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Studies on HEBM and Sintering Process via Sol-Gel Method on Alumina and Copper Alumina Nanocomposites

P Murali[1], Dr. G V S Sarma[2]

[1] Masters in Nanotechnology, centre for Nanotechnology, Andhra University, AP, India
[2] Assistant Professor in Andhra University, Chemical Engineering, Andhra Pradesh, India

Abstract: **These Nanocomposites are synthesized by Sol-gel process named as Alumina and copper Alumina. They are calcined at 600°C. In this High energy ball milling and High temperature sintering process was introduced for these calcined composites. XRD and SEM images are obtained for them to characterize. After the High Energy Ball Milling process the same samples are sintered at 300°C and obtained XRD and FTIR images to calculate crystalline size and lattice strain (%). The other process via sol-gel was sintered at 1000°C and characterized by XRD and FTIR techniques. The following conclusions were drawn as HEBM is not suitable to form a HEBM is not suitable to form a crystalline phase whereas low temperature sintering after milling is favoured for crystalline phase for both pure Alumina and Copper Alumina Nanocomposites. High temperature sintering is also a possible technique for the formation of pure alumina and copper aluminate nanocomposite $CuAl_2O_4$ spinel form is obtained.**

Keywords: **Sol-Gel method, XRD, SEM, FTIR, Nanocomposites, HEBM, Sintering.**

I. INTRODUCTION

The sol-get method relies on the transformation of a sol obtained from metallic alkoxides or organometallic precursors [4]. This sol which is a solution containing particles in suspension is polymerized at low temperature, in order to form a wet gel. The solvent is removed by drying the gel and therefore the next step is a proper heat treatment.

Some of the advantages of the sol-gel method are its versatility and the possibility to obtain high purity materials, the provision of an easy way for the introduction of trace elements [1], allowance of the synthesis of special materials and energy savings by using low processing temperature. The main advantages of sol-gel method, as compared to traditional methods, are lower processing temperatures [2], control over purity, composition and easy introduction of doping elements.

After the preparation of heterogeneous precursor in the form powder/precipitation from the above methods, there is a need to proceed to get nano composite particles. Then it has to be characterization to know its homogeneity of the product and ensuring the material performance. The characterization methods are done with FT-IR Vibration stretch frequency of metal-oxygen bonds, XRD -Extent of crystallization of the sample, particle size, Lattice strain. SEM Particle shape, size, morphology.

The present investigation is envisaged to generate basic data on the nano composites of Alumina, and Alumina with copper by adopting standard method to study. Synthesization by sol-gel process of alumina and alumina with copper. Preparation of nano particles of the above composites at different speeds to study characters. Characterization of the composites of different combinations by the following methods crystallinity by XRD, surface morphology by SEM, lattice strain%, IR-Bonding.

II. EXPERIMENTAL PROCEDURE

In this process of preparation these nano composites these nanocomposites involves by the following steps a). Precursor prepared by sol-Gel process b). Preparation of powder by ultra grinding with high energy ball mill and sintering c). Characterization of these composites through XRD, FTIR, and SEM. Aluminum nitrates were prepared by mixing calculated portions of copper nitrate and aluminum nitrate with definite amount of citric acid. To prepare alumina and copper alumina through sol-gel process on every combination 100ml ammonia and 20ml ethylene glycol is mixed. The mixed precursors were kept in a beaker and put it on a hot place at 70^{o} C for 10 hours. The obtained materials are calcined at 600^{o} C for 3 hrs, to remove nitrates and unwanted solvents.

The pre-calcined alumina and copper alumina composites are chosen for the ball milling process. One of the prepared composite, alumina composite was milled at 21 hrs and 26hrs whereas the copper alumina composite was milled at 18 hrs in planetary motion. After this, powder sample of the above composites were subjected to the SEM and XRD analysis. The results obtained through XRD and SEM shown that some agglomeration and porosity were noticed. Then, those samples were again calcined at 300^{o} C to vanish the porosity completely and till we get the results properly.

The pre-calcined alumina, copper alumina composites are involved for the sintering process. The sintering process was operated at 1000^{o} C for 6 hours for all the four samples. These composites were characterized through XRD, and FTIR spectra.

III. RESULT & DISCUSSIONS

Experiments were carried out to prepare composites of Alumina, copper substituted alumina and characterizing them by adopting various available techniques such as XRD, FTIR etc. In this connection, so many steps have to be taken to study the Crystallinity, lattice strain per cent and IR absorbance of the prepared nano composites, and preparation of precursor by sol-gel, powdering them by high energy ball milling(HEBM) , calcination and sintering process to avoid porosity and agglomeration. The work done for this project has been divided into two sections. First section consists of the general observations on the Sol-Gel process for the composites and calcination process. Second section deals with the synthesis of nanocomposites by HEBM, sintering process and characterization of nanocomposites through the properties such as Crystallinity, lattice strain and IR absorbency by adopting the techniques XRD, SEM and FTIR.

Section -1:

General Observations:

The dissolution with Ethylene glycol: citric acid (EG:CA) and inorganic metal salts with low temperatures makes the precursor powders predominantly a mixture of homogeneously distributed metal oxides is an intermediate single phase compound with stoichiometry of the metal ions. The viscosity of the solution drastically increases during the polymer chain augmentation. The nature of the cations affect the rate of viscosity increases, which indicates that metal ions play an important role in cross-linking the polymer chains by means of complex formation. During the first stage of the polymer growth in the solution it provides necessary environment to prevent cation segregation, and later relatively rigid polymer network traps cation preserves the initial homogeneity of the solution.

Citric acid is well soluble in Ethylene Glycol, which provides a wide range of CA:EG ratios with the sol-gel process and makes it possible to tune the conditions of synthesis for each particular system. Chemical interaction between citric acid and Ethylene Glycol with metal nitrates are occurs in the room temperature where the used ammonia is used as a fastest evaporation of vaporizable phases. The solvent removal and the nitrates are decomposed during the low temperature range of decomposition. The gelation, with a slow growth and a particular phase of alumina and copper substituted alumina's are formed during the sol-gel synthesis, he obtained precursors are calcined to remove the Nitrates, particular dissolved solvents and content of the composites, so they are calcined at 600^{o}C for 3 hrs.

Section II:

Studies on ball milling:

The precalcined precursor materials are subjected to the high energy ball milling process to prepare the powders for nano composites of the desired materials.

Ball milling of Alumina:

Alumina copper alumina have been subjected to the grinding process using high energy Ball mill PM-100 for 21 hrs, 26hrs and 18hrs (copper alumina) respectively. Initially, 6 gms of alumina mixed with toluene, is milled in high energy ball mill PM-100 with a planetary motion with tungsten carbide balls at a weight of 50gms for 21hr at 400 rpm speed at an interval of 15 min for every hour. Powders formed by this process, have been sent to the scanning Microscopic photographs to study the surface morphology through their images. Images obtained from SEM have given below. Magnification of the grain size of the nanocomposite powder has magnified up to the size of 10,000X.

The figures of different timings of high energy ball milling (i.e. 21hrs, 26hrs) SEM images for Alumina with the same magnification. The image of 21hrs milling time shows agglomerated nano-particles of alumina composite. The morphology of the material existed with agglomerations because the material was not calcined after the HERB process.

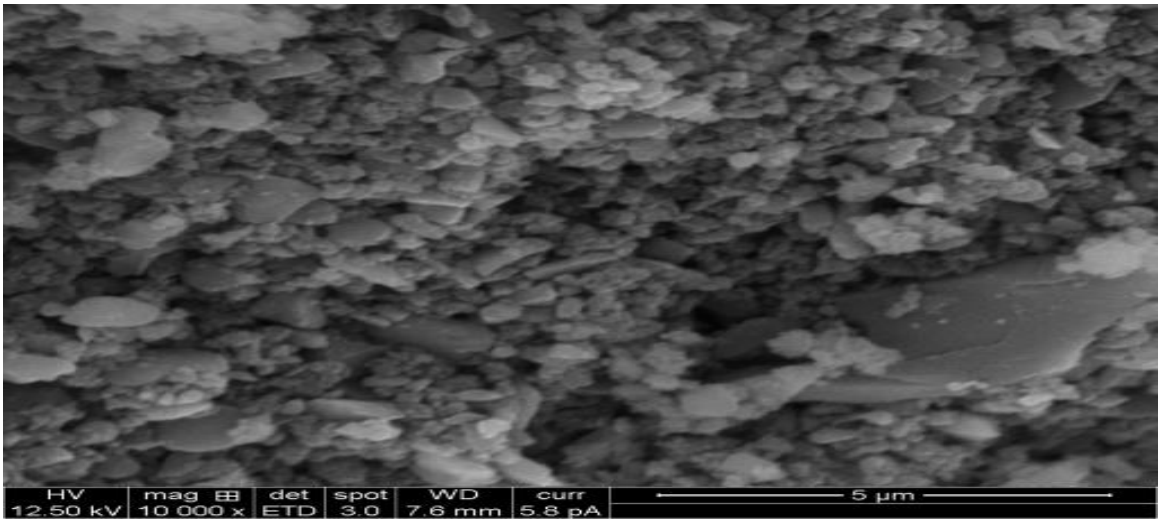

Fig 1.1.a SEM images of Al_2O_3-21 hrs

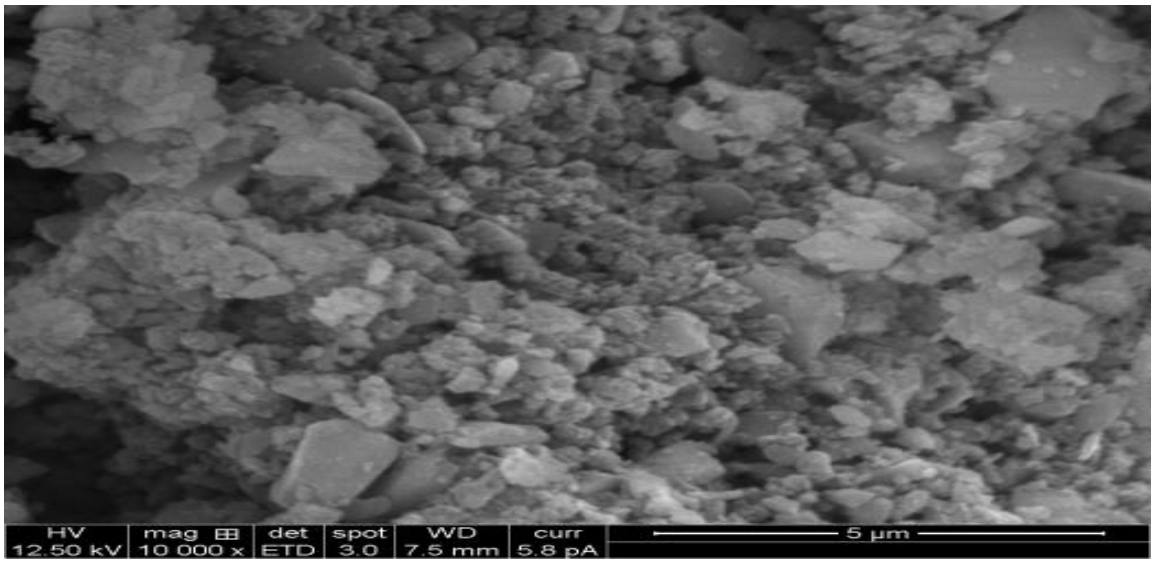

Fig 1.1.b SEM images of Al_2O_3-26 hrs

Ball milling of copper Alumina:

The surface morphology of the CuoAl_2O_3 nanocrystals obtained after 18hrs high energy ball milling was investigated by scanning electron microscopy images. Fig 1.1.c shows that the SEM images of prepared product in the presence of citric acid. SEM image of the product indicates nano crystals are in the agglomerated state as there is no specific development of crystallization.

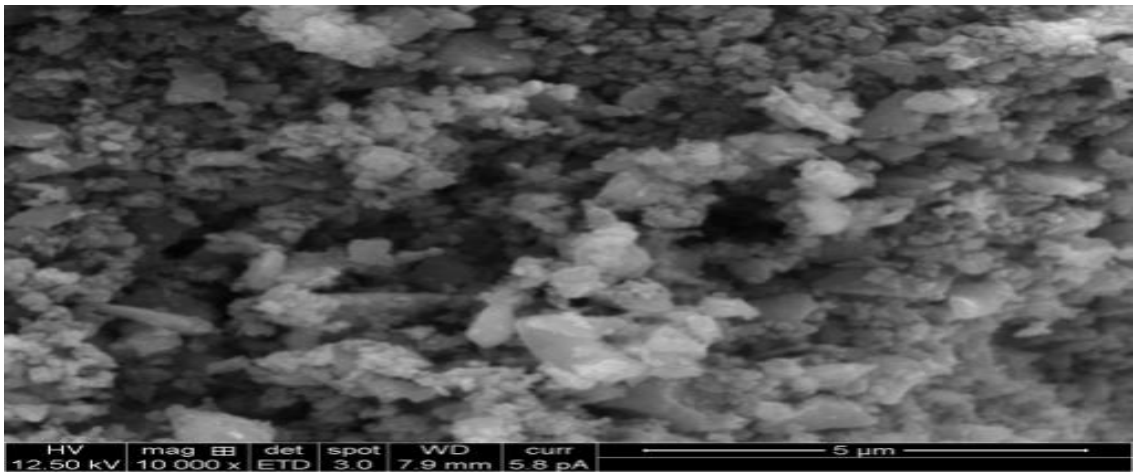

Fig 1.1.c SEM images of Copper Alumina

XRD Analysis of the Alumina and Copper Alumina:

The XRD diffractograms of the SEM images of figures noticed from all the three diffractograms that no crystalline structure has been occurred from the prepared nanocomposites, ball milled at different times. That means no specific peak development has been observed from the diffractograms which support the lack of crystalline in the lattice of the developed composites due to formation of agglomeration among the nanocrystals of the composites.

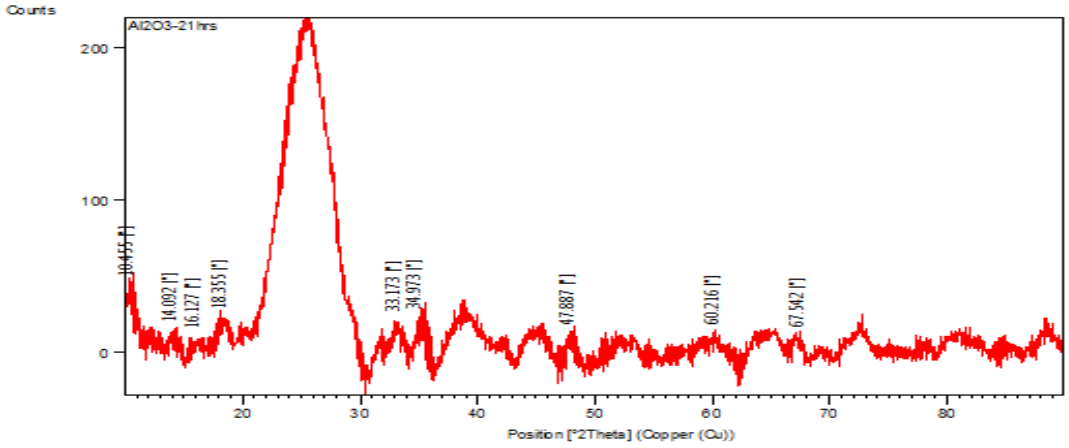

Fig 1.2.a XRD images of Al_2O_3-21 hrs

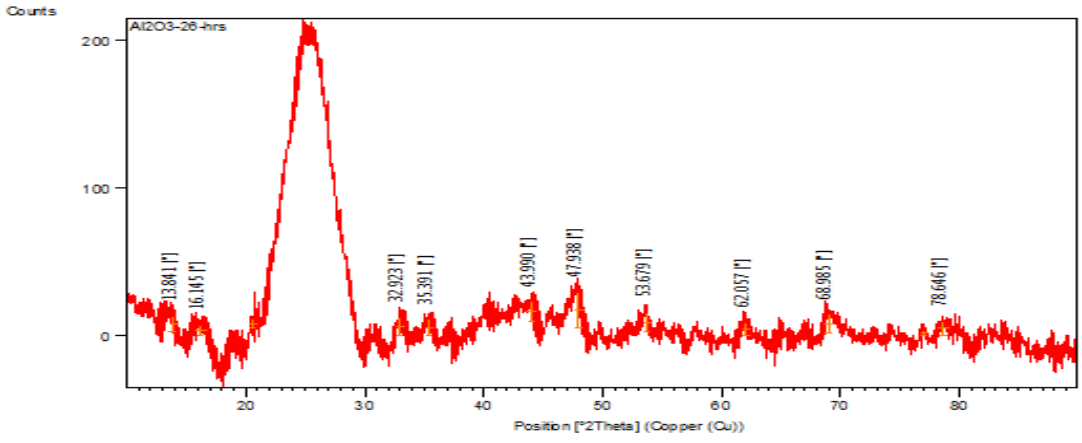

Fig 1.2.b XRD images of Al_2O_3-26 hrs

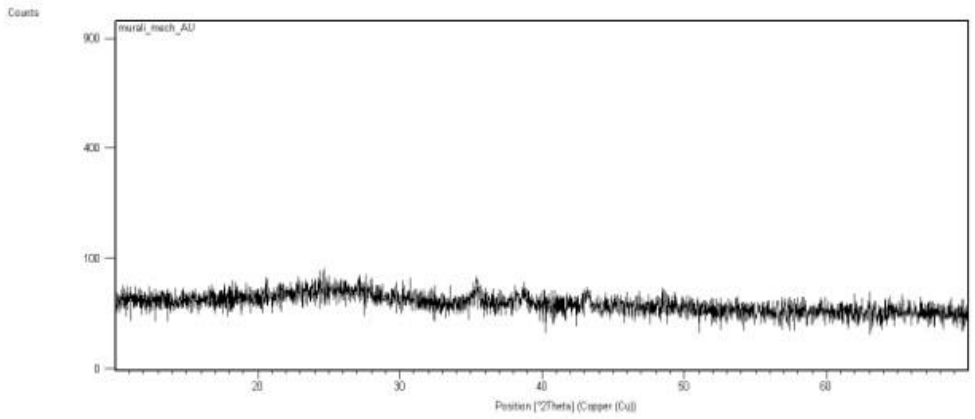

Fig 1.2.c XRD images of Copper Alumina

Ball Milled Al_2O_3 after low temp sintering:

The powder of composite Al_2O_3 after HEBM for 26hrs is subjected and considered to Low Temperature sintering (300ºC) for 2 hours. During the sintering, the colour of the Alumina has been turned into white from black. The black colour of the powder at this temperature shows the existence of organic materials, and also confirmed by XRD pattern so that these compounds have prevented the formation of crystal structure [1] from fig.1.2.b. As shown by the XRD pattern at low at 300ºC, there are broad peaks which are indications of crystallite structure formation and nanosized dimensions [7] have reported the same type of broad peaks of Al_2O_3 at 750ºC due to low temperature sintering has brought down the rate of crystallinity with respect to temperature from fig.2.1.a.

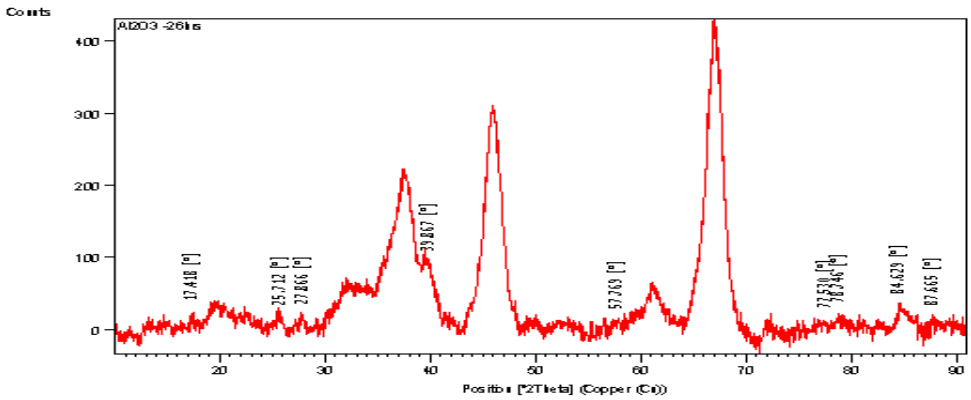

Fig.2.1.a XRD image of Ball mill Al_2O_3-26 hrs after low temp sintering

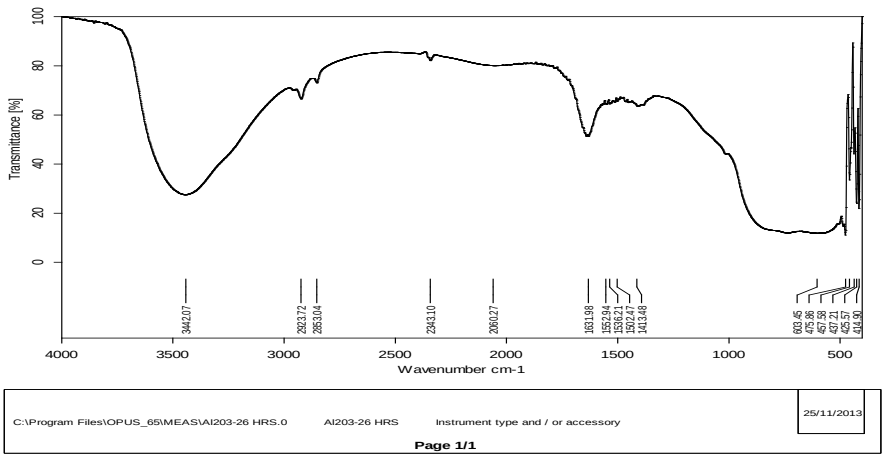

Fig.2.1.b FTIR Spectra 500-4000cm^{-1} of Ball Mill Al_2O_3-26 hrs after Low temp Sintering

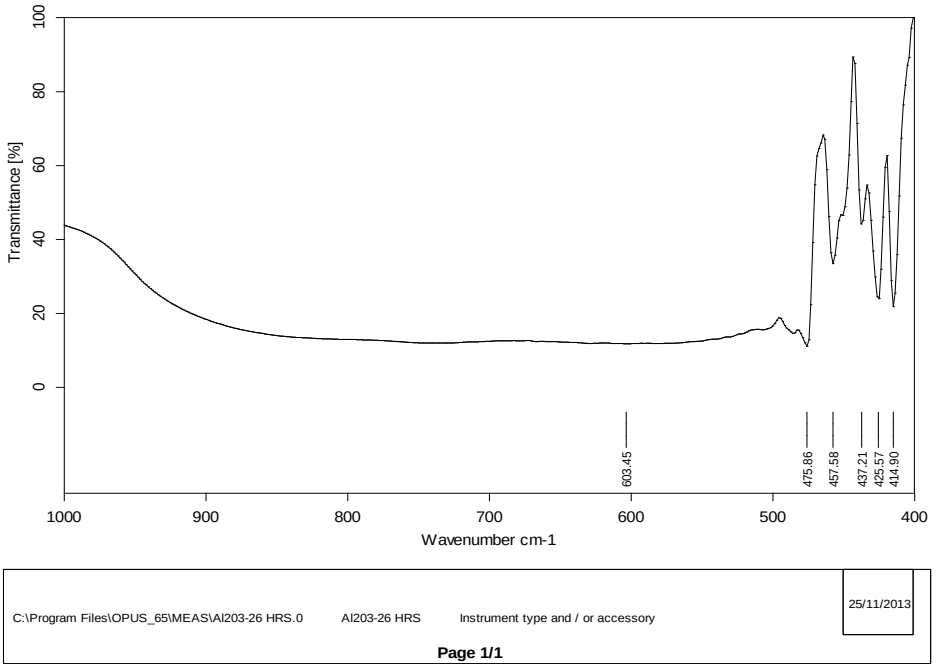

Fig.2.1.c FTIR Spectra 400-1000cm^{-1} of Ball Mill Al_2O_3-26 hrs after Low temp Sintering

It is revealed from the figures 2.1.b & 2.1.c of FTIR spectrum that the sharp absorption peaks is observed at 400 to 600 cm^{-1} for our metal oxide compound which are identified to be the characteristics of absorption bands of alpha Al_2O_3[6].

***Ball Milled CuoAl$_2$O$_3$ after low temp sintering*:**

The powder of composite $CuoAl_2O_3$ after HEBM for 18 hrs is subjected to low temperature sintering (300ºC) for 2 hours. During the sintering, the colour of the copper Alumina composite has been turned into brown from black.

We have done similar work with citric acid and without citric acid calcined at 800ºC done by [4]. Their diffractograms indicate that each sample is nanophasic spinel cubic with lattice sizes of 8.064 Aº. Yanyan et al. Nanocrystalline spinel $CuAl_2O_4$ is formed at high temperature and at the low temperature only CuO and $CuAl_2O_3$ is formed not $CuAl_2O_4$. Our XRD patterns fig.2.2.a, 2.2.b, 2.2.c agrees with their results [4], but our peaks are sharper than the peaks obtained by them. This feature supports the increase in the crystallinity of the composite due to the lower calcined after grinding with HEBM for two hours.

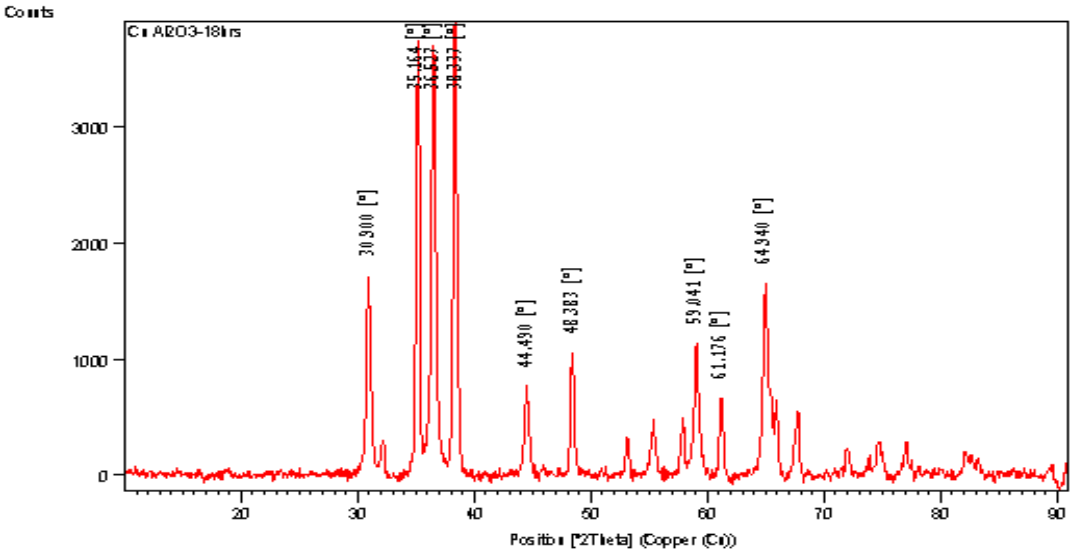

Fig 2.2.a XRD images of CuO Al_2O_3 after low temp Sintering

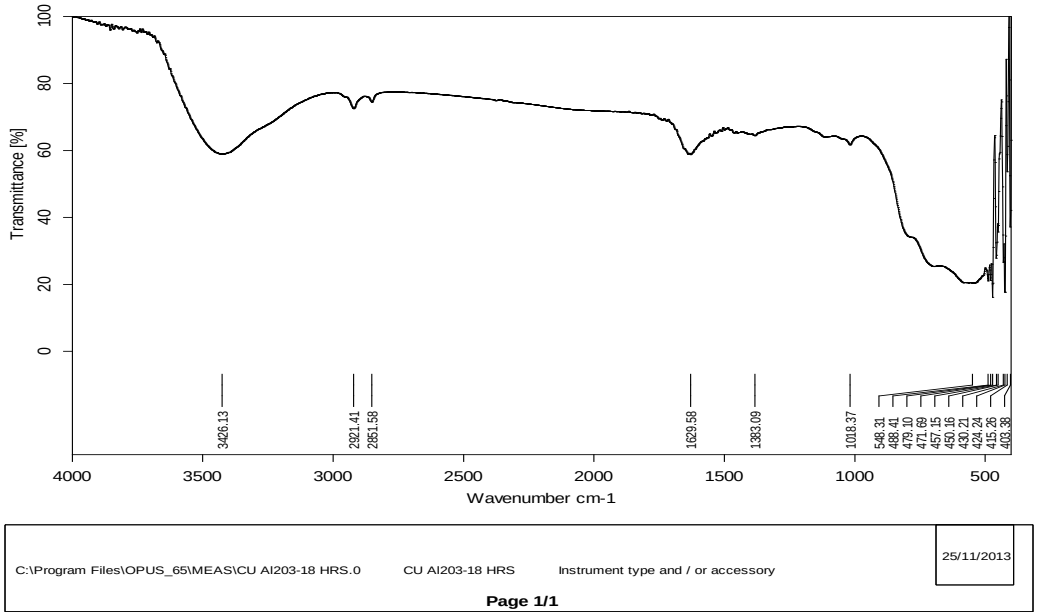

Fig 2.2.b IR Spectra 500-4000cm^{-1} of Ball Mill CuoAl$_2$O$_3$ after Low temp Sintering

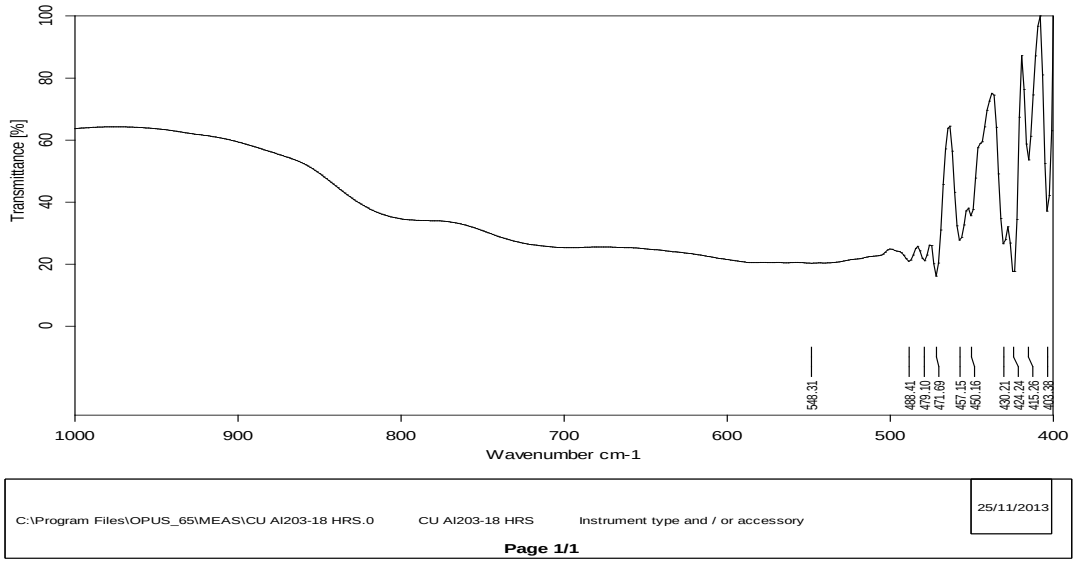

Fig 2.2.c IR Spectra 400-1000cm^{-1} of Ball Mill CuoAl$_2$O$_3$ after Low temp Sintering

The figures represent the FTIR measurements which are used to identify and characterize the resulting spinel nanocrystals. Our FTIR measurement is very much similar to the result obtained by Madoud salavati-Niasari et al [3]. In this case (figures) copper-oxygen stretching frequencies appeared at the range of 400-600 cm^{-1} and associated with the vibrations of Cu-O, Al-O and Cu-O-Al bonds [10, 12]. This supports that the crystal formed might be spinel.

Studies on the High Temperature Sintering process and characterization by XRD and FTIR spectra:

And the preparation of precursor of the nanocomposites by sol-gel process, the precursor is subjected to the calcined process at 600ºC for 3 hours and allowed the same to the sintering at 1000ºC for 6 hours. We obtained the XRD patterns and FTIR measurement for (Alumina, Cu-Alumina) composites to characterize them.

Precalcined Al_2O_3:

The powder of precalcined Al_2O_3 was analyzed for phase analysis using X-ray diffractometer and for Fourier transforms infrared spectroscopy to study the absorbency. The XRD patterns of the sintered Al_2O_3 at 1000ºC temperature is shown in figures which reflect crystalline form of gamma Al_2O_3 with certain level of peak position iterated among FWHM and 2θ position and coincides with the result [1, 11]. They also noticed that the increase of calcinations temperature, crystallinity of gamma Al_2O_3 improved and crystallized in a defective spinel lattice with aluminium located in tetragonal

position. Such a lattice is unstable. The size of crystal grain is 33.3 nm with lattice strain % 0.341 is calculated with the Scherer's calculator.

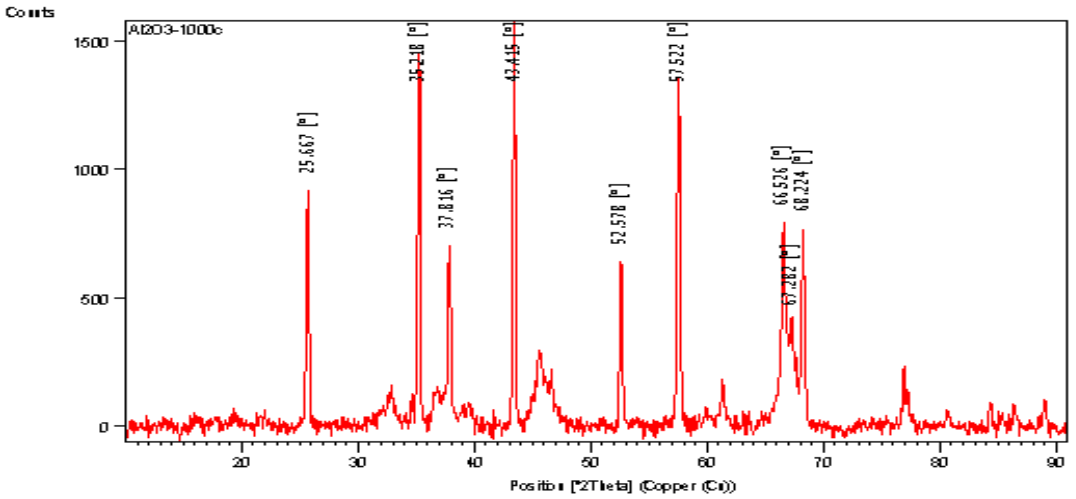

Fig 3.1.a XRD images of Al_2O_3-26 hrs after Sintering

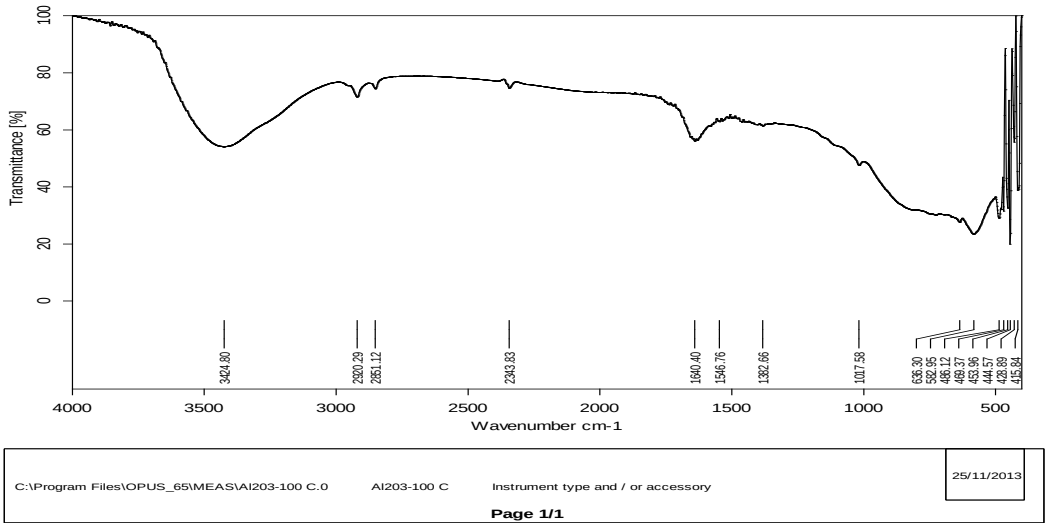

Fig 3.1.b IR Spectra 500-4000cm^{-1} of Al_2O_3-26 hrs after Sintering

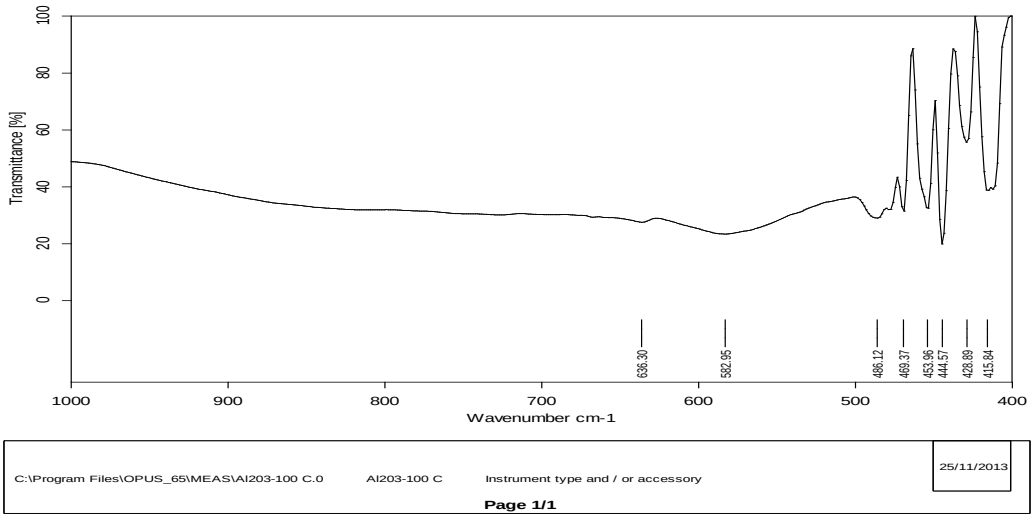

Fig 3.1.c IR Spectra 400-1000cm^{-1} of Al_2O_3-26 hrs after Sintering

When we compare the diffractograms with the low temp sintered XRD pattern shows amorphous. It is supporting that there must be a phase transformation as the temperature increases in the sintering process. IR spectra of the precalcined Al_2O_3 at 1000ºC are shown above fig 3.1.b&3.1.c. It is observed from the spectra that it has four main strong absorption bands at 3400 cm^{-1} band (1), 1595 cm^{-1} and 1540 cm^{-1} band (2), 1394 cm^{-1} band(3) and 620 cm^{-1} band (4), which corresponds to [11] (O-H) and (C-H) and (C=C) and (-CH_3) and (AL-O).

Precalcined Copper Alumina ($CuoAl_2O_3$):

The precalcined copper oxide alumina is sintered at 1000ºC to observe change in its crystalline nature and absorbance. We obtained the XRD patterns and FTIR measurement.

The figure 3.2.1a XRD patterns of the sintered $CuoAl_2O_3$ at 1000ºC with sharp peak heights. These XRD data are compared with the data obtained by [4, 10]. Both are nearly showing the same pattern, support our data information of pure spinel $CuAl_2O_4$ nanopowders at high temperature and at low temperature only CuO is formed not of $CuoAl_2O_3$. Our XRD patterns are also support their results. The average crystalline size of the nanocrystals calculated by XRD data using Scherer's equation is 28.4 nm with lattice strain % of 0.445%

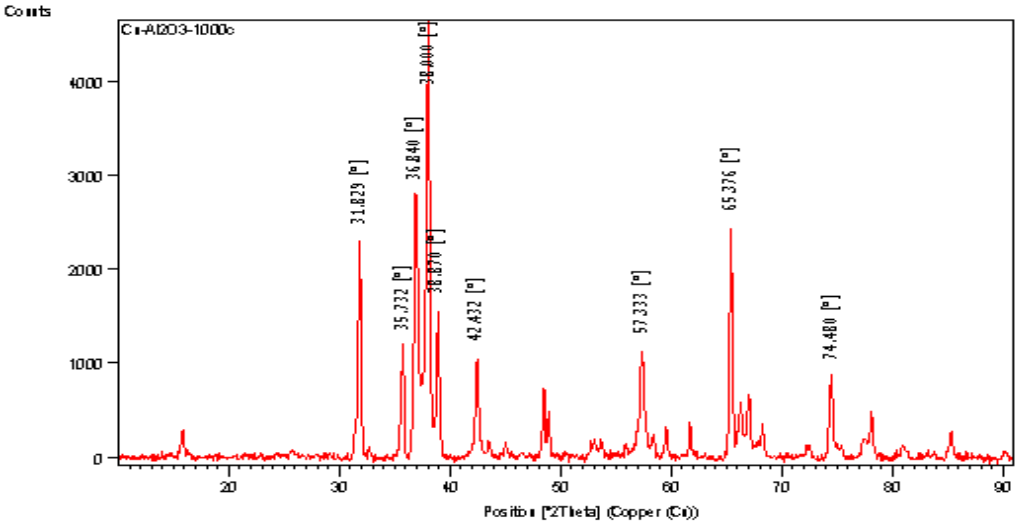

Fig 3.2.a XRD images of precalcined $CuOAl_2O_3$ at 1000^{0}C

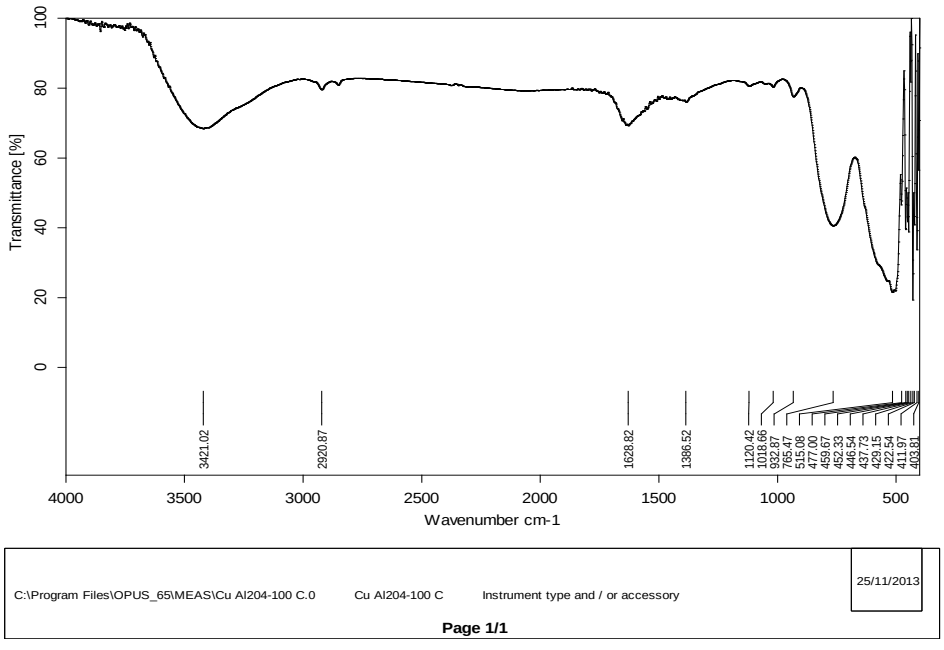

Fig 3.2.b IR Spectra 500-4000cm^{-1} of precalcined $CuOAl_2O_3$ at 1000^{0}C

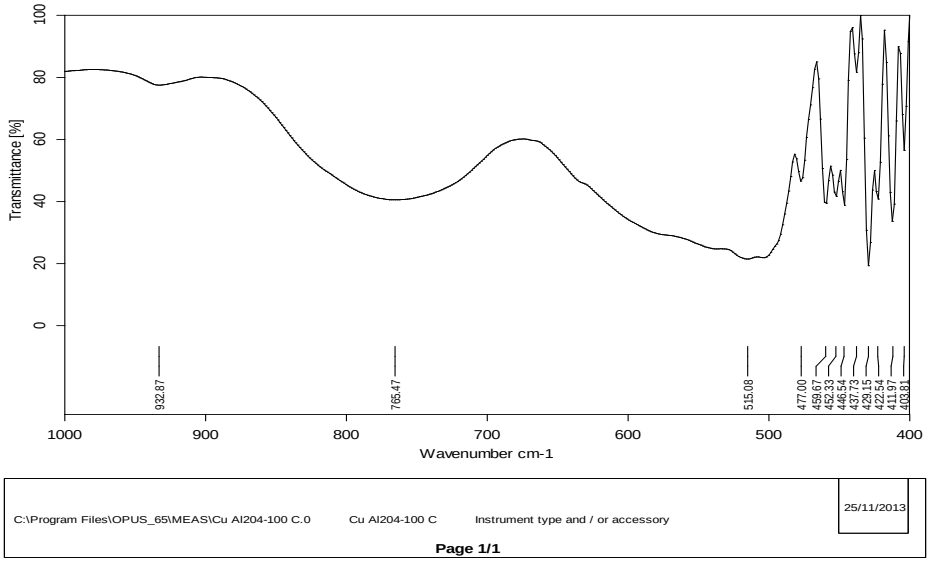

Fig 3.2.c IR Spectra of 400-1000cm^{-1} of precalcined $CuOAl_2O_3$ at 1000^{o}C

Figures are FTIR spectra of $CuAl_2O_4$ nanocrystals prepared with citric acid and calcined at 1000^{o}C. spectra reveals that the absorption peak around 3500-3100 cm^{-1} due to OH longitudinal vibration of water, the absorption peak around 1650cm^{-1} belonging to bending vibration of H-O-H in the water molecule. It is also observed from the figure that the stretching frequencies appeared in the range of 500 to 800 cm^{-1}.

IV. CONCLUSIONS

The Nanocomposites are prepared by Sol-Gel procedure named as Alumina and Copper Alumina. They are calcined to remove the Nitrates. Alumina and Copper Alumina are subjected to high energy ball milling (HEBM) and characterized by X-Ray Diffractometer technique and Scanning Electron Microscope. These two HEBM powders are again sintered at low temperature (300^{o}C). Again, XRD and FTIR data is collected for these two samples. The calcined composites are again sintered at high temperature i.e. 1000^{o}C. And they are characterized through XRD and FTIR. Finally crystalline size and lattice strain % are calculated using Scherer's formula. Based on the above experimental data, XRD Patterns and FTIR spectra, the following conclusions are drawn from the study.

The XRD patterns and SEM photographs of the high energy ball milling of the two nanopowders of Alumina and Copper-Alumina suggested that HEBM is not suitable for characterization of nanomaterials as high agglomeration is formed in both cases. Low temperature sintered samples of Alumina and Copper-Alumina (HEBM) have shown crystalline phase whereas HEBM are not shown any crystallinity. Data on the (XRD & FTIR) for high temperature sintered nanocomposites the following statements a) XRD patterns of Al_2O_3 indicates that the presence of gamma Al_2O_3 with the crystalline size of 33nm with lattice strain % 0.341. FTIR spectra support the presence of bonds: (O-H) and (C-H) and (C=) and (-CH3) and (Al-O).b) XRD patterns of $CuAl_2O_4$ showed that the formation of nanocrystal of $CuAl_2O_4$ with the crystalline size of 28 nm with lattice strain % 0.445. FTIR spectra support the same. The above conclusions are subjected to the range of concentration and ratios of the chemicals used in the present study.

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