Section A-Research paper

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GROWTH MECHANISM AND OPTICAL PROPERTIES OF Bi_2O_3-Al_2O_3 NANO CRYSTALLINE MATERIALS

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Abstract: In the present scenario, the machine size decreases with time spent and price increases with advances. The materials at nano-scale shows peculiar behavior as of their bulk particulates and resulted advanced multifunction properties were adhered by particulates. The type of synthesis techniques and other physical parameters such as calcinations temperature, pH and dilution were responsible for its properties changes and advancements. In present study the Bi_2O_3 doped Al_2O_3 Nano particulates were prepared by microwave-modified co-precipitation method at different calcinations temperature. i.e. 200^{o}C, 400^{o}C and 600^{o}C for fixed duration 2 hours. The calcined powder samples were examined by different instrumentation techniques such as XRD, UV-Vis–NIR spectroscopy, FTIR & HRTEM etc. The XRD study reveals that the particulates are nano-sized in the range 26 nm to 38nm at 200^{o}C to 600^{o}C respectively. The crystallite sizes proved its ascending trend with the rise of calcination temperatures. The IR spectroscopy were deployed to check the functional group present in samples and concluded the purity of samples and the IR- peak at 743cm^{-1}, 744cm^{-1} and 750cm^{-1} at 200^{o}C, 400^{o}C and 600^{o}C for fixed duration 2 hours respectively and were might be due increase of lattice energy to O-Al-O vibrations however an additional peak were observed in samples at 200^{0}C at around 1015cm^{-1} and indicated that Aluminum hydroxide was formed at lower temperature and an addition peak were exhibited at position 484 cm^{-1} and may be attributed by O-Bi-O vibration of Bismuth ion incorporated in Al_2O_3 nano particulates at lattice sites. The UV-Vis spectra concluded at the sharp peak occurred at about 310nm and shows that the particulates were nano in size and optical band gap at 3.6 eV. The FESEM image shows that particulates are truncated spherical in shape and agglomerated in nature.

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Keywords: Bi_2O_3-Al_2O_3 nanoparticulates , XRD, UV Spectroscopy, FTIR & FESEM, HRTEM etc.

1.INTRODUCTION

Nanotechnology and nanosized materials are extensive, interdisciplinary zones that comprehend bio-chemistry, physics, materials science, electronics engineering and many more. The contemporary way will deliver an assessment on a few of the 'ultimate ideologies behind nano-techniques and nano-substances and their vivacious character in different sensing assets and presentations.[1] The course will deliberate attention-grabbing interdisciplinary technical and production acquaintance at the nano-dimensions to understand fundamental physical differences at the nano-sensors.[2] Metal oxide nanomaterials represent a growing asset in many industries, especially with their heightened chemical, physical, and electronic properties compared with their bulk counterparts.[3] Aluminum oxide (Al_2O_3) is a semiconducting material of p-type having variable band gap depending on α,□ γ ,Δ- Al_2O_3 components.[4] Bismuth oxide has been utilized in number of applications from the nineteenth century for the cure/treatment of infections caused by bacteria [5] but its use being less from the mid of the 20th century after the flexible bismuth encephalopathy (viral infection) happened in Australia and France. Nevertheless, bismuth-based medical articulation still being utilized for stomach problems treatments/cure as bismuth subsalicylate, bio-active conjugates, colloidal bismuth sub-citrate etc.[6] Organo-bismuth by-products are not the only collection of huge interest as nano-structured oxides and related substances have attract more attention of the scientific community because of their low-cost fabrication procedure, high versatility and stability in terms of structural analysis[7]. Moreover, the large atomic number of bismuth (Bi) transfers high energy radiation fading higher than that of lead (Pb) at an nearly negotiable danger of toxicity.[8] It is acquired in a highly purified (supreme) form for those implementations where it is utilized as a replacement for lead (Pb). Generally, bismuth(Bi) is utilized in form of oxo-halides, halide, oxides and nitrate derivatives.[9] There are remarks that doping of bismuth with group thirteen elements/materials like as Aluminium (Al) is an efficient way to gain larger thermos-electric activity.[10] Because of their small atomic radius i.e. 135 pm, Aluminum atoms can be interstitially substituted into the Bi-Se-Te layered morphology to generate lattice distortion and brings about a decrement of matrix and electronic thermal conductivity leading to improved thermos-electric characteristics.[11]

2. Synthesis Mechanism of Bismuth Oxide (Bi_2O_3) doped Aluminium Oxide (Al_2O_3) Nanostructured materials

All the starting chemicals used in the present work were of analytical grade(AR grade).The appropriate concentration of bismuth nitrate($Bi(NO_3)_3.5H_2O$ and Aluminum nitrate($Al(NO_3)_3.9H_2O$) (HIMEDIA, India) solution was prepared in 100 ml of de-ionized or doubly distilled water. Then conc. NaOH (sodium hydroxide) solution was poured with stirring

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to the above solution at 25^{o}Cand the resulting mixture was constantly stirred at room temperature (about 25^{o}C) for 2 hours by using magnetic stirrer. Thereafter, the solution is kept for ageing process for 24 hrs. After the completion of reaction, the resulting white precipitates were filtered and washed with de-ionized water and then ethanol (Merck) for several times to remove the by-products or impurities. The filtered cake was dried in air at 100°C for 15 min with 2 sitting in microwave oven. The as-synthesized samples were calcined at different temperature and for fixed time duration of 2 hours in air to obtain Bi_2O_3 doped Al_2O_3 nanostructured materials. The resulted white powder form samples were stored in air tight sample holder and used for further characterization techniques.

3. Characterization Techniques

The Al_2O_3 based nanostructured were analyzed by XRD using a PANalytical X'Pert-Pro powder diffractometer with CuK_{α} radiation (λ=1.5406Å) in the range of 10^0–80^0in SAIF, Punjab University, Chandigarh. The result based morphology of the nanoparticles was studied by HRTEM (JSM-6360 JEOL) and facility was availed at CIL PU, Chandigarh. The electronic band gap energy of nanoparticles were estimated by absorption spectra recorded using Hitachi 330 double beam spectrophotometer. The crystallite size and structural properties of the nanostructured materials were also observed from photograph recorded from Field effect Scanning Electron Microscope (FESEM), Model JSM−6700) at SAIF PU, Chandigarh .Fourier Transform Infra-red spectra were recorded on a Perkin Elmer RX-FTIR Spectrometer.

3.1 X-Ray Diffractometer (XRD) Investigations

Bismuth oxide (Bi_2O_3) incorporated Aluminum oxide nano-particulates were made by using chemical co-precipitation modus of sample preparation. The prepared and calcined samples were studied with the help of diffraction by X-Ray's to know about the crystalline nature of the samples and the size of nano-powder grains. The XRD study was done by use of Time Per Step 57.3 instrument available at SAIF, PU Chandigarh. The obtained data was used to determine the grain size that was calculated by using origin software and shown in below table 1.

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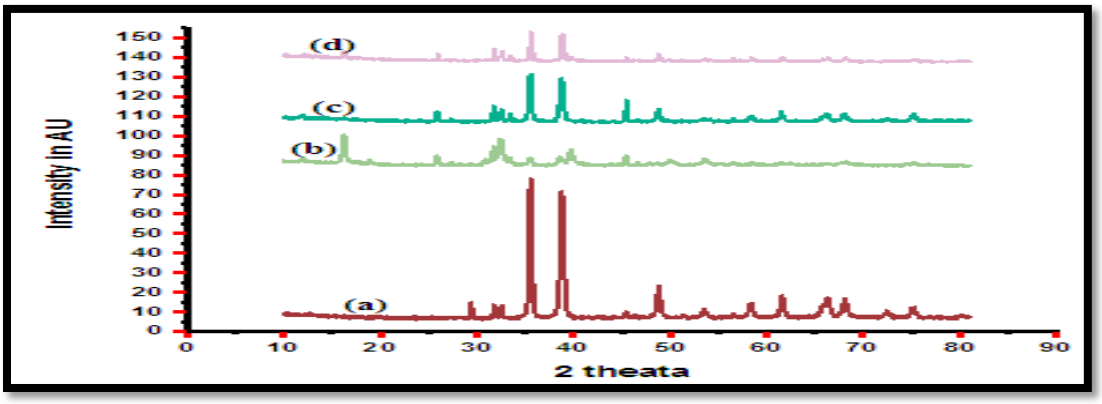

Figure 1: XRD plot of (a) pure Al$_2$O3 (b) Bi$_2$O$_3$- Al$_2$O$_3$ (10%) bismuth oxide incorporated aluminium oxide nano stuffs annealed for fixed duration of 2 hours at (a)200^0 C (b) 400^0 C (c) 600^0 C

The graph plotted among two theta and intensity shows sharp peaks which means, obtained nano-stuff is of crystalline nature. The intensity of peaks got diminished on addition of bismuth oxide as compared to pure Aluminium oxide which illustrate that the crystalline behavior of the samples was reduced. The intensity further goes on decreasing with increasing in temperature with same amount of dopant which also explores about the reduction in crystalline behavior of the nano-powder. The granular dimensions also got improved on keeping the concentration of dopant constant and changing the calcination temperature. The alps of Aluminium oxide as well as bismuth oxide were present in the samples that were matched by JCPDS file no. 00-400-2817. Peaks for both metal oxides were noticed at two theta positions (20.51, 22.43, 24.02,28.41, 30.97 and many more) which were matched by origin software. The perusal of image shown in **Figure 1** explores that no major shifting exists in peaks position. The FWHM got altered for each specimen which illustrate that bismuth got incorporated among Aluminium and made a new structure. The comparative graph of pure Aluminium and bismuth oxide doped Al_2O_3 with uniform doping and various ignition temperatures was explored in **Figure 1**. The peaks existing in accordance with hexagonal structure of Bi_2O_3-Al_2O_3 nano-composites.

Table 1: Crystallite size of bismuth oxide (Bi$_2$O$_3$) (10%) incorporated Aluminium oxide (Al$_2$O$_3$) nano-stuffs annealed at different temperature for duration of two hours.

Sr. No.	Calcinations temperature (^{o}C)	2 Theta (Degrees)	FWHM (Radians)	Crystallite size (nm)
1	200^{o}C	32.7	0.72	12.46 nm
2	400^{o}C	39.8	0.42	21.47 nm

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3	**600^{o}C**	**35.7**	**0.334**	**27.24 nm**

The tabulated data reflected that the crystallite size increases with increase of calcined temperature. It may be caused by the increase of oxidation rate with rise of temperature.

3.2 UV-VIS-NIR Spectroscope Analysis

All the samples were examined by UV- Visible NIR spectroscopy in wavelength range of 200nm -700nm by Hitachi 330 double beam spectrometer. The absorption spectrum were represented in graphical form and shown in **figure 2**.

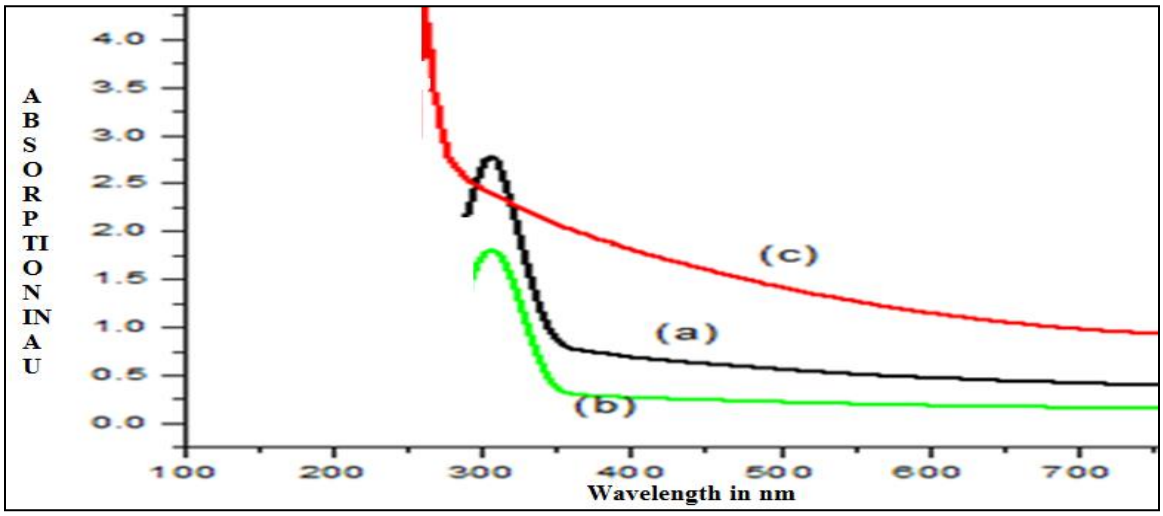

Figure 2: UV-VIS plot for 10% bismuth oxide doped Al_2O_3 NPs annealed at temperature 200^{o}C, 400^{o}C & 600^{o}C for 2-hour duration.

The effect of calcination temperature 200^{o}C, 400^{o}C & 600^{o}C for fixed duration of 2-hour were shown in figure 2 and perusal of image shows that all the samples were in nm range and the absorption peak lying between 200 to 400 nm range.

Table 2: Energy band gap for 10% bismuth oxide doped Al_2O_3 annealed at temperature 200^{o}C, 400^{o}C & 600^{o}C for fixed duration .

Sr. No	Nano-particulates	Ignition temperature	Ignition time period	Band gap energy
1.	**10% Bi_2O_3 - Al2O3**	**200^{o}C**	**2hrs**	**3.3 eV**
2.	**10% Bi_2O_3 - Al2O3**	**400^{o}C**	**2hrs**	**3.4 eV**

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3.	**10% Bi_2O_3 - Al2O3**	**600^oC**	**2hrs**	**3.6 eV**

The tabulated data reflected that the band gap energy increases with increase of ignition temperature for bismuth oxide incorporated aluminium oxide nanostructured materials at 10% concentration and it might be due to increase of quantity of γ-Al2O3 composition in calcined samples at higher temperature.

3.3 Fourier Transform Infra-Red (FTIR) Perusals

The samples were examined in wave no. range 400-4000 cm^{-1}. The IR data were shown in graphical form in **figure 3** . The wave number (cm^{-1}) is shown on abscissa and transmittance rate on ordinate were represented in graph.

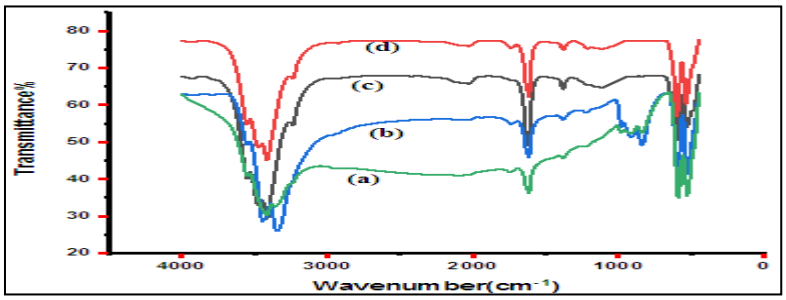

Figure 3: FTIR spectrum of bismuth oxide incorporated aluminium oxide nano stuffs annealed at different temperature for 2 hours (a) Pure Al_2O3 (b) $Al_2O_3 – Bi_2O_3$(10%) at 200^oC (c) $Al_2O_3 – Bi_2O_3$ (10%) at 400^oC(d) $Al_2O_3 – Bi_2O_3$ (10%) at 600^oC

The FTIR spectrum for the pure Al_2O_3 and 10% bismuth oxide (Bi_2O_3) doped Al_2O_3 nano-structured materials annealed at 200^{o}C, 400^{o}C &600^0 C temperature for the time period of 2 hours has been studied by using data obtained by use of Perkin elmer instrumentation at SAIF, Panjab University Chandigarh. The study of the spectrum explores the various Infra-Red broad Alps/peaks around at (3446, 3306, 1612, 975,827 and 504) cm^{-1}. A broad band around 3500 -3330 cm^{-1} and another wide band across 1700 -1500 cm^{-1} have been examined. These numerous alps/peaks assigned to a confining mode of -OH group of various vibration mode and may be exists due to water content occurs in surroundings. The peaks at 827 cm^{-1}& 504 cm^{-1} had been assigned to various metal oxide (MOs) vibrations like as Al-O-Al the vibration modes of Al_2O_3 nano substance. The investigation of various alps/peaks exhibit that the value of transmittance increases with the increase in the calcination temperature.

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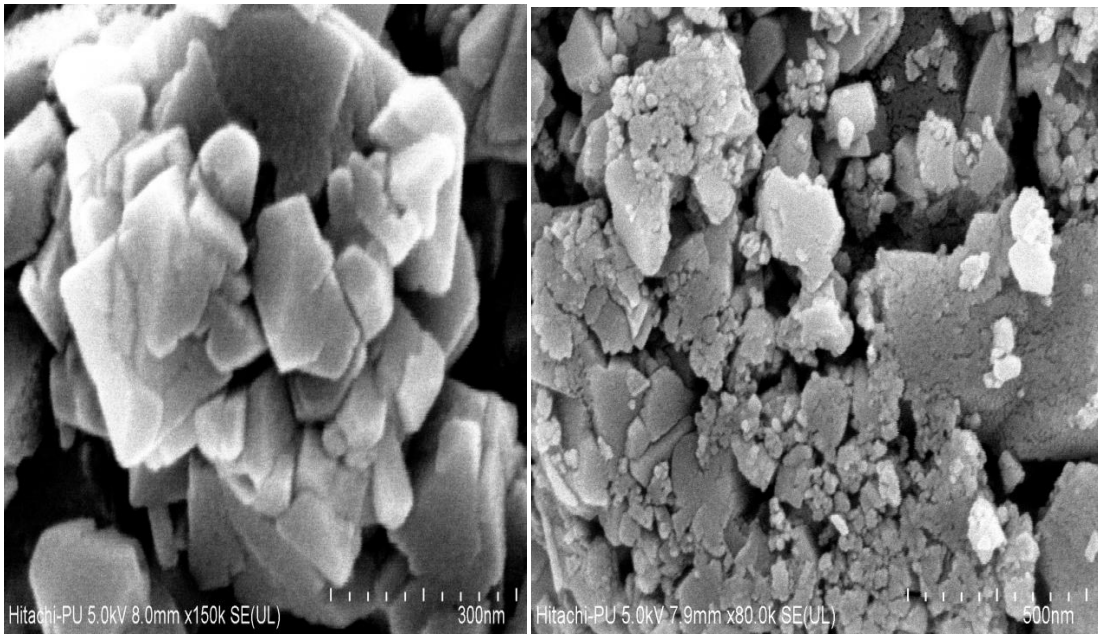
3.4 FESEM Analysis

The FESEM is effective and non-destructible route which avail wide-ranging statistics about the alignment, shape, arrangement and morphology of the scanned materials. The FESEM were employed to examine the surface morphology of samples under the applied conditions voltage 5 KV in image size 8.0 mm* 150 K SE(UL) in scaling 300nm in **figure 4(a) and 4(b)**



(a) (b)

Figure 4 : FESEM image of (a) Pure-Al_2O_3 (b) 10 % Bi_2O_3 doped Al_2O_3 nano-stuffs ignited at temperature 600^0 C for 2 hrs

The persuals of image quoted in **figure 4 (a) & (b)** shows that nanostructured material samples were polycrystalline in nature. The samples showed different transmittance and reflectance. The difference in optical phase transmittance and reflectance may be caused by incorporation of Bi^{2+} ions in Al_2O_3 lattice. The representative field emission scanning electron microscope images for bismuth oxide doped Aluminum oxide nano-dimensioned materials exhibits that substance are inhomogenous in size, cluttered in macrocosm and truncated spherical in contour or crispy in formation.

3.5 High Resolution Transmission Electron Microscope interpretation

High resolution transmission electron microscope (HRTEM) images are explored in **Figure 5(a) and 5 (b)** below for bismuth oxide (Bi_2O_3) doped Aluminium oxide nano-dimensioned substances calcined at $600\ ^0$C for fixed time period of two hours.

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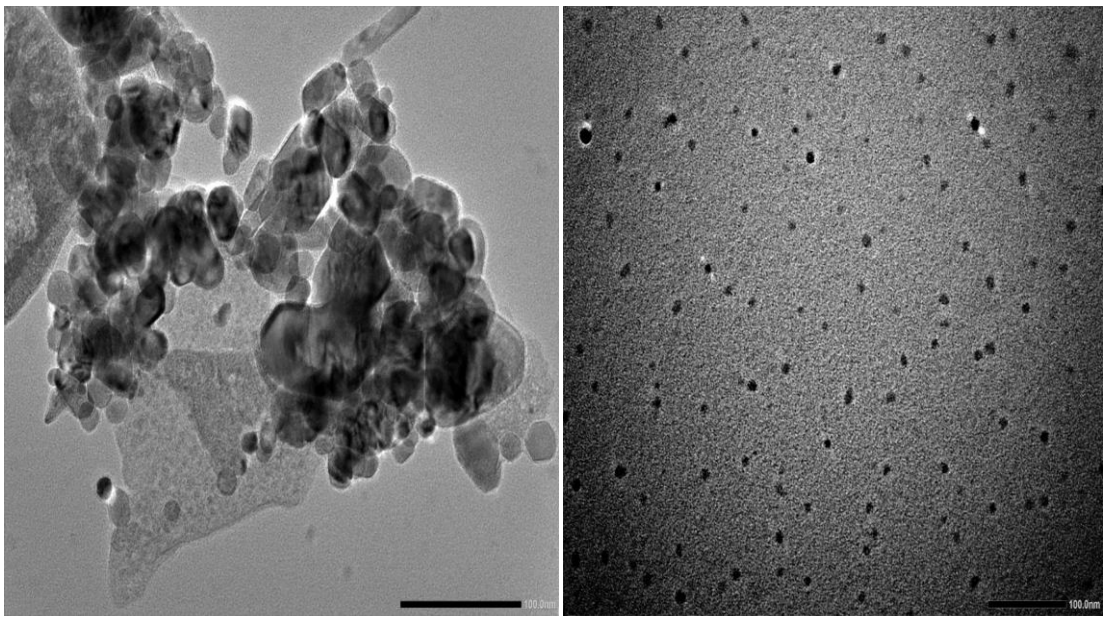

(a) (b)

Figure 5: HRTEM image of (a) Pure-Al_2O_3 (b) 10 % Bi_2O_3 doped Al_2O_3 nano-stuffs ignited at temperature 600^0 C for time duration of 2 hrs.

Examination of the images explores that the dimensions of the nano-structured substances lies in confine of 20 nm to 23 nm and aggregate grain size determined out to be 21 nm. The HRTEM summary are in accordance with those of XRD outcomes.

Conclusion:

The bismuth oxide incorporated Aluminium oxide (Al_2O_3) nano-dimensioned particles have been prepared by using the chemical co-precipitation modus and the obtained cake were calcined at different calcination temperature (200^{o}C, 400^{o}C and 600^{o}C) for duration of 120 minutes in muffle furnace. The effect of calcination temperature were studied and concluded that the size of nanoparticulates increases with calcination temperature and exhibited hexagonal crystal structure. The IR spectroscopy contains as usual pics of hydroxyl ion and verified that (Bi_2O_3) 504 cm^{-1} peak observed with (Al_2O_3) 827 cm^{-1} crystals had been assigned to various metal oxide (MOs) vibrations like as Al-O-Al the vibration modes of Al_2O_3nano substance. The optical study indicates that the semiconducting nature of nanoparticulates decreases with increase of temperature. The microscopic images of FESEM and HRTEM shows that nano-particulates have hexagonal crystalline nature and average grain size in accordance with XRD outcomes.

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