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Preparation of dissimilarly structured ferrite compounds by sol–gel auto-combustion method

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Ferrites with the spinel-type $NiFe_2O_4$ (NiF), $CoFe_2O_4$ (CoF) and hexagonal $BaFe_{12}O_{19}$ (BaM) structure were obtained using the auto-combusting reaction method. After the temperature-initiated auto-combusting reaction, different oxide mixtures were obtained. In the next step by calcination at 800 °C for BaM and CoF and at 1000 °C for NiF, corresponding ferrite compounds of a high level of purity were obtained. Auto-combustion reaction temperature was determined by thermogravimetry (TG) analysis. The obtained substances (crystalline phases) and their crystallite size were investigated by X-ray diffraction (XRD) analysis. Powder-forming particle sizes were characterized by atomic force microscopy (AFM) and by scanning electron microscopy (SEM). AFM images revealed particles of nanometer dimensions under 50 nm.

Introduction

Ferrites, due to their electric and magnetic properties, have been widely used in high-frequency techniques, electronics, electroacoustics, magnetic elements of memory, etc. for many decades [1–3].

Different oxide compounds can be prepared by almost all existing techniques of solid state chemistry. Nowadays, attention is focused on the application of nanoparticles, which leads to the development of various techniques of synthesis having a common feature – all reagents in them are mixed on the atomic or molecular level [4–8]. Most popular among them are the co-precipitation method [4]; the precursor method [5]; the sol–gel method [6]; the hydrothermal method [7]; the microemulsion method [8]. The above-mentioned methods have various typical drawbacks: the reaction may result in products with a wide particle size distribution; the composition of the obtained compounds may be inhomogeneous; expensive reagents are needed to perform the reaction; to maintain the reaction process, elevated operating temperatures are often required; most of these procedures include a complicated preparation technique [9].

The above disadvantages are the reason why at present, to obtain different oxide compound nanoparticles, sol–gel auto-combustion method is used. The advantage of this method is that it can be performed relatively easily, without using special equipment, and low energy consumption is characteristic of the method. The sol–gel auto-combustion method gives a homogeneous powder with a high level of purity and a low particle size distribution [3].

The method is based on dissolution of corresponding metal salts and an organic complexing agent; after gelation, the obtained gel should be dried before the oxidation-reduction reaction. The auto-combustion proceeds within a few seconds, resulting in oxide mixture formation. The obtained oxide mixture is annealed, and a corresponding pure ferrite compound can be obtained [10].

The reaction is affected by the nature of the organic complexing agent, the stability of the metal ion complex and the flame temperature of the auto-combustion reaction. In their turn, the stoichiometric ratio of the composition, the crystallite size of the obtained compound, the specific surface area and agglomeration tendency of particles, as well as the content of admixtures and the magnetic properties of compounds are affected [11].

As organic complexing agents, frequently ethylene glycol ($C_2H_6O_2$) [12], glycine ($C_2H_5NO_2$) [13], hydrazine (N_2H_4) [11], carbamide (CH_4N_2O) [13], citric acid ($C_6H_8O_7{\cdot}H_2O$) [25] are used. In our work, synthesis of different ferrite compounds was performed using citric acid which is known to form stable metal ion complexes [11]. It is well known that by increasing metal ion complex stability the selective deposition of metal ions is decreased, resulting in the invariability of the composition stoichiometric ratio [11].

Frequently, for obtaining sol–gel auto-combustion precursor solutions, nitrates and complexant agents were used, while the pH level was adjusted by adding ammonium hydroxide (NH_4OH). Changes of pH affect the rate of the auto-combustion reaction; as a result, the size of the obtained particles and admixture content could be reduced [15]. By increasing the pH level of the solution, the morphology of dried gels is affected – fluffy, less dense, three-dimensional network structures with on elevated pore content are formed. This effect is due to the increasing content of volatile gases during the gel-forming process [15]. Additionally to the consequences described above, with increasing the pH level increases the content of the crystallized ammonium nitrate (NH_4NO_3) phase in the dried gel [16]. The decomposition of ammonium nitrate leads to O_2 liberation. At the same time, at pH ≥ 8, metal ion complexes become unstable, and the stoichiometric ratio of the composition again may be affected [14].

The aim of present report is evaluate the efficiency of the sol–gel auto-combustion method in synthesizing nanoparticles of various ferrite compounds with a dissimilar structure.

Experimental

$NiFe_2O_4$, $CoFe_{12}O_{19}$ and $BaFe_{12}O_{19}$ compounds were synthesized using the sol–gel auto-combustion reaction method. The detailed process can be described as follows (Fig. 1). The analytical grade $Fe(NO)_3 \cdot 9H_2O$, $Co(NO)_3 \cdot 6H_2O$, $Ni(NO_3) \cdot 6H_2O$, $Ba(NO_3)_2$ and citric acid ($C_6H_8O_7 \cdot H_2O$) were used as raw materials. The stoichiometric amount of nitrates and citric acid was first dissolved in distilled water to form a clear solution. The molar ratio of nitrates to citric acid was 1 : 1. The next stage was neutralization of the solution by adding ammonium hydrate (NH_4OH) till pH 7 was reached. Then the solution was evaporated by intensive stirring and heating at 90 °C for approximately 1–4 hours. Evaporation of the solution caused formation of a highly viscous gel. To dispose of residual water, the gel was placed in a laboratory oven and dried at 90 °C. The dried gel was placed in a muffle furnace in which the auto-combustion reaction was initiated at the experimentally determined temperature of 250 °C. The final residue was calcined at different temperatures which were 800 °C for BaM and CoF and 1000 °C for NiF.

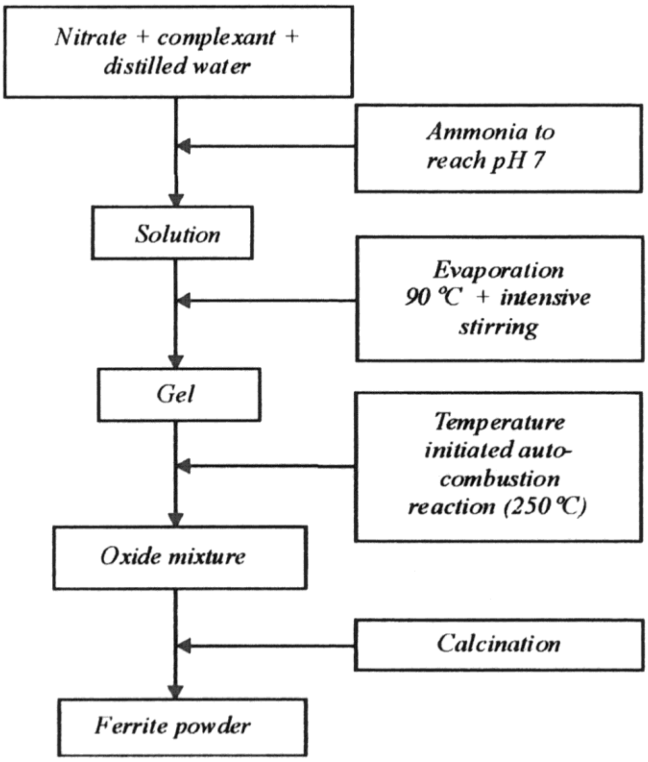

Fig. 1. Scheme of ferrite powder preparation

The auto-combustion reaction initiation temperature was determined with a *Mettler Toledo TGA/SF* thermogravimetry (TG) device. Thermal analysis data were collected in the range 25–800 °C at the heating rate of 20 °C/min under ambient atmosphere.

The powders obtained after combustion and calcination and crystallite size were characterized by X-ray diffraction spectra (XRD) applying a *Rigaku Ultima+* difractometer and CuKα radiation. The particle dimension of the obtained compounds was investigated using as atomic force *Digital Instruments CP-II* scanning probe microscope (Veeco Instruments Inc.) in a non-contact mode. Samples for AFM analysis were prepared by making a colloidal ferrite–heptane system dropped on a daze sheet. The microstructure analysis of ferrite powders was carried out using a *FEI Phenom* scanning electron microscope (SEM).

Results and discussion

It is well known that during the auto-combustion reaction the process of oxide formation involves liberation of gaseous products, which is accompanied by a decrease of mass. Thus, TG the thermogravimetry of the corresponding ferrite auto-combustion initiation temperature could be determined (Fig. 2). The auto-combustion initiation temperature of precursor gels is in the range of 200–220 °C. In spite of the obtained results, to perform the synthesis of ferrites with a possibly highest completeness, the gel auto-combusting reaction was initiated at 250 °C.

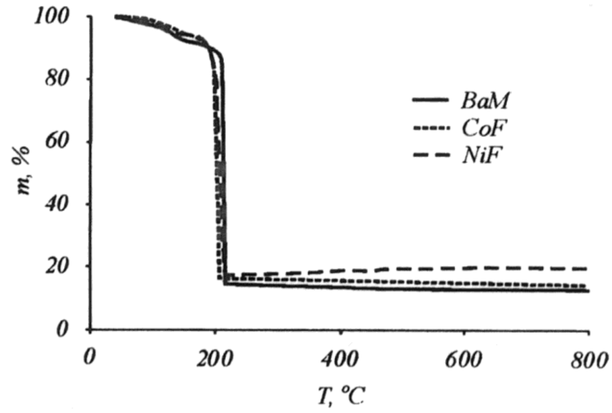

Fig. 2. TG curves of dried gels

Data of XRD analysis characterize the completeness of the auto-combustion reaction resulting in the desired spinel structure ferrite powders of NiF and CoF and BaM with the m-type hexagonal structure, which show the efficiency of the calcination procedure. BaM, NiF and CoF compound particular XRD patterns, which characterize both the auto-combustion reaction and the products of calcinations, are shown in Figures 3, 4 and 5.

The XRD patterns of the combustion reaction products of the calculated composition corresponding to BaM and NiF show several individual crystalline phases (Figs. 3, 4). In the case of CoF, the composition of the designed $CoFe_2O_4$ phase develops after the self-combustion reaction, without performing calcination at elevated temperature (Fig. 5). Performing calcination, almost in each case, a pure desirable ferrite phase develops. An exception is BaM, where alongside the $BaFe_{12}O_{19}$ phase, also the $BaFe_4O_7$ phase is formed (Fig. 3). This could be explained by the formation of precipitates during the gel formation process.

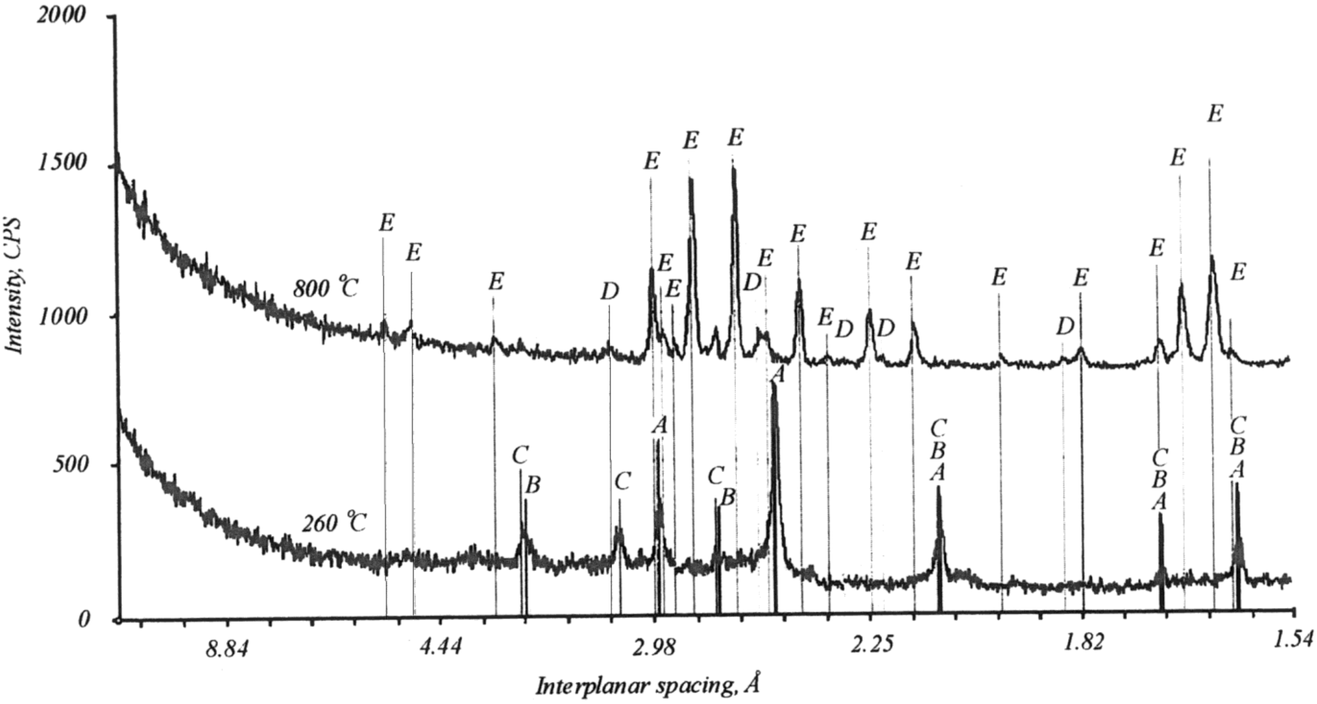

Fig. 3. XRD patterns of self-propagated and annealed BaM powders. A – $Y\text{-}Fe_2O_3$; B – $BaCO_3$; C – $BaFe_2O_4$; D – $BaFe_4O_7$; E – - $BaFe_{12}O_{19}$

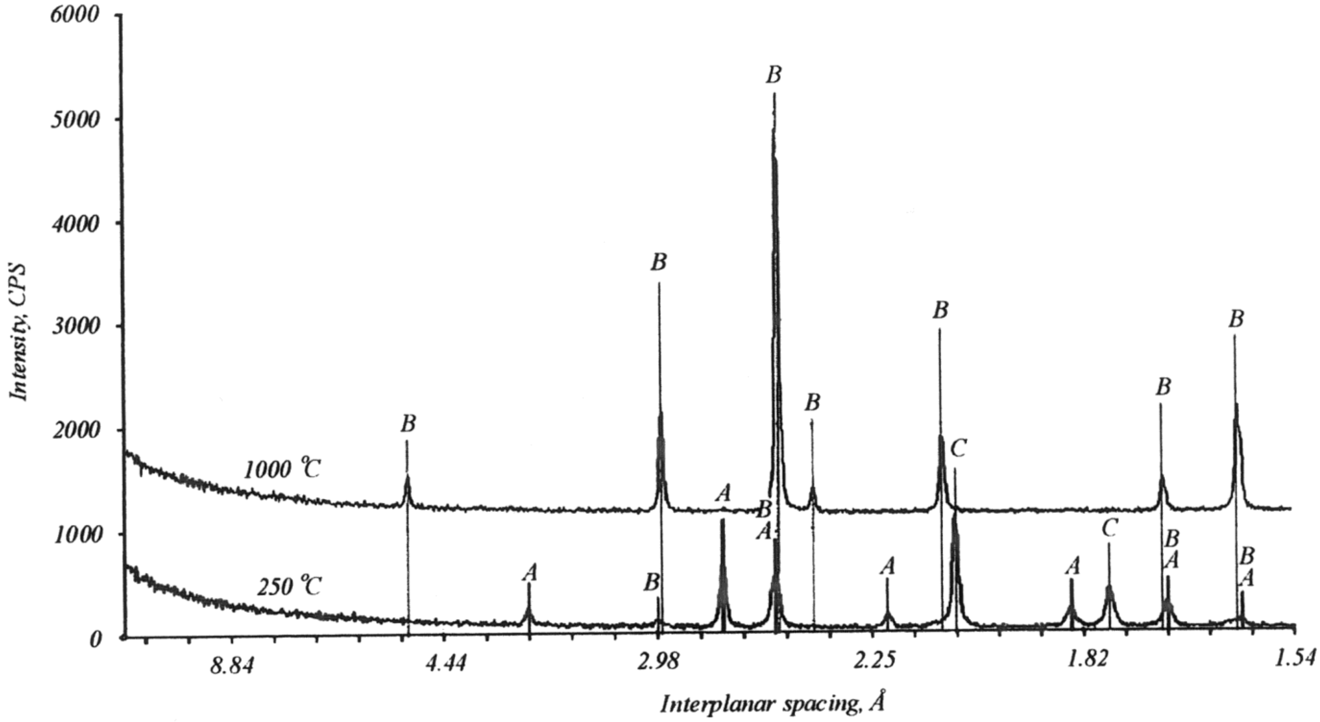

Fig. 4. XRD patterns of self-propagated and annealed NiF powders. A – $\alpha\text{-}Fe_2O_3$; B – $NiFe_2O_4$; C – Ni

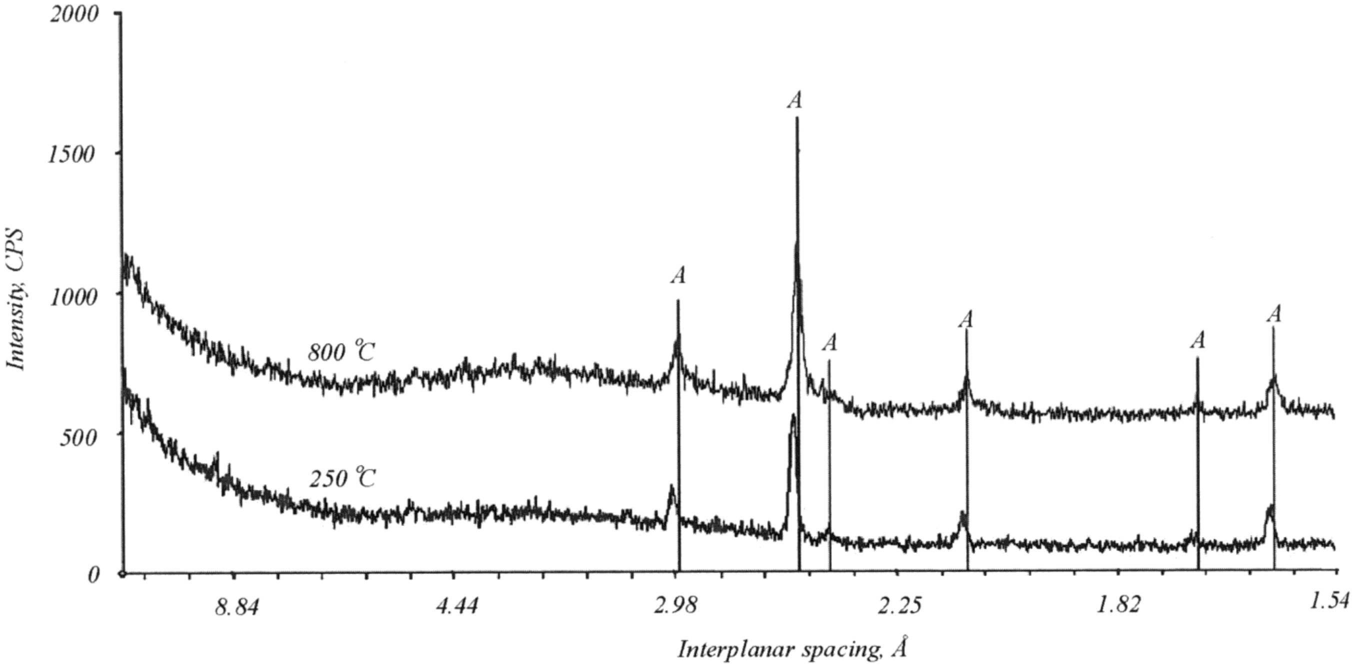

Fig. 5. XRD patterns of self-propagated and annealed CoF powders. *A – $CoFe_2O_4$*

The crystallite size of synthesized compounds was calculated by the X-ray line broadening method using the Scherrer formula:

$$D = \frac{\lambda}{B \cdot \cos\Theta},$$

where D is the average crystallite size, nm; λ is the X-ray radiation wave length, nm; B is the X-ray diffraction peak width at its half of height, rad; Θ is the Bragg's angle, degree.

The obtained results are presented in Table.

Table. Average calculated crystallite size of synthesized ferrite powders

Specimen	Average crystallite size, nm
$BaFe_{12}O_{19}$	27.7
$NiFe_2O_4$	30.6
$CoFe_2O_4$	33.4

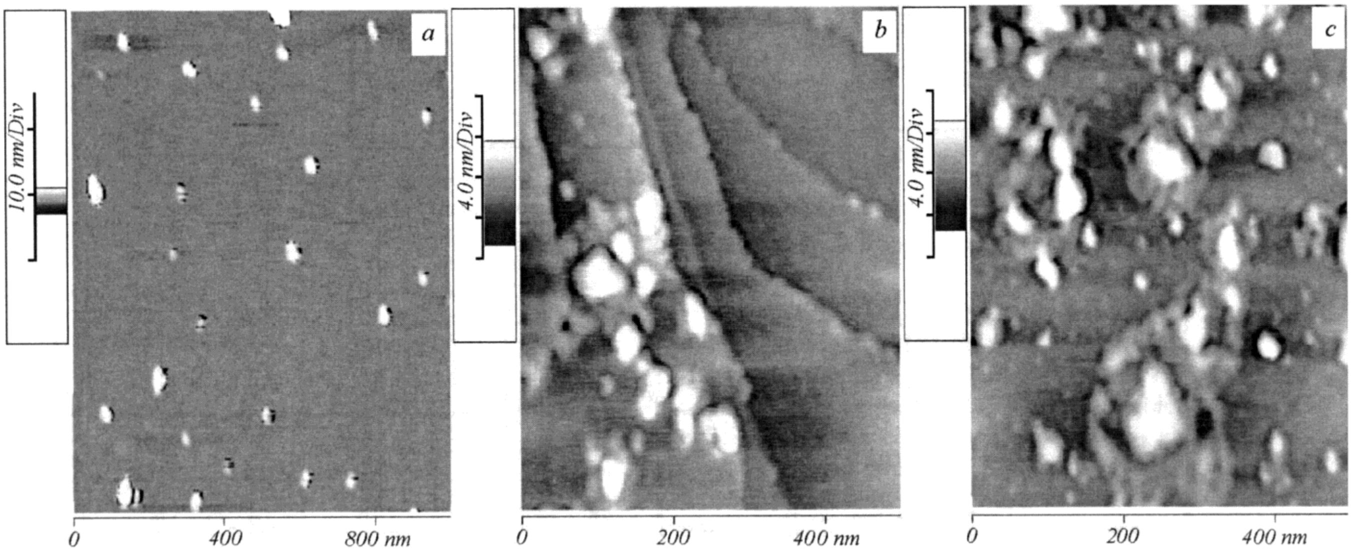

Fig. 6. AFM pictures of annealed ferrite powders: *a* – NiF, *b* – BaM, *c* – CoF

Figure 6 shows non-contact AFM images of annealed NiF, BaM, CoF ferrite powders. The average particle size and distribution are presented in Figure 7. One can see that all compounds the average particle size of all compounds is below 50 nm, also, the compounds that are burned at a higher temperature are characterized by a larger average particle size, which can be explained by the sintering processes during powder calcination.

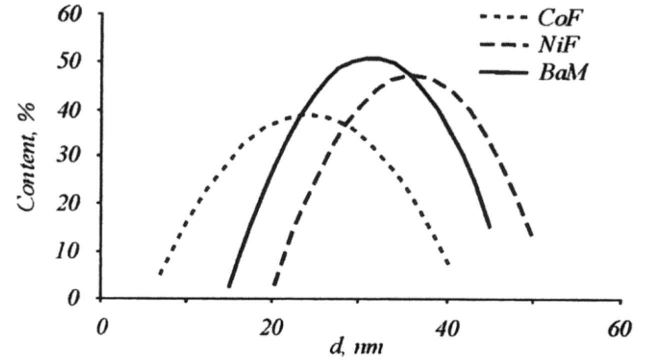

Fig. 7. Average particle size and particle size distribution for various ferrite compounds

The SEM image of calcinated BaM powder is shown in Figure 8. We see that sub-micrometer-sized primary particles are agglomerated into larger secondary particles and located in loosely packed agglomerates. The SEM microphotograph shows also the highly porous nature of the agglomerates. However, the obtained images do not allow evaluating the size of separate particles.

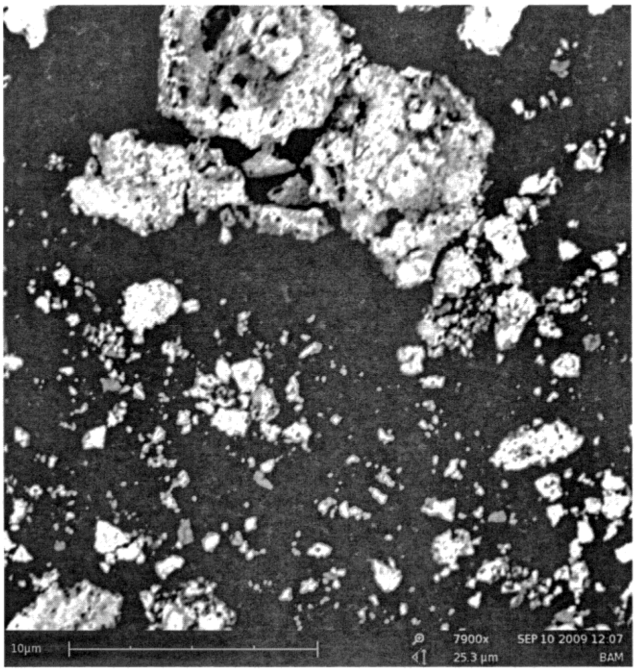

Fig. 8. SEM images of annealed BaM powder particle agglomerates

Conclusions

1. Gels containing metal nitrate and citric acid which can burn in on auto-combustion way were developed.
2. The X-ray diffraction patterns of calcinated samples almost in all cases confirm the desired single-phase ferrite structure.
3. The sol–gel auto-combustion reaction method is effective for obtaining nanosized dissimilarly structured $CoFe_2O_4$, $NiFe_2O_4$, $BaFe_{12}O_{19}$ ferrite particles.

Acknowledgments

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SKIRTINGŲ STRUKTŪRŲ FERITŲ KOMPONENTŲ GAVIMAS ZOLIŲ–GELIŲ SAVAIMINIO DEGIMO METODU

Santrauka

Špinelių struktūros feritų – $NiFe_2O_4$ (NiF), $CoFe_2O_4$ (CoF) ir heksagoninės struktūros ferito – $BaFe_{12}O_{19}$ (BaM) milteliai gauti zolių–gelių savaiminio degimo metodu. Po 250 °C temperatūroje inicijuotos savaiminio degimo reakcijos buvo gauti oksidų mišiniai. Inicijavimo reakcijos temperatūra nustatyta termogravimetrinės analinės būdu. Kitoje stadijoje šie oksidų mišiniai buvo kaitinami 800 °C temperatūroje tam, kad susidarytų BaM ir CoF feritai. Nikelio ferito gavimo atveju mišinys kaitinamas 1000 °C temperatūroje. Nustatyta, kad po kaitinimo susidarė didelio grynumo laipsnio nanometrų eilės

dydžio reikiami feritiniai junginiai. Kristalinių fazių sudėtis, kristalėlių dydis bei jų morfologija tirti rentgenodifrakcinės, atominės jėgos (ASM) ir skenuojančiosios elektroninės mikroskopijos (SEM) metodais. ASM ir SEM tyrimų rezultatai rodo, kad feritų dalelės yra iki 50 nanometrų.