ON FERRIMAGNETIC GLASS-CERAMICS BASED
ON B_2O_3 AND $MnFe_2O_4$*

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Relative boundaries of glass-formation for given quenching conditions are shown for the system $MnO-Fe_2O_3(-PbO)-B_2O_3(-SiO_2)$. 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 $BaO-Fe_2O_3-B_2O_3$ with up to about 50% of Fe_2O_3, yielding upon crystallization magnetoplumbite $BaO \cdot 6Fe_2O_3$. Schultz [10] crystallized glasses in the system $PbO-Fe_2O_3-SiO_2$ with 10–30% Fe_2O_3 into glass-ceramics containing $PbO \cdot 6Fe_2O_3$. Colline et al. [5] and Schultz [11] have found the system $R_2O-Fe_2O_3-SiO_2$ suited for crystallization of the spinel $Li(Na)FeO_2$ from glasses containing up to 26% Fe_2O_3. More complex glass systems resulting in crystals of ferrites $M^{2+}Fe_2O_4$ were investigated by Rogers et al. [9] ($CaO-Al_2O_3-B_2O_3-SiO_2$ with 12% Fe_2O_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_2O_3. In all these systems typical heat-treatments required were 600–900° for 1–60 hours.

The system chosen for the present work was $MnO-Fe_2O_3(M^{2+}O)-B_2O_3$ $(-SiO_2)$, because of established magnetic properties of manganese ferrite [1, 2] and the ease of glass formation at relatively low B_2O_3 content [9]. A large number of exploatory glasses crystallizable to high ferrite contents were, indeed,

obtained in this study. Batches (80 cm³) 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° for about 30 minutes in refractory crucibles, cast on stainless steel preheated to about 100° and pressed to 2 mm plates. Arbitrary relative boundaries of glass formation were established for the given quenching conditions (see Fig. 1).
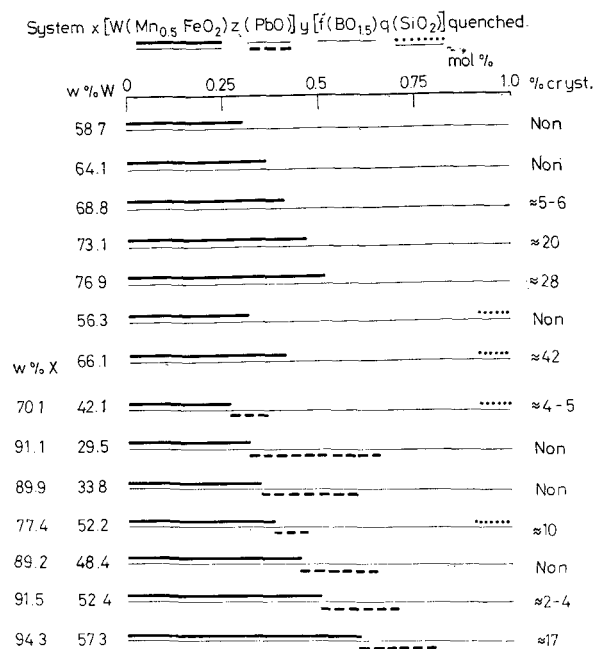

Fig. 1. Diagramatic representation of initial glass composition in the system containing manganese ferrite and PbO

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 ($a = 8.51$ Å), prepared by repeated sintering at 1300° of hot-pressed $MnCO_3 - Fe_2O_3$ mixtures, and glass $0.65\ BO_{1.5}\ 0.05\ SiO_2\ 0.05\ BaO\ 0.05\ PbO\ 0.1\ MnO\ 0.1\ Fe_2O_3$. 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.

The investigation of glass-forming regions was, for the sake of convenience, related to the following atomic ratio formulation: $x(wMn_{0.5}FeO_2zM^{2+}O)\,y\,(f\,BO_{1.5}$

g SiO_2) where M^{2+} is a divalent metallic cation other than Mn or Fe. The approximate empirical regions of glass formation noted under the given experimental conditions in this basic system are shown in Fig. 1. Contamination by Al_2O_3 and SiO_2 from the corroded crucibles was checked analytically to about 5 wt. % (for instance glass of 0.4 ferrite and 0.6 boric oxide showed 35.6 wt. % of Al_2O_3 + + SiO_2 + B_2O_3 compared to the theoretical content of 31.2 wt. % of B_2O_3). Glass-forming regions for the system containing PbO and BaO comparable to systems reported elsewhere[6, 10 – 13, 19] were also investigated.

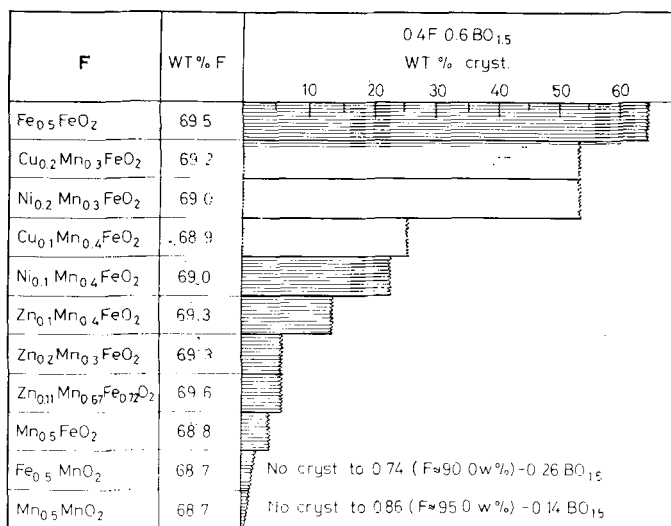| F	WT % F	0.4F 0.6 BO$_{1.5}$ WT % cryst.					
		10	20	30	40	50	60
$Fe_{0.5}FeO_2$	69.5						
$Cu_{0.2}Mn_{0.3}FeO_2$	69.2						
$Ni_{0.2}Mn_{0.3}FeO_2$	69.0						
$Cu_{0.1}Mn_{0.4}FeO_2$	68.9						
$Ni_{0.1}Mn_{0.4}FeO_2$	69.0						
$Zn_{0.1}Mn_{0.4}FeO_2$	69.3						
$Zn_{0.2}Mn_{0.3}FeO_2$	69.3						
$Zn_{0.11}Mn_{0.67}Fe_{0.72}O_2$	69.6						
$Mn_{0.5}FeO_2$	68.8						
$Fe_{0.5}MnO_2$	68.7	No cryst to 0.74 (F≈90.0 w %) –0.26 BO$_{1.5}$					
$Mn_{0.5}MnO_2$	68.7	No cryst to 0.86 (F≈95.0 w %) –0.14 BO$_{1.5}$					

Fig. 2. Diagramatic representation of the crystallization tendency for a constant ratio ferrite : boric oxide = 0.4 F : 0.6B_{15}O

The relative solubility of the ferrite-forming materials with the glass has been evaluated in terms of crystal amount detected for a given ratio ferrite: B_2O_3 as illustrated in Fig. 2. The empirical results may be summarized by an approximate series of increasing compatibility chosen in general accord with the concepts invoking field strength (charge over radius), covalency, high symmetry and stability of crystalline phases formed: $Cu^+ - Fe^{2+} - Cu^{2+} - Fe^{3+} - Ni^{2+} - Mn^{2+} - Zn^{2+} - Mn^{3+} - Ba^{2+} - Pb^{2+}$.

It is well-known in glass technology that the desired states Mn^{2+} and Fe^{3+} are favored over the combination if both manganese and iron ions are present in oxide glass melts. The analytical determination of the oxygen showed oxygen deficiency for samples dissolved in HCl under a CO_2 atmosphere and titrated by Ce^{4+} solution in H_2SO_4 using ferroin as indicator. Together with the low value of a for the crystallized ferrite this indicates that some of the manganese remains in the glassy phase, or that some the Al^{3+} or Si^{4+} from the contaminators has

been introduced into the spinel phase. The formula of the ferrite precipitating is thus believed to be $Mn_xFe_{3-x}O_4$ where $x < 1$.

The crystallization of ferrite, $MnFe_2O_4$, on controlled reheating of quenched melts occurs because this phase is the most stable one in the system if oxygen transport into the glass bulk is negligible. On continuing the temperature increase
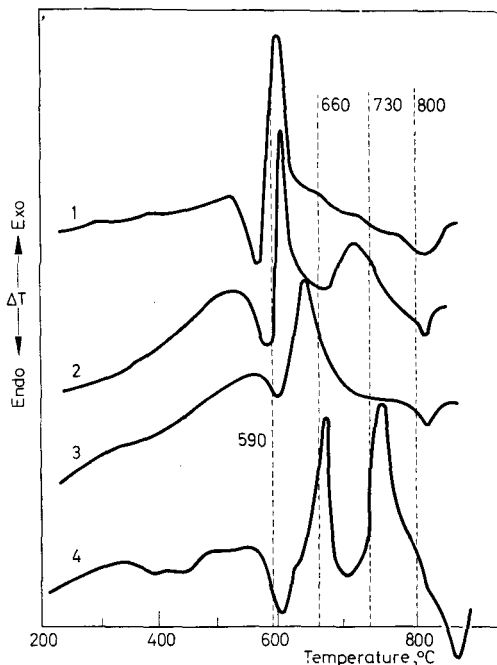

Fig. 3. DTA traces for quenched glass systems: 1) $0.46\ Mn_{0.5}FeO_2 + 0.34\ BO_{1.5} + 0.2\ PbO$; 2) $0.35\ Mn_{0.5}FeO_2 + 0.65\ BO_{1.5}$; 3) $0.45\ Mn_{0.5}FeO_2 + 0.25\ BO_{1.5} + 0.3\ BaO$; 4) $0.30\ Mn_{0.5}FeO_2 + 0.60\ BO_{1.5} + 0.1\ SiO_2$

this metastable spinel is oxidized [3] to Mn_2O_3 (bixbyte) and Fe_2O_3 (hematite) with their wide range of mutual solid solutions [2] as soon as the decreasing glass viscosity permits a sufficient oxygen supply. Both these processes are accompanied [2] by a heat release which permits the determination of the region of ferrimagnetic phase occurrence.

Heat-treatments for the controlled crystallization were thus successfully chosen from preliminary investigations by DTA [18, 21] as shown in Fig. 3 for four traces of the investigated types of glasses. The fully automatized instrument of Stone with Pt cells heated in a protecting steel vessel in a Pt furnace was used under a controlled heating rate of $10°/min$. The first large exothermic peak at $570-680°$ corresponds to the crystallization of manganese ferrite as confirmed by X-ray investigations of samples heat-treated at 590 and 660°. The second smaller exo-

thermic peak at $690-810°$ is associated with the ferrite decomposition and borates formation. The addition of SiO_2 enhances this peak, while PbO and/or BaO diminishes it, which indicates that these ingredients change the condition of the oxidation. The heat liberated (ΔH) during the crystallization was calculated from the area under the respective first peaks [22] after calibration using the quartz $\alpha \to \beta$ transformation and the heat of K_2SO_4 fusion, the temperatures of which fall into the same range as that of glass crystallization. The value of ΔH calculated per molecular content of ferrite crystallized was estimated as about 4 kcal/mole, which appears to be at the lower end of the values (4−8 kcal/mole) found by calorimetric measurements of $MnFe_2O_4$ formation [2] from MnO and Fe_2O_3. On considering these glasses similar to diluted melts of ferrite in glass the heat of solidification ($\cong 30$ kcal/mole) [2] should be regarded as the maximum value for ΔH comparison. The difference can be accounted for by, besides the dissolution effect, the high ordering of Mn and Fe ions in glass.

For the purpose of preliminary characterization some room-temperature electric and magnetic properties were determined (see Table 1) on solid samples crystallized under controlled conditions, specifically at 590, 660, 730 and 800° for 12, 10, 6 and 2 hours, respectively (heating and cooling rates were 2°/min in air). Informative measurements of DC electric conductivity were made by a twopoint contact method on silver paste as the surface contact with no special precautions

Table 1

Theoretical content	Heat-treatment	Weight % of spinel phase (by X-ray)	Dielectric constant at 1 MHz	Dielectric losses [%] at 1 MHz	Specific electric conductivity, $\Omega^{-1} \cdot m^{-1}$	Init. spec. magnetic susceptibility, $cm^3 \cdot g^{-1}$
0.6 $BO_{1.5}$	Glass	$\cong 5$	16.5	7.5	$6.5\ 10^{-11}$	$1.32\ 10^{-3}$
	590°, 12 hr	$\cong 16$	25.5	21	$1.5\ 10^{-11}$	$2.56\ 10^{-3}$
	660°, 10 hr	$\cong 54$	22	17.5	$0.5\ 10^{-11}$	$7.67\ 10^{-3}$
0.4 $Mn_{0.5}FeO_2$	730°, 6 hr	$\cong 42$	23.5	27.5	$0.8\ 10^{-11}$	$5.93\ 10^{-3}$
	800°, 2 hr	$\cong 0$	35.5	34.5	$2\ \ \ 10^{-8}$	$0.85\ 10^{-3}$
0.6 $BO_{1.5}$	Glass	none	11	3	$0.4\ 10^{-12}$	$0.25\ 10^{-3}$
0.1 SiO_2	660°, 10 hr	$\cong 34$	16	4.5	$8.0\ 10^{-12}$	$5.65\ 10^{-3}$
0.3 $Mn_{0.5}FeO_2$	730°, 6 hr	$\cong 41$	20.5	6.5	$0.5\ 10^{-12}$	$5.77\ 10^{-3}$
	800°, 2 hr	$\cong 0$	53.5	34	$6\ \ \ 10^{-9}$	$0.32\ 10^{-3}$
0.34 $BO_{1.5}$	Glass	none	20	3.5	$4.5\ 10^{-12}$	$0.03\ 10^{-3}$
0.2 PbO	590°, 12 hr	$\cong 4$	21.5	2.5	$6.0\ 10^{-12}$	$0.7\ \ 10^{-3}$
0.46 $Mn_{0.5}FeO_2$	730°, 6 hr	$\cong 18$	27.5	22.5	$4.5\ 10^{-10}$	$2.63\ 10^{-3}$
0.4 $BO_{1.5}$	Glass	$\cong 3$	13	1	$9.0\ 10^{-13}$	$0.18\ 10^{-3}$
0.2 BaO	660°, 12 hr	$\cong 13$	14.5	1.5	$1.5\ 10^{-13}$	$2.31\ 10^{-3}$
0.4 $Mn_{0.5}FeO_2$	730°, 6 hr	$\cong 18$	15.5	3	$2.5\ 10^{-13}$	$3.16\ 10^{-3}$
	800°, 2 hr	$\cong 40$	19.5	4	$7.5\ 10^{-13}$	$4.98\ 10^{-3}$

against electrode polarization. Loss factors and dielectric constant were determined simultaneously using an AC bridge at 1 MHz. Exploatory susceptibility measurements were made by a modified Guy method by weighing small glass balls in a very low magnetic field outside the magnet poles after calibration with known substances.

Table 1 together with the DTA plots (Fig 3. prove that the addition of BaO and partly PbO stabilize the ferrite phase up to higher temperatures ($\approx 700-800°$)) whereas in the basic Mn—Fe—B—O system or in that containing some SiO_2 the decomposition of ferrite occurs around 700°.

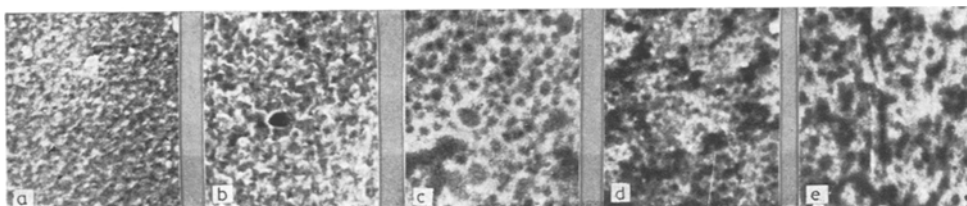Fig. 4. Electroscanning micrographs of glass sample 0.35 $Mn_{0.5}FeO_2$ + 0.65 $BO_{1.5}$ after different heat-treatments: a) quenched glass; b) 590° — 12 hr; c) 660° — 10 hr; d) 730° — 6 hr; e) 800° — 2 hr. Etching procedure after grinding and polishing 15 sec (2 HF + 1 CH_3COOH+ + 10 H_2O), then 25 sec (2 HCl + 1 HNO_3 + 5 H_2O), and finally 10 sec (1 HCl + 15 H_2O). Gold-plated in vacuum. Electron scanning microscope TOELCO (Japan) and Polaroid picture

The initial formation of Mn and Fe-rich regions tending to nucleate and crystallize is not easily followed by X-ray diffraction or DTA. Electron micrography supplies some evidence of the development of the ferritic phase. In Fig. 4 a set of pictures is shown for a borate glass with a theoretical content of 64 wt.% $MnFe_2O_4$ heated at different temperatures. Phase separation is already noticeable in the quenched glass (a) and becomes more pronounced below and close to the temperature of crystallization (b). Above this temperature well-developed differentiation and formation of ferrite grains becomes evident (c). Next, disintegration due to decomposition of ferrite is observed (d) until a new, possibly borates structure is reached (e). Liquid-liquid phase separation may play a role in the process of origination of the ferritic crystalline phase. The interpretation of the compositional areas in the electron micrographs was supported by non-dispersive X-ray spectrometry, in terms of the local concentration of Fe and Mn elements.

The maximum or optimum ferrite content of a ferritic glass-ceramic is obviously limited by the minimum content necessary in glass, as far as manganese ferrite alone cannot form the precursor glass. Nevertheless, the controlled formation of a well-defined diluted ferrite ceramic may be attractive for specific materials in which well-defined separation of tiny crystals may be desirable. Alternatively, a microstructure with a continuous precipitated phase can be developed. It may be possible to orient the magnetic phase during the precipitation by applying an

external field. It is of interest to study stability areas, domain formation, and oxidation kinetics at lower temperatures, etc. in diluted ferritic glass-ceramics. Initial experiments in this direction are now being performed [23] by the Magnetic Group of the Institute of Solid-State Physics in Prague.

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