Optimization of fuel to metal nitrate ratio for synthesis of phase pure $BaZn_{0.2}Zr_{0.2}Fe_{11.6}O_{19}$

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Abstract: *$BaZn_{0.2}Zr_{0.2}Fe_{11.6}O_{19}$ were synthesized by sol–gel auto combustion route using tartaric acid as fuel. XRD data reveals pure phase upto 1.00 M and presence of Fe_2O_3 impurity phase beyond 1.00 M. SEM micrographs revealed irregular shapes and sizes of particles. Magnetic measurements revealed the presence of magnetic ordering in all the samples. The H_c was found to be minimum in 1.25 M sample where as M_r and M_s were found to be maximum in 1.00 M sample. The optimum fuel to metal nitrate ratio was found to be 1.00 M.*

Keywords: *M-type Barium hexaferrite; Sol-gel auto combustion; Fuel to metal nitrate ratio; Saturation magnetization; coercivity.*

1. Introduction

The M-type hexaferrite are useful for making permanent magnets, microwave devices, electromagnetic shielding devices and magnetic recording devices [1, 2]. Among M-type hexaferrites, Barium based (BaM) are most useful and widely studied. For practical applications, it is desirable to obtain highly crystalline BaM having very narrow size distribution. In this regard, sol-gel-auto-combustion technique can be of significance for synthesis of BaM. The properties of synthesized BaM samples using sol gel auto combustion method depends upon various factors like pH, metal nitrate to fuel ratio, calcination temperature and type of fuel used [3,4, 5]. Fuel to metal nitrate ratio is known to affect the surface morphology, particle size as well as the magnetic properties of BaM [4, 6]. A number of fuel materials such as Stearic acid, citric acid, sucrose, citric acid-ammonia, ethylene glycol-citric acid combination etc. have been explored for BaM synthesis [7, 8]. However, very few reports of tartaric acid as fuel for sol gel synthesis are available in literature. In this study we report the impact of variation of metal nitrate to citric acid fuel ration on the physical properties of $BaZn_{0.2}Zr_{0.2}Fe_{11.6}O_{19}$ via sol-gel auto-combustion method.

2. Experimental

$BaZn_{0.2}Zr_{0.2}Fe_{11.6}O_{19}$ was synthesized by dissolving a mixture in double distilled water of analytical grade chemical: Barium nitrate, Ferric nitrate, Zinc nitrate, Zirconyl nitrate and tartaric acid. Tartaric acid is used as fuel (different fuel to metal nitrate ratio 0.5 M, 0.75 M, 1.0 M, 1.25 M and 1.5 M). The resultant solution was heated at 80-100°C for 3-4 hours with continuous magnetic stirring. With continuous heating excessive water evaporates and viscous dark brown gel was formed. This gel was put in oven at 200-250°C for 1-2 hour after which auto combustion occurs resulting in a precursor powder material. Grounded precursor was calcined at 900°C for 6 hours in muffle furnace to get crystalline $BaZn_{0.2}Zr_{0.2}Fe_{11.6}O_{19}$ phase. Rigaku Miniflex diffractometer equipped with Cu-α radiation, was used to collect data in the 20-80° 2θ range a step size of 0.005. Magnetic studies were carried out with vibrating sample magnetometer (Microsense EV-90) at room temperature. Surface morphology and EDAX was determined by FESEM (JEOL, JSM-7100) at an operating voltage of 20KV.

3. Results and discussion

3.1 Structural analysis

The XRD diffraction of the various $BaZn_{0.2}Zr_{0.2}Fe_{11.6}O_{19}$ samples have been shown in **Figure 1**. A comparison of the data (2θ peak positions) with the literature revealed that all the samples (except at 1.25 M and 1:50 M) are phase pure.

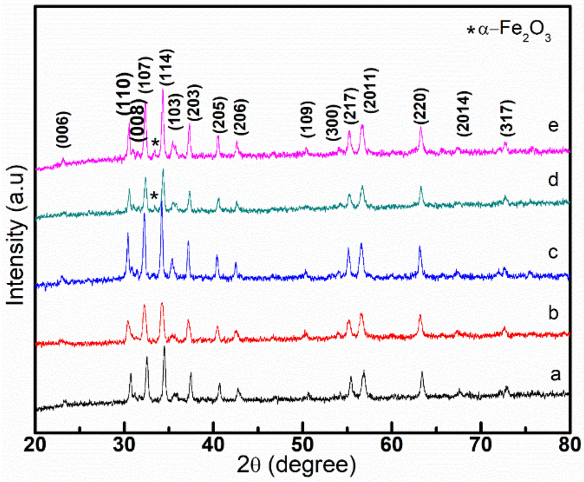

Figure 1. XRD diffractograms of $BaZn_{0.2}Zr_{0.2}Fe_{11.6}O_{19}$ samples synthesized at a) 0.50 M, b) 0.75 M, c) 1.00 M, d) 1.25 M, and e) 1.50 M fuel to metal nitrate ratio.

The impurity peaks have been marked with '*' and these correspond to α-Fe_2O_3 phase. It should be noted that the samples synthesized at fuel to metal nitrate ratio of 0.5 M and 0.75 M are not highly crystalline as indicated by the presence of some low intensity broad peaks in these samples. Thus, the fuel to metal nitrate ratio of 1.0 M turns out to be the most optimal for synthesis of highly crystalline and phase pure BaM. It should be noted that the role of the fuel is to provide heat by oxidation and chelation of metal ions. Thus, the lower crystallinity at lower fuel to metal nitrate ratio (<1.0) results from insufficient heating (due to lower amount of fuel) while the phase impurities at >1.0 ratio result from excessive heating [5-8]. The "a" and "c" have been found out to be 5.8927 and 23.2461 (using LeBail refinement) for 1.0 M sample. The c/a ratio has been found to be <3.98 for all the sample implying that they are M-type hexaferrites.

3.2 Surface Morphology and Elemental analysis

Figure 2 presents the FESEM micrographs of $BaZn_{0.2}Zr_{0.2}Fe_{11.6}O_{19}$ samples synthesized at different fuel to metal nitrate ratio and EDAX data corresponding to 1.00 M sample. These micrographs reveals the presence of irregular shaped particles in all the samples.

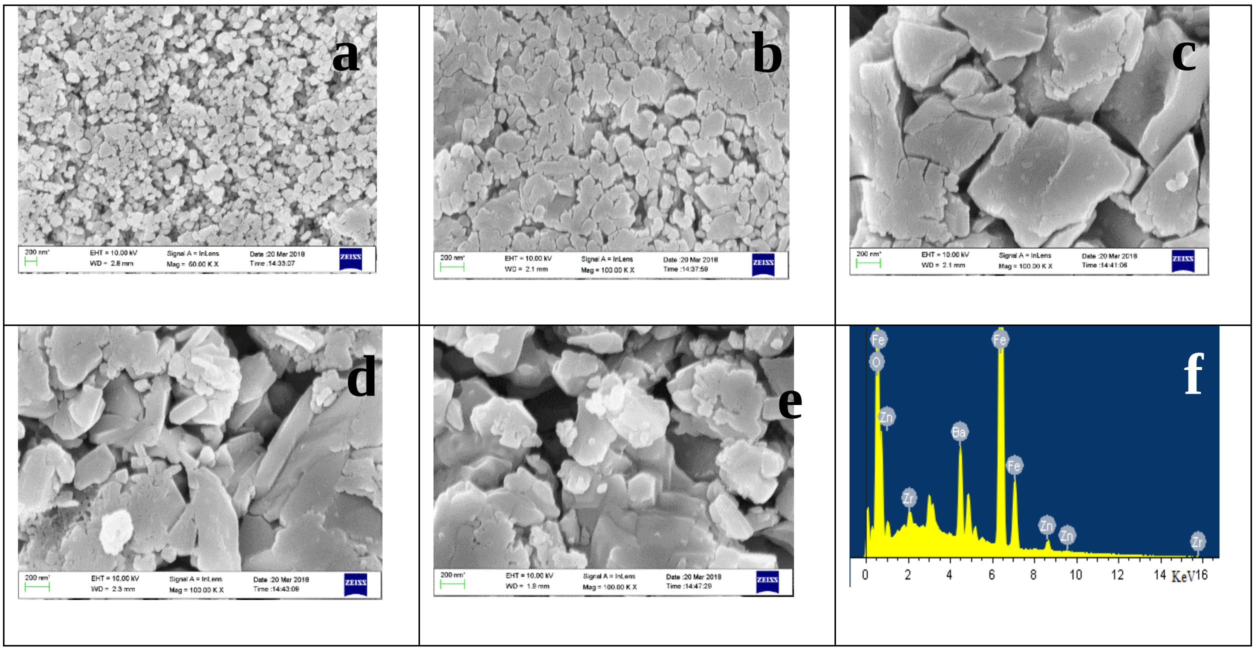

Figure 2. FESEM micrographs of $BaZn_{0.2}Zr_{0.2}Fe_{11.6}O_{19}$ samples synthesized at a) 0.50 M, b) 0.75 M, c) 1.00 M, d) 1.25 M, and e) 1.50 M fuel to metal nitrate ratio. The EDX data corresponding to 1 M sample is shown in (f).

The samples 0.50 M and 0.75 M appear to be more homogeneous with respect to particle size distribution. The grain size has been observed to increase from ≈ 200 nm (in 0.50 M sample) to ≈ 1.37 μm (in 1.00 M sample. The particle size increases marginally from 1.0 M to 1.25 M sample. However, the particle size decreases for >1.25 M samples. The continuous increase in particle size upto metal nitrate to fuel ratio of 1 M, is because of increasing fuel concentration towards its optimal value (1.0 M). However, beyond 1.00 M, higher tartaric acid content generates excessive gases and high pressure of released gases results in more porous structure, reduction of particle size and appearance of impurity phases (as was observed in the XRD data). The EDX data of the 1.00 M sample is shown in Figure 2f. The data reveals the presence of Ba, Zn, Zr, Fe and O in nearly stoichiometric proportions.

3.3 Magnetic Studies

The M-H data measurements of various samples has been shown in Fig. 3. It is clear from the figure that all the sample exhibit non-linear M-H loops which are not saturated even at the highest value of applied magnetic field. The presence of hysteresis loops in all the samples indicates the presence of magnetic order in all the samples. Various magnetic parameter (M_s, H_c and M_r) of all the samples have been listed in Table 1. It is clear from the table that M_s values increases with increase metal nitrate to fuel ratio upto 1.0 M, beyond which it starts decreasing due to formation of impure phase (α-Fe_2O_3), the canted antiferromagnetic behavior of α-Fe_2O_3 is responsible for reduction in magnetic properties [4]. However, the H_c continuously decreases with increasing metal nitrate to fuel ratio upto 1.25 M, beyond which it increases due to decrease in particle size. Thus our coercivity data is nicely correlated to the inverse of the particle size which is also well reported in literature [8]. The magnetic parameters are best for 1.0 M sample which again reveals that the optimal fuel to metal nitrate ratio is 1.0 M.

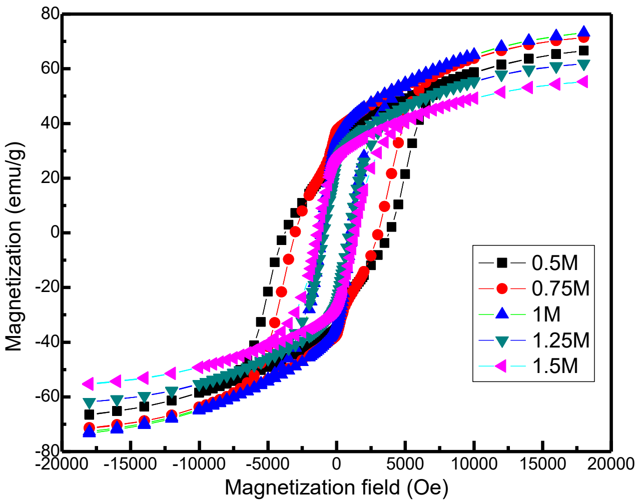

Figure 3. The *M-H* hysteresis loop of $BaZn_{0.2}Zr_{0.2}Fe_{11.6}O_{19}$ samples synthesized 0.50 M, 0.75 M, 1.00 M, 1.25 M, and 1.50 M fuel to metal nitrate ratio.

Table 1. Magnetic parameters of various $BaZn_{0.2}Zr_{0.2}Fe_{11.6}O_{19}$ samples.

Metal nitrate to fuel ratio	H_c (Oe)	M_r (emu/g)	M_s (emu/g)	M_r/M_s
0.50 M	3789	34.98	66.6	0.525
0.75 M	3028	36.56	71.49	0.511
1.00 M	1099	36.99	72.4	0.510
1.25 M	932	35.2	61.9	0.568
1.50 M	1345	32.4	55.4	0.584

4. Conclusions

$BaZn_{0.2}Zr_{0.2}Fe_{11.6}O_{19}$ powder were successfully synthesized by sol-gel auto combustion method using tartaric acid fuel. The XRD data confirmed the phase purity upto 1.0 M samples. FESEM data confirmed an increase in particle size upto 1.25 M. EDAX data confirms the stoichiometry of the prepared samples. The highest value of saturation magnetization and remanence were observed for 1.0 M sample which were attributed to its highest crystallinity and phase purity. The coercivity data was observed to be inversely related to particle size. The XRD, FESEM and magnetic data confirms the optimal fuel to metal concentration to be 1.0 M.

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6. References

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