Novel ZnAl$_2$O$_4$:SiO$_2$ Nano-composites for High Temperature Refractory Applications

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Abstract. High Temperature properties in nanocomposites have received significant attention in recent years due to its potential as an efficient refractory material. Nano-enabled spinel refractory products are finding widespread application owing to their enhanced temperature withstanding limits coupled with excellent abrasion resistance. Several synthesis techniques have been employed to develop these spinel nanopowders. Sol-Gel synthesis provides lower processing temperatures, control over purity, composition and easy introduction of doping elements. In this work an in-situ sol-gel route was adopted for preparation of novel nanocrystalline ZnAl$_2$O$_4$ dispersed in silica matrix. The gels of composition 5%ZnO–6%Al$_2$O$_3$–89%SiO$_2$ were developed by using tetraethyl ortho silicate, zinc nitrate, aluminium nitrate and ethyl alcohol as precursors. The transparent gels were converted to xero gel and subsequently to crystalline phase by controlled heat treatment. The structure and thermal behavior of these nanopowders was studied by utilizing various characterization techniques. Differential Scanning Calorimetry and Thermo Gravimetric Analysis were performed on the xero gel in inert argon atmosphere indicating the crystallization of spinel ZnAl$_2$O$_4$ and formation of oxide network. X-ray diffraction spectra were studied for samples heat treated at different temperatures in the range of 800 deg C to 1200 deg C confirming the formation of crystalline ZnAl$_2$O$_4$ phase. Fourier Transfer Infrared specta 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). 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. This approach may enable rapid and cost-efficient manufacturing of bulk refractory nanocomposites for supporting the industrial demands of stringent continuous processes with higher availability.

1. Introduction
Nano-enabled refractory materials are being developed in order to meet stringent demands in high temperature processes, which could offer improved service life with minimum shutdowns. Spinel presents itself as a promising structural material for mechanical and thermal applications because of its excellent high-temperature properties such as strength, hardness and chemical stability.

Synthesis of nanostructured spinel based composites, 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 shock resistance, 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 advantages of Sol gel synthesis route are lower processing temperatures, control over purity, composition and easy introduction of doping elements [8-10]. In this paper, we are presenting a novel in-situ sol gel route for ZnAl$_2$O$_4$ nanocomposite and its characterization using x-ray diffraction, infra-red spectroscopy and atomic force microscopy techniques.
2. Experimental Procedure

In-situ sol-gel synthesis route was adopted for developing gel samples with the composition 5%ZnO–6%Al2O3–89%SiO2. 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(NO3)2.6H2O and Al(NO3)3.9H2O 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. 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 Fig 1.

![Flow Chart for Sol Gel Synthesis of Nanocomposites](image)

**Figure 1: Flow Chart for Sol Gel Synthesis of Nanocomposites**

Post synthesis, Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) were 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° to 90° 20 with Cu Kα radiation wavelength λ = 1.540598 Å in steps of 0.1°. 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 investigated by Atomic Force Microscopy (AFM).
3. Results & Discussion

DSC and TGA scan of dried gel sample shown in Figure 2 indicated an endothermic peak at 382 K corresponding to loss of water molecules present in the dried gel capillaries. The exothermic peak at 1180 K is for the crystallization of spinel ZnAl$_2$O$_4$. A step-like change at 1112 K corresponds to glass transition because of the formation of oxide network.

![Figure 2: DSC and TGA Results for Dried Gel](image)

The synthesis of sol to gel and insitu reaction for the formation of ZnAl$_2$O$_4$/SiO$_2$ is described as follows –

\[
(C_2H_3O)SiOH + Zn(NO_3)_2 + Al(NO_3)_3 + H_2O \xrightarrow{298 \text{ K}} ZnO.Al_2O_3.SiO_2 \text{(Gel)} \quad (1)
\]

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

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

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

X-ray diffraction pattern of the dried gels heat treated in the temperature range 1073 – 1473 K, shown in Figure 3, indicates that the sample, heat treated upto 1073 K is amorphous in nature. This is evident 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\textsubscript{2}O\textsubscript{4} phase. It is also seen that on heating above 1273 K, the broad peak at 22° disappears, indicating rupture of this glassy matrix.

Scherrer’s equation can be used to calculate the crystallite size:

\[
D = \frac{K \cdot \lambda}{\beta \cos \theta}
\]

where,
\(\lambda\) - X-ray wavelength (1.540598 Å)
\(\beta\) - Full width half maximum (FWHM) of the peak
K - Shape factor (0.89)

Using the above equation, the calculated average crystallite size is 29 nm.

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. The peaks of metal hydroxyl and nitrate groups are not present for heat treated samples. The peaks between 1650 to 1635 cm\(^{-1}\) and between 950 and 940 cm\(^{-1}\) may be attributed 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 respectively[11,12].
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 observed that with increase in heat treatment temperature, the metal hydroxide peaks get weaker, and the Si-O-Si peaks get stronger, confirming the 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 increases with increase in the heat treatment temperature of the samples.

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 was observed that there was a tendency of the particles to agglomerate in the dispersion medium. The spherical particles in the image are ZnAl$_2$O$_4$/SiO$_2$ nanocomposites. The measured crystalline sizes were in the range of 23 – 28 nm.
4. Conclusions
A novel method for synthesis of ZnAl$_2$O$_4$/SiO$_2$ spinel nanocomposites was investigated using laboratory scale precursors. Calcination studies were carried out to arrive at nanocrystalline phase which was verified by x-ray diffraction patterns. The phase and microstructural evolution was optimized and characterized by differential scanning calorimetry and fourier transform infra-red spectroscopy. Nano-size crystals were confirmed by atomic force microscopy and Scherrer’s equation. The synthesis strategy adopted here might open a new route for development of refractory nanocomposites with enhanced performance for future applications.

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