Characterization of nanocrystalline ZnFe$_2$O$_4$ prepared by using polyvinyl alcohol gel method

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Nanometer-sized ZnFe$_2$O$_4$ particles have been prepared by using polyvinyl alcohol gel method without any intermediate phase formation. Particle sizes could be controlled in the range of 6.3-13.9 nm by a suitable heat treatment from 723 to 923 K. The crystal structure and particle morphology have been examined with XRD and TEM. EPR technique has also been used to investigate the obtained ZnFe$_2$O$_4$ samples. All samples have a broad EPR signal with a g value of about 2.006. The quantitative EPR measurement shows that the line width and the intensity of the Fe$^{3+}$ signals depend on the calcination temperature and the particle size.

Nanocrystalline materials are of interest due to their unique physical, mechanical and chemical properties. Several procedures such as laser vapour reaction, rf sputtering, etc. have been employed to prepare nanocrystalline particles. Recently, a Sol-Gel method was found to be effective for preparation of nanocrystalline ferrite within a SiO$_2$ matrix. We report herein the preparation of nanocrystalline ZnFe$_2$O$_4$ by the polyvinyl alcohol (PVA) gel method at low temperatures, and its crystal structure properties, particle morphology and EPR features.

**Experimental**

**Sample preparation**

Nanocrystalline ZnFe$_2$O$_4$ was prepared by the PVA gel method as follows:

Zn and Fe nitrates (AR) in a 1:2 molar ratio of cations, were dissolved together in the minimum amount of deionized water to get a clear solution. Polyvinyl alcohol (polymerization degree 2000) was used to make a gel. The aqueous solution of PAV was added to the nitrate solution and then dehydrated at temperatures in the range 333-353K. The gelation slowly proceeded and a light red gel-type precursor was obtained. The precursor was then calcined in the temperature range of 723-923K for 2h in air to prepare ZnFe$_2$O$_4$ nanocrystalline particles with different sizes.

\[
\begin{align*}
\text{Zn(NO}_3\text{)}_2 + 2\text{Fe(NO}_3\text{)}_3 + 8\text{H}_2\text{O} &\rightarrow \text{Zn(OH}_2\text{)}_2\text{Fe(OH}_3\text{)(Sol) + 8HNO}_3 \\
\text{Zn(OH}_2\text{)}_2\text{Fe(OH}_3\text{)(Sol)} &\rightarrow \text{Zn(OH}_2\text{)}_2\text{Fe(OH}_3\text{)(Gel)} \\
(\text{Dehydration in the range of 333-353K}) & \\
\text{Zn(OH}_2\text{)}_2\text{Fe(OH}_3\text{)(Gel)} &\rightarrow \text{ZnFe}_2\text{O}_4(\text{nanocrystalline}) + 4\text{H}_2\text{O (gas)} \\
(\text{Calcination in the range of 723-923 K}) &
\end{align*}
\]

The thermal decomposition behaviour of the precursor was investigated by using thermogravimetry and differential thermal analysis (Dupont 9900) in air at a heating rate of 10°C min$^{-1}$. The crystalline structure of the samples were identified from the X-ray diffraction patterns taken on a Rigaku D/max-$\gamma$ diffractometer using CuK$\alpha$ radiation. Particle size and morphology were observed by transmission electron microscopy (JEM-1200EX/S). The electron paramagnetic resonance technique was used to examine the EPR features of ZnFe$_2$O$_4$ samples calcined at different temperatures. EPR spectra were recorded at room temperature with a Varian E-115 spectrometer operating in the X-band ($\nu=9.2$ GHz) with 100 KHz field modulation. EPR parameters were calibrated by comparison with a standard Mn$^{2+}$/ZnS (1-6 line distance, 34.05 mT) and 2,2-diphenyl-1-picrylhydrazyl (DPPH, $9.7\times10^{15}$ spins, g=2.0036).

**Results and discussion**

Figure 1 shows the TG and DTA curves for the gel-type precursor. The initial slight weight loss below 523K in the TG curve may be attributed to the loss of adsorbed water or other substances such as free nitric acid from the surface of the precursor. Subsequently, a strong exothermic peak in DTA curve with drastic weight loss is observed in the range 523-773K, which corresponds to the conventional oxidative decomposition of PVA-based phases. Above 773K, there is no distinct change in TG/DTA curves, indicating the completion of PVA-chain and nitrate decomposition.

The X-ray diffraction patterns of samples calcined at different temperature are shown in Fig. 2. The six broad peaks, centered at 20=29.86°, 35.16° 42.78°.
Fig. 1—TG-DTA curves of the gel-type precursor for zinc ferrite nanocrystalline particles [heating rate: 10°C min⁻¹ in air]

Fig. 2—X-ray diffraction patterns of ZnFe₂O₄ samples calcined at different temperatures for 2h followed by slowly cooling [(a), 723K; (b), 773K; (c), 823K; (d) 923K].

52.96°, 56.58° and 62.26°, coincide well with the ZnFe₂O₄ crystal reflections [220] (d₁=2.986Å), [311](d₂=2.550 Å),[400] (d₃=2.109 Å),[422] (d₄=1.728Å), [511] (d₅=1.625Å), [440] (d₆=1.486Å), respectively. It is evident that in all the cases the spinel phase could be produced at a rather low temperature compared to the conventional solid- ceramic techniques (1573K) and the diffraction peaks are fairly broad, particularly for the low temperature calcination. The peak intensities are also lowered with the decreasing calcination temperature. The peak broadening and lowering in intensities may be caused by the small particle size and the interface structure with a large volume fraction and disorder⁸.

Crystallite size of the zinc ferrite samples as calculated from Scherrer's formula are shown in Table I—Heat treatment schedule and particle sizes in ZnFe₂O₄ nanocrystalline particles

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Calcination temp. (K)</th>
<th>Particle size (nm)</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>723</td>
<td>6.7</td>
<td>Thin-red</td>
</tr>
<tr>
<td>2</td>
<td>773</td>
<td>8.5</td>
<td>Brown-red</td>
</tr>
<tr>
<td>3</td>
<td>823</td>
<td>12.7</td>
<td>Brown-red</td>
</tr>
<tr>
<td>4</td>
<td>923</td>
<td>13.9</td>
<td>Thick-red</td>
</tr>
</tbody>
</table>

Table 1. The crystallite size of the ferrite phase as obtained in the present investigation varies from 6.7 to 13.9 nm, depending on the calcination temperature. From Fig. 2, it may be seen that no change in the crystal structure occurs in the XRD patterns of the powders. The only effect is that the X-ray line broadening gradually decreases and the intensity of diffraction peaks gradually increases with increasing calcination temperature, which is due to the perfection of crystal lattice and the growth of the crystallites at higher temperature⁹ (see Table 1).

Isothermal heating of the gel-type precursor was also carried out in flowing nitrogen and argon atmospheres to check the effect of atmosphere on the formation of the ZnFe₂O₄ phase. It was found that the formation of ZnFe₂O₄ was not affected by the surrounding atmosphere, in air as well as in flowing nitrogen and argon atmosphere, only the monophase ZnFe₂O₄ was produced when the calcination temperature was higher than 723K. Thus, the minimum calcination temperature for the formation of pure crystalline ZnFe₂O₄ phase was found to be about 723K, which is lower than the temperature (1073K) employed in conventional ceramic processing method. The lower crystallizing point of ZnFe₂O₄ was ascribed to the greater reactivity of the homogeneously dispersed PAV-based precursor powders employed and the crystallite size⁹.

Transmission electron micrograph (TEM) of ZnFe₂O₄ sample calcined at 723K and 3b shows the selected area diffraction (SAD) pattern of the same sample. It is easily seen that the particles are very small and fairly uniform. The average size of the particles is ca. 10 mm which is in agreement with the XRD results. The selected area diffraction pattern of the same sample shows that the characteristic rings of ZnFe₂O₄ are fairly diffused, which also shows the small size of the particles. The SAD patterns of the other three samples were much more distinct which shows the increasing size of the particles with increasing calcination temperature.
The EPR spectra of ZnFe₂O₄ nanocrystalline particles have been recorded at room temperature. Typical EPR spectrum is shown in Fig. 3. The EPR spectrum shows a broad signal with a g value of about 2.006, which is attributed to the paramagnetic centers, i.e., Fe³⁺ ions. Furthermore, we performed quantitative EPR measurements and the results are shown in Table 2. It is concluded that the dependence of both the line width and the intensity of the Fe³⁺ signals is on the particle size and the calcination temperature. When the calcination temperature is below 873K, both the width of line and intensity of the EPR signals increase with increase in calcination temperature and particle size, whereas above 873K they decrease with further increase in calcination temperature. The linewidths of clusters are determined by two effects: exchange coupling and dipolar interactions between the Fe³⁺ ions. The former results in an exchange narrowing of the resonance, while the latter gives rise to line broadening. At low calcination temperatures, the dipolar interactions dominate (not well-crystalline clusters) and there is an increase in EPR line widths when the particles grow in size. On the other hand, high calcination temperatures give highly crystalline materials and exchange narrowing dominates over dipolar interactions. Consequently, the line widths decrease with increasing cluster size.

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References