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# Changes in Physical Properties of Zinc Aluminates Ceramics upon Doping

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***Abstract:*** **Zinc aluminates ($ZnAl_2O_4$) being of spinal shape has drawn considerable attention as a catalytic material in making ceramics. It can improve the properties of the host like high thermal stability, high mechanical resistance, and simpler crystal structure and affects the optical spectra [1-4]. Moreover zinc aluminates tend to eliminate sintering of starting materials due to a strong material-support interaction. Zinc sulphate ($ZnSO_4$), alum ($Na_2SO_4$-$Al_2O_3$-24 $H_2O$), potassium per magnet ($KMnO_4$), and urea ($NH_2$-CO-$NH_2$) were used as starting materials. In this process urea is used as a chelating agent.**

***Keywords:*** **Spinal structured zinc aluminate, look of fired sample, chelating agent, SEM of samples.**

## 1. INTRODUCTION

Nano sized zinc aluminate powder crystals were prepared by sintering method. Zinc aluminate ($ZnAl_2O_4$), is a naturally occurring mineral. Zinc aluminate has drawn considerable attention as a catalytic material with improved properties due to its higher thermal stability, higher mechanical resistance, and low surface activity [1-2]. Nano sized zinc aluminate crystals (which apparently look like powdery) were prepared in these investigations by heating the homogenised ingredients at $600^OC$ temperature. Zinc sulphate ($ZnSO_4$), alum ($Na_2SO_4$-$Al_2O_3$-24 $H_2O$), potassium-di-chromate ($K_2Cr_2O_7$) and fine urea ($NH_2$ - CO - $NH_2$) powder were used as starting materials and same process was adopted as was done with Mn [3-4]. The addition of Mn to zinc aluminate allows an increase in the specific surface area and desired specification of the crystal morphology. However the catalytic isobutene dehydration properties remain unchanged. The addition of Mn to zinc aluminate causes an increase in the specific surface area [5]. Moreover, zinc aluminate tends to minimise the need of sintering of noble metals due to its strong metal–support interaction [6-8]. Zinc aluminate ($ZnAl_2O_4$) is a member of the class of inorganic spinal materials. These spinal oxides are generally wide-band-gap semiconductors; the optical band gaps are reported to be about 3.8eV for ($ZnAl_2O_4$) [2]. It has been widely used as catalyst, ceramic and electro-conductive materials. In high temperature processes sintering and chemical stability are the properties of the most significance for the catalytically active phases. Besides, it is widely used for coating electro - conductive material because of its high thermal stability, high mechanical strength and excellent optical properties. Optical properties make it useful for ceramic, pigments and coatings [9].

Zinc aluminate is normally prepared by a solid state reaction between zinc oxide and aluminium oxide. However, for ensuring complete reaction; a temperature above $1000^o$ C has to be maintained for several days [10]. On the theoretical front, we are not aware of any studies except that which leads to the prediction of the stability of the normal spinal structure over the inverse structure for $ZnAl_2O_4$ [11]. We have therefore embarked upon a detailed theoretical study of these zinc-based spinal oxides. In an earlier work, we have reported the results of an atomistic simulation study [12] that included derivation of inter atomic potentials, and determination of the equation of state and compressibility behaviour at the octahedral and tetrahedral sites in the spinal lattice, and the energetic of point defects in $ZnAl_2O_4$. Zinc aluminate is a well-known wide band gap semiconductor with cubic spinal structure and transparent for wavelengths greater than 320 nm. Therefore, $ZnAl_2O_4$ can be used for ultraviolet photo electric devices [13]. Therefore, $ZnAl_2O_4$ can be used for ultraviolet photo electric devices. Furthermore, spinal zinc aluminate is useful in many reactions as catalytic support. Zinc aluminate ($ZnAl_2O_4$) is a member of the class of inorganic materials called spinals. They have a close-packed face-centred-cubic structure [14] with *Fd*3*m* space group symmetry. Further, in the polycrystalline form, these are found to be

highly reflective from 300 nm and above which is well within the ultraviolet regime of the spectrum. This has attracted considerable interest amongst researchers for a variety of applications. For example, they are being studied as candidate materials for reflective optical coatings in aerospace applications [15]. Zinc aluminate, being a mixture of oxide of aluminium and zinc, is a naturally available mineral commonly called as gahnite with a normal spinal structure having all zinc cations in the tetrahedral and all aluminium cations in the octahedral voids of *fcc* lattice of oxygen anions. Zinc aluminate is a widely used as catalyst in chemical reactions viz. synthesis of methanol and synthesis of styrene from aceto-phenones [16].

In the present paper, the synthesis of $ZnAl_2O_4$ nano powder crystals formed by sintering method. Cr was taken from ($K_2Cr_2O_7$) and Mn was taken from $KMnO_4$ for doping. The disadvantages of solid-state reaction are in-homogeneity, need of high sintering temperature and low surface area available for interaction. Sintering is a method for synthesising materials from powder, by heating the material in a sintering furnace below their melting point (solid state sintering) but critical for its particles attain sufficient energy to adhere to each other. Sintering is traditionally used for manufacturing ceramic objects, and has also finds use in such fields as powder metallurgy.

**1.1 Requirements and precautions of sintering method:**

The material preparation by the above referred powder technology needs:

1. Very high levels of purity and uniformity of starting materials.
2. Doping of impurity entails simpler subsequent prefabrication process (fewer steps) that it makes possible.
3. Stabilization of the details of repetitive operations, by control of grain size during the input stages.
4. Absence of binding contact between segregated powder particles – or "inclusions" (called stringing) – as often occurs in melt processes.
5. No deformation is needed to produce directional elongation of grains.
6. Its capability to produce materials of controlled, uniform porosity.

Sintering is effective when the process reduces the porosity and enhances properties such as strength, translucency and thermal conductivity; yet, in other cases, it may be useful to increase its strength but keep its gas absorbency constant. During the firing process and as it continues; grain size becomes smaller and more spherical because the particle's surface tends to flow into the pores within it. It is based on the difference between vapour-pressure and cross-sectional area of the pore's neck.

## 2. WORKING

The method of making zinc aluminate nano material comprises of following steps:-

a. To provide a growing seed and growing device, comprising of a heating apparatus with reacting chamber.

b. Placing growing substrate and a quantity of reacting materials into the reaction chamber.

c. Heating the reaction chamber to a temperature of 600$^oC$.

**2.1 Material Preparation:**

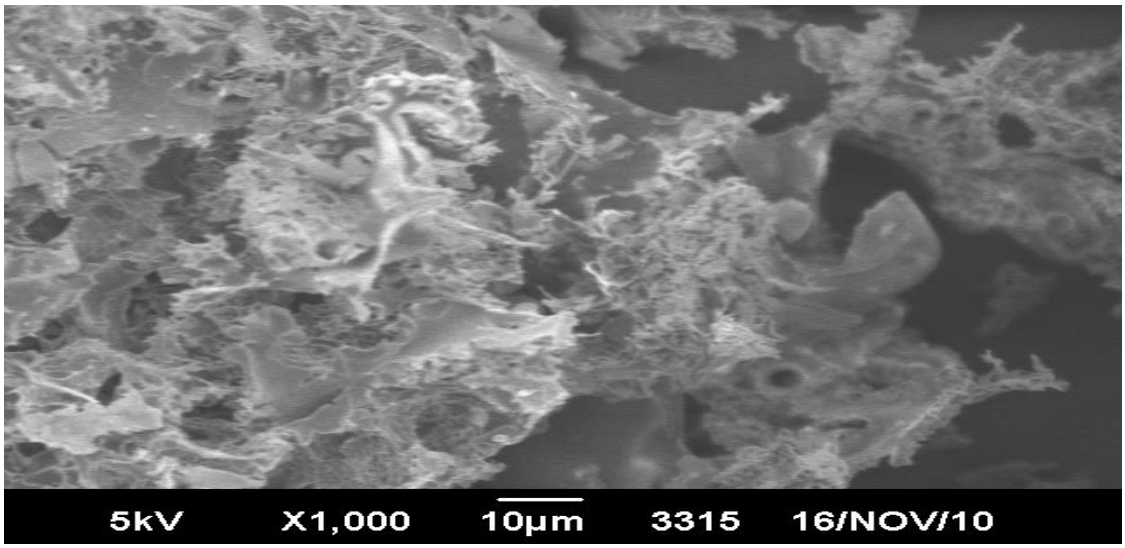
1. Take a definite quantity of zinc sulphate ($ZnSO_4$) powder (750 mg), alum ($Na_2SO_4$-$Al_2O_3$-24 $H_2O$) powder (1500 mg) and urea ($NH_2$ CO $NH_2$) powder (750 mg).
2. Grind the zinc sulphate powder, alum powder and urea. Now place the mixture into a furnace.
3. Heating the mixture to a temperature at 600$^oC$ for 15 minutes to obtain zinc aluminate nano material.
4. Leave a part of the material (A) into the furnace when the temperature decreases gradually.
5. Again take different quantity of alum powder (1500 mg), zinc sulphate powder (750 mg), urea powder (750 mg) and Cr impurity from potassium dichromate (10 mg).
6. Now grind it and put the mixture in to furnace at 600$^oC$ then allow a part of it material (B) into the furnace and let cool it down.

7. Now again take different quantity of alum powder (1500 mg), zinc sulphate powder (750 mg), urea powder (750 mg) and Mn impurity from potassium per magnet (10 mg).
8. Now grind it and put the mixture in to furnace at 600$^{o}$C then keep a part of it (C) in the furnace and let cool it down.
9. The remaining part of each sample is used for observing change if any in its physical nature.

Here A denotes un-doped material and B, C indicates doped material. The comparison between doped and un-doped zinc aluminate spinal is done as per regular practice indicated here.

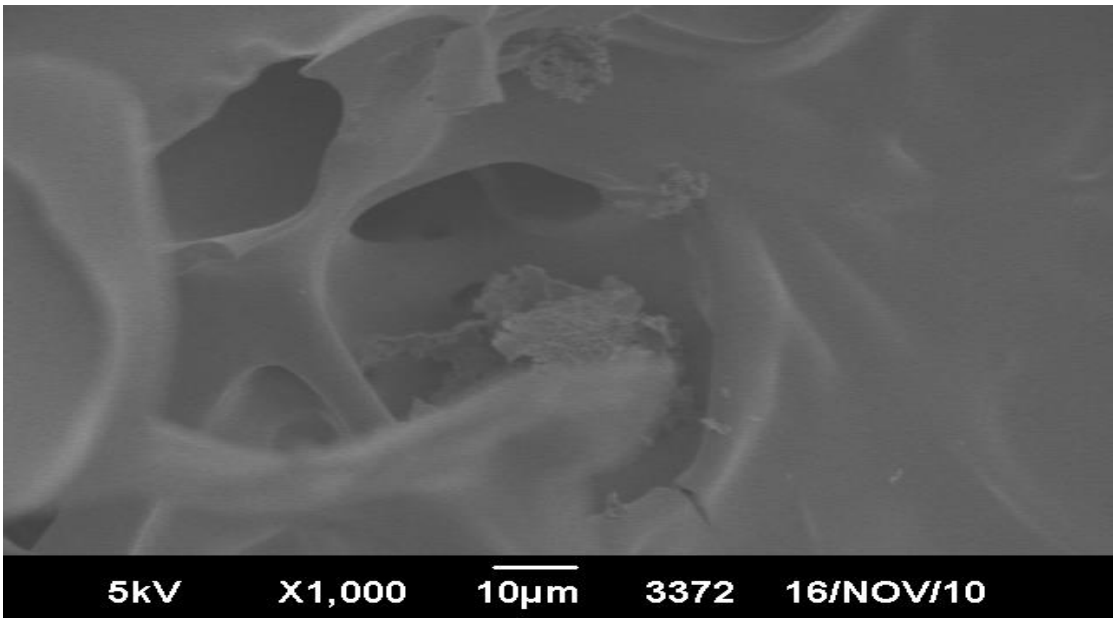
## 3. RESULT AND DISCUSSION

The temperature of the formation of zinc aluminate was found to be 600$^{o}$C at a reaction time 15 minutes. At short reaction time the reaction rate is obviously depends upon the number of nucleons sites or content point of alumina or zinc. If we increase the reaction time the rate of reaction time increases and the rate of reaction become increasingly dependent upon the rate of diffusion of zinc. SEM studies were undertaken and results of it are narrated below.

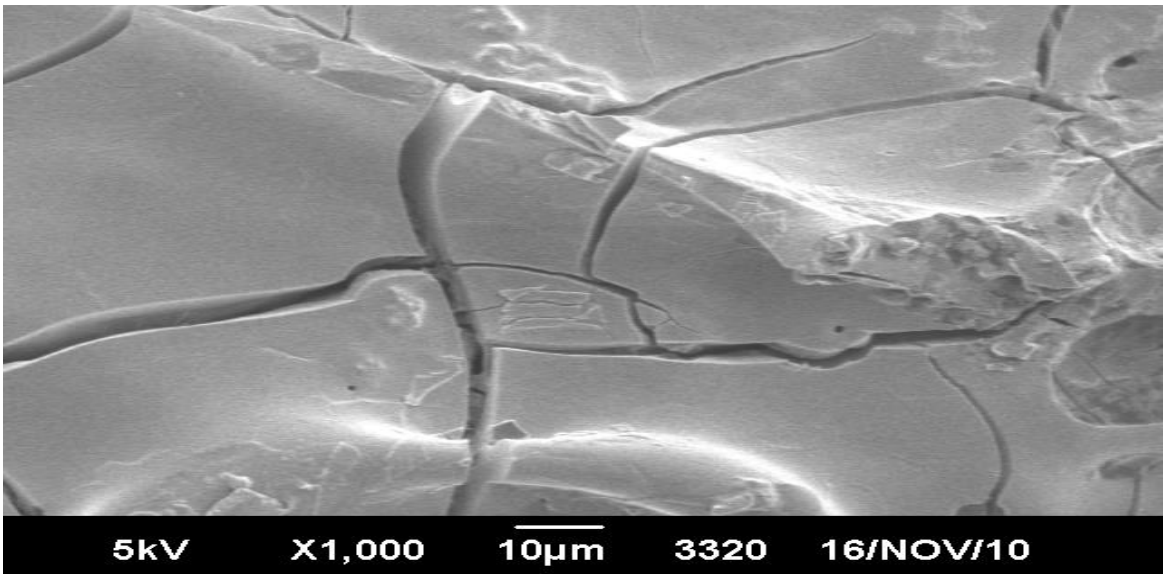



**SEM images of material (A) :**

In the SEM images and photograph of material "A" (un-doped) we shows that the surface of the material is porous and upper surface looks like the moon surface which has small hole like structure while internal surface appears to be of the spinal form.



**SEM images of material (B):**




**SEM images of material (C):**

When the doped sample "B" with $K_{22}Cr_2O_0$, we found that the material becomes hard and their surface has spinal form. Material also has porosity on the surface.

When the doped sample "C" with $KMnO_4$, we found that the material becomes very smooth but very hard. Its surface does not appear to be of spinal form. The material also has no porosity on its surface.

**3.1 Comparison between doped and un-doped zinc aluminate:**

| Sample | Temperature $^oC$ | Type | Surface | shape | colour |
|---|---|---|---|---|---|
| A (Un-doped) | 600 | Soft | Crystals seem to be attached irregularly on to each other. Porous and upper surface looks like moon<br>Internal surface- spinal form | Irregular shape | White |
| B (doped) | 600 | Hard | Surfaces are smooth and appear like powder.<br>Porous and spinal form | Regular shape | Light pink |
| C (doped ) | 600 | Hard but very smooth | Micro crystalline | Regular shape | cream |

## 4. CONCLUSION

The relative reactivity of the formation of zinc aluminates by the powder method shows conspicuous difference in their SEM images. The images suggest that diffusing different species in $ZnAl_2O_4$ is a one of the way to transfer / displace Zn from zinc aluminate which is obvious from surface-layers of the material in to the alumina particles. So the porous material may find useful for devices dealing with thermal conductivity.

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