

A novel technique for the preparation of fine ceramic oxides

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Abstract. In this paper, we put forward a novel and simple chemical route for the preparation of fine ceramic oxides i.e. ferrites using triethylammonium carbonate as the precipitating agent. The particles were studied and characterized by X-ray diffraction and scanning electron microscopy. The emphasis is on the superiority of this technique over other chemical and conventional routes.

Keywords. Ceramic oxide; spinel; triethylammonium carbonate.

1. Introduction

The compounds of AB_2O_4 type with spinel structure have been studied by several researchers (Keeffe 1961; Goodenough 1963; Blasse 1965; Ghare and Sinha 1968; Rao and Subba Rao 1970), as they exhibit interesting structural, electrical and magnetic properties which vary with the nature of ions, their charge and site distribution amongst tetrahedral and octahedral sites. These fine particles of ceramic oxides find application in the field of electrical and electronics industries. The conventional preparation of these ceramic powders depends entirely on solid-state reactions. Besides being painfully time-consuming, such processes are affected by serious limitations of large inter-grain diffusion of various atomic species leading to multiphase final products with wide particle-size distribution. To overcome these, chemical routes such as gel-precipitation (Fletcher and Hardy 1968; Marcilly *et al* 1970; Delmon and Droguest 1974; Baythoun and Sale 1982), coprecipitation using oxalates and citrates etc (Carcilly *et al* 1970; Anderson and Sale 1979; Bednorz *et al* 1987; Capone *et al* 1987; Wang *et al* 1987) have gained acceptance in recent years for their ability to give finer sinteractive particles with higher density and improved homogeneity.

In this paper, we report a novel and simple technique for the preparation of such fine amorphous ceramic oxides. In this study it was aimed at producing ferrites of Ni(II), Zn(II), Cu(II) and Co(II) ions from their corresponding salt solutions using triethylammonium carbonate (organic carbonate) as the precipitating agent. The effect of polymer coating of the precursors over the particle-size of these oxides was also studied. The particles obtained were characterized by X-ray diffraction (XRD) patterns, energy-dispersive X-ray spectroscopy (EDAX) and scanning electron microscopy (SEM).

2. Experimental procedure

Mixtures of ferric salt solutions and the corresponding salt solutions of the desired ferrites were prepared. The compositions chosen were based on the stoichiometry of $NiFe_2O_4$, $ZnFe_2O_4$, $CuFe_2O_4$ and $CoFe_2O_4$. These mixtures were separately poured into an excess of freshly prepared solution of triethylammonium carbonate (Pramanik *et al* 1990), with continuous stirring. The precipitates obtained were filtered, washed and

dried. It was then ground and calcined at 900°C for 150 min. The precursors were decomposed/oxidized to form the respective ferrites.

To study the effect of polymer adsorption over these oxides, the above procedure for the preparation of ferrites was repeated in the presence of 2.5% solution of polyvinyl alcohol (PVA) in the solution-mixture before precipitation.

The products obtained were characterized by XRD patterns (figures 1 and 2) recorded using a Philips PW-1710 X-ray diffractometer and Cu-K_α radiation. The composition and formation of these ferrites were confirmed by EDAX using AN 10,000 EDAX link

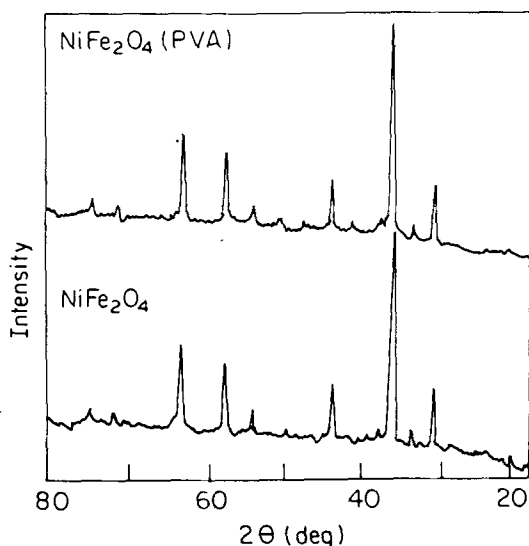


Figure 1. XRD pattern of NiFe₂O₄ in (a) absence of PVA and (b) presence of PVA.

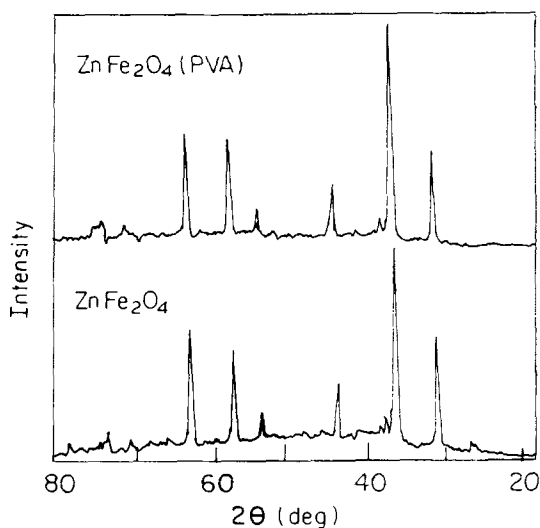


Figure 2. XRD pattern of ZnFe₂O₄ in (a) absence of PVA and (b) presence of PVA.

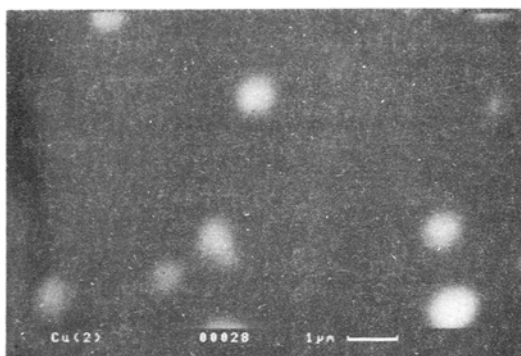


Figure 3. Scanning electron micrograph of CuFe₂O₄.

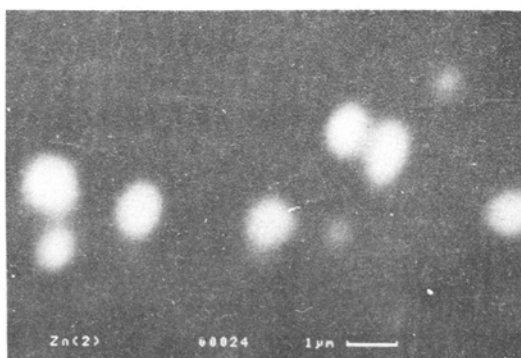


Figure 4. Scanning electron micrograph of ZnFe₂O₄.

system. SEM studies, using the model CAMSCAN series 2 DV, revealed the fine particle nature of the prepared ferrites (figures 3 and 4).

3. Results and discussion

The novelty of the organic carbonate precipitating technique over that of an inorganic carbonate process lies in its simplicity. These organic carbonates can be easily burnt off during calcination of the precursors to give the desired oxides, thus avoiding thorough washings. The inherent difficulty in using inorganic carbonates arises due to their persistence in the precursors and the laborious chemical treatment involved in their removal. Though the use of ammonium carbonate as a precipitating agent is an exception to this, our studies showed that its tendency to leach Ni(II) and Cu(II) ions from the precursors restricts its use.

The comparative study of XRD patterns of the calcined oxides obtained in the presence of PVA and in the absence of the same, shows no significant change in the peak-intensity and the peak-width reflecting the fact that no marked change in particle-size occurs in the presence of PVA (figures 1 and 2). SEM studies confirm this fact. These observations may be attributed to the possibility that the triethylammonium carbonate solution when added to salt solutions, for the precipitation, gives a gel-network structure in which the precursors' nuclei gets embedded and the particle-size

growth is restricted. As the organic carbonate solution itself acts like a polymeric reagent, the presence of a polymer coating on the precursors does not significantly serve the purpose of further restricting the particle-size growth.

SEM studies revealed the particle-size range to be between 1 and 3 μm . The observed densities of the ferrites varied from 95–97% from the theoretical densities. In conclusion, it has been possible to successfully obtain high yield of single-phasic, fine, amorphous, homogeneous ferrite particles with minimum chemical treatment using triethylammonium carbonate precipitating technique. Moreover this method is cost-effective since triethylamine can be easily recovered from the filtrate for reuse. Dimethylammonium carbonate, trimethylammonium carbonate and diethylammonium carbonate may also be used in place of triethylammonium carbonate for the precipitation of ferrites and other mixed-oxide systems (Pramanik *et al* 1990).

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