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## **LiFe<sub>5</sub>O<sub>8</sub> and BaFe<sub>12</sub>O<sub>19</sub> Fine Particles Crystallised in a Glassy Matrix**

We investigated the magnetic and microstructure properties of the Fe<sub>2</sub>O<sub>3</sub> - Li<sub>2</sub>O - B<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> - BaO - B<sub>2</sub>O<sub>3</sub> - Sb<sub>2</sub>O<sub>3</sub> glass strips (with dimensions 50 mm long, 6 mm wide and about 30±100 μm thick) subjected to various heat treatments. The irreversible structure changes produced by heat treatments, were investigated by X-ray diffraction and magnetic measurements. The magnetic behaviour is discussed in terms of the evolution of the size of LiFe<sub>5</sub>O<sub>8</sub> and BaFe<sub>12</sub>O<sub>19</sub> crystals dispersed in the glassy matrix, with thermal annealing.

Keywords: glass-ceramic, crystallization, magnetization, coercivity

### **1. Introduction**

Fine magnetic particles are scientifically and technologically very important. The particles are of great scientific interest in developing a better understanding of magnetic phenomena. From the technological point of view they find wide applications in many types of materials including magnetic tapes, ferrofluids, catalysts, medical diagnostics, drug delivery systems, and pigments in paints and ceramics. Many investigations have been performed on magnetic materials having fine particles (NORRISH; NAKATSUKA, JEYADEVAN; ROSENBERG et al.; SATO et al.; DAVIES et al.). The magnetic fine particles have properties which are different from those of the corresponding bulk materials. This results from reduced sizes and effects of magnetic interactions between particles. Oxide fine particles exhibit unusual physical and chemical properties and are very promising in applications like catalysts or magnetic recording medium (where every bit corresponds to a monodomain particle) with high recording density (estimated of 60 Gbit/in<sup>2</sup>).

In this paper we present some results for the oxide composites containing Li or Ba-M ferrite fine particles randomly dispersed in a glassy matrix. These materials known as glass-ceramics were obtained by glass crystallisation method (GCM) which permits a gradual control of particle size. This method uses the crystallisation of a thermodynamically metastable amorphous state of a selected chemical composition under suitable conditions of temperature, time and atmosphere. The recent interest in the preparing of this family of materials arises from the fact that glasses are less prone than ceramics to processing flaws arising from packing defects. For example, large agglomerates can produce flaws in the sintering ceramics (REEVE; EVANS; LANGE, METCALF). But glasses usually sinter to full density even when the green microstructure is nonuniform. Therefore, in the optimum process for preparation glass-ceramic, the glass should be formed to full density before the onset of crystallisation. By magnetic measurements and X ray diffraction we investigated the hybrid materials. We focus our attention on the relation between annealing temperature, crystal size and magnetic properties (magnetisation and coercivity).

In some earlier papers ( REZLESCU, REZLESCU 1994; REZLESCU et al. 1994) we showed that by the thermal treatments of the oxide glasses  $\text{Fe}_2\text{O}_3\text{-Li}_2\text{O-B}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3\text{-BaO-B}_2\text{O}_3\text{-Sb}_2\text{O}_3$  the crystallisation of Li and Ba ferrites occurs into the metastable glass and the resultant material is a glass-ceramic (ferriglass).

## 2. Experimental

Two systems are studied:  $\text{Fe}_2\text{O}_3\text{-Li}_2\text{O-B}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3\text{-BaO-B}_2\text{O}_3\text{-Sb}_2\text{O}_3$ . The fabrication procedure of the oxide glasses was the rapid cooling of the melt. As starting materials,  $\text{H}_3\text{BO}_3$ ,  $\text{BaCO}_3$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{Sb}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  (chemical purity greater than 99.5%) were used.  $\text{B}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_3$  were chosen, on the one hand, because having low melting points they can favour the melting at lower temperatures and, on the another hand, these atoms are matching the criteria of glass formation (STANWORTH): cation valence  $\cdot 3$ ; cation radius  $\cdot 1,5 \text{ \AA}$ ; electronegativity between 1.8 and 2.1. For the glass formation it is very important to obtain a very high cooling speed of the melt in order to avoid crystallisation. We were able to obtain a cooling rate of about  $10^7 \text{ deg/s}$  of the melt by the method of the copper rollers (CHEN, MILLER). The samples obtained were ribbons with a thickness of 30 to 100  $\mu\text{m}$ , 5-6 mm width and about 40 - 50 mm long. More detailed information about preparation is given in (REZLESCU et al. 1994).

The structure analysis of the obtained products was carried out by X-ray diffraction with a DRON diffractometer, using Fe  $K\alpha$  radiation. The obtained ribbons were treated successively at various temperatures (between 20 and 800  $^\circ\text{C}$ ) to crystallise the ferrite particles within the matrix. The glass crystallisation was detected by X-ray diffraction and magnetic measurements (specific magnetisation  $\sigma$  and coercivity  $H_c$ ). The mean particle size  $D$  was determined using Scherrer's formula. The magnetic properties ( $\sigma$  and  $H_c$ ) of the samples were measured with a vibrating sample magnetometer up to a maximum field of 8.8 kOe.

## 3. Results

At room temperature, the X-ray diffraction has shown that except for a few very small crystallites of Ba hexaferrite (magnetoplumbite-M type) the products were mainly in an amorphous phase. Probably the cooling rate of  $10^5 \text{ deg/s}$  was insufficient to avoid the nucleation of some crystallites of Ba hexaferrite. The percentage of the Ba hexaferrite crystallites dispersed in the glass matrix was estimated to be between 1.5 and 2 %. The Li containing ribbons were nonmagnetic, while the other sample was magnetic.

In order to investigate the thermal evolution of the obtained samples, the specific magnetisation was measured in a 8.8 kOe magnetic field, during both heating and cooling in air, in a dynamic regime, between 20 and 800 $^\circ\text{C}$ , with a heating rate of about 5 deg/min. Figures 1 and 2 display the variation of the specific magnetisation  $\sigma$  (at 8.8 kOe) versus temperature. For the system with lithium it was revealed (Fig.1) the occurrence of a magnetic phase at about 515 $^\circ\text{C}$ ; up to temperature of 515 $^\circ\text{C}$  there was no appreciable magnetisation. Above this temperature, a ferrimagnetic behaviour was observed up to about 650 $^\circ\text{C}$ . The obtained Curie temperature (650 $\pm$ 10 $^\circ\text{C}$ ) is compatible with the one we measured on the  $\text{LiFe}_5\text{O}_8$  single crystals grown in our laboratory by flux method (655 $^\circ\text{C}$ ) (REZLESCU et al. 1996). This proves the Li-ferrite crystallisation in the glass matrix. During the cooling from 780 to 20 $^\circ\text{C}$  a higher magnetisation was obtained below 650 $^\circ\text{C}$  by the crystallisation of a greater amount of Li ferrite at higher heating temperatures. Concerning the Ba system, this has a small magnetisation, of about 2 emu/g, at room temperature, which slowly decreases

during the heating (Fig.2), up to about 470°C; above this temperature the sample behaves paramagnetically. During the cooling of the same sample, from about 800°C, we found out a ferrimagnetic behaviour under 465°C.

Fig. 1: Comparison between the temperature dependence of the specific magnetisation in the ribbons with composition  $\text{Li}_2\text{O}-\text{Fe}_2\text{O}_3-\text{B}_2\text{O}_3$  and that of  $\text{LiFe}_5\text{O}_8$  hexaferrite

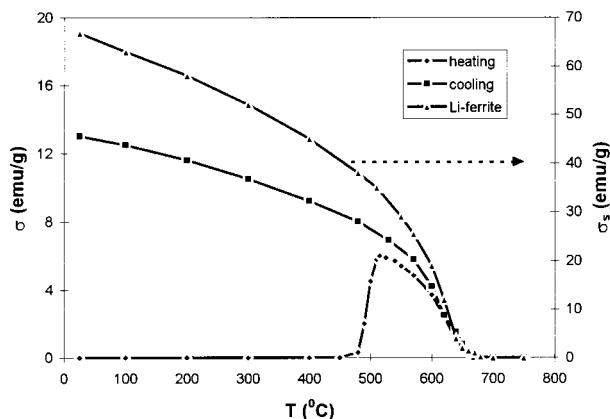
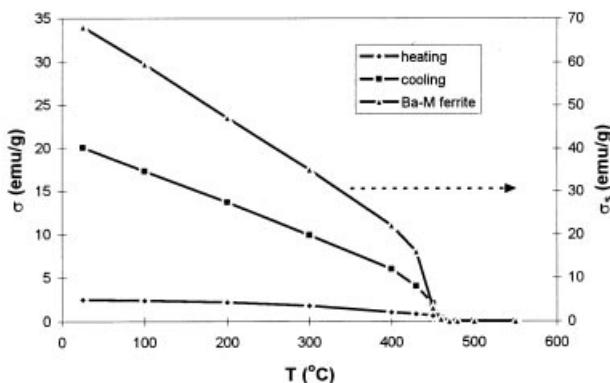


Fig. 2: Comparison between the temperature dependence of the specific magnetisation in the ribbons with composition  $\text{BaO}-\text{Fe}_2\text{O}_3-\text{B}_2\text{O}_3-\text{Sb}_2\text{O}_3$  and that of  $\text{BaFe}_{12}\text{O}_{19}$  hexaferrite



Comparing the shape of the magnetisation versus temperature curve, obtained during the cooling process, with that of the Ba hexaferrite bulk sample (see Fig.2), which has  $T_c = 450^\circ\text{C}$ , it was evidenced that the magnetic phase crystallised within the glass matrix during heating at high temperatures is the Ba hexaferrite and its Curie temperature does not depend on the presence of the glassy matrix. Moreover, the temperature behaviour of the  $\sigma$  during heating-cooling shows that the crystallisation process of the hexaferrite does not occur up to the Curie temperature as in case of Li ferrite but at higher temperatures. X-ray diffraction confirmed that the product contains barium ferrite crystallites of the M structure (Ba M), whose amount increases with temperature.

By heat treatments for a long time (2 h for each treatment) at several temperatures, between 200 and  $800^\circ\text{C}$ , the X-ray analysis and magnetisation measurements revealed the start of the crystallisation at lower temperatures. In this case the longer annealing time favours the nucleation process at lower temperatures. Evolution of the specific saturation magnetisation and the crystal size as a function of the annealing temperature  $T_a$  for the both systems investigated is shown in Figures 3 and 4. The saturation like behaviour of  $\sigma$  for Li containing ribbons treated at higher temperatures than  $530^\circ\text{C}$  is the result of the crystallisation of the whole amount of Li-ferrite via diffusion within the glass host. Of

course, due to the dispersion of the ferrite particles in a non-magnetic matrix, the specific magnetisation of this magnetic glass-ceramic is much lower than that reported by us for Li ferrite single crystal (62.5 emu/g) (REZLESCU et al. 1996).

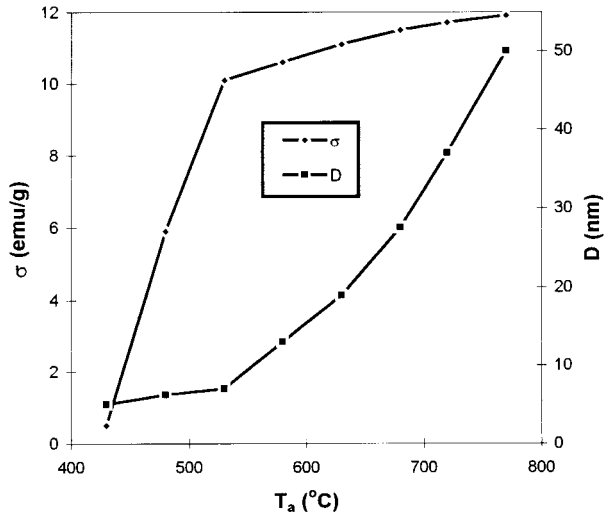


Fig. 3: Effect of the annealing temperature on the specific magnetisation and on the average  $\text{LiFe}_5\text{O}_8$  grain size development in the glassy matrix, measured at room temperature

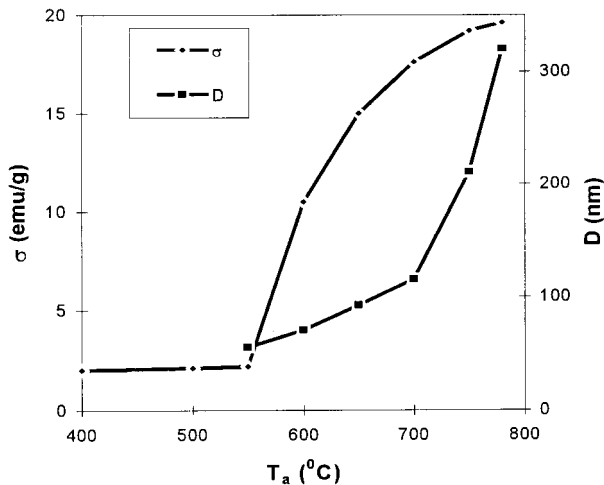


Fig. 4: Effect of the annealing temperature on the specific magnetisation and on the average  $\text{BaFe}_{12}\text{O}_{19}$  grain size development in the glassy matrix, measured at room temperature

Thus the  $\sigma$  values may give information on the percentage of  $\text{LiFe}_5\text{O}_8$  crystallised in the amorphous material. For the ribbons with barium (Fig.4) the crystallisation process does not occur at low temperatures. This fact point out the existence of a critical temperature at which the crystallisation of Ba-M ferrite begins and which is higher than the Curie temperature. From experimental results, the temperature of 600°C seems to be the beginning of the Ba-hexaferrite nucleation. The evolution of the crystal size as a function of the annealing temperature investigated on the same samples is given in Figures 3 and 4 too.

One can observe that the mean crystallites size exhibit a slight increase at low annealing temperatures and the important increase of the crystals was obtained at high temperatures. It is expected that the size maximises at some temperature just below the onset of melting.

The relationship between  $\sigma$  and  $D$  was found to be  $\sigma \sim D^3$ , for the initial portion of  $\sigma = f(T_a)$  curve and  $\sigma \sim D^{0.08}$ , for the second portion (REZLESCU et al. 1997).

It is known that the crystallisation of a glass implies two phenomena: nucleation and crystal growth by diffusion (GORNERT et al.; OUCHI; BEALL, DUKE). At low annealing temperatures, a nucleation and a little increase of isolated grains, randomly dispersed within the glassy matrix takes place. Above 580°C two simultaneous processes which can be considered as controlling of the grain growth seem to produce: a normal grain increase due to the progressive crystallisation and, on the other hand, a formation of agglomerated clusters, in which the larger grains grow at the expense of the smaller by a “penetrating” process. We assumed that this configuration modification does not essentially change the magnetisation, although the grain size does increase as the grains “penetrate” one another inside the agglomerates (the increase in the grain size corresponds to the elimination of the small intraagglomerated grains). On the other hand, it must also be mentioned that normal grain growth due to the progressive crystallisation takes place. This process slightly affects the magnetisation value.

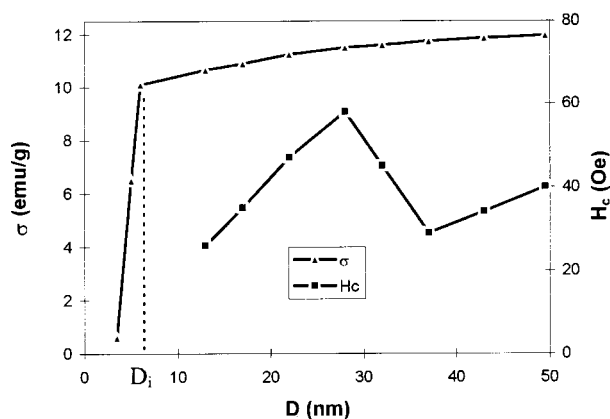


Fig. 5: Specific saturation magnetisation  $\sigma$  and coercivity  $H_c$  as a function of crystallised particle sizes for heat-treated Li ferrite samples at different temperatures

It is known that the coercivity of a fine particle material is one of its most significant parameters; this gives information on the magnetic state and on the quality of the material. A fundamental property of  $H_c$  is its dependence on the grain size  $D$ . Figure 5 reveals the specific saturation magnetisation  $\sigma$  and coercivity  $H_c$  as a function of the average size  $D$  of the ferrite grains for the Li-ferrite vitroceraic. The coercivity increases with the increasing grains, and then, for a further increase of the grains, it decreases. In order to explain this decrease, domain wall nucleation was considered a possible mechanism. The transition from the single to multidomain magnetisation mechanism (it is easier to displace a domain wall than to rotate the individual atomic spins) will lead to a decrease of  $H_c$ . In this connection we estimate the critical grain size for a single domain particle with formula (SMIT, WIJN)

$$D_{\text{crit}} = (9 \sigma_w / 2 \pi M_s^2),$$

where  $\sigma_w = (2 k_B T_c |K_1|/a)^{1/2}$  is the wall density energy,  $|K_1|$  is the magnetocrystalline anisotropy constant,  $T_c$  the Curie temperature,  $M_s$  the saturation magnetisation,  $k_B$  the Boltzmann constant and  $a$  the lattice constant. For the sizes  $D > D_{\text{crit}}$ , the particles are already multidomains. Below this critical size, the particle is a uniformly magnetised single-domain. For Li ferrite,  $\text{LiFe}_5\text{O}_8$ , using  $|K_1| = 8 \cdot 10^4 \text{ erg/cm}^3$  (ARAI, TSUYA),  $M_s = 310 \text{ Gauss}$ ,  $a = 8.37 \cdot 10^{-8} \text{ cm}$ ,  $T_c = 933 \text{ K}$ , it was calculated a critical grain size,  $D_{\text{crit}}$  of about 75 nm. From

experimental results we appreciated a  $D_{\text{crit}}$  of about 30 nm. If the grain size is larger than  $D_{\text{crit}}$  the domain walls appear and the magnetisation process requires a smaller energy compared to the rotation of the atomic spins.

For Ba hexaferrite, using the numerical values pertaining to this ferrite,  $T_c = 720$  K,  $a = 3 \cdot 10^{-8}$  cm,  $|K_{\parallel}| = 3.3 \cdot 10^6$  erg/cm<sup>3</sup> and  $M_s = 380$  Gauss (SMIT, WIJN), the theoretical value of  $D_{\text{crit}}$  is about 460 nm, which is in reasonable agreement with the evaluation from X-ray diffraction, of 330 nm for the vitroc ceramic treated at 780°C. After Kubo (KUBO et al.) and Gornert (GORNERT et al. 1990, GORNERT et al. 1991) a particle of  $\text{BaFe}_{12}\text{O}_{19}$  having an average size larger than 1  $\mu\text{m}$  displays a multidomain magnetic behaviour, while those with sizes smaller than 10 nm show a superparamagnetic behaviour. If the single domain particle size is too small, the thermal fluctuations become important, the anisotropy energy ( $K_{\text{ef}} \cdot V$ ) becomes comparable or smaller than the thermal energy ( $k_B T$ ),  $k_B T \geq K_{\text{ef}} \cdot V$ , and the magnetic behaviour called "superparamagnetism" appears (BEAN). ( $K_{\text{ef}}$  is effective anisotropy constant including shape and magnetocrystalline anisotropies (DORMANN)). Therefore, there is an inferior limit for the single domain particle size,  $D_i$ . Below this, a superparamagnetic state characterised by zero coercivity can appear. For  $\text{BaFe}_{12}\text{O}_{19}$ ,  $D_i$  was evaluated to 4 nm, which is in agreement with the one we measured on the green material, thermally non treated. Thus, the decrease of the number of superparamagnetic particles with the increase of the single-domain particle size can explain the initial increase in  $H_c$  (Fig.5).

The experimental dependence of  $H_c$  on the grain size for the two systems can be plotted qualitatively as in Figure 6 in accord to (KRONMULLER). One may distinguish four zones:

- I. For very small so-called superparamagnetic particles with  $D < D_i \approx 4$  nm; the reversion of  $\sigma$  takes place by a thermally activated process.
- II. For particles with  $D_i < D < D_{\text{trans}}$ ; the reversion of  $\sigma$  is independent of the size and takes place by a uniform rotation process.
- III. For larger particle sizes,  $D_{\text{trans}} < D < D_{\text{crit}}$ ; an inhomogeneous magnetisation process with decreasing coercive field takes place.
- IV. For large particles,  $D > D_{\text{crit}}$ ; the single domain particles become multidomain particles, in which the reversion of the magnetisation takes place by domain wall displacements.

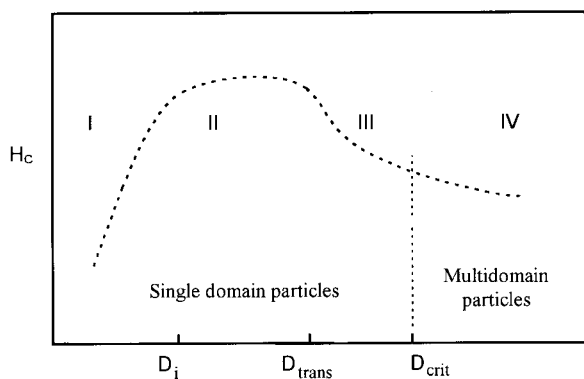


Fig. 6: Qualitative dependence of  $H_c$  on the average grain size  $D$ . The four zones are determined by the three diameters: for the thermal activation ( $D_i$ ), transition to inhomogeneous rotation ( $D_{\text{trans}}$ ) and the formation of multidomain particles ( $D_{\text{crit}}$ ).

The annealing time evolution of the magnetisation and mean grain size was investigated too. Figure 7 shows the dependence of  $\sigma$  and  $D$  on the annealing time, at  $T_a = 780^\circ\text{C}$ , for Ba sample. As initial state of the material is the one that resulted from the precedent treatment, at  $750^\circ\text{C}$ . One can see that the specific magnetisation increases abruptly during the first 10 minutes of the thermal treatment and the mean size of the crystallites increases significantly

during 60 minutes. For larger annealing time, the increase of the magnetisation is small. This is due to the crystallisation of the whole amount of ferrite within the glass host. The grain growth is slower because of the paramagnetic matrix. For ultra high density magnetic recording media, the grain size should be small in order to reduce the noise in reproduced output. From these results it was found that the annealing time of about 10 minutes at the temperature of 780°C is enough to crystallise without an important grain growth.

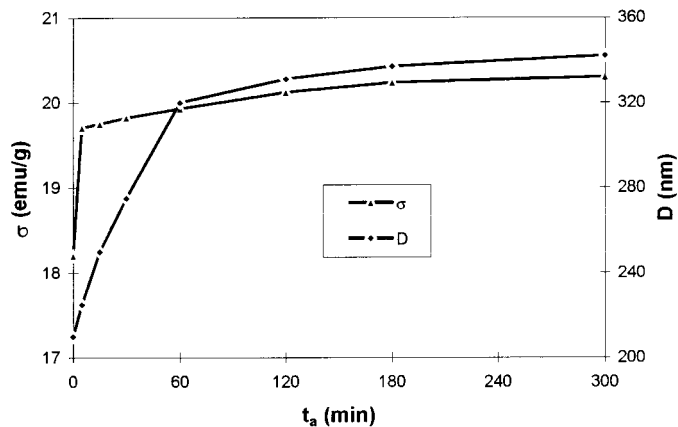


Fig. 7: Variation of specific magnetisation  $\sigma$  and average grain size  $D$  versus annealing time  $t_a$ , at the constant  $T_a = 780^\circ\text{C}$ , for the Ba-M ferriglass

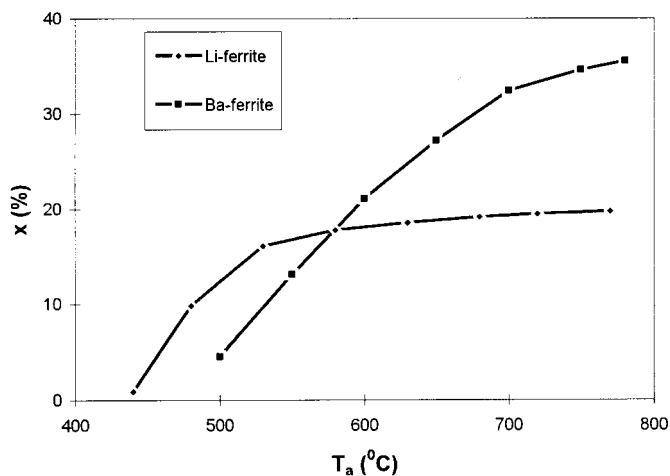


Fig. 8: Estimated fraction of crystallised phase in glassy matrix by heat treatments of two hours

The ferrite powder, after the final thermal treatment, was extracted from the amorphous matrix by dissolving the residual matrix with dilute acetic acid (20%). The remained residual mass was washed and dried. By X-ray diffraction we found that the powder contains only barium-M ferrite,  $\text{BaFe}_{12}\text{O}_{19}$ , or lithium ferrite,  $\text{LiFe}_5\text{O}_8$ . The specific magnetisation measured on these powders at 8.8 kOe ( $\sigma^*$ ) is about 55.8 emu/g for Ba-M ferrite and 60.8 emu/g for Li ferrite. If the specific magnetisation measured after each thermal treatment is normalised to the specific magnetisation measured on the ferrite powder obtained after the final treatment, one can evaluate the percent of crystallised ferrite in the glassy mass after each thermal treatment (Fig.8). One can remark a larger crystallisation percent at higher annealing temperatures for Ba-M ferrite.

#### 4. Conclusions

Formation of fine ferrite particles in glass ribbons by isothermal treatments and their influence on the magnetic properties of glass-ceramic were analysed. Two glass systems were studied:  $\text{Li}_2\text{O}-\text{Fe}_2\text{O}_3-\text{B}_2\text{O}_3$  and  $\text{BaO}-\text{Fe}_2\text{O}_3-\text{B}_2\text{O}_3-\text{Sb}_2\text{O}_3$ .

The magnetic properties of the glass ceramics are closely linked to the crystal size developed in the glassy matrix by thermal annealing. By manipulating the annealing temperature the crystal growth can be controlled to obtain the vitroc ceramic materials with predetermined properties. Also, glass crystallisation by heat treatments offers a facile possibility to obtain powders of very fine magnetic particles for many practical applications.

#### References

- ARAI, K.S.; TSUYA, N.: J. Phys. Soc. Jap. **33** (1972) 1581  
 BEALL, G.H.; DUKE, D.A.: Glass-Ceramic Technology in Glass Science and Technology - Vol.21 - Glass Forming Systems (p.404), Editors D. R. Uhlman and H. J. Kreidi, Academic Press, New York 1983  
 BEAN, G.P.: J. Appl. Phys. **26** (1955) 13  
 CHEN, H.S.; MILLER, C.F.: Rev. Sci. Instrum. **41** (1970) 12367  
 DAVIES, K.J.; WELLS, S.; CHARLES, S.W.: J.Magn.Magn.Mater. **122** (1993) 24  
 DORMANN, J.L.: Rev. Phys. Appl. **16** (1981) 275  
 EVANS, A.G.: J.Am.Ceram.Soc. **65** (1982) 497  
 GORNERT, P.; SINN, E.; SCHUPPEL, W.; PFEIFFER, H.; ROSLER, M.; SCHUBERT, Th.; M. JURISCH, M.; R. SELLGER, R.: IEEE Trans. Magn. **26** (1990) 12  
 GORNERT, P.; SINN, E.; ROSSLER, M.: Key Eng. Mater. **58** (1991) 129  
 KRONMULLER, H.: Micromagnetism and Magnetization Process in Modern Magnetic Materials, in Science and Technology of Nanostructured Magnetic Materials (p.657), Edited by G. C. Hadjipanayis and G. A. Prinz, Plenum Press, New York and London 1990  
 KUBO, O.; IDO, T.; YOKOYAMA, H.; KOIKE, Y.: J. Appl. Phys. **57** (1985) 4280  
 LANGE, METCALF, M.: J.Am.Ceram.Soc. **66** (1983) 398  
 NAKATSUKA, K.; JEYADEVAN, D.: IEEE Trans.Magn. **30** (1994) 4671  
 NORRISH, A. H.: Studies of Magnetic Properties of Fine Particles and their Relevance in Materials Science (p.181), Editors J. L. Dormann and D. Fiorani, Elsevier Science Publishers, London 1992  
 OUCHI, K.: IEEE Trans. Magn. **26** (1990) 24  
 REEVE, K.D.: Am.Ceram.Soc.Bull. **42** (1963) 452  
 REZLESCU, E.; REZLESCU, N.: phys. stat. sol. (a) **143** (1994) k111  
 REZLESCU, N.; REZLESCU, E.; PASNICU, C.; CRAUS, M.L.: J. Magn. Magn. Mat. **131** (1994) 273  
 REZLESCU, E.; REZLESCU, N.; CRAUS, M.L.; PASNICU, C.; REZLESCU, L.: Cryst. Res. Technol. **31** (1996) 739  
 REZLESCU, E.; REZLESCU, N.; CRAUS, M.L.: J. Phys.(France) **7-C1** (1997) 553  
 ROZENBERG, A. S.et al.: Russian Chem.Bull. **44** (1995) 858  
 SATO, T.; IJIMA, T.; SEKI, M.; INAGAKI, T.: J.Magn.Magn.Mater. **65** (1987) 252  
 SMIT, J.; WIJN, H.P.J.: Les Ferrites, Dunod, Paris 1961  
 STANWORTH, J. E.: J. Am. Ceram. Soc. **54** (1971) 61

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