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Influence of the metal nitrates to citric acid molar ratio on the combustion process and phase constitution of barium hexaferrite particles prepared by sol–gel combustion method

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Abstract

A novel sol–gel combustion process was used to synthesize the ultrafine particles of barium hexaferrite. The nitrate–citrate gels were prepared from metal nitrates and citric acid solutions under various molar ratios of the metal nitrates to citric acid of 0.5, 1, 1.5 and 3 by sol–gel process. The results showed that the nitrate citrate gels exhibit a self-propagating behavior after ignition in air at room temperature. The thermal decomposition of nitrate–citrate gels and the phase evolution of calcined powder were investigated respectively by DTA/TG and XRD techniques. Scanning electron microscope was used to characterize the microstructure of the products. The results revealed that the formation temperature and the crystallite size of barium hexaferrite are influenced significantly by the molar ratio of the metal nitrates to citric acid. The formation temperature of barium hexaferrite decreases with increasing the molar ratio of the metal nitrates to citric acid.

Keywords: A. Sol–gel processes; A. Calcination; C. Magnetic properties; D. Ferrites; E. Hard magnets

1. Introduction

Hexagonal hard ferrites such as $BaFe_{12}O_{19}$ are currently magnetic materials with great scientific and technological interest, because of their relatively, high Curie temperature, high coercive force and high magnetic anisotropy field as well as excellent chemical stability and corrosion resistivity [1]. In the past decade, there has been an increasing interest in methods for the preparation of fine particles of barium hexaferrites, because of its emerging application in perpendicular magnetic recording media. The synthesis method strongly determines its homogeneity, particle size, shape, and magnetic characteristics [2].

The classical ceramic method for preparing barium hexaferrite requires a high calcining temperature (∼1200 °C), which induces sintering and aggregation of particles. Furthermore, the milling process to reduce the particle size from multi-domain to single domain, generally yields nonhomogeneous mixtures on a microscopic scale and induces lattice strains in the material [3]. In order to achieve highly homogeneous ultrafine particles of barium hexaferrite and to avoid the milling process, various techniques such as chemical coprecipitation [4], hydrothermal [5], sol–gel [6,7], glass crystallization [8], microemulsion [9], citrate precursor [10] and salt melt methods [11] have been developed. However, a number of difficulties in obtaining high purity, ultrafine and homogeneous particles of barium hexaferrite with narrow size distribution have been pointed out by several investigators.

Synthesis of barium hexaferrite powders by a sol–gel combustion technique is focused in the present work. This is a novel way with a unique combination of the chemical sol–gel process and the combustion process based on the gelling and subsequent combustion of an aqueous solution containing salts of the desired metals and some organic fuel, giving a voluminous and fluffy product with large surface area. This process is less complicated than the others. In the present study, a metal nitrates-citric acid solution has been used to prepare barium hexaferrite. The effects of metal nitrates/citric acid ratio (henceforth referred to as MN/CA ratio) on the combustion process and phase constitution of barium hexaferrite particles were investigated.

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2. Experimental procedure

Nanostructured barium hexaferrite powders were synthesized using the sol–gel combustion method. The starting materials were iron nitrate, barium nitrate, citric acid and ammonia, all of analytic purity. Appropriate amount of $Fe(NO_3)_3{\cdot}9H_2O$ and $Ba(NO_3)_2$, in a molar ratio of 11, were dissolved in a minimum amount of deionized water. Citric acid was then added into the prepared aqueous solution to chelate Ba^{2+} and Fe^{3+} in the solution. The mixed solution was neutralized to pH 7 by adding liquor ammonia. The neutralized solution was evaporated to dryness by heating at 100 °C on a hot plate with continuous stirring. As water evaporated, the solution became viscous and finally formed a very viscous brown gel. Increasing the temperature up to about 200 °C led to the ignition of the gel. The dried gel burnt in a self-propagating combustion manner until all gels are completely burnt out to form a loose powder. Finally, the as-burnt powders were calcined in air at 800 and 850 °C for 1 h with a heating rate of 10 °C/min to obtain barium hexaferrite nanoparticles. For studies on the effect of variation in citric acid content, four samples were prepared with molar ratios of metal nitrates to citric acid (MN/CA) of 0.5, 1, 1.5 and 3 that are named in with A1, A2, A3 and A4, respectively.

The thermal decomposition behavior of the gels was examined by simultaneous DTA/TG in air with the heating rate of 10 °C/min on the LINSEIS L70/2171 TGA and DTA instruments. The phase identification of the gel precursor, the as-burnt and calcined powders were performed using X-ray diffraction (XRD) on a Philips PW-1730 X-ray diffractometer using Cu Kα radiation ($\lambda = 1.5405$ Å). The average crystallite size of the powders was measured by X-ray line-broadening technique employing the Scherrer formula. The particle morphology examined by a scanning electron microscope (Cambridge S360).

3. Results and discussion

The experimental observation showed that nitrate–citrate gels with all four molar ratios of metal nitrates to citric acid exhibited self-propagating combustion behavior. When the dried gels were ignited, the combustion rapidly propagated forward until all the gels were burnt out completely to form a loose powder with a large amount of microscopic pores. Fig. 1 shows the SEM micrograph of as-burnt powder derived from sample A2.

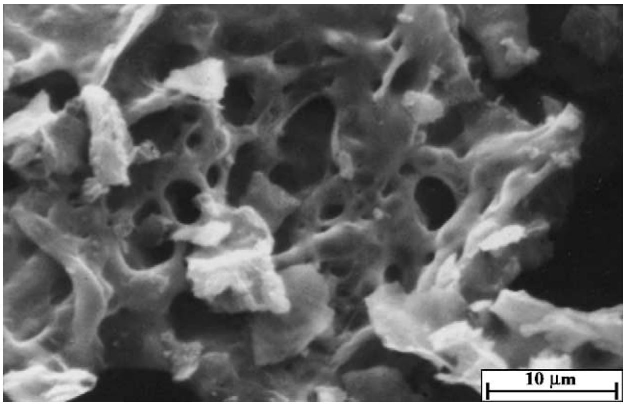

Fig. 1. SEM micrographs of as-burnt powder derived from sample A2.

The auto-catalytic nature of the combustion process of nitrate–citrate gels was studied by thermal analysis (DTA/TG) of the dried gels. The DTA/TG results for the nitrate–citrate dried gels prepared with different ratios of nitrates to citric acid are shown in Fig. 2. Generally, on the DTA curves of the gels with different MN/CA molar ratios, one endothermic peak and two exothermic peaks appear at about 100, 200 and 360 °C, respectively, except for the gel with MN/CA = 3 that there is only one exothermic peak at 200 °C. The endothermic peak around 100 °C in the DTA curve with a small weight loss (∼2%), is due to the loss of residual water in the gel. The first sharp exothermic peak at about 200 °C with a concurrent large weight loss of ∼70% could be due to the reaction of nitrates with citric acid. Whereas, the decomposition of unreacted starting citric acid remained after combustion could be responsible for the exothermic peak at about 360 °C. During the combustion, large amounts of gases such as H_2O, CO, CO_2 and NO are liberated.

In the starting materials C, H, Ba and Fe could be considered as reducing elements with corresponding valences of +4, +1, +2 and +3, respectively. O is regarded as an oxidant element with valences of −2, the valence of nitrogen is taken as zero. The total calculated valence of metal nitrates by arithmetic summation of oxidizing and reducing valences is negative whereas for citric acid is positive. Therefore, the combustion can be considered as a thermally induced anionic, redox reaction of the gel wherein the citrate ion acts as reductant and nitrate ions acts as oxidant. Since the nitrate ions provide an in situ oxidizing environment for the decomposition of the organic component, the rate of oxidation reaction increases slightly. The combination of the lowering of the reaction temperature and the increase rate results in a self-propagating combustion of the nitrate–citrate gel.

It was observed in this investigation that the position of two decomposition reactions is changed with the MN/CA molar ratio of the gel. With increasing the MN/CA molar ratio, the first exothermic peak become stronger and the second one become weaker and the corresponding weight loss decreases and finally, completely disappear for the gel with MN/CA molar ratio of 3. Therefore it could be said that the combustion rate is affected with the molar ratio of nitrates to citric acid; the highest rate is achieved with the MN/CA molar ratio of 3.

The X-ray diffraction studies (XRD) have been carried out on the dried gel, as-burnt powder, and the powders calcined at 800 and 850 °C for 1 h. Fig. 3 shows the XRD patterns of the A1, A2 and A3 dried gels. The obtained dried

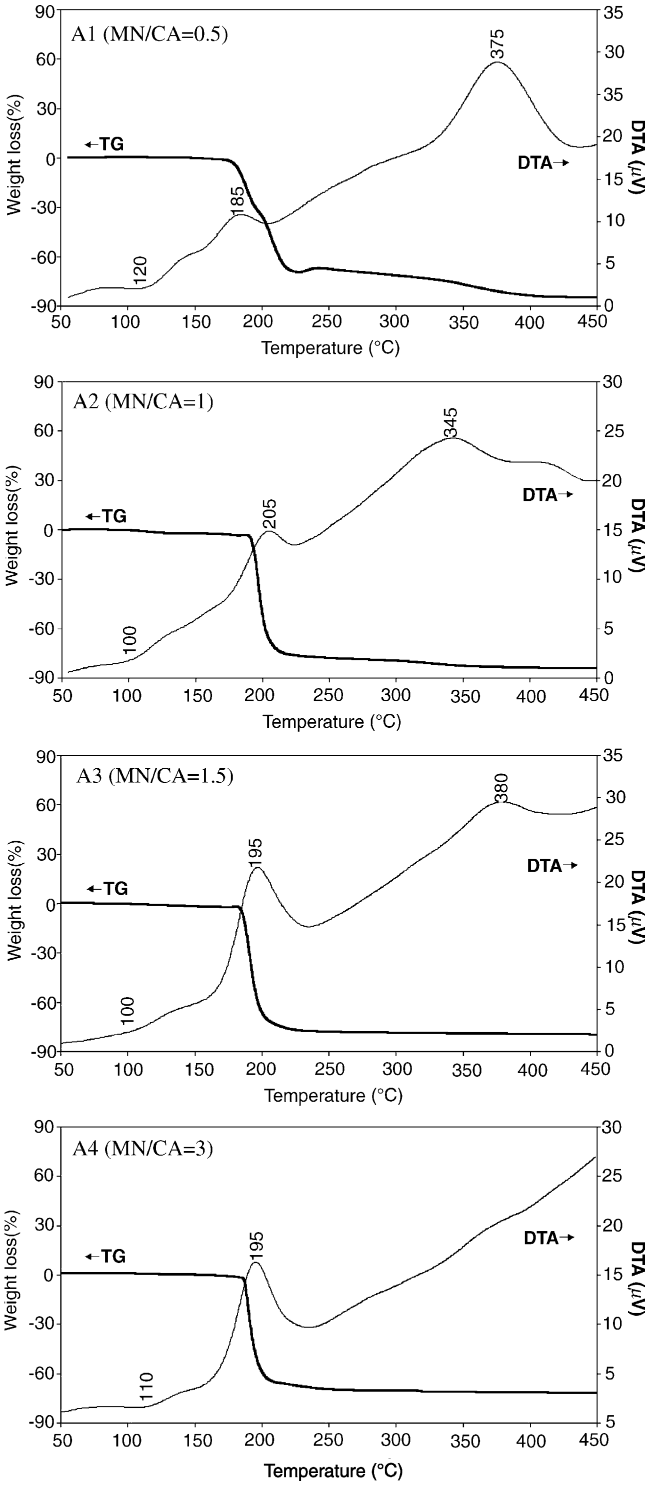

Fig. 2. DTA/TG curves for the nitrate–citrate gels with different MN/CA molar ratio.

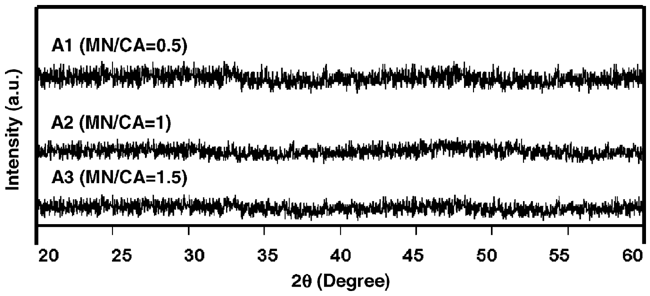

Fig. 3. XRD patterns of the nitrate–citrate gels with different MN/CA molar ratio.

gel in all three samples are found to be amorphous. The released heat in the process of exothermic decomposition has been observed to be sufficient for complete conversion of the metal compounds to metal oxides and carbonates. The XRD patterns of as-burnt powder of samples A1, A2 and A3 are shown in Fig. 4, which indicate the presence of γ-Fe_2O_3 as a major phase and some other minor phases such as α-Fe_2O_3, $BaCO_3$ and BaO_2 which confirms the completion of the decomposition process. The interaction between CO or CO_2 generated from citric acid decomposition and Ba^{2+} ions leads to formation of $BaCO_3$ and it's amount decreases as the MN/CA molar ratio increases because of decreasing the carbon content of the system. The XRD pattern of sample N1 shows the presence of some residual organic

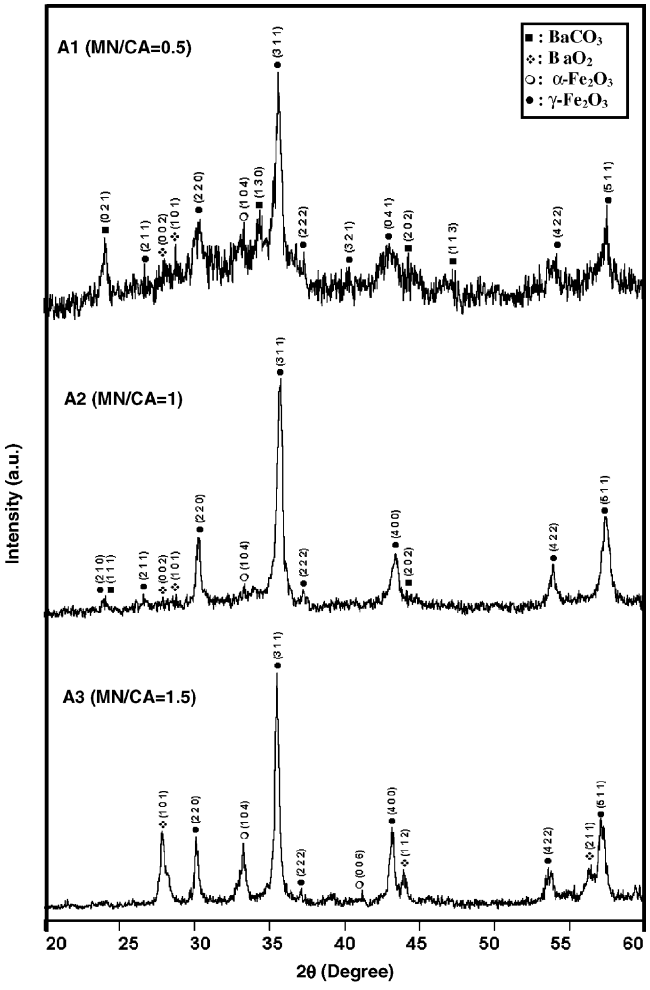

Fig. 4. XRD patterns of as-burnt powders derived from the nitrate–citrate gels with different MN/CA molar ratio.

phases. This is in good agreement with DTA/TG results. The broadening of the XRD peaks indicates the particles are sub-micron in size. It was also observed that the diffraction peaks become narrower with decreasing of citric acid content, suggesting an increase in the crystallite size. Because the combustion takes place more complete and more vigorous then the heat liberated increases that leads to more particle growth. On the other hand, the more citric acid content leads to more amounts of removal gases such as CO and CO_2 during the combustion, then result in more porous ash and removing the more thermal energy by gases from the system. The more pore leads to more difficult diffusion of atoms and the more removal gases bring into the more temperature losses. Both of these factors act as an agent to reduce the growth rate of particles during the combustion.

The crystallite size of as-burnt powders were calculated from the X-ray peak broadening of the (2 2 0) diffraction peak using the Scherrer formula [12]:

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

where D is the crystallite size in nm, λ is the radiation wavelength (0.15405 nm for Cu Kα), β is the corrected halfwidth, and θ is the diffraction peak angle. The calculated crystallite sizes are 17.2, 34.3 and 68.6, respectively for A1, A2 and A3 samples. As expected, crystallite size decreases with increasing citric acid content.

Effects of MN/CA molar ratio of the starting solution on the phase constitution of the gel derived barium hexaferrite powder could be seen in Fig. 5, which shows XRD pattern of the samples A1, A2 and A3 after calcination at 800 °C for 1 h. It may be pointed out that calcined powder at 800 °C obtained from all the three samples contains the same oxide and carbonate phases, the only difference being in their relative quantities.

Increasing the citric acid content leads to decrease the intermediate phases such as α-Fe_2O_3, γ-Fe_2O_3 and $BaFe_2O_4$ whereas the $BaFe_{12}O_{19}$ increases and appears as a major phase for sample A1. It also causes barium hexaferrite to grow bigger. Increasing citric acid contents in starting solution causes more compositional homogeneity of the gel, because more citric acid is ionized then more carboxylic groups ($COOH^-$) to chelate Fe^{3+} and Ba^{2+} are generated. As the carbon chains in citrates are decomposed during combustion and calcination, adjacent Fe^{3+} and Ba^{2+} ions which are homogeneously distributed throughout the matrix can more easily and completely come into contact and form crystal lattice of barium hexaferrite. In addition using the excess citric acid leads to some remained unreacted organic material that during a exothermic reaction after combustion decomposes. The thermal energy due to organic material decomposition lead to raise the particle crystallinity and to carry out the reactions more completely so the formation temperature of barium hexaferrite decreases. Fig. 6 shows the XRD pattern for the sample A1 calcined at 850 °C and indicates the formation of single phase barium hexaferrite at this temperature for the gel prepared with MN/CA = 0.5.

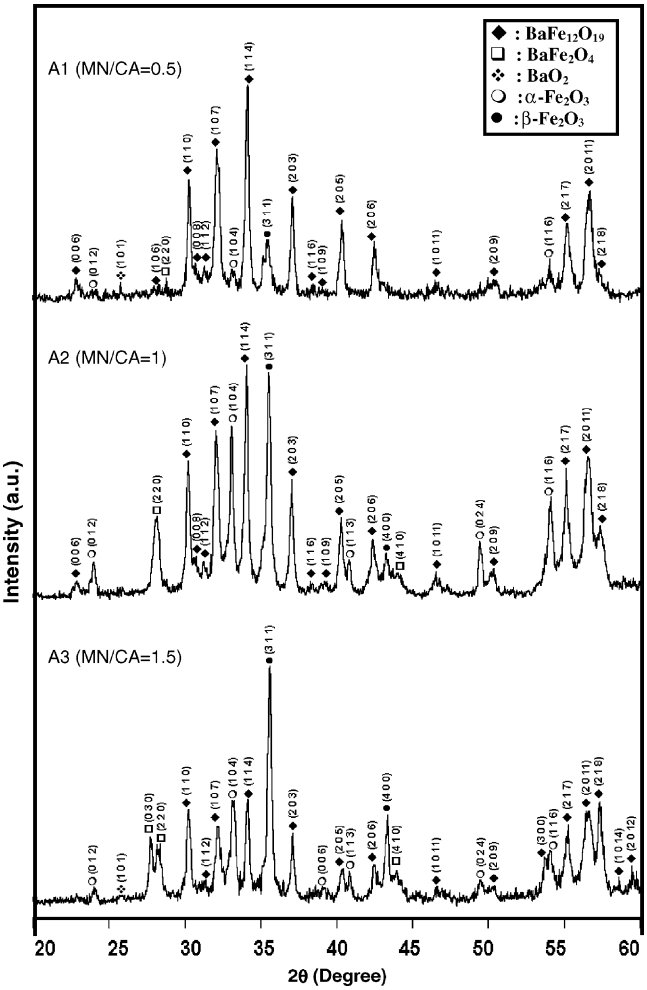

Fig. 5. XRD patterns of powders derived from the nitrate–citrate gels with different MN/CA molar ratio and calcined at 800 °C.

The crystallite sizes of barium hexaferrite particles calcined at 800 °C measured using the Scherrer formula and (1 1 0) reflection. The calculated crystallite sizes are 41.2, 34.2 and 29.4 nm, respectively for A1, A2 and A3 samples. As expected for samples calcined at 800 °C, the crystallite

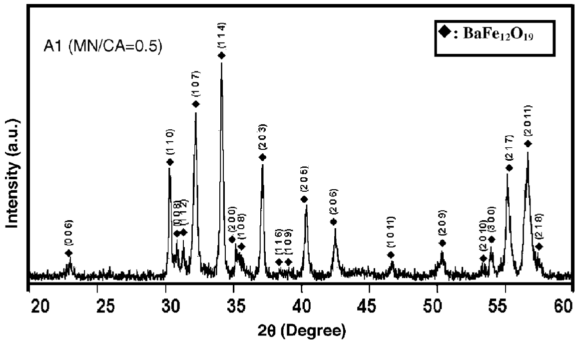

Fig. 6. XRD pattern of powder derived from the nitrate–citrate gels with MN/CA molar ratio of 0.5 and calcined at 800 °C.

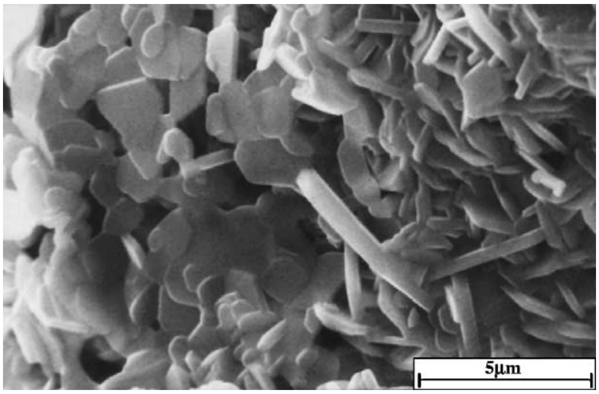

Fig. 7. SEM micrographs of powder derived from the nitrate–citrate gels with MN/CA molar ratio of 0.5 and calcined at 800 °C.

size increases with increasing the citric acid content. The formation temperature of barium hexaferrite decreases due to the increasing of citric acid content, so samples with lower formation temperature and calcined at the same temperature have the more time to grow. The crystallite sizes of barium hexaferrite particles for sample A1 calcined at 850 °C measured using the Scherrer formula is 82.3 nm that reveals the particle size growth with increasing the calcination temperature.

Typical SEM image of the sample A2 calcined at 1100 °C for 1 h shown in Fig. 7, indicates the plate-like particles of barium hexaferrite with a mean particle diameter of 3 μm.

4. Conclusion

Nano-size particles of barium hexaferrite have been synthesized at a relatively low temperature by the sol–gel combustion method using a gel including citric acid as a fuel and metal nitrates as a reductant. The combustion rate is associated with the molar ratio of nitrates to citric acid and its rate is must vigorous and rapid for the gel with MN/CA molar ratio of 3. The formation temperature of barium hexaferrite was decreased on increasing the citric acid contents in the starting solution. Single phase barium hexaferrite was formed at a relatively low temperature of 850 °C for sample synthesized with MN/CA molar ratio of 0.5.

Acknowledgements

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