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XRD, DTA and TGA investigations of the $BaFe_{12-x}Al_xO_{19}$ (x=0.3, 0.9 and 1.2) solid solutions

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By X-ray diffraction, differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA) were investigated $BaFe_{12-x}Al_xO_{19}$ hexaferrites with various concentrations of Al (x = 0.3, 0.9 and 1.2). Crystal structure of compounds was determined, and it determined that under normal condition (P = 0 GPa, T = 300 K) they possess structure is hexagonal symmetry with the space group $P6_3/mmc$. Replacing Fe^{3+} ions Al^{3+} with ions, on account of reducing ion radius, decrease of indices of parameters was occurred. This crystal structure is saved in a temperature range 30 - 950 ºC and structural phase transition do not occur. Energy supplied to a system is fully swallowed by a system, monotonic decrease is occurred in TGA curve and in DTA curve endo and exo effects do not occur.

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1. Introduction

M-type hexagonal barium ferrite ($BaFe_{12}O_{19}$) and solid solutions based on it are one of the most interesting and studied multiferroics [1]. Hexaferrites have large magnetocrystalline anisotropy, high Curie temperature, relatively large magnetization, as well as its excellent chemical stability and corrosion resistivity. The value of anisotropy energy constant such materials exceed values of garnet ferrites in a hundred times more. Such excellent functional properties made it possible their practical applications such as in permanent magnets, microwave devices, absorbing materials ("Stealth" technology) and magnetic recording devices [2, 3, 4, 5]. Hexaferrites are well-known ferrimagnetic materials with strong uniaxial anisotropy and this anisotropy field can be controlled by the substitution of Fe^{3+} ions. These substitutions aim at developing materials with improved characteristics, which make hexaferrites suitable for technological applications. Little had been reported on the Al^{3+} substituted barium ferrites. The structural and magnetic properties of these materials seem to vary with the preparation method and the Al concentration [2, 6, 7, 8]. Moreover, the microwave absorption properties have been reported to be affected by Al- substitution [2, 9, 10].

The crystal structure of $BaFe_{12}O_{19}$ is hexagonal with the space group $P63/mmc$ [11]. At ambient conditions, the lattice parameters are a = b = 5.886(2) Å and c = 23.143(7) Å [11]. The unit cell, which includes two formula units (Z=2), contains 38 oxygen ions, 24 ferric ions and 2 barium ions. Iron ions occupy the nine 6-fold octahedral sites (12k, 2a and 4fVI), the one 5-fold trigonal site (2b) and the two 4-fold tetrahedral sites (4fIV). Barium ions occupy 2d sites. The spin orientations of each sites are 4fIV and 4fVI: (down); 2a, 2b and 12k: (up).

In this work, X-ray diffraction (at room temperature) and DTA analysis (a temperature range of 30 – 950 ºC) have been investigated and analyzed in an attempt to explore the effect of Al substitution for Fe the crystal structure of $BaFe_{12-x}Al_xO_{19}$ (x = 0.3, 0.9, 1.2).

These studies are needed to refine crystal structure parameters, phase homogeneity and temperature stability of the solid solutions.

2. Experimental

The investigated samples $BaFe_{12-x}Al_xO_{19}$ (where x = 0.3, 0.9 and 1.2) have been obtained from high purity oxides Fe_2O_3, Al_2O_3 and carbonate $BaCO_3$ using 'two-steps' topotactic reactions (conventional solid reaction method).

- At first the oxides and carbonate have been mixed with design ratio. Then the prefiring has been performed at 1200 °C in air during 6 h. We used intermediate grinding for homogenization and improving the quality of the obtained ceramics.
- Final synthesis was carried out at 1300 °C in air during 6 h. After synthesis the samples have been slowly cooled (100 $^{o}C\cdot h^{-1}$). The formation of $BaFe_{12-x}Al_xO_{19}$ (where x = 0.3, 0.9 and 1.2) powders can be represented as follows:

$$BaCO_3 + (12-x)/2Fe_2O_3 + x/2Al_2O_3 \rightarrow BaFe_{12-x}Al_xO_{19} + CO_2 \uparrow$$

To perform X-ray diffraction study, powder samples were prepared from these single crystals to be analyzed on a D8 ADVANCE powder diffractometer (Bruker) with the following parameters: 40 kV, 40 mA, Cu K_α radiation (λ = 1.5406 Å). The analysis was performed in a TTK723K thermal chamber in the room temperature.

The decomposition course of the precursor in the flowing air was performed using simultaneous DTA–TGA thermal analyzer (Perkin Elmer, STA 6000), to investigate the appropriate calcination temperatures and possible phase transformation, from 25 to 1000 °C with a heating rate of 5 °C/min. In the kinetic measurements, the non-isothermal TGA curves were obtained at heating rates of 1, 2 and 3 °C/min [12].

3. Results and discussion

The X-ray diffraction spectra of $BaFe_{12-x}Al_xO_{19}$ obtained at different compounds are shown in Fig. 1. The diffraction spectra at an ambient pressure at room temperature in the angular range $5° \leq 2\theta \leq 80°$, correspond to a hexagonal crystal structure with the space group *P*63/*mmc*. The unit cell parameters at normal conditions are listed in the Table 1, which agrees well with the previous results [11].

It is clear from obtained results that by replacing Fe ions with Al in compound $BaFe_{12}O_{19}$, decrease is observed cell parameters. This is an effect occurring on account of reduction of ion radius by replacing Fe^{3+}(0.645 Å) ions with Al^{3+} (0.535 Å) ions. Parameters *a* and *b* decrease more rapidly than the parameter *c* with increasing of concentration substitution. Perhaps this is due to the selective distribution of aluminum ions in the positions located in the *ab* plane. This leads to anisotropic compression of the unit cell with increasing concentration of aluminum in the plane *ab*.

DTA and TGA research methods are considered to be the very exact methods to carry out analyses of a composition of synthesized crystals. If there is crystal water in a composition of a sample, if any element remains in a composition of a sample independently during synthesis process and structural phase transitions occured, these effects are observed both in TGA and DTA curves. In order to study structural phase transitions and that there are supplements in a composition of synthesized $BaFe_{11.7}Al_{0.3}O_{19}$, $BaFe_{11.1}Al_{0.9}O_{19}$ and $BaFe_{10.8}Al_{1.2}O_{19}$ samples in a temperature range 30-950 ºC DTA and TGA analyses has been carried.

Table 1. Lattice constants a, b and c, c/a ratio and cell volume of $BaFe_{12-x}Al_xO_{19}$ samples.

x	*a* = *b* (Å)	*c* (Å)	*c*/*a*	*V* ($Å^3$)
0.3	5.884(3)	23.170(1)	3.937(6)	694.793
0.9	5.881(3)	23.170(2)	3.939(6)	694.080
1.2	5.870(1)	23.127(2)	3.939(8)	690.159

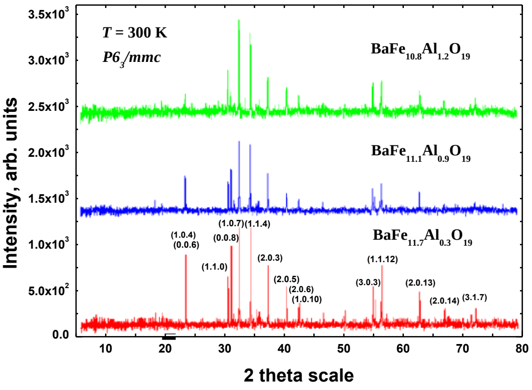

Fig. 1. X – ray diffraction pattern of the $BaFe_{12-x}Al_xO_{19}$ (x = 0.3, 0.9 and 1.2) powders being calcined at room temperature.

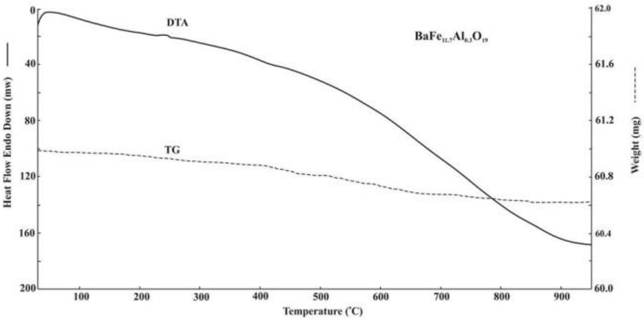

Fig. 2. Differential thermal analysis and thermo-gravimetric analysis curves of $BaFe_{11.7}Al_{0.3}O_{19}$.

Considerable changes are not observed in TG (mass) curve of $BaFe_{11.7}Al_{0.3}O_{19}$ sample with initial mass of 61.9 mg (Fig. 2). In a given temperature interval 1.4 mg decrease is observed in a mass, and it constitutes 2.26 %. In connection with that there is no any effect in TG curve, endo and exo effects are not observed in DTA curve. Monotonic decrease is occurred in DTA curve in $BaFe_{11.7}Al_{0.3}O_{19}$ compound, means swallow of energy flow supplied physically by a system. It enables to say that in this system not happens structural phase transition in a temperature interval 30-950 ºC. At higher temperatures, possibility of smashing into pieces or melting is high.

Analogical curves are also obtained for other samples (Fig. 3 and Fig. 4).

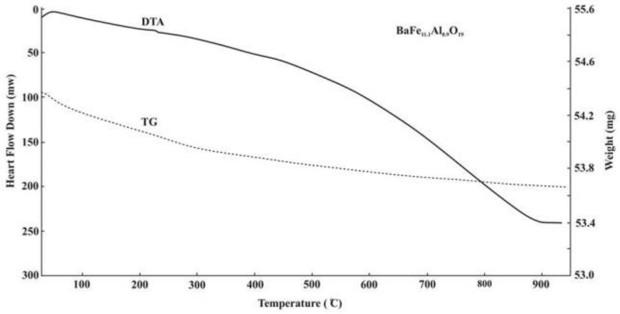

Fig. 3. Differential thermal analysis and thermo-gravimetric analysis curves of $BaFe_{11.1}Al_{0.9}O_{19}$.

Decrease in the amount of 2 mg is occured of mass in a given temperature interval for a sample of $BaFe_{11.1}Al_{0.9}O_{19}$ of which original mass is 55.4 mg and it constitutes 3.61 %. Decrease in the amount of 1.5 mg is occured in a mass in a given temperature interval for a sample of $BaFe_{10.8}Al_{1.2}O_{19}$ of which original mass is 122.9 mg and it constitutes 1.22 %.

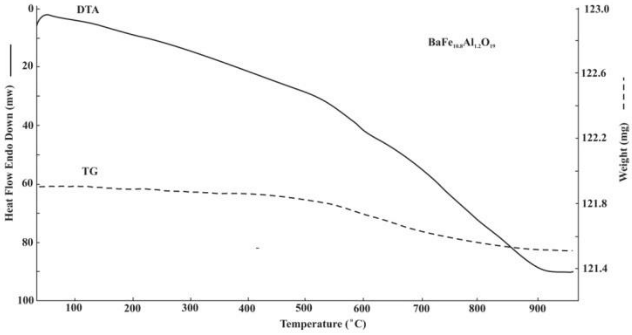

Fig. 4. Differential thermal analysis and thermo-gravimetric analysis curves of $BaFe_{10.8}Al_{1.2}O_{19}$.

4. Conclusions

The crystal structure of $BaFe_{11-x}Al_xO_{19}$ (x=0.3, 0.9 and 1.2) solid solutions are determined in a normal condition. It was determined that they possess crystal structure is hexogonal symmetry with the space group P63/mmc. Replacing Fe^{3+} ions with Al^{3+} ions, on account of reducing ion radius, decrease of indices of parameters was occurred. Structural phase transition is not occurred in temperature range 30-900^{0}C. Energy supplied to a system is fully swallowed by a system, monotonic decrease is occurred in TGA curve and in DTA curve endo and exo effects do not occur. This data confirms the thermal stability and uniformity of the phase of the synthesized compounds in a wide temperature range. The challenge for future research is to refine the parameters of the crystal and magnetic structure by neutron diffraction and determination of the electromagnetic energy absorption coefficients for practical applications. Diamagnetic substitution is capable of changing the magnetic structure and magnetic properties of multicomponent oxides. It is known that the diamagnetic substitution may be the reason for deviation from strict collinearity in the direction of the magnetic moments in a single ferromagnetic structure ferrites. And it may be the reason for formation of the frustrated magnetic structure too. For determination the dominant mechanism of induced by substitution is required neutron diffraction studies of the crystal and magnetic structure of the solid solutions. Studies by neutron diffraction can also to give an answer about the degree of cation ordering in the structure of hexagonal ferrites substituted M-type.

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