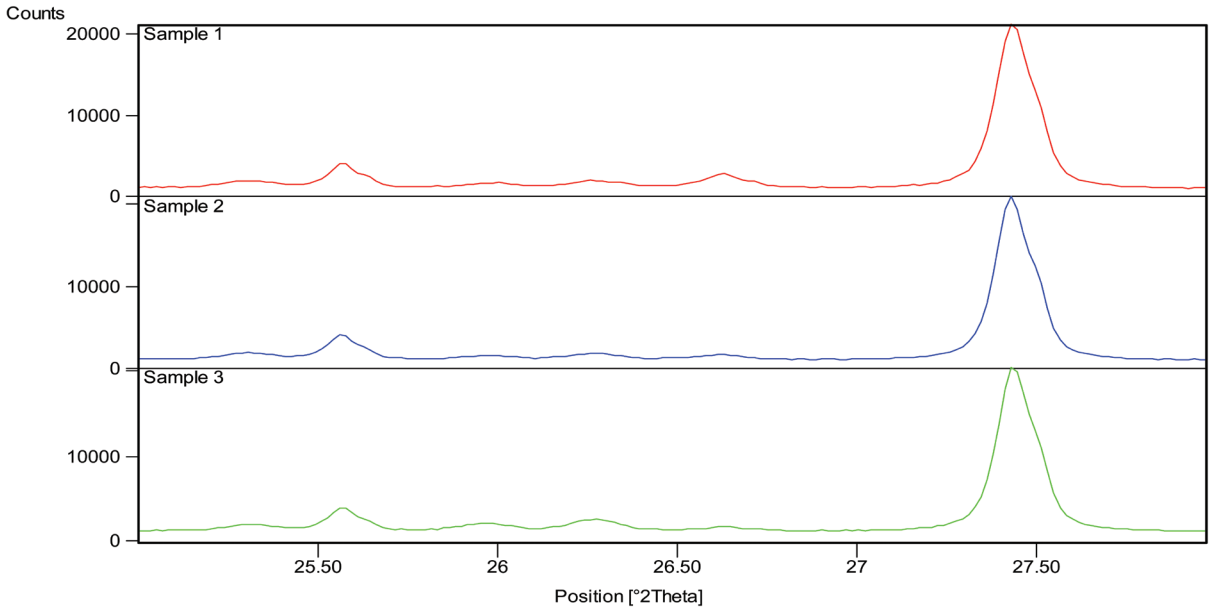

FIG. 6 VARIATION OF MULLITE IN ALUMINA BASED PORCELAIN INSULATORS SAMPLES

TABLE 3

MULLITE IN ALUMINA BASED PORCELAIN INSULATORS SAMPLES

Sl.No	Calibration slope	$I_{O\ Mullite}$	$I_{Ti\,O2}$	$I_{O} / I_{Ti\,O2}$	% I_M = $(I_{O} / I_{Ti\,O2}) / 0.0032$
1	0.0032	447.36	18813.22	0.02377	7.48
2	0.0032	458.64	19366.71	0.02368	7.40
3	0.0032	505.15	18943.81	0.02666	8.33
4	0.0032	996.65	19951.52	0.04999	15.62

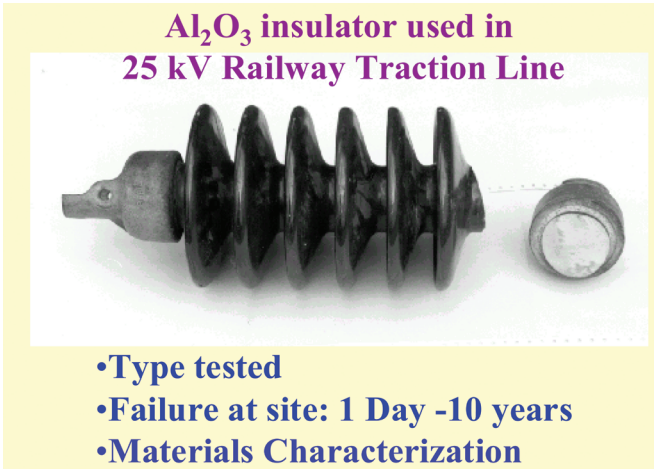

FIG. 7 A SEM MICROSTRUCTURE OF

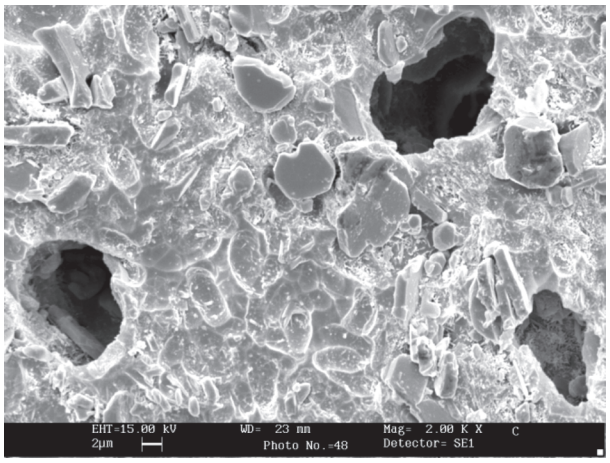

FIG. 7 B FAILED PORCELAIN FAILED INSULATOR

Based on the results, it has been found that sample 1, 2 and 3 have optimum mullite content, which reflects the good quality of the insulators, whereas sample 4 have high mullite concentrations, which might have been instrumental in the failure of the insulator. The SEM microstructure of sample 4 (failed insulator) is given in Figure 7a and macro picture of a sample of a failed alumina based porcelain insulator is shown in Figure 7b. The mullite content in alumina based porcelain insulator samples are given in Table 4.

TABLE 4

% MULLITE IN SAMPLES

Conducted samples	% Mullite
Sample 1	7.48
Sample 2	7.40
Sample 3	8.33
Sample 4	15.62

11.0 CONCLUSIONS

a. Titanium oxide has been used as the internal standard and calcium Fluoride has been used as the diluent in the study.

b. The calibration curve based on I_m/ I_{TiO2} found to be following a straight line tend as can be seen from the plot. The unknown mullite content has been successfully quantified in the alumina based porcelain insulators with the intensities observed from the XRD data and interpreting them with calibration curve. The variation is justified with interpreting them with the calibration curve and with scanning electron microscope analysis.

c. The method has been successfully used in benchmarking the alumina based porcelain insulators.

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