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Glass-Ceramic Containing Lithium Ferrite: Magnetic and Structural Properties

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Abstract: The magnetic and microstructural properties of Fe_2O_3–Li_2O–B_2O_3 glass strips (with dimensions 50 mm long, 6 mm wide and about 30–100 μm thick), which were subjected to various heat treatments in order to induce a variable amount of magnetic crystalline phase ($LiFe_5O_8$ crystals) within the glassy matrix, were investigated. The irreversible structural changes produced by the heat treatments between 200 and 770°C were studied by X-ray diffraction, from which the average crystal block size, $\bar{D}$, was also determined. Crystals of ferrite, with sizes ranging from 3·5 to 50 nm depending on the annealing temperature, were observed. Correspondingly, it was shown that the crystalline fraction in the glassy mass increases with increasing annealing temperature. The magnetic behaviour is discussed in terms of the evolution with thermal annealing of the size of $LiFe_5O_8$ crystals, dispersed in the glassy matrix. Taking into account the dependence of the magnetic properties on the crystallite size, the fine control of the crystal growth by thermal annealing can be exploited in the future for the production of glass-ceramics with pre-determined properties. Also, the resulting glass-ceramic, named ferriglass, offers an opportunity for studying the various effects of fine particle magnetism. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

The recent interest in the preparation of the family of materials known as glass-ceramics 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,[1–3] but glasses usually sinter to full density even when the green microstructure is non-uniform. Therefore, in the optimum process for preparation of glass-ceramics, the glass should form to full density before the onset of crystallization.

In an earlier paper[4] we have shown that by thermal treatments of the ternary oxide glasses Fe_2O_3–Li_2O–B_2O_3, the crystallization of Li-ferrite into a metastable glass occurs and the resultant material is a glass-ceramic (ferriglass).

The glass crystallization method by thermal treatments is attractive because it can be conducted at lower temperatures and, therefore, allows greater control over phase separation and crystallization.

It seems then necessary to study the relationship between thermal treatments, crystalline phase formation, crystal size and magnetic properties. In this work we extend previous reports dealing with the relationship between all these parameters.

2 EXPERIMENTAL

The glass-ceramic (Li-ferrite glass) was produced by the glass crystallization method (GCM). An Fe_2O_3–Li_2O–B_2O_3 flux melt is quenched at 10^4–10^5 grad/s between two rotating rollers to form glass ribbons of 30–100 μm in thickness and 4–5 mm long. The non-crystalline structure of the glass was confirmed by X-ray diffraction. These ribbons were annealed successively at various temperatures (430, 480, 530, 580, 630, 680, 720 and 770°C) to crystallize the Li-ferrite particles within

the matrix. More detailed information about preparation is given in Refs 5 and 6.

The glass crystallization was detected by X-ray diffraction and magnetic measurements (specific saturation magnetization σ_s and coercivity H_c). The mean particle size $\bar{D}$ was determined using Scherrer's formula. The magnetic properties of the samples were measured with a vibrating sample magnetometer.

3 RESULTS AND DISCUSSION

The glass ribbons were completely amorphous, and the X-ray pattern is typical of a glass heated above its melting point and then quenched.

First, the partial crystallization of the glass ribbons was revealed by measurement of the specific saturation magnetization during "normal" heating of the glass in air, with a heating rate of about 5 °C/min, between 20 and 700°C. Figure 1(a) displays the specific saturation magnetization (at 8·8 kOe) as a function of the heating temperature. There was evidence of the occurrence of a magnetic phase at about 515°C; up to a temperature of 515°C there is no appreciable magnetization.

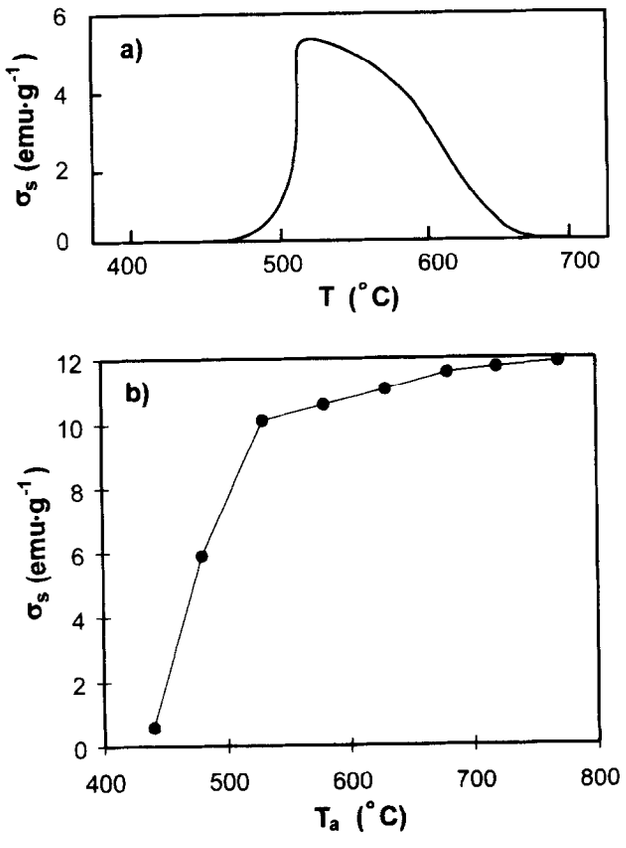

Fig. 1. (a) Specific saturation magnetization σ_s measured at 8·8 kOe, vs temperature. (b) Influence of the annealing temperature, T_a, on the specific saturation magnetization σ_s measured at room temperature.

Above this temperature, a ferrimagnetic behaviour to about 650°C is observed. Above 650°C the sample behaves like a paramagnetic material. The obtained Curie temperature (650 ± 10°C) is close to that measured on the $LiFe_5O_8$ single crystals, prepared by us using the flux method, that suggests the crystallization of Li-ferrite in the glass matrix. Then, the glass ribbons were annealed successively at different temperatures between 430 and 770°C, for 2 h at each temperature.

The X-ray analysis performed on the annealed samples revealed Li-ferrite crystallization at lower temperatures (430°C). No crystalline phases were observed in the glass heat-treated below 430°C. The difference between the two crystallization temperatures arises because the longer treatment time favours the formation of a homogeneous temperature distribution within the ribbons.

Evolution of the specific saturation magnetization, measured at room temperature, vs annealing temperature T_a is shown in Fig. 1(b). An abrupt increase in σ_s can be noticed for samples annealed in the temperature range 430–530°C, which may be attributed to the Li-ferrite crystallization. The saturation-like behaviour of σ_s for high annealing temperatures is the result of the crystallization of the whole amount of Li–ferrite via diffusion within the glass host. Of course, due to the dispersion of the ferrite particles in the matrix, the specific magnetization of this magnetic glass-ceramic is much lower than that reported for bulk ferrite.[7]

It is known that the crystallization of a glass implies two phenomena: nucleation and crystal growth by diffusion.[5] The evolution of the crystal size as a function of the annealing temperature investigated on the same sample is given in Fig. 2. One can remark: (i) a slight increase of mean crystallite size at low annealing temperatures; (ii) an important increase of the crystals beyond a

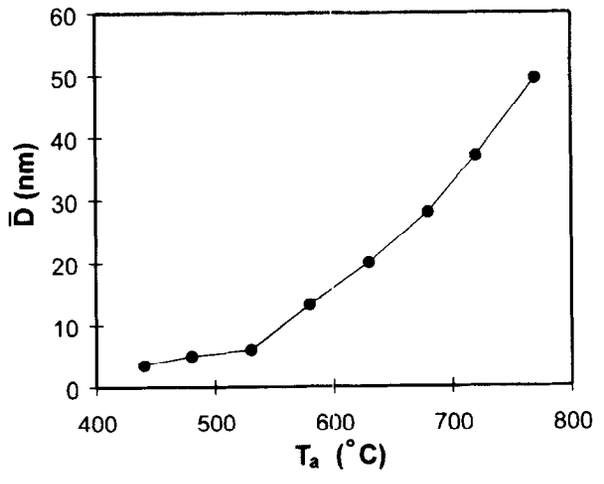

Fig. 2. Effect of annealing temperature on the average $LiFe_5O_8$ grain size development in the glassy matrix.

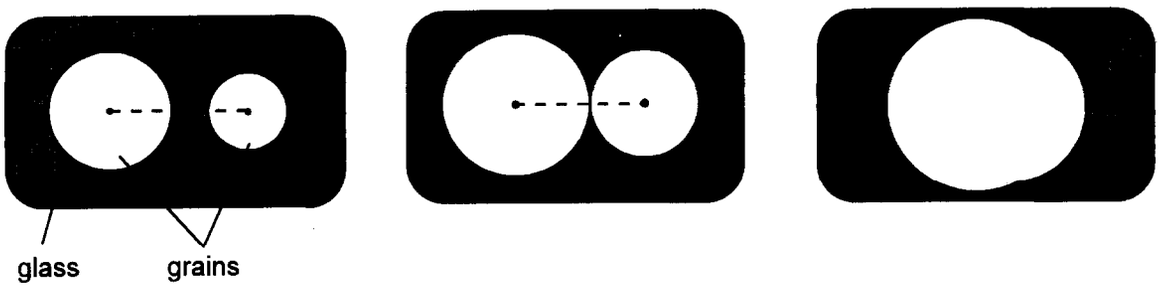

Fig. 3. Illustration of the structural changes produced during the heat treatments for two grains.

temperature of 580°C; and (iii) the mean grain size does not become constant above 770°C. It is expected that the size maximizes at some temperature just below the onset of melting. These results can be explained as follows: the annealing at low temperatures, between 430 to 530°C, results in the nucleation and a small increase in the number of isolated grains, randomly dispersed within the glassy matrix. Above 580°C, two simultaneous processes seem to take place which could be considered as controlling the grain growth. On one hand, with increasing grain sizes some grains will just touch one another leading to the formation of agglomerates. With increasing annealing temperatures, within these agglomerates, the larger particles can grow at the expense of the smaller, as shown in Fig. 3. We assumed that with this configuration modification there is essentially no change in magnetization, 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 progressive crystallization takes place, which affects, to a small extent, the magnetization value.

Special attention is given to the relationship between the average grain size and the magnetic properties of crystallized glass. Figure 4 reveals the specific saturation magnetization σ_s and coercivity H_c as a function of the average grain size $\bar{D}$. A sharp decrease of the magnetization for grain sizes below 6 nm was obtained. At larger grain sizes (or high annealing temperatures), σ_s increases slowly and begins levelling off at grain sizes of 40–50 nm. Thus, a critical average particle size $\bar{D}_c$, below which the magnetization of the ferrite-glass declines rapidly, can be defined. From Fig. 4 the relationship between σ_s and $\bar{D}$ is found to be: $\sigma_s \sim \bar{D}^3$ for $\bar{D} < \bar{D}_c$ and $\sigma_s \sim \bar{D}^{0.08}$ for $\bar{D} > \bar{D}_c$. The sharp decrease of the σ_s values may be due to either a decreasing fraction of superparamagnetic particles with increasing mean crystal size (crystallites smaller than 10 nm are superparamagnetic)[8] or an imperfect occupation of the two magnetic sub-lattices of spinel ferrite at lower annealing temperatures. Further investigations are needed to support the latter hypothesis.

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. From Fig. 4 one can observe that H_c increases with increasing grain size, shows a maximum at about 28 nm, and then decreases sharply.

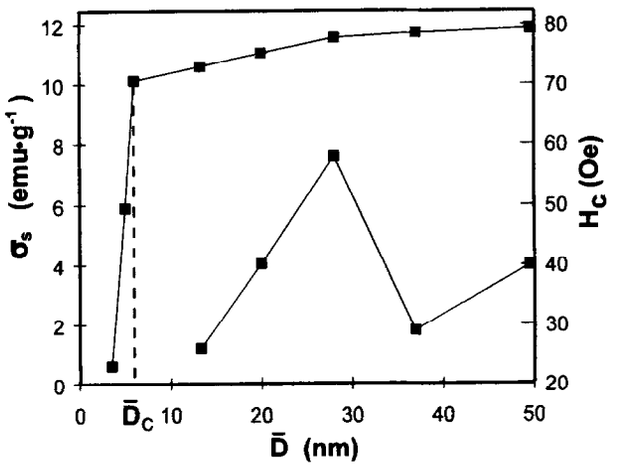

Fig. 4. Specific saturation magnetization σ_s and coercivity H_c vs average grain size $\bar{D}$ correlation for heat-treated samples at different temperatures.

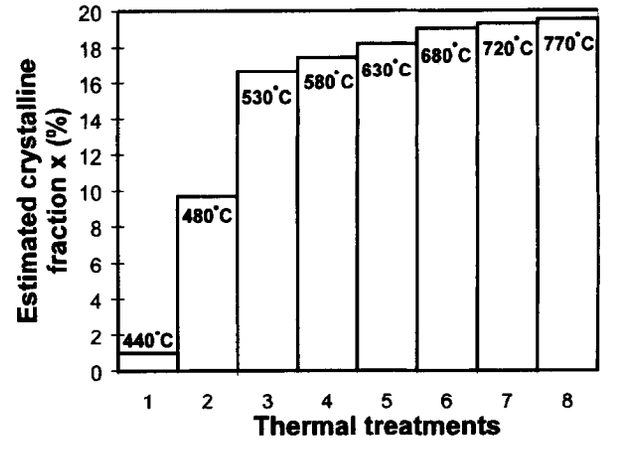

Fig. 5. Estimated fraction of crystallized phase ($LiFe_5O_8$) in the glassy matrix by heat treatments.

In order to explain the decrease in H_c above 28 nm, domain wall nucleation was considered as a possible mechanism. The transition from the single to multi-domain magnetization mechanism for larger sizes (of about 28 nm) will lead to a decrease of H_c. For crystal sizes below 10 nm, no appreciable coercivity is found.

Finally, the Li-ferrite sub-micrometre particles were separated by dissolving the residual matrix with dilute acetic acid and the specific saturation magnetization was measured, $\sigma_s' = 60{\cdot}8\ \text{emu}\cdot\text{g}^{-1}$. If the specific saturation magnetization measured after each treatment is normalized to σ_s', the fraction x of magnetic crystalline phase ($LiFe_5O_8$) in the non-magnetic host was determined. Evolution of this fraction vs annealing temperature is given in Fig. 5. One can observe an important increase of the crystallized phase after annealing at 480 and 530°C, from 0·98% to 16·65%, when one can suppose that multiple nucleation and growth of isolated crystals in the whole amorphous mass takes place. At higher annealing temperatures, the increase in the number of crystallites within the agglomerated formation leads to a slower increase of the estimated fraction.

4 CONCLUSIONS

The following conclusions can be drawn from the above work:

(a) The magnetic properties of the Li-ferrite glasses are closely linked to the crystal size of $LiFe_5O_8$ developed in the Li_2O–Fe_2O_3–B_2O_3 glass by crystallization. By varying the heat treatment temperature of the composite, a sharp decrease in the specific saturation magnetization for crystallite sizes below 6 nm was obtained. This result may be attributed to both a decrease of superparamagnetic grain number with increasing mean average grain size and an imperfect occupation of the two sub-lattices of the ferrite at low temperatures. For the decrease in H_c above 28 nm, multi-domain nucleation was supposed as a possible mechanism.

(b) The glass crystallization method (GCM) is convenient to produce vitroceramics with pre-determined properties, since their structural and magnetic properties can be adjusted by the manipulation of the heat treatment conditions. Also, this method allows one to obtain powders of very fine magnetic particles, with grain sizes of 10–50 nm, for many practical applications.

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