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Influence of stoichiometry and calcination condition on the microstructure and phase constitution of $NiFe_2O_4$ powders prepared by sol-gel autocombustion method

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The phase constitution and the microstructure of $NiFe_2O_4$ powders prepared by a sol-gel autocombustion route have been studied in this research. Amorphous gels, as-burnt powders with a varying Fe/Ni ratio and calcined powders at temperatures between 600–1000 °C for 1h, were investigated by using DTA/TG, XRD and SEM techniques. The results show that different Fe/Ni ratios in the starting solution and different calcination affect the crystal size of the synthesized powder and the phase constitution. SEM micrograph also shows a particle size less than 100 nm.

1 Introduction Nickel ferrite is a soft ferrite having low magnetic coercivity and high electrical resistivity. The high electrical resistivity and good magnetic properties make this ferrite an excellent core material for power transformers in electronics and telecommunication [1, 2]. These ferrites are commonly produced by conventional ceramic processes [3], involving high temperature (≥1200 °C) solid-state reactions between the constituent oxides/carbonates. However, the method has some inherent drawbacks such as: (1) Poor compositional control, (2) chemical inhomogeneity, (3) coarser particle size and (4) introduction of impurities during ball-milling/grinding. In addition, the coarse and non-uniform particles, on compacting, result in the formation of voids or low-density areas in the green compacts. Wet chemical methods such as coprecipitation using mixed metal sulphate solutions kept at 100 °C by NaOH [4], coprecipitation using metal nitrates by hydrazine [5], coprecipitation using metal nitrates by diethylamine [6] and sol-gel method [7] have over come these drawbacks and produced homogeneous, fine and reproducible ferrite powders using aqueous solutions of salts of constituent ions. In this work the sol-gel autocombustion preparation of $NiFe_2O_4$ was carried out using aqueous solutions of ferric nitrate, nickel nitrate, citric acid and ammonia. This resulted in the formation of single phase ferrite powder after combustion which further characterized by XRD, DTA/TG and SEM measurements.

2 Experimental procedure The chemical materials used in experiments were ferric nitrate nonahydrate (≥99.5%, Merck), nickel nitrate (97%, Merck), citric acid (99.5%, Merck) and ammonia to prepare $NiFe_2O_4$ ferrite material. The ferrite powder was synthesized as follows. Appropriate amounts of metal nitrates and citric acid were first dissolved in minimum amount of de-ionized water to make a clear solution. Molar ratio of nitrates to citric acid was 1:1. A small amount of ammonia was added to the solution

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to adjust the PH value at about 7. During this procedure, the solution was continuously stirred using a magnetic agitator. Then, the mixed solution was poured into a dish and heated and stirred continuously to transform into a xerogel. In a proper temperature ignition started and the dried gel burnt in a self-propagating combustion manner until all the gel was burnt out completely to form a loose powder. Thermogravimetric (TG) and differential thermal analysis (DTA) of the precursor gel were carried out at a heating rate of 10 °C/min. The combusted powder was then calcined at different temperature for 1 h. The phase identification of the gel precursor and the as-burnt powder as well as the calcined powder was performed using XRD with CuK_α radiation. The microstructure of the calcined powder was observed by scanning electron microscop (SEM).

3 Results and discussion

3.1 DTA-TG characterization of dried gels The combustion process of the nitrate-citrate gels was investigated by thermal analysis (DTA and TG) of the dried gels. Fig. 1 shows the DTA and TG plots of the dried gel with Fe/Ni of 2. As expected, the decomposition reaction is strongly exothermic. The exothermic peak, at ~236 °C, is relatively sharp and intense. This indicates that the decomposition of the gel occurs suddenly in a single step, as observed in other systems [8–10]. The weight reduction associated with this exothermic reaction was approximately 80%. This is probably attributed to the exit of water steam, NO_2 and CO_2. However the citrate gels without NO_3^- ion, washed out with deionized water before gelation, did not exhibit auto-combustion behavior. Moreover, it was observed that the combustion process depends on the concentration of Fe. Figure 2 shows the DTA plots for the dried gel with Fe content of 1 and 2. Comparing the two plots, we can see that the exothermic peak at~236 °C reduces with increasing the Fe content. It is believed that the main exothermic peak corresponds to the reaction between nitrate ions and carboxylate anions.

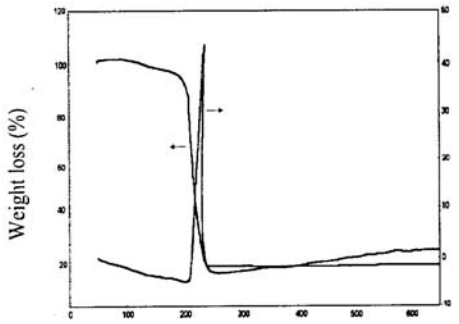

Fig. 1 DTA and TG plots of the dried nitrate- citrate gel.

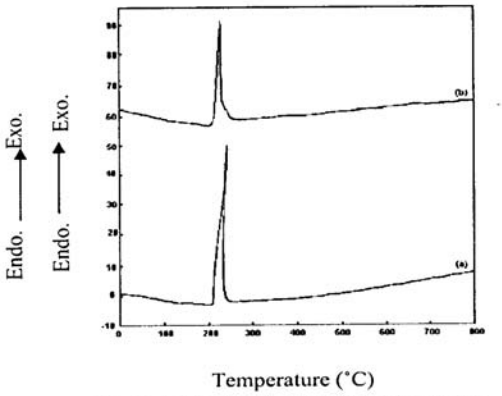

Fig. 2 DTA plots for the dried gel with Fe content of 1 (a) and 2 (b).

3.2 Influence of the Fe/Ni ratio The variations of the phase constitution with the different Fe/Ni ratios are presented in Fig. 3, for the dried gels and as-burnt powders respectively. It is clear that the dried gels are amorphous in nature. All the as-burnt powders with the different ratios of Fe/Ni have nickel ferrite with spinel structure. This indicates that the $NiFe_2O_4$ ferrite in opposite of $BaFe_{12}O_{19}$ [11–13] can be directly formed after auto-combustion of gel. The results seem to indicate that Fe/Ni = 2 yield the best

phase constitution because intermediate phases as $FeNi_3$ and NiO which deteriorate the magnetic properties are eliminated.

3.3 Influence of the calcination temperature on the phase constitution Figure 4 shows the effect of the calcination temperature on phase constitution of powders calcined at the range of 600–1000 °C which processed with a Fe/Ni ratio of 2. The phases observed in range 600–900 °C were α-Fe_2O_3 and $NiFe_2O_4$ and only at 1000 °C single phase $NiFe_2O_4$ could be obtained. Hence, increasing the calcinationtemperature was beneficial in order to eliminate the intermediate phases which deteriorate the magnetic properties and to form single phase $NiFe_2O_4$. Figure 5 also shows the Scanning Electron Micrograph of the calcined powder at 1000 °C for 1h with a particle size of < 100 nm.

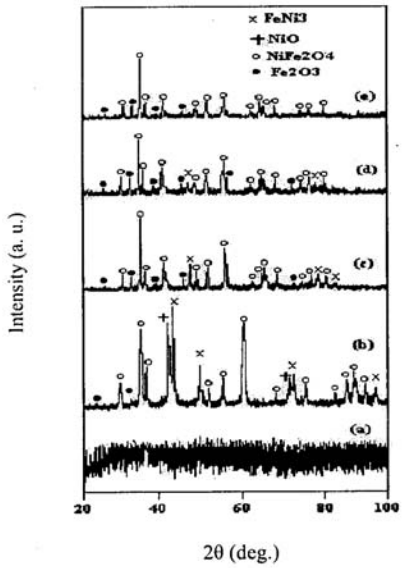

Fig. 3 XRD patterns for the (a) dried gel and (b-e) as-burnt powders with different contents of Fe/Ni, (b) x=0.5, (c) x=1, (d) x=1.5 and (e) x=2.

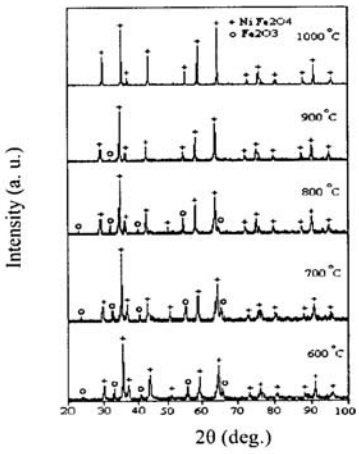

Fig. 4 XRD patterns corresponding to calcined powders at several temperatures for 1 h with a Fe/Ni ratio of 2.

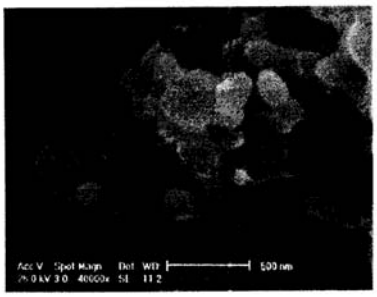

Fig. 5 SEM photograph of calcined powder at 1000 °C for 1h.

4. Conclusions A series of nitrate-citrate gels were prepared from metal nitrates and citric acid by a sol-gel process in order to synthesize $NiFe_2O_4$ ferrite. The nitrate-citrate gels can burn in a self- propagating combustion way. After combustion, the gel is directly transformed into nanocrystalline ferrite powder. The combustion process is an oxidation- reduction reaction in which the NO_3^- ion is oxidant and the carboxyl group is reductant. The studies of the effect of the Fe/Ni ratio and calcination temperature on the phase constitution indicated that Fe/Ni = 2 and calcination at 1000 °C resulted in formation of single phase $NiFe_2O_4$. By this method ferrite powders with particle size of less than 100 nm were synthesized.

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