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A novel method for the synthesis of nano-sized $MgAl_2O_4$ spinel ceramic powders

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This study describes the preparation and characterization of $MgAl_2O_4$ spinel ceramic powders by a polyacrylamide gel method with $Al(NO_3)_3{\cdot}9H_2O$ and $Mg(NO_3)_3{\cdot}6H_2O$ as the raw materials, acrylamide as the monomer, N,N-mehtylenebisacrylamide as the cross-linking agent, and deionized water as the solvent. The nanopowders were studied by X-ray diffraction (XRD) and a transmission electron microscope (TEM). The results showed that the nanopowders having a typical spinel structure are ultrapure and nano-sized. Due to the hindering effect of the polyacrylamide network, the average grain size of the $MgAl_2O_4$ spinel is approximately 20 nm. Moreover, it is confirmed that the optimal sintering temperature for synthesizing the $MgAl_2O_4$ spinel ceramic nanopowders is 900 °C, which is about 600-1000 °C lower than that of the traditional solid-state method.

Key words: polyacrylamide, network gel, spinel, nanopowders.

Introduction

Due to the excellent refractoriness (melting point ≈ 2135 °C), high resistance against chemical attack, good mechanical strength both at room temperature and elevated temperatures, low dielectric constant and good optical properties, $MgAl_2O_4$ spinel is a very important ceramic material and widely used in many fields, such as a refractory, transparent optical ceramic, in catalysis, humidity sensors, and etc [1-4].

It is well known that good properties of ceramics are a result of proper formation processing, sintering conditions and the favorable properties of the starting powder [5]. The purity and reactivity of $MgAl_2O_4$ spinel powder are inuenced by the synthesis method. In recent years, several techniques such as solid-state, coprecipitation, sol-gel and freeze-drying have been used for the synthesis of $MgAl_2O_4$ spinel ceramic powders [6-8]. However, the solid-state route which suffers from inhomogeneity and high-synthesis temperatures (1500-1900 °C) cannot be used to prepare ultrafine $MgAl_2O_4$ spinel powders. Similarly, the $MgAl_2O_4$ spinel powders which are prepared by the freeze-drying method agglomerate densely. The procedure of the sol-gel technique is tedious. The grain size of $MgAl_2O_4$ spinel prepared by coprecipitation method is not uniform and pure.

A polyacrylamide gel, a novel method for synthesis ceramic powders, is of great simplicity and provides ultrafine powders at relatively low temperatures. In a previous study [9] $YBa_2Cu_3O_{7x}$ powders were prepared by a polyacrylamide gel method. Recently, Pan et al. synthesized bismuth oxide nanoparticles by the polyacrylamide gel route [10]. In the present study, the polyacrylamide gel method was adopted to prepare $MgAl_2O_4$ spinel ceramic nanopowders.

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Experimental

Desired quantities of acrylamide (the monomer), N, N-mehtylenebisacrylamide (the network cross-linking agent) and $(NH_4)_2S_2O_8$ (the initiator) were added in turn to an aqueous solution of aluminum nitrate and magnesium nitrate with concentrations (Al^{3+} : 0.2 mol/l; Mg^{2+} : 0.1 mol/l). The mixed solution was stirred vigorously over a water bath at 60 °C, and the mixing solution turned into gel at 78 °C with the slow increase of water bath temperature. The gel was dried at 100 °C for 24 h in a vacuum drier. The xerogel thus formed was sintered in a muffle furnace in an air atmosphere at 800, 900 and 1000 °C. Finally, the flocculent micropowders were obtained and studied by X-ray powder diffraction, using a D8 Discover X-ray diffractometer with Cu Kα radiation (λ = 0.154184 nm), operated at 40 KV and 100 mA. TEM images were recorded with a Hitachi H-7650 at an accelerating voltage of 80 kV. The micropowders were sonically dispersed in ethanol for 30 minutes, dropped onto and dried on a carbon-coated TEM copper grid.

Results and Discussion

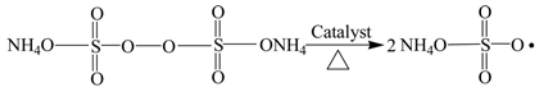
Reaction mechanism of polyacrylamide gel

The acrylamide polymerizes via a radical polymerization mechanism. Owing to the activated double bond of N, N-mehtylenebisacrylamide, a polyacrylamide network gel was obtained. The molecular reaction process is made up of three elementary reactions, chain initiation, chain pro-

pagation and chain termination. Therein, the reaction rate of the chain initiation is the lowest, so it is the key factor in the polymerization rate. Here, $(NH_4)_2S_2O_8$ is the initiator of polymerization. It can decompose slowly to the sulphate ($NH_4SO_4\cdot$) which is able to make the monomer and the network cross-linking agent activated. Then the chain propagation reaction begins.

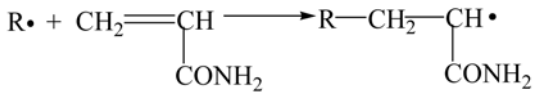
The chain initiation process can be divided into two steps:

(1) two primary radicals are produced via the homolysis of the initiator ($NH_4SO_4\cdot$ is the radical, expressed as R·):

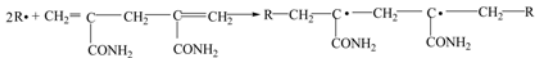


(1)

(2) the monomer radicals are obtained because of the addition reaction between the monomer and the primary radical:

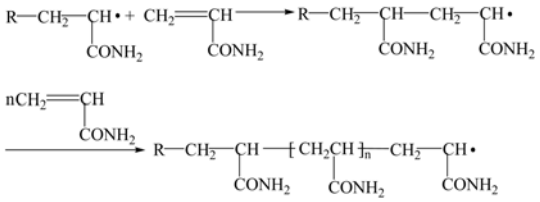


(2)



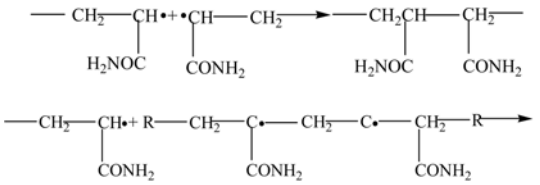
(3)

Chain propagation is the process in which the monomer radical is continuously regenerated with a new monomer (acrylamide) during the polymerization reaction. The reactive end-groups are transferred to that last unit of the chain.

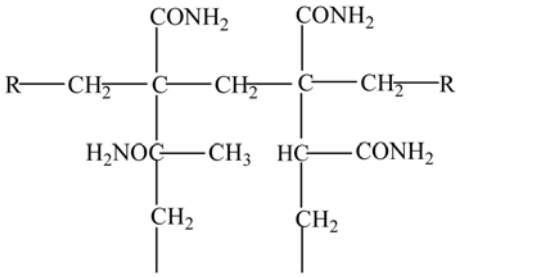


(4)

Chain termination is the chemical reaction leading to the destruction of the monomer radical and the formation of the stable polymer (polyacrylamide):



(5)



(6)

Then, the staggered-dimensional network structure of polyacrylamide where the $MgAl_2O_4$ spinel ceramic-precursor molecules are distributed uniformly is prepared. The hindering effect of the network gel greatly reduces the agglomeration of the $MgAl_2O_4$ spinel molecules, which is helpful in the preparation of small-size and less- agglomeration nanopowders.

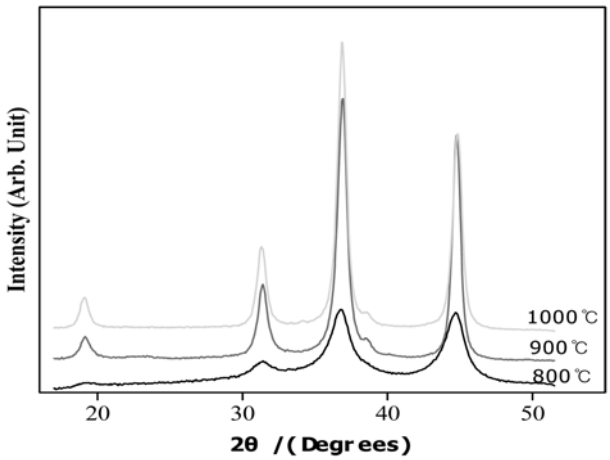


Fig. 1. XRD patterns of the samples under different sintering temperature

Phase composition and morphological characterization

The XRD patterns of the samples which were prepared by the sintering of the xerogel at different sintering reaction temperatures are shown in Fig. 1. All samples crystallized only in a pure $MgAl_2O_4$ spinel phase (JCPDS 21-1152). However, the sample sintered at 800 °C showed low and blunt peaks, which gives a clear indication that the sample was not well crystallized. The XRD patterns of the samples sintered at 900 and 1000 °C are little difference. Therefore, the optimal sintering temperature is 900 °C, which is remarkably lower than that of the traditional solid-state method, which is, 1500-1900 °C.

Moreover, the broadened diffraction peaks which are observed indicate that the crystal size of samples is very fine. The crystallite size of the sample sintered at 900 °C is calculated to be 19.69 nm according the Scherrer formula:

$$D = \frac{K\lambda}{\beta cos\theta} \tag{7}$$

in which K is a numerical constant with a value of 0.89, λ is the wave-length, β is the half-value breadth of the diffraction peak and θ is the Bragg angle.

A TEM image of the superfine $MgAl_2O_4$ spinel ceramic powder (Fig. 2) shows that the $MgAl_2O_4$ nanoparticls are of ellipsoid-like shape and loosely aggregated. The average particle size is approximately 20 nm, which is in good agreement with the XRD result.

Conclusions

A polyacrylamide gel process was used for the preparation

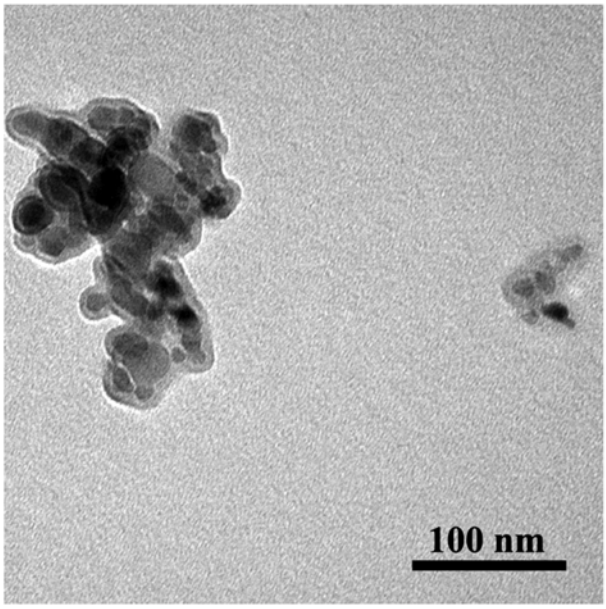


Fig. 2. TEM image of the sample sintered at 900 °C for 1 h.

of $MgAl_2O_4$ spinel ceramic nanopowders. The average grain size of the $MgAl_2O_4$ spinel was approximately 20 nm. Moreover, the sintering temperature for synthesizing the $MgAl_2O_4$ spinel ceramic nanopowders was 900 °C, about 600-1000 °C lower than that of the traditional solid-state method.

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