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THE COMPARATIVE ANALYSIS OF CHANGE IN OPTICAL PROPERTY WITH CALCINATION TEMPERATURE IN CE DOPED AL_2O_3 NANOSTUFF

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ABSTRACT

Background: Nanoparticles are specialized particles that exhibit less predictable optical, chemical as well as physical properties, there is a constant change in its property as it reaches the atomic scale levels **[1]**.

Methods: For the scope of this research, Cerium is doped with Al_2O_3 to create a Nanoparticle. The formed calcined samples were under analysis at separate temperature conditions **[2]** and various characterization techniques were carefully analyzed. The levels of temperature considered for the analysis scope were 200ºC, 400ºC and 600ºC **[3]**. The concentration considered in Al_2O_3 for Cerium dopant was 20%. This was a practical study involving deployment of characterization techniques, i.e. P-XRD diffraction, UV visible, Fourier transformation IR technique, TEM/SEM techniques. With P-XRD spectroscopy, the resultant sample provided key insights on Al atom with doping of CeO_2. The crystalline size (~30.95 nm) of the Nanoparticle using this technique was derived using Debye Scherer method **[4]**.

Results: A clear observation during the analysis was revealed, according to which the Nanoparticle grain size was constantly reduced as temperature levels were elevated **[5]**. Deeper analysis revealed that an increased lattice strain on the calcined sample caused dislocation of the atom structure which resulted in realignment of bonding between Al_2O_3 atom and Ce atom **[6]**. The trend was confirmed by FTIR graphs where metal oxide material and moiety were present at relative positions in the synthesized samples. Similar conditions in the UV visible spectrum showed that a gradual increase in temperature levels increased wavelength, causing energy levels to drop, the phenomenon is known as a redshift pattern **[7]** where there is a constant change in insulating property to di-electric behavior for the Nanoparticle **[8]**. UV visible analysis also depicted an abrupt absorption peak in the spectrum at 200nm wavelength which confirmed formation of Nanoparticle. It was also observed that elevated levels of temperature caused rightward shift of the wavelength in optical band gap thereby showing a diminishing conducting property **[9]**. In the TEM analysis, a surface investigation **[10]** of Ce doped Al_2O_3 Nanoparticle in the calcined sample showed a uniform size and spherical shape of the Nanoparticle.

Conclusion: Nanocomposite material was formed with P-XRD, FTIR, TEM, SEM and UV methods with a constant dopant concentration at different temperature levels and vice versa.

Keywords: Nanoparticle composites, P-XRD, FTIR, TEM, UV, Nanostructure

I. INTRODUCTION:

The metal oxides of Aluminum that contain different concentrations of Cerium oxide are referred to as Alumoxidalopoates **[11]**. The Ce dopant structure impacts different physical, magnetic, anti-bacterial and anti-polluting properties of Nanoparticles. If the constituents of Al alloy is to be analyzed, it is apparent that Aluminum resides in a free state however this phenomenon is less observed for the fact that there is strong bonding of Aluminum with Silicon, Oxygen and Fluoride particles present in the alloy. There are numerous metals that would provide properties like lightness, better ductility, superior conductivity or high mechanical strength when analyzed in isolation however Aluminum is one of the rarest metals **[12]** that provides all these properties together due to which it is resistant to corrosion, highly recyclable and possess ductile capabilities at scale. Aluminum metal oxides have found numerous applications in the field of biomedical sciences and has seen

Rapid expansion in popularity of this class of materials also owing to its cost effective and viability of further research in this area **[13]**. Aluminum oxide finds numerous use cases in the medical industry, used as a coating material for automobiles, aircrafts; The Gamma-Alumina alloy is commonly used as a catalyst in microsatellite construction, satellites, and space. The Aluminum oxide nanoparticles also possess strong anti-bacterial properties that have gained immense interest in the last 10 years. The rapid growth in semiconductor or magnetic Nanoparticles has been well beyond just a moderate scientific or technical advancement (Paul, 2012), Magnetic or Non-magnetic properties of Nanoparticles was discovered through research into the behavior of Nano-particles during methods deployed in the previous years (Ohno, 2010). There are numerous physical features that greatly impact the Nanoparticle composition and includes aspects such as chemical composition, physical grain limits due to differing concentrations, varying Oxygen composition, etc. These aspects actually give rise to many opportunities when exploring the Nanoparticle composition and that has been the point of discovery in this research. The magnetic and electronic properties of Nano-particles have got it a lot of attention in the yesteryears. Nano-particles are used in a numerous ways for lab experimentation, procedures, Bio imaging as magnetic beads and as electrodes, electrophoresis ology and endocrinology (Manna *et al*., - 2008 and Layek & Verma- 2016, Nano *et al*. 2012). Comparatively, the chemical processes for Nano particles are less complex when compared with other types. For the scope of this research work, Cerium oxide solution was co-precipitated with Aluminum oxide at a 20% concentration level and the chemical properties were analyzed at different temperature levels. A co-processing technique would have taken more time but have yielded the same result and hence this method was preferred. The primary aim of this study was to build on existing knowledge and discover newer properties of Nano particles. Due to its regenerative properties, Cerium oxides tend to exhibit antioxidant properties. During redox (cycling) reaction, an oxidized form is generated along with the 4 + 3 oxidation state. In this research, the use of Germanium oxide in medical applications has been investigated where it was found that wherever varying oxygen levels was an effective measure of treating diseases, Cerium oxide played a key role. Cerium is one of the metals that belong to the rare earth metals group which has characteristics like silver shining, silky & elastic nature, and softness, ductile, etc. 58 is the atomic number of this element where it has an optimal state along with four other oxidation states. Since it is a rare earth metal, it has a limited industrial significance however de-acidification properties of Cerium oxide improve its significance for medical use by humans without any significant biomedical effects on the body. The other variant known as Cerium nitrate **[14]** works as an effective antimicrobial agent however there is still significant research required in the area to estimate how it can prove to be one of the effective measures of fighting against the disease-causing bacteria. A recent study **[15]** on concentrated Cerium nitrate and Aluminum nitrate indicated that Cerium (III) Oxide (CN) Nano (organic compound) precipitation can be formed using the laic acid process (inorganic amine base). This process showed significant removal of Phosphorous metals from the water samples consisting of varying purity levels. Moreover the Nano-manufacturing method is environmentally friendly and more cost effective. Considering an example of Phosphorous Impurities removal, an effective method would be by forming a Nanoparticle that in most sense is distinct in terms of varying components. Aluminum dioxide, as an example, would be expected to act as an alkaline adj. & manganese complex bi-reducing bimetallic Oxides would accumulate impurities involving Aluminum, as already proven before (mulligan *et al* -2001). Nano crystalline matter most likely find use in applications where thermal expansion is required due to which Nanoparticle conductivity and electrical resistance become essential properties as well.

II. MATERIALS AND METHODS:

1. **Process of formation of a Nanoparticle where Al_2O_3 doped in Cerium**

   It is important to mention that the chemicals taken for this research work were A.R. grade (99.9% purity as per lab scaling). Himedia was the supplier of 1M of Aluminum nitrate Nona hydrate solution that has the chemical formulae of Al $(NO)_3.9H_2O$ and similarly the Cerium Nitrate hex-hydrate solution was sourced from the same supplier at a concentration level of 0.2M. The chemical formulae for the chemical is Ce $(NO_3)_2.6H_2O$ for the purpose of my experiment.

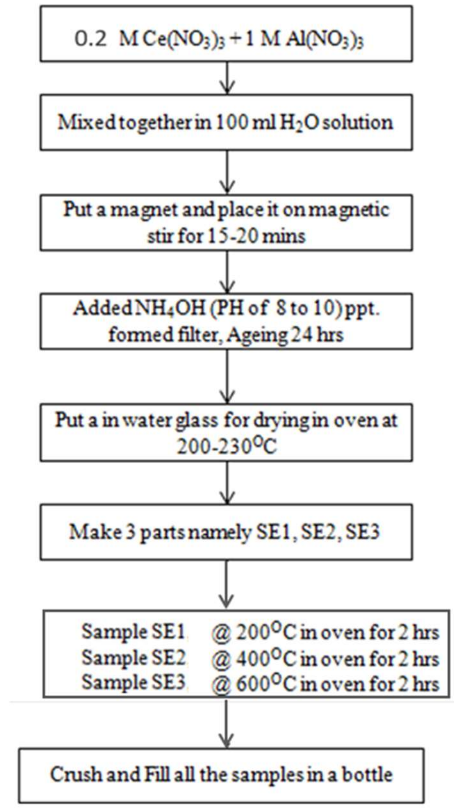


Fig 2.1 Flow chart of synthesis mechanism

The preparation method followed for doping the Aluminum with Cerium oxide was co-precipitation method that included taking 21.3 grams of Aluminum and was doped with 0.2M Cerium nitrate solution ~8.68 grams, with 100 ml dissolution with water and continuously stirring it for a few minutes. It took some time for the mixture to settle and then a magnet was put into the sample for initiating magnetic stirring at controlled temperature for about ~20 minutes to a point where a clear solution is seen. The next step requirement was to provide a slightly basic medium. During precipitation process it was important to ensure that the hydrogen ion must be in the range of 8 to 10 which is a basic medium range. As the formation of precipitate is seen in the mixture, the same was filtered by Whitman filter paper and was left for about a day for getting settled. Once the filtration process was complete, the reaction mixtures was rinsed with a portion of distilled water for additional impurities to be removed, following which it was placed on a watch glass container & then into the oven which was set at $200^{O}C$ to form a dry cake. 3 separate China dishes were taken and the reaction mixture was placed in each of these, a temperature was set up at $200^{O}C$, $400^{O}C$ and $600^{O}C$ respectively for 2 hours. These 3 samples, which are hydroscopic in nature were crushed and placed into different sample tubes.

III. RESULTS AND DISCUSSION

3.1 XRD characterization:

As seen in the graph 3.1 below, the grain size of nanoparticle formed by doping Cerium in Aluminum oxide was investigated using P-XRD technique at 20% dopant concentration and the temperature levels are gradually increased from $200^{O}C$, $400^{O}C$ to $600^{O}C$. Due to a significant lattice strain, it was seen that there was a clear dislocation of atomic structure of the nanoparticle, the diffraction peaks were visible and this was majorly attributed to the Aluminum atom, that consolidated at the position of Ceria like a CeO_2 the FCC structure according to the standard file JCPDS card no. JCPDS – (00-004-0787) and JCPDS – (00 – 004 – 0787).

Table 3.1 XRD pattern peak concentration & increasing temperature

S. No.	XRD sample	Conc% of dopant	2 hour temperature level	Position (2θ)	FWHM (β)	Grain size
1	XS1	20%	$200^{o}C$	-	0.09	31.211
2	XS2	20%	$400^{o}C$	-	0.09	31.109
3	XS3	20%	$600^{o}C$	28.821	0.09	30.95

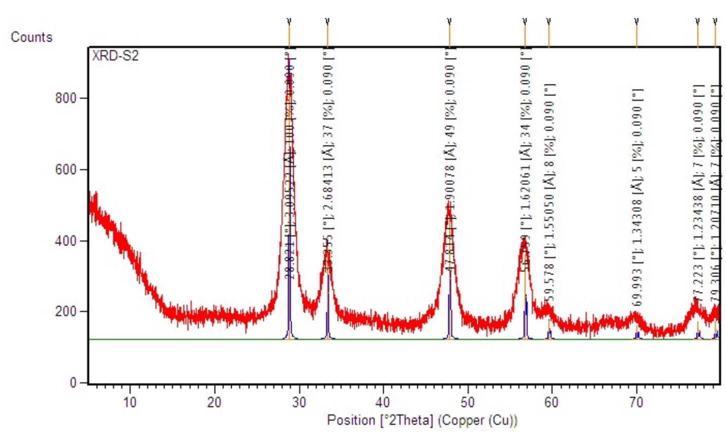


Figure 3.1 XRD of Ce doped Al_2O_3 Nano stuffs

Table 3.2 XRD pattern peak at constant concentration with increasing temperature

S. No.	XRD Sample	Conc% of dopant	2 hour temperature level	Contracting peak 1	Contracting peak 2
1	XS1	20%	200°C	47.691	59.325
2	XS2	20%	400°C	47.814	59.331
3	XS3	20%	600°C	47.937	59.578

On analyzing the results, it is observed that due to transformation of Ce^{2+} ions into Ce^{3+} ions a right shift is seen in the contracting peak and length of bond that exists between the Ce & O ions kept diminishing as well as the size reducing due to higher availability of Ce^{3+} ions as the temperature level is elevated. The phenomenon was clearly confirmed by conducting calculations as per the Debye Scherer method, given below:

$D = k\,\Lambda / \beta \cos\theta$

Where k = shape factor = 0.89

Λ = wavelength = 1.54 A°

β = FWHM = given in the above table

Cosθ = Angle (position) = given in the table

3.2 SEM & TEM study: The study is carefully targeted at deploying different types of characterization techniques to investigate metal oxide formation doped with Nano stuff at varying temperature levels.

Transmission electron microscopy (TEM) analysis technique:

A surface analysis of Al_2O_3 with Cerium Nano stuff in figure 3.2 shows the spectroscopy transmission graphs with/without any Cerium dopant into Al_2O_3. TEM analysis showed that the Nanoparticle had a spherical shape and no material difference was observed before/after doping and those had retained a spherical shape.

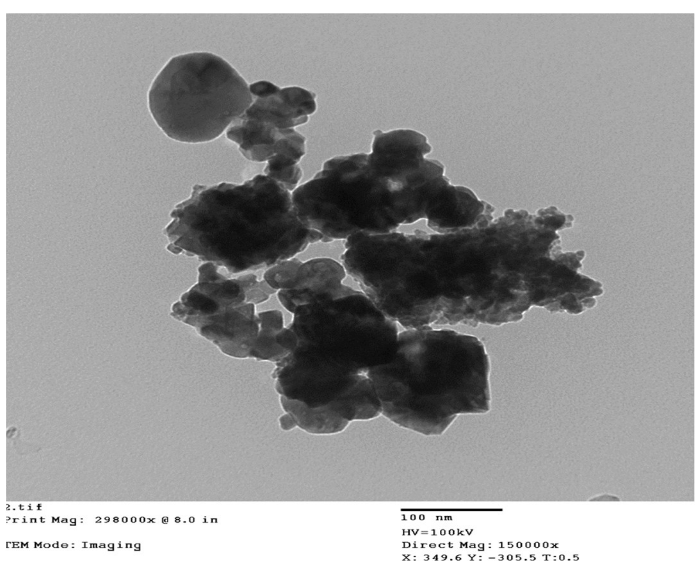


Fig 3.2: TEM-1 spectroscopy Ce (20% doped Al_2O_3)

Scanning electron microscopy (SEM): SEM technique produced a desired result where $Al_2O_3.CeO_2$ Nano stuff was calcined at 200^OC temperature for 2. It was seen that the Nanoparticle's exhibited a size uniformity, spherical & symmetrical shaped and cluttered in macro-form. Given below figure SEM-1.

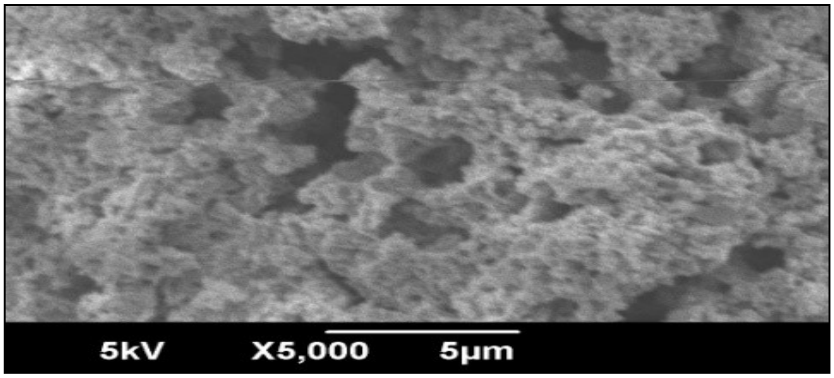


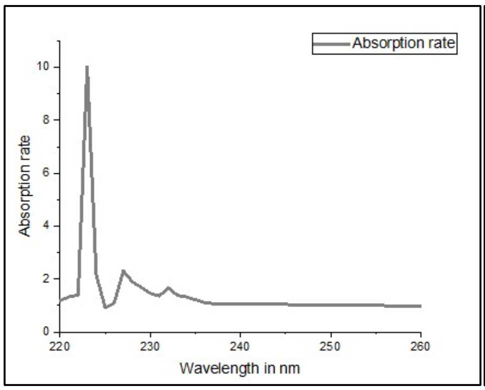
Fig 3.3: SEM-1 spectroscopy Ce (20% doped Al2O3)

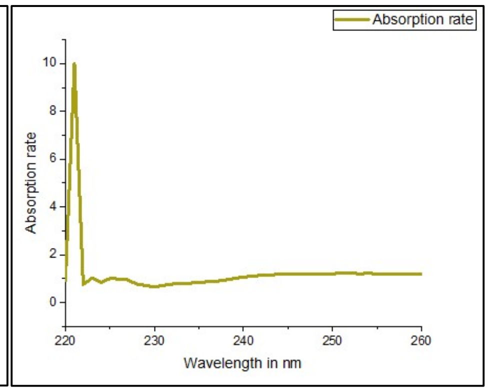
3.3 UV-VIS absorption spectrum analysis:
A scale of 200-1200nm was considered to analyze the spectroscopic results for the sample after disseminating it through UV screening in its absolute form after mixing ethanol and forming a homogeneous mixture. A cubic shaped sample holder was considered for the process & ensure the ethanol purity to its highest levels. The graph plots generated largely depend on the data of the Nano samples that depict the adsorption level for the Ce doped Al_2O_3 specimen. The calcination was conducted for 2 hours at a constant concentration of 20% and increasing temperature of 200ºC, 400ºC, 600ºC. The analysis results are depicted in the below table.

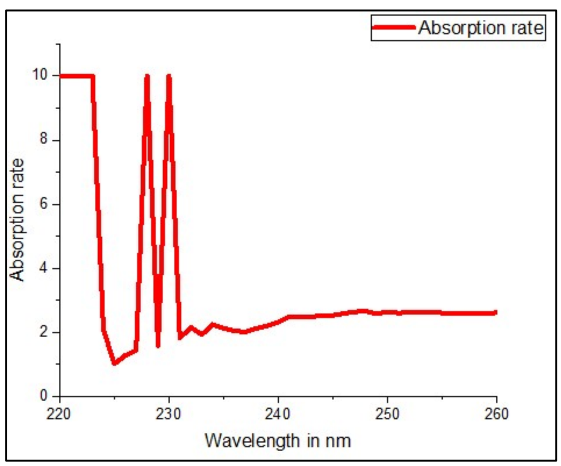
Table 3.3 UV visible spectra data of wavelength with change in Temp.

S. No.	At a constant Conc. 20% with raising temperature in ºC	Wavelength in nm	E = 1240/ λ (Energy)
SU1	200	231	5.367
SU2	400	222	5.585
SU3	600	233	5.321

The band edges of a metal oxide nanoparticle usually fall between range of 100-400nm and in the experimentation stage it came out to be around 233 nm which clearly depicted a UV visible spectrum data of λ (wavelength) with varying temperature of dopant material at constant conc. The same is taken as 200ºC, 400ºC and 600ºC vis-à-vis wavelength values of 231, 222 and 233 nm respectively as also depicted in the table 3.3. Formation of nanoparticle is clearly confirmed for these values. There is also a change in insulator to dielectric behavior seen for the nanoparticle formation. Moreover as the temperature level is increased, there is a clear decrease in energy band gap levels showing a well-known UV pattern known as Red shift pattern that is considered as a bathochromic shift with values depicted as 5.367, 5.585 and 5.321 respectively against the given temperature range values. A second review of UV spectrum stated that at the maximum value of lambda there is an advancing shift towards the right thereby confirming a shrink in the optical band gap and increased conducting behavior of Nanoparticle during calcination procedure.







3.4 Fourier transform infrared spectroscopy (FTIR)

A popular technique for analysis of Ce doped Al_2O_3 to substantiate the functional composition changes was FTIR where at a 20% concentration and different temperature levels for calcination i.e. 200ºC, 400ºC and 600ºC respectively were considered. The time period considered for this analysis is 2 hours and Perkin Elmer instrumentation that is at SAIF, PU and Chandigarh facility was leveraged to produce these results In fig-3.4, the Fourier transformation peaks of Ce doped Al_2O_3 at different levels of temperature can be seen, for sample FS1, different FTIR peaks can clearly be seen at: 3913.3, 3780.1, 3321.1, 2094.8, 1764, 1628.9, 1579.2, 1383.9, 1163.1, 1069.7, 1885.3 and 786.6 cm^{-1}. A 400-1200 cm^{-1} FTIR range is observed. The broad point of peak is seen at the level of 1063.1 $cm^{-1}$and another sharp peak can be seen at 1069.7 cm^{-1}. It hence confirms that an Al $(OH)_3$ group is present with a strong Al-O-O-H bond. The position wavelength at 885.3, indicates strong bonding of C-O bond due to presence of CeO_2 and Ce_2O_3 Nano particles. The graph 3.4 below shows these results

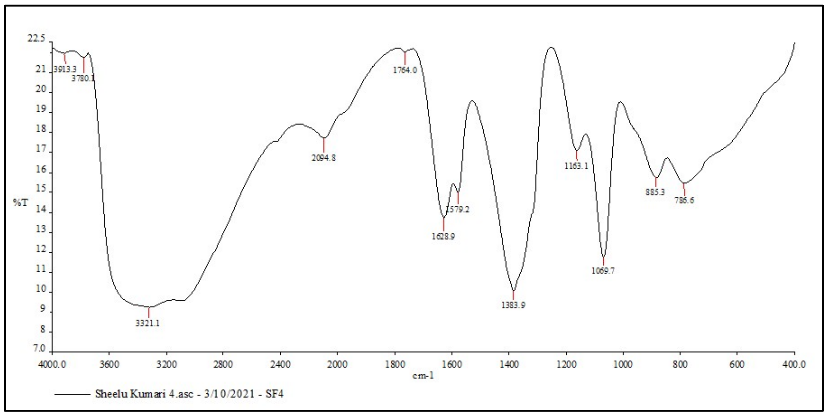


Fig 3.4: FTIR spectrum for Nano experimental sample for FS1

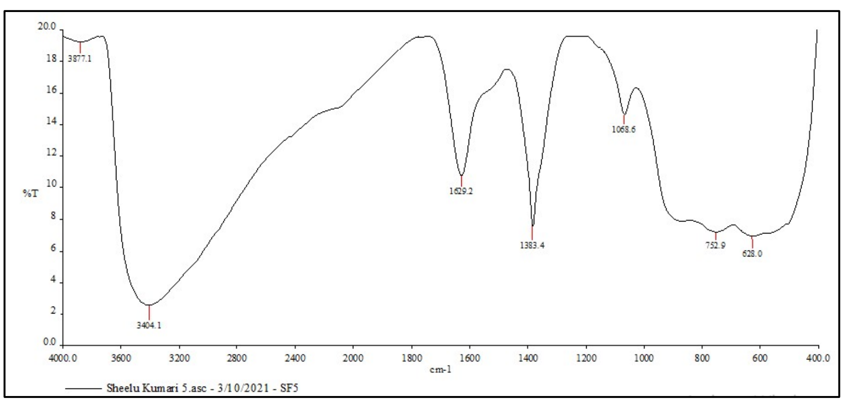


Fig 3.5 FTIR spectrum for Nano experimental sample for FS2

At 400ºC and 20% concentration, different FTIR peaks can clearly be seen at: 3877.1, 3404.1, 1629.2, 1383.4, 1068.6, 752.9 and 628 cm-1. In this FTIR spectrum, 1629 position of peak showed a strong presence of γ-Al_2O_3.The result was verified by comparing it with a standard JCPDS file ISSN-C2344-2344, [Unics (2020) 26:5747-5756] and RSC.Adv-2019, 9, 7388-7399. Further, at 1068.6 position a strong bonding structure, i.e.

Aluminum with hydroxyl group was also evident. At 752.9 level, a strong C-O bond that depicted CeO_2 was also formed. The peak 628.0 depicted presence Al_2O_3 Nano stuff showing a strong Al-O bond.

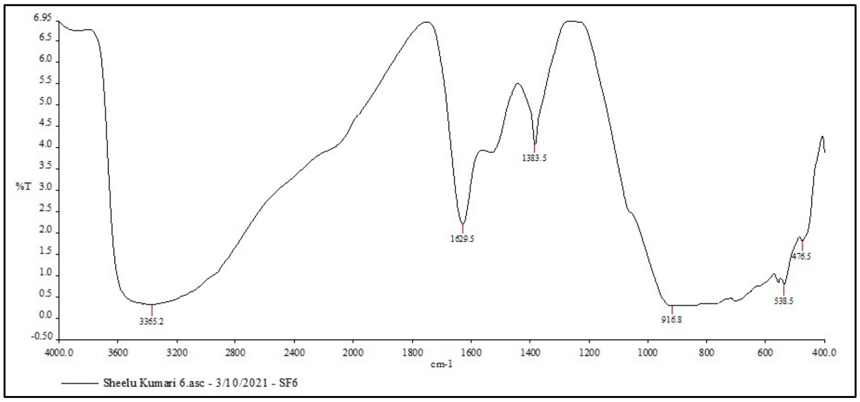


Fig 3.5 FTIR spectrum for Nano experimental sample for FS2

At 600ºC and 20% concentration, different FTIR peaks can clearly be seen at: 3365.2, 1629.5, 1383.5, 916.8, 538.5 and 476.5 cm-1. The 916.8 peak is clearly visible due to presence of γ-Al2O3 available as Nanoparticle metal oxide and the peak 538.5 is also due to the same reason. 476.5 peak indicated availability of Ce-O intense bond structure to formation on nanoparticle (CeO_2).

CONCLUSION:

A reasonable conclusion of this experimental research is that when Al_2O_3 was doped with Cerium, a Nanocomposite material was formed with co-precipitation method. All characterization techniques mentioned in the paper conclude formation of Cerium as well as Aluminum, in the as-synthesized Nano-composite sample. The calcination was conducted at a constant dopant concentration but different temperature levels, confirmed the phenomenon. P-XRD spectra showed a decrease in the grain size with higher temperature level as lattice strain causes assimilation of Al atom in Ceria as Cerium oxide. Various peak positions in FTIR graph also confirmed the formation of Nanoparticle at different peak levels, same was the case with UV-visible spectrum range of 200-400nm that confirms nanoparticle formation. Increasing temperature levels showed red shift pattern, changes from insulating to dielectric behavior, increased optical band gap again confirming the original hypothesis. TEM graphs depicted a uniform and spherically arranged structure of the Nano particle as well.

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