Rev.Adv.Mater.Sci. 18(2008) 553-556

INFLUENCE OF CHEMICAL COMPOSITION ON PHASE CONSTITUTION AND MAGNETIC PROPERTIES OF MAGNETS PROCESSED BY DEVITRIFICATION OF $BaO\text{-}Fe_2O_3\text{-}B_2O_3$ GLASSES

Waldemar Kaszuwara[1], Artur Witkowski[1], Marcin Leonowicz[1] and Piotr Pawlik[2]

[1]Warsaw University of Technology, Faculty of Materials Science and Engineering, ul. Wołoska 141, 02-507 Warszawa, Poland

[2]Czestochowa University of Technology, Institute of Physics, Al. Armii Krajowej 19, 42-200 Częstochowa, Poland

Received: March 29, 2008

Abstract. An interesting method of the processing of hard ferrites comprises amorphisation of the starting material by rapid solidification followed by subsequent devitrification of the glassy precursor. The B_2O_3 was used as a vitrification agent. Chemical composition of the alloys from the $BaO\text{-}Fe_2O_3\text{-}B_2O_3$ system has a decisive effect on the phase constitution and magnetic properties of the final product.

In this study, the influence of the amount of the BaO in the $X BaO 6Fe_2O_3B_2O_3$ (X=1-5) system on the phase constitution and properties of the magnets was studied. After rapid solidification the material comprised both amorphous and crystalline phases. Up to BaO content X=2 precipitation of Fe_3O_4 was observed; for the higher contents phases containing Ba appeared. After devitrification at 950 °C for 1h, for BaO content X=3, only the phase close to the hexagonal barium ferrite $Ba_{0.91}Fe_{11.68}O_{18.2}$ was obtained. For lower and higher BaO concentrations, Fe_2O_3 and spinel $BaFe_2O_4$, respectively were observed. The best coercivity was obtained for the $2BaO6Fe_2O_3B_2O_3$, whereas the remanence attained maximum for the BaO in the range from X=2 to X=3.

1. INTRODUCTION

In recent years one can observe growing interest in the development of hard barium and strontium ferrites, which arises from the ability of improvement their magnetic properties by microstructure refinement to the nanoscale [1], with the potential applications for high density recording media. Mechanical alloying and mechanical milling are being developed in order to produce nanoscale ferrites [1]. Some reports are related to the processing of nanoferrites by devitrification of the glass phase. The main advantage of this method is the possibility of producing of bulk materials. As starting substrates barium/strontium oxide or barium/strontium carbonate, Fe_2O_3 and glass-forming oxide are used. The appropriate mixture of starting materials is subjected to homogenisation annealing. As a result a composition consistent with the phase equilibrium diagram can be obtained [2-4]. The material is subsequently melted and rapidly solidified. Further devitrification begins at about 550 °C.

The major problem for the processing of high performance magnets is composition optimization. Such data is not available in the literature. In this study the effect of the BaO content on the phase constitution and magnetic properties of the magnets produced by devitrification of the $XBaO6Fe_2O_3B_2O_3$ glasses was studied and discussed.

Corresponding author: Waldemar Kaszuwara, e-mail: wkaszu@inmat.pw.edu.pl

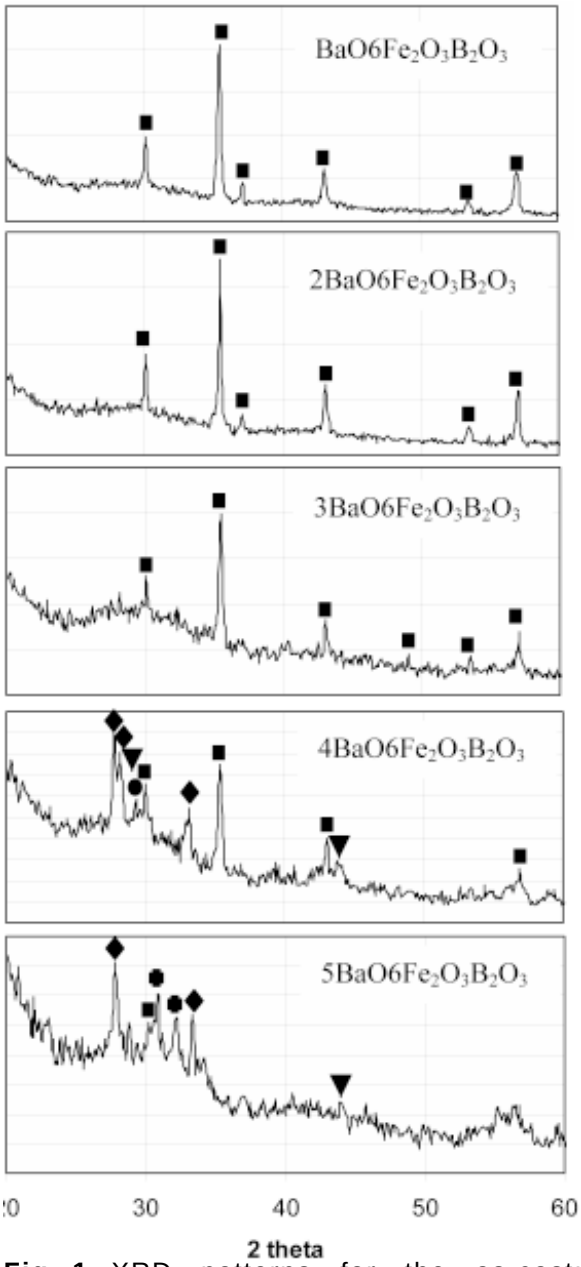

Fig. 1. XRD patterns for the as-cast: *X*BaO6$Fe_2O_3B_2O_3$ (*X*=1-5). ■ - Fe_3O_4, ◆ - $BaFe_2O_4$, ● - Ba_2FeO_4, ● - $Ba_2Fe_2O_5$, ▼ -$FeAl_2$.

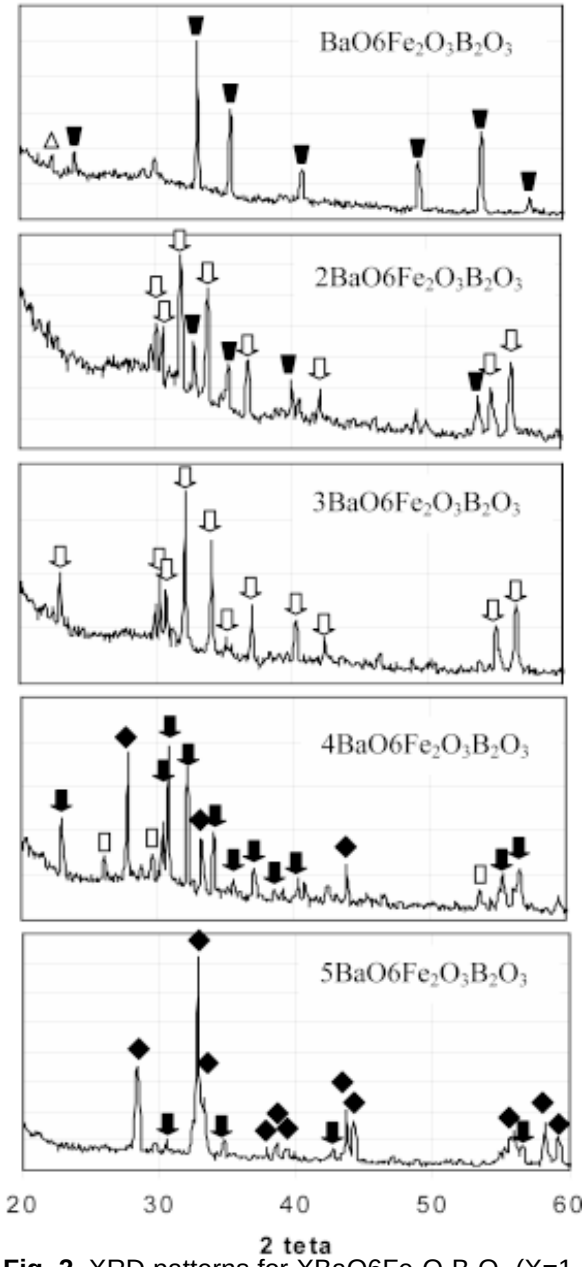

Fig. 2. XRD patterns for X$BaO6Fe_2O_3B_2O_3$ (X=1-5) annealed at 950 °C for 1h. ▼ - Fe_2O_3 ◆ - $BaFe_2O_4$ ⇩ - $Ba_{0.91}Fe_{11.68}O_{18.02}$, ⬇ - $BaFe_{12}O_{19}$, ▯ -Ba_2SiO_4, △ - $BaSi_4O_{10}$.

2. EXPERIMENTAL

As starting substrates, a mixture of barium carbonate ($BaCO_3$), iron oxide - Fe_2O_3 and boron oxide - B_2O_3 were used. The final compositions matched the formula XBaO $6Fe_2O_3$ B_2O_3, where X=1-5. The mixtures of powders were cold pressed and annealed at 1000 °C for 24h in air. Then, the produced starting materials were melted using a gas burner and cast by suction casting to the die having 2 mm bore. The as-cast specimens were annealed at 950 and 1100 °C, for 1h in air. The phase structure was studied using X-ray diffraction (XRD). The crystallite size of the $BaFe_{12}O_{19}$ phase was evaluated from the (114) diffraction peak using a

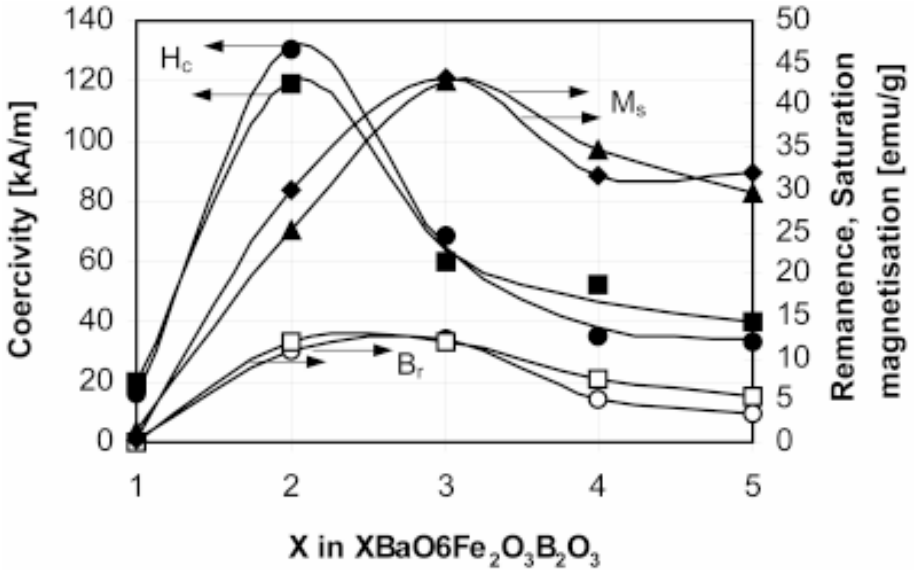

Fig. 3. Effect of BaO contents (*X* in *X*BaO6$Fe_2O_3B_2O_3$) on the remanence B_r, saturation magnetisation M_s, and coercivity for the materials annealed at 950 °C (□, ◆, ■ respectively) and 1100 °C (○, ▲, ● respectively).

Scherrer equation. The magnetic properties were studied using vibrating sample magnetometer (VSM).

3. RESULTS AND DISCUSSION

The chemical analysis of the materials showed that they were contaminated with Al and Si from the used crucible. The impurities contents is generally at a level of 5-6 at.%. The oxides of Si and Al, introduced in the course of casting, act similarly to B_2O_3 as an amorphisation agent.

The phase constitutions of the as-cast materials were evaluated by XRD analysis (Fig. 1). The processing conditions applied did not result in full amorphisation. For the BaO contents from *X*=1 to *X*=3 the Fe_2O_3 peaks are present. On the basis of the diffraction patterns one can conclude that the increase of the BaO content leads to the growing proportion of the amorphous phase, which contains all barium oxide. For the BaO contents *X*=4 and *X*=5 the phases containing Ba, i.e. $BaFe_2O_4$, Ba_2FeO_4 and $Ba_2Fe_2O_5$ appear. Individual peaks representing phases formed by the impurities of Al and Si are also visible. One can conclude that, up to *X*=3, the BaO concentrates in the amorphous phase.

Annealing (devitrification) of the studied materials at 950 °C for 1h changes their phase constitution (Fig. 2). For the composition BaO6$Fe_2O_3B_2O_3$ the Fe_2O_3 is formed. For the BaO content *X*=2, the XRD pattern shows a presence of peaks which match those of the hexagonal barium ferrite ($Ba_{0.91}Fe_{11.68}O_{18.2}$). This phase is accompanied by the Fe_2O_3. For *X*=3, the exclusively existing phase is $Ba_{0.91}Fe_{11.68}O_{18.2}$. In the sample 4BaO6$Fe_2O_3B_2O_3$, a stoichiometric barium ferrite $BaFe_{12}O_{19}$ is present, accompanied with some proportion of a ferrite richer in Ba, having spinel structure – $BaFe_2O_4$. For the 5BaO6$Fe_2O_3B_2O_3$, the $BaFe_2O_4$ ferrite is the major phase, however, some small peaks, from the hexagonal ferrite, were also detected.

Optimal phase structure, in respect to the magnetic properties, should comprise the crystallites of hexagonal barium ferrite separated by the glassy phase consisting of oxides B_2O_3 and BaO. The phase structure closest to the optimal one was obtained for the 3BaO6$Fe_2O_3B_2O_3$. At the deficit of BaO, the iron oxides are formed in the microstructure, whereas at the excess of this phase the phases rich in Ba are obtained.

The magnetic properties depend on the devitrification temperature, although the differences in the coercivity, after annealing at 950 and 1100 °C, respectively are not substantial. The highest remanence was achieved for the 3BaO6$Fe_2O_3B_2O_3$, which contains single phase $Ba_{0.91}Fe_{11.68}O_{18.2}$ (Fig.

3). The deviation from this composition causes formation of the phases having lower magnetisation, what results in a lower remanence. The highest coercivity was obtained for the $2BaO6Fe_2O_3B_2O_3$, which contains some proportion of magnetically soft Fe_2O_3 (Fig. 3). Determination of the crystallite size were performed using the Scherrer formula for the hexagonal barium ferrite $Ba_{0.91}Fe_{11.68}O_{18.2}$, for the specimens with X=2 and 3, and for the crystallites of the $BaFe_{12}O_{19}$, for the specimen with X=4. The respective values are: 58 nm for X=2, 67 nm for X=3 and 87 nm for X=4. One can conclude that increasing proportion of the amorphous phase, resulting from the increase of the BaO content, promotes diffusion and leads to the crystallite growth of the barium ferrite phase. An increase of the crystallite size results in a reduced coercivity, however, it is rather doubtful that such a small difference in the crystalline size would cause 50% coercivity decrease. Also the fact that for X=2 higher coercivity was achieved for the sample annealed at 1100 °C than at 950 °C points that the crystallite size is not a decisive factor. Increase of the BaO contents, from X=2 up to X=3, enables transformation of the entire Fe to the barium ferrite (for X=2 part of Fe remains in a form of Fe_2O_3) and increase of the proportion of the $BaFe_{12}O_{19}$. Increasing amount of this phase is evidenced by growing saturation magnetization (M_s) of the specimen with BaO content X=3. Assuming that the M_s value is proportional to the amount of the hexagonal barium ferrite, one can assess that the proportion of this phase grows by about 45%.

4. CONCLUSION

It is evident that the optimal composition, providing the best magnetic properties, is the one containing about 2BaO. Proper phase constitution in the material containing 3BaO suggests that optimisation of the processing conditions for this composition would enable to achieve better properties.

REFERENCES

[1] P.G.Bercoff and H.R.Bertorello *// J. Magn. Magn. Mat*. **187** (1998)169.
[2] D.D.Zaitsew, P.E.Kazin, Yu.D.Tret'yakow and M.Jansen // *Rusian Journal of Inorganic Chemistry* **11** (2003) 1717.
[3] D.D.Zaitsew, P.E.Kazin, Yu.D.Tret'yakow and M.Jansen // *Inorganic Materials* **12** (2003) 1319.
[4] H.Sato // *Mater. Trans. JIM* **11**(1996) 1672.