ON FERRIMAGNETIC GLASS-CERAMICS BASED ON B$_2$O$_3$ AND MnFe$_2$O$_4$* 

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(Received March 9, 1972) 

Relative boundaries of glass-formation for given quenching conditions are shown for the system MnO--Fe$_2$O$_3$(--PbO)--B$_2$O$_3$(--SiO$_2$). The crystallization tendency of manganese ferrite is investigated by DTA, X-ray and electron microscopy. 

Ceramic ferromagnetic materials have been fabricated by solid-state reactions including conventional sintering [1-3] and/or hot pressing, promotion of solid-state reactions and sample densification through addition of less than 10 wt. % of glass-forming materials [4] and crystallization of vitreous melts by slow cooling or reheating [5-18]. The latter method may permit the best grain control if suitable glasses are formulated [7], melted, quenched, nucleated and crystallized under controlled conditions [19]. Layton and Herzog [20], Famy et al. [6], Shirk and Buessem [13], and Tanigawa and Tanaka [15] have investigated glasses in the system BaO--Fe$_2$O$_3$--B$_2$O$_3$ with up to about 50 % of Fe$_2$O$_3$, yielding upon crystallization magnetoplumbite BaO·6Fe$_2$O$_3$. Schultz [10] crystallized glasses in the system PbO--Fe$_2$O$_3$--SiO$_2$ with 10--30 % Fe$_2$O$_3$ into glass-ceramics containing PbO·6Fe$_2$O$_3$. Colline et al. [5] and Schultz [11] have found the system R$_2$O--Fe$_2$O$_3$--SiO$_2$ suited for crystallization of the spinel Li(Na)FeO$_2$ from glasses containing up to 26 % Fe$_2$O$_3$. More complex glass systems resulting in crystals of ferrites M$^{2+}$Fe$_2$O$_4$ were investigated by Rogers et al. [9] (CaO--Al$_2$O$_3$--B$_2$O$_3$--SiO$_2$ with 12 % Fe$_2$O$_3$) as well as by Shaw et al. [12], Smith [14] and particularly Tashiro et al. [16], who started from lithium, magnesium and aluminium silicates containing up to 50 % Fe$_2$O$_3$. In all these systems typical heat-treatments required were 600--900° for 1--60 hours. 

The system chosen for the present work was MnO--Fe$_2$O$_3$(M$^{2+}$O)--B$_2$O$_3$ (--SiO$_2$), because of established magnetic properties of manganese ferrite [1, 2] and the ease of glass formation at relatively low B$_2$O$_3$ content [9]. A large number of exploatory glasses crystallizable to high ferrite contents were, indeed, 

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obtained in this study. Batches (80 cm$^3$) mixed from pure materials milled in a glass ball mill for 10 hours were reacted for about 15 minutes at about 900°C, quickly heated to, and melted at 1270 – 1380°C for about 30 minutes in refractory crucibles, cast on stainless steel preheated to about 100°C and pressed to 2 mm plates. Arbitrary relative boundaries of glass formation were established for the given quenching conditions (see Fig. 1).

The investigation of glass-forming regions was, for the sake of convenience, related to the following atomic ratio formulation: $x(w\text{Mn}_{0.5}\text{Fe}_{2}O_{3}z\text{M}^{2+}\text{O})y(f\text{BO}_{1.5}$

Samples were inspected for crystallinity by a horizontally mounted X-ray powder diffractometer (General Electric) with MoKα radiation using a Zr filter. The diffraction patterns of the phases precipitating from the glasses corresponded to cubic spinels, a being within 8.43 – 8.49 Å. The patterns obtained were compared to those of standard powder mixtures of crystalline manganese ferrite ($a = 8.51 \text{ Å}$), prepared by repeated sintering at 1300°C of hot-pressed MnCO$_3$ – Fe$_2$O$_3$ mixtures, and glass 0.65 BO$_1.5$0.05 SiO$_2$ 0.05 BaO 0.05 PbO 0.1 MnO 0.1 Fe$_2$O$_3$. To estimate the amount of crystalline phase in the sample, the intensities of at least five diffraction lines were compared with those of a standard mixture. In this evaluation of crystallinity and microstructure small nucleation and phase separation may have remained undetected.

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