

INFLUENCE OF CALCIUM ON PROPERTIES OF STRONTIUM AND BARIUM FERRITES FOR MAGNETIC MEDIA PREPARED BY COMBUSTION

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For preparation of the strontium ($\text{SrFe}_{12}\text{O}_{19}$) and barium ($\text{BaFe}_{12}\text{O}_{19}$) hexaferrite powder, with CaO additive used in magnetic recording we used a new method, which is an improved variant of the coprecipitation method. According to this method, named self combustion, the reacting substances are metal nitrates and ammonium hydroxide. The CaO additive improves the coercivity of hexaferrites and a better control of the grain growth is achieved.

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1. Introduction

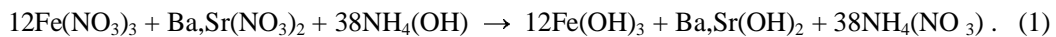
M-type hexagonal ferrites ($\text{BaFe}_{12}\text{O}_{19}$ and $\text{SrFe}_{12}\text{O}_{19}$) are known for their high uniaxial magnetocrystalline anisotropy with the easy axis of magnetization along the hexagonal c-axis and their chemical stability [1]. These have been used in bulk form for many applications due to their hard magnetic properties, for example, as permanent magnets. In the last time, these ferrites have drawn a great interest for magnetic recording media [2,3]. Hexagonal ferrites thin films have higher coercivity and lower saturation magnetization in comparison to Co-alloy films [4]. Hexagonal ferrites show good chemical and thermal stability which would result in longer storage life of the media. Various techniques have been developed to prepare hexagonal ferrites powder with good recording characteristics [5]. The application of hexagonal ferrites in the magnetic media industry requires materials with strict control of homogeneity, morphology and magnetic properties resulting from their preparation and heat treatments.

In this study hexaferrite fine powders were prepared by a novel method which consists in coprecipitation and quick combustion [6]. The main feature of this method is that the crystallization of hexaferrite particles is performed in the proces of solid phase diffusion of the cations. In this method, named self combustion, the reacting substances are metal nitrates and ammonium hydroxide and the coprecipitation of metal hydroxides takes place into a colloidal medium. By quick combustion of a dried gel one obtained a powder with nanogranular structure. Due to the high propagation velocity of the combustion fronts and extremely high heating rates, the combustion reaction will results in a fine-grained product. By heat treatments of the combusted powders, the growth of the hexaferrite crystallites can be controlled. Thus, this method offers the possibility for preparing the hexaferrite submicron powders with a coercivity suitable for recording applications. It was investigated the effect of the annealing time on the grain size and magnetic properties on the undoped and CaO doped Ba and Sr hexaferrite powders prepared by rapid combustion.

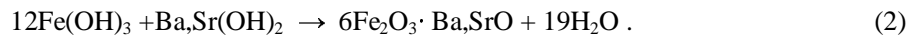
2. Experimental

A solution containing metal (Fe, Ba or Sr) nitrates was mixed with an aqueous solution of 10 wt% polyvinil alcohol. Then, small amounts of ammonium hydroxide solution with 25 wt% concentration was dropped to adjust the pH value (pH ~ 8). It results a sol of metal hydroxides and ammonium nitrate, according to the reaction:

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The resulting mixture was dried at 100 °C and the sol turned into a dried brown gel. When the dried gel was ignited in a corner, a combustion wave spontaneously propagates through the whole gel, converting the hydroxides into oxides and the synthesis between oxides begins:



It results a dark brown fine powder. This powder was pressed in a disk shape and the discs were subjected to heat treatments in air, for different times. For annealing, the samples were introduced into a hot furnace. The nanometric structure of the powder obtained by combustion was evidenced by X-ray powder diffraction (average crystallite size is smaller than 50 nm). The microstructure and morphology of the powder were studied by a high resolution scanning electron microscopy (SEM). The magnetic measurement (specific magnetization, M and coercivity, H_c) were performed by a vibrating sample magnetometer operating up to a maximum field of 10 kOe, on the spheres (of about 4 nm diameter) obtained from discs.

3. Results and discussion

The as prepared powders by combustion were characterized by a relatively large specific magnetization ($M = 44.7$ emu/g, for $\text{SrFe}_{12}\text{O}_{19}$ and $M = 31$ emu/g for $\text{BaFe}_{12}\text{O}_{19}$), small coercivity ($H_c = 520$ Oe for $\text{SrFe}_{12}\text{O}_{19}$ and $H_c = 350$ Oe for $\text{BaFe}_{12}\text{O}_{19}$) and very small crystallites (about 50 nm). Because the propagation velocity of the combustion front is extremely high, the hexaferrite crystallites have not time to increase.

For recording media a high coercivity is necessary to stabilize small bits. It is known that the grain size is significant for achieving high H_c . In order to obtain an adequate size for hexaferrite crystallites, the powder obtained after combustion was thermally treated at high temperatures between 800 and 1000 °C.

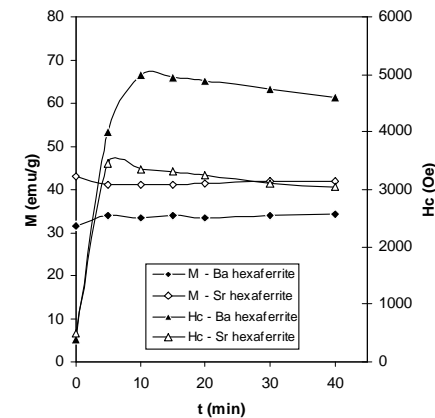


Fig. 1. Magnetic properties of Sr and Ba hexaferrites treated at 1000 °C in dependence on the annealing time.

Fig. 1 shows the influence of the annealing time on the static magnetic properties (M and H_c) for hexaferrites treated at $1000\text{ }^\circ\text{C}$. As can be seen after a short annealing time (5 minutes), the specific magnetization slightly decreases for Sr hexaferrite but slightly increases for Ba hexaferrite. For longer annealing time than 20 minutes, the specific magnetization remains almost constant. The coercivity exhibits important increase for short time treatment (about 5 – 10 minutes). H_c increases from 350 Oe to about 5000 Oe for Ba hexaferrite and from 520 Oe to 3400 Oe for Sr hexaferrite. By increasing the annealing time, the slightly lower values of H_c are observed in the both samples compared to those of first minutes. The decrease of H_c for longer annealing time is interpreted on the basis of the microstructure changes. The grain size increases with increasing annealing time as can see Fig. 2. In the larger crystallites, the multidomain structure it is possible to occur and the magnetization by domain wall displacement is easier than by spin rotation. The measurements were carried out on both powder and pressed samples and the results were almost the same.

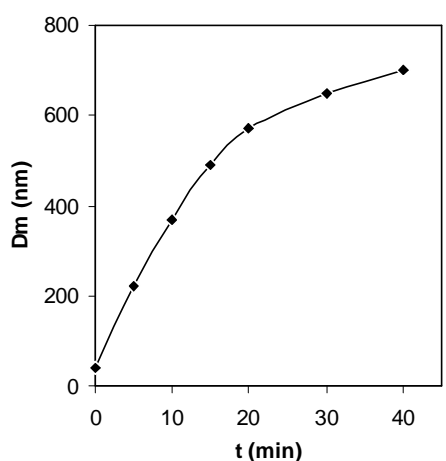


Fig. 2. The influence of annealing time at $1000\text{ }^\circ\text{C}$ on the crystallite size for Ba hexaferrite.

In this work, we tried to optimize the static magnetic properties of hexaferrites by using calcium addition. The Ca additive was introduced as calcium nitrate in the initial nitrate solution.

The variation of the magnetic properties as a function of annealing time for samples containing 1 mol Ca to 1 mol hexaferrite is illustrated in Fig. 3. One can remark that by means of calcium addition, a noticeable improvement of H_c (from 3400 Oe to 6000 Oe) was achieved for Sr-hexaferrite after annealing at $800\text{ }^\circ\text{C}$, for short time (5 – 10 minutes). For longer annealing time (40 minutes) both H_c and M are almost time independent. This fact is a proof that the grain growth process takes place in the first minutes of a thermal treatment. Such high H_c value for Ca doped Sr hexaferrite was attributed to a much finer grain size in comparison with grain size of Ca-doped Ba-hexaferrite annealed at higher temperature, of $1000\text{ }^\circ\text{C}$.

In Fig. 4 is given SEM micrograph on the fracture surface of Ca doped Ba-hexaferrite sample heat treated at $1000\text{ }^\circ\text{C}$ for 10 minutes. One can see particle agglomerations and crystallites of about $0.5\text{ }\mu\text{m}$ in which multidomain structure can occur and thus smaller H_c values were measured. The decrease of magnetization for Ca doped samples can be explained if it supposed that Ca ions enter into the hexagonal structure [7, 8]. In this case, the wall displacement or spin rotation may be impeded by the lattice strain generated by the Ca ions incorporated in structure, taking into account the ionic radius difference between Ca (1.14 \AA) and Ba (1.49 \AA) or Sr (1.32 \AA) ions [9]

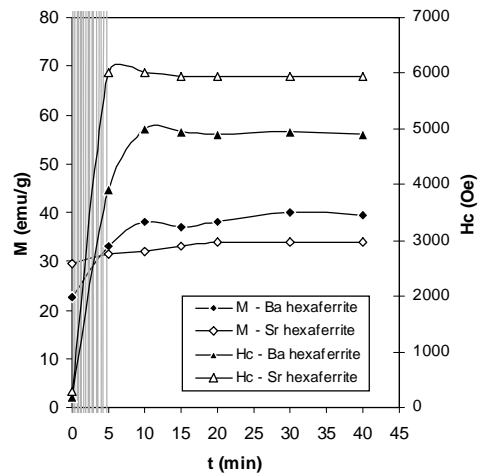


Fig. 3. Magnetic properties of Sr and Ba hexaferrites doped with 1 mol Ca treated at 800 °C and 1000 °C respectively, in dependence on the annealing time.

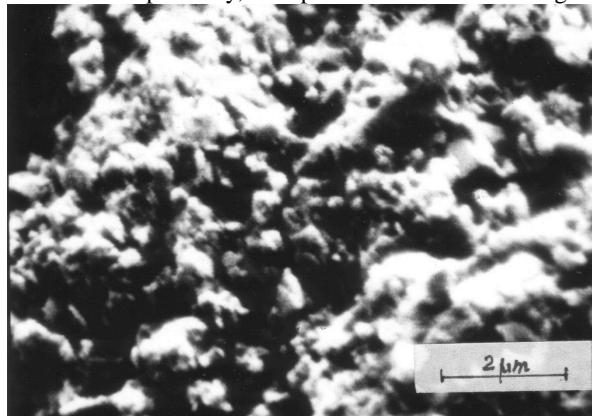


Fig. 4. SEM micrograph for the sample $\text{BaFe}_{12}\text{O}_{19} + 1 \text{ mol Ca}$ heated at 1000 °C for 10 minutes.

4. Conclusions

In this paper, the influence of thermal treatment time and calcium additive on the grain size and the magnetic properties (magnetization M and coercivity H_c) of the hexagonal ferrites powders ($\text{BaFe}_{12}\text{O}_{19}$ and $\text{SrFe}_{12}\text{O}_{19}$) obtained by selfcombustion method have been studied. By annealing for about 5 - 10 minutes, hexaferrite crystallites increase and the powders exhibit isotropic magnetic properties and a fine granular structure. CaO addition improves the coercivity of the Sr hexaferrite. The obtained results suggest that the post-annealed hexaferrite powders can be a promising candidate for recording magnetic media.

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