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Sol Gel Synthesis and Characterization of $ZnAl_2O_4$:SiO_2 Nanopowders for Refractory Applications.

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Abstract: In-Situ Sol-Gel synthesis route was adopted for preparation of nanocrytalline $ZnAl_2O_4$ dispersed in silica matrix for potential application as a refractory material. The gels of composition 5%ZnO–6%Al_2O_3–89%SiO_2 were developed at a temperature of 298 K by using tetraethyl ortho silicate, zinc nitrate, aluminium nitrate and ethyl alcohol as precursors. The transparent gels were converted to xero gel by controlled drying at 313 K and subsequently to crystalline phase by heating at 1273 K. The structure and thermal behavior of the nanopowders was characterized by TGA, DSC, XRD, and FTIR. The crystallite size measured by AFM was in the range 23 – 28 nm and the mean size calculated using Scherrer's equation was 29 nm.

Keywords: Nanomaterials, Spinels, Sol-Gel, X-ray diffraction, FTIR spectroscopy, Atomic force microscopy.

1. INTRODUCTION

It has become indispensible to develop efficient, stable and better performing refractories for supporting the industrial demands of stringent continuous processes with higher availability. Developments in the refractory field based on conventional concepts and techniques have been conducted exhaustively. Application of nanotechnology in refractories presents a promising alternative for developing novel materials with enhanced performance.

Synthesis of nanostructured metal aluminates, with spinel structure, dispersed in silica glassy matrix have drawn great interest of research owing to their potential applications in refractories, high alumina cement, optical and as oxidation catalysts [1-4]. These materials are found to exhibit enhanced properties such as thermal stability at elevated temperatures, wear resistance and increased hardness [5-6]. Synthesis of nanomaterials depends on the ability to control the size and distribution of the particles in the host matrix, the mixing modes of the reactants and drying techniques [7]. The main advantages of sol gel method, as compared to traditional methods, are lower processing temperatures, control over purity, composition and easy introduction of doping elements [8-10]. In this paper, we have reported the synthesis of nanocrytalline $ZnAl_2O_4$ dispersed in silica matrix through novel insitu sol-gel route and its characterization by XRD, FTIR, DSC, TGA and AFM.

2. EXPERIMENTAL PROCEDURE

2.1 Precursors

Tetraethylorthosilicate (TEOS, 99% Fluka), absolute alcohol (EtOH, 99.5%), aluminium nitrate nonahydrate $Al(NO_3)_3.9H_2O$, zinc nitrate hexahydrate $Zn(NO_3)_2.6H_2O$ and distilled water have been used in this work. The chemicals were used without any further purification.

2.2 Synthesis Process

In-situ sol-gel synthesis route was adopted for developing gel samples with the composition $5\%ZnO–6\%Al_2O_3–89\%SiO_2$. Two solutions were made simultaneously at a controlled temperature of 298 K with continuous stirring at 500 rpm for 60 minutes. First solution was made by mixing $Zn(NO_3)_2.6H_2O$ and $Al(NO_3)_3.9H_2O$ in distilled water according to their respective molecular weight percentages as mentioned above. Second solution was made by mixing TEOS, EtOH and distilled water in order to obtain the ratio of water to TEOH as 16:1. The two solutions were mixed and stirred at 500 rpm at 298 K for one hour and then allowed to age at the same temperature for 24 hours for gel formation. The gel was then dried at 313K for 6 weeks to form xero gel. The xero gel was calcined at 1073 K for 2 hours and then heat treated between 1173 – 1473 K for 5 hours at a heating rate of 1 K/min. The flow sheet for the synthesis process is shown in Figure 1.

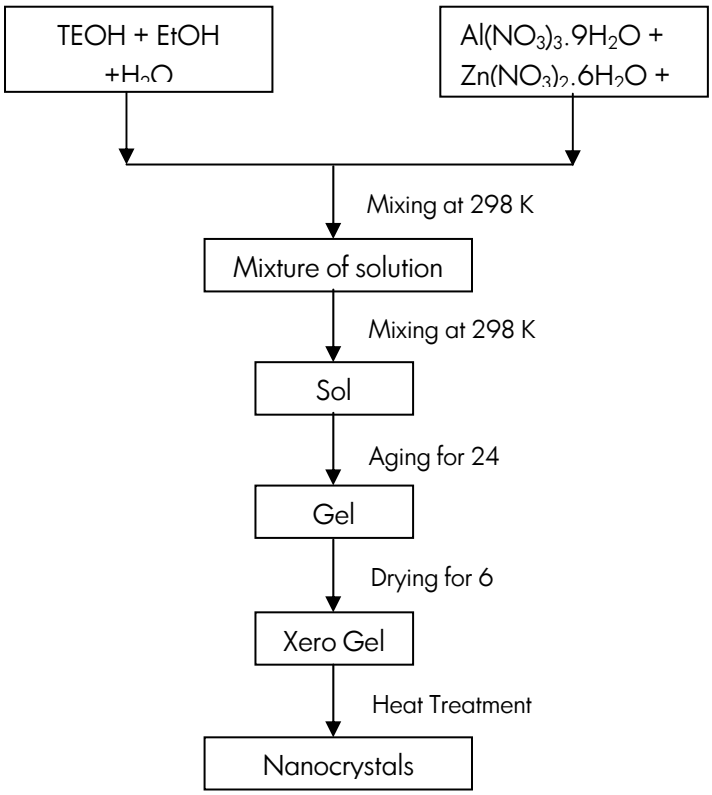

Figure 1: Sol Gel Synthesis of Nanocrystals

2.3 Characterizations

Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) was performed on the xero gel in inert argon atmosphere with a purge rate of 100 ml/min and heating rate of 5K/min. X-ray diffraction spectra were studied for samples heat treated at different temperatures in the range 10^o to 90^o 2θ with Cu Kα radiation wavelength λ = 1.540598 Å in steps of 0.1^o. Fourier Transfer Infrared specta (FTIR) was recorded to understand the mechanism of development of glass from xero gel and the various bond-formations during the transformation. The morphology and crystallite size of nanocrystals were observed by Atomic Force Microscopy (AFM).

3. RESULTS & DISCUSSION

3.1 Differential Scanning Calorimetry & Thermogravimetry

A DSC and TGA scan of dried gel sample is shown in Figure 2. The endothermic peak at 382 K corresponds to loss of water molecules present in the dried gel capillaries. The exothermic peak at 1180 K indicates the crystallization of spinel $ZnAl_2O_4$. A step-like change at 1112 K may correspond to glass transition because of the formation of oxide network.

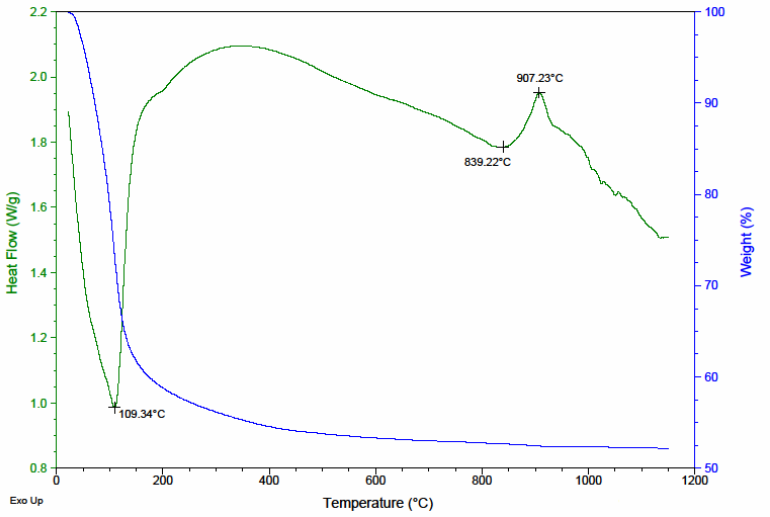

Figure 2: DSC and TGA Curve for Dried Gel

The synthesis of sol to gel and insitu reaction for the formation of $ZnAl_2O_4/SiO_2$ is described as follows –

$$(C_2H_5O)_3SiOH + Zn(NO_3)_2 + Al(NO_3)_3 + H_2O \xrightarrow{298\ K} ZnO.Al_2O_3.SiO_2\ (Gel) \quad (1)$$

$$ZnO.Al_2O_3.SiO_2\ (Gel) \xrightarrow{1073\ K} ZnO.Al_2O_3.SiO_2\ (Glass) \quad (2)$$

$$ZnO.Al_2O_3.SiO_2\ (Glass) \xrightarrow{1273\ K} ZnAl_2O_4/SiO_2\ (Nanocrystals) \quad (3)$$

The total reduction of weight observed is 45%, which can primarily be attributed to the loss of water and ethanol.

3.2 X-ray Diffraction Characterization

X-ray diffraction pattern of the dried gels heat treated in the temperature range 1073 – 1473 K is shown in Figure 3. It is evident that the sample, heat treated upto 1073 K is amorphous in nature, as indicated from the broad peak centered at 22°, which is characteristic of the diffraction pattern of the amorphous SiO_2 glassy matrix. The diffraction pattern of sample heat treated at 1273 K for 5 hours shows clear diffraction peaks at 31.3°, 36.8°, 55.7°, 59.3° and 65.2° of 2θ value. On comparison with JCPDS data, these peaks confirm to the formation of crystalline $ZnAl_2O_4$ phase. It is also seen that on heating above 1273 K, the broad peak at 22° disappears, indicating breaking of the glassy matrix.

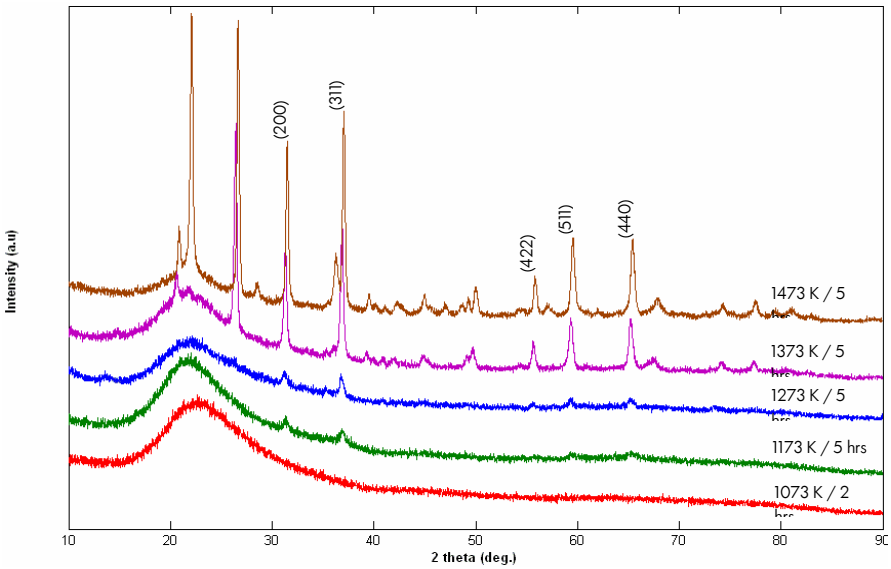

Figure 3: X-ray Diffraction Pattern for Heat Treated Samples

The crystallite size was calculated using Scherrer's equation:

$$D = K\lambda / (\beta \cos\theta) \qquad (4)$$

Where λ is the X-ray wavelength (1.540598 Å), β is the full width half maximum (FWHM) of the peak and K is the shape factor (0.89). Using the above equation, the average crystallite size is calculated as 29 nm.

3.3 Fourier Transfer Infrared Characterization

FTIR spectra of the gel sample and heat treated samples in the wave number range 3800 to 600 cm^{-1} is shown in Figure 4. The spectrum of xero gel has a strong and broad absorption peak between 3500 cm^{-1} and 3380 cm^{-1} indicating the vibration modes of metal hydroxyl groups. Xero gel spectrum also has peaks at 1376 cm^{-1} and 816 cm^{-1} corresponding to the presence of nitrate groups. These peaks metal hydroxyl and nitrate groups are not present for heat treated samples. The peaks between 1650 to 1635 and between 950 cm^{-1} and 940 cm^{-1} may be attributed to respectively to stretching and bending vibrational modes of O-H of molecular water and the Si-OH stretching of surface silicon hydrogen bond to molecular water [11,12].

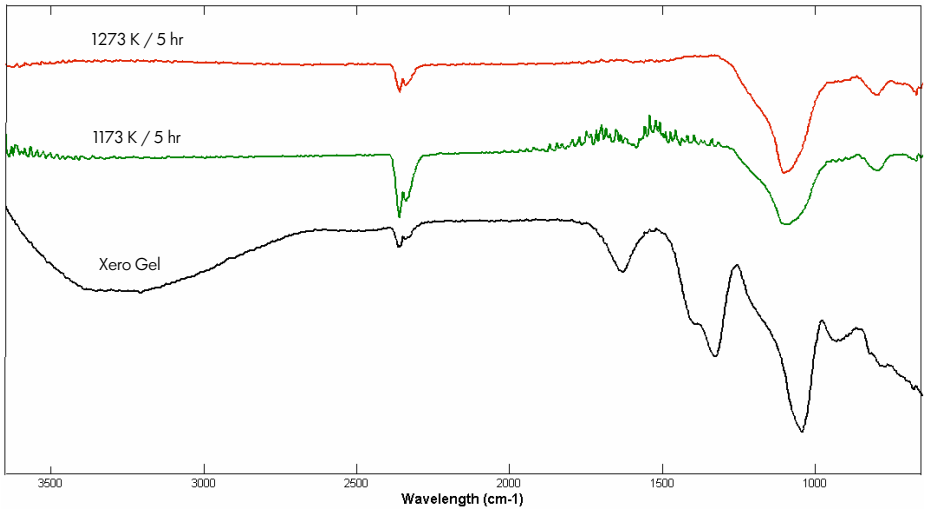

Figure 4: FTIR Spectra for Dried Xero Gel and Heat Treated Samples

The peaks at 1105 cm^{-1} and 795 cm^{-1} signifies the stretching and bending vibrations of Si-O-Si bonds which are present in heat treated samples [13]. It is seen that with increasing temperature, the metal hydroxide peaks get weaker, and the Si-O-Si peaks get stronger, indicating formation of glass network. The appearance of absorption peaks at 670 cm^{-1} for sample heat treated at 1273 K is characteristic of the spinel structure [14]. The intensity of spinel peaks increase with increase in the heat treatment temperature of the samples.

3.4 Atomic Force Microscopy

Atomic Force Microscopy (AFM) in non-contact mode was carried out on the sample heat treated at 1273 K for 5 hours. Powder sample was dispersed in acetone and water using ultrasonic mixer and analyzed on a mica plate by taking a drop of the dispersed powder. The typical micrographs are shown in Figure 5. It can be seen that there is a tendency of the particles to agglomerate in the dispersion medium. The spherical particles in the image are $ZnAl_2O_4$ nanocrystallites. The measured crystalline size were in the range of 23 – 28 nm.

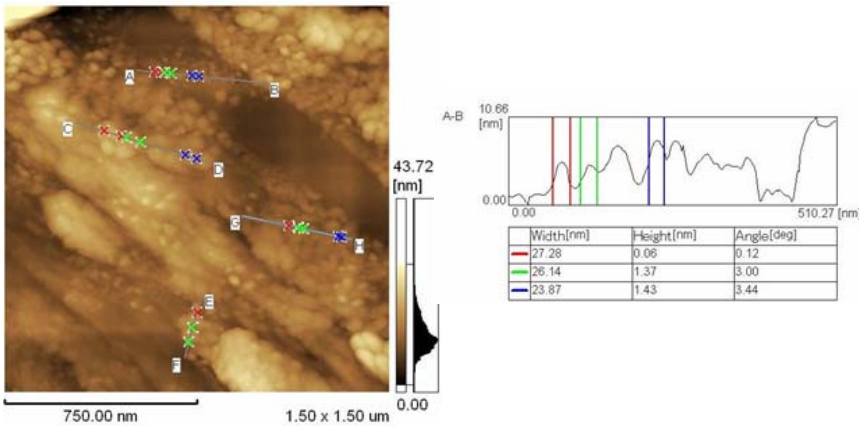

Figure 5: AFM Micrographs of Powders Heat Treated at 1273 K for 5 hours

4. CONCLUSIONS

Nanopowders of $ZnAl_2O_4/SiO_2$ were prepared using insitu sol-gel process as a promising material for refractory applications. XRD pattern confirmed the presence of nanocrystalline phase of $ZnAl_2O_4$ of samples heat treated at 1273 K for 5 hours. The phase and microstructural evolution was characterized by DSC and FTIR. Size of the nanocrystals measured by AFM was in the range of 23 – 28 nm and calculated using Scherrer's equation was 29 nm. Further study will be carried out in order to analyze the performance of these nanopowders in actual process conditions.

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