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GLASS-FORMATION, PHASE RELATIONS AND MAGNETIC PROPERTIES OF THE SPLAT-QUENCHED SYSTEM OF LASER-MELTED (Fe, Mn)$_2$O$_3$–(Bi, B)$_2$O$_3$

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Presintered rods of oxide mixtures in the system (Fe, Mn)$_2$O$_3$–(Bi, B)$_2$O$_3$ were melted crucible-free with the help of a laser while suspended in a rhodium-wire microheater. The molten hanging drop was then quenched by pressing between two small copper plates mounted at the ends of tweezers inside a globular reflector. The crystalline phases of Fe_2O_3, $Fe_4Bi_2O_9$ and $FeBiO_3$ gradually disappeared when the cooling rate was increased from about 10^2 to an estimated maximum of 10^4 deg s^{-1}. Substitution of B instead of Bi, and Mn instead of Fe, substantially changes the phase relations and facilitates glass-formation. The glasses exhibit magnetic interactions of antiferromagnetic type; only $FeBiO_3$ provides magnetic measurements explainable on the basis of weak ferromagnetism, probably caused by canted spins of the antiferromagnetic sublattice.

According to the ordinary criteria for glass formation developed before use of the fast quenching techniques, the B_2O_3 content of the previously [1–3] investigated (Fe, Mn)—B—O compositions was not sufficient to allow ready glass formation. It was found [1] that the cation shift from $Mn^{3+} \rightarrow Mn^{2+} \rightarrow Fe^{3+}$ to Fe^{2+} decreases the glass-forming ability of splat-quenched melts (between two copper plates into specimens approximately 2 mm thick), the upper limit of the Fe_2O_3 content being 20 mol%. Incorporation of Mn and Fe ions into the glass network follows the above sequence, as corroborated by our findings relating to ferrite precipitation on the crystallization of (Fe, Mn)$_2$O$_3$—B_2O_3 glasses, showing an enrichment of Fe in $Mn_xFe_{3-x}O_4$ (x = 0.15 and 0.3, as found by X-ray diffraction measurement of the lattice constant [1] and Curie temperature determination via the specific magnetization [2], respectively) in comparison with the starting formula $MnFe_2O_4$. This is in agreement with a recent study on the (Fe, Co)Mn_2O_3—SiO_2 system [4].

Interesting studies have been made on the influence of the different admixtures on the stabilities of these gases, analysed on the basis of DTA and magnetic measurements. SiO_2 tends to form a separate network within the original B_2O_3

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matrix, two separated regions of glass-formation being exhibited, while the glass-formation ability remains unaffected. On the other hand, Al_2O_3 tends to enter the B_2O_3 matrix and to span its network into three dimensions, which results in a relative gain in its glass stability. Alkali metal cations, with their relatively large ionic radius, deform the B_2O_3 network in their vicinity. These regions act as potential nuclei sites for subsequent crystallization upon reheating, thereby decreasing the glass-forming ability, although the melting temperature is lowered [3]. A BaO additive [1] behaves similarly, despite the essential increase in the glass-transition temperature in comparison with that of glass containing K_2O. A positive effect on the glass-formation ability is associated with the addition of PbO or Bi_2O_3, the latter being analysed in greater details here.

Experimental

The samples investigated were prepared from Fe_2O_3, Mn_3O_4, B_2O_3 and Bi_2O_3 analysed for cation content. The well-homogenized mixture was premelted at about 1150°, quenched, crushed and then melted in a platinum crucible for about 15 min at about 1300°. For high contents of Bi_2O_3, either 1% of V_2O_5 was added to prevent the Bi-initiated corrosion of the Pt crucible, or a presintered sample was melted crucible-free by means of a laser, while suspended in a rhodium-wire microheater (Fig. 1). Quenching of the melt was carried out either by our standard method of pouring/dropping the melt in between two copper plates, or by a new

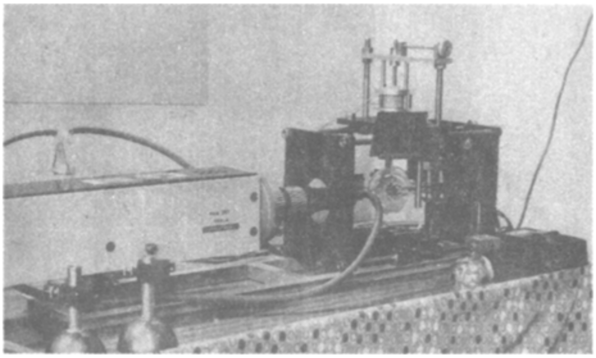

Fig. 1 Overall view of the CO_2 cw-laser (left) aided high-temperature microfurnace (right), which is half-open (one hemispherical reflector removed) to expose the inner view of the Rh-wired heater. The upper part serves to rotate the sample, with a twin-roller quenching instrument placed underneath. The maximum temperature achieved with full power supply to both heaters was about 2500° (estimated via a Rh–W thermocouple inserted into the sample)

modified method, similar to that conveniently called the pendant drop melt extraction, with complementary laser heating [5–7]. The end of a rotating presintered rod-like specimen was heated by a focused laser beam (while the surrounding microheater ensured a more homogeneous temperature distribution). The hanging molten drop was then pressed in between two small copper plates mounted at the ends of tweezers placed inside the globular reflector (Fig. 2), the resulting thickness being about 0.5 mm. Quenching rates from 10^2 up to 10^4 deg s^{-1} were probably achieved [8], although not experimentally determined. The quenched specimens (Fig. 3) were examined by means of X-ray powder diffraction for the content of crystalline phases. DTA runs were also carried out to measure the tendency of the individual glasses to devitrify. The magnetic susceptibilities in the temperature range from 4.5 K up to room temperature were measured by means of a modified Faraday method, using an inhomogeneous magnetic field (Fig. 4). For the determination of phase relations in this system, the known phase diagrams and X-ray data on related phases were utilized. The less known system B_2O_3—Fe_2O_3—Mn_2O_3 was checked in independent annealing experiments.

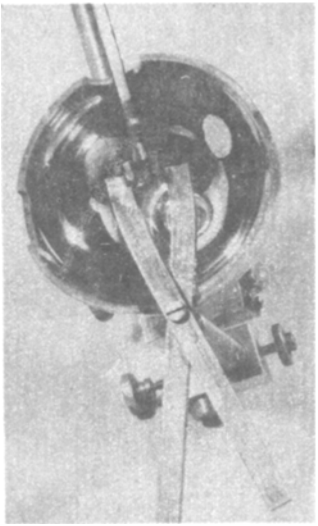

Fig. 2 Detailed view of the globular reflector, made from quartz plated with Ag13Pd, with the sample rod suspended on a ceramic support and with the quenching instrument consisting of a miniature tweezer-like holder ended by two small copper plates, serving to splat the melted drop hanging down the sample

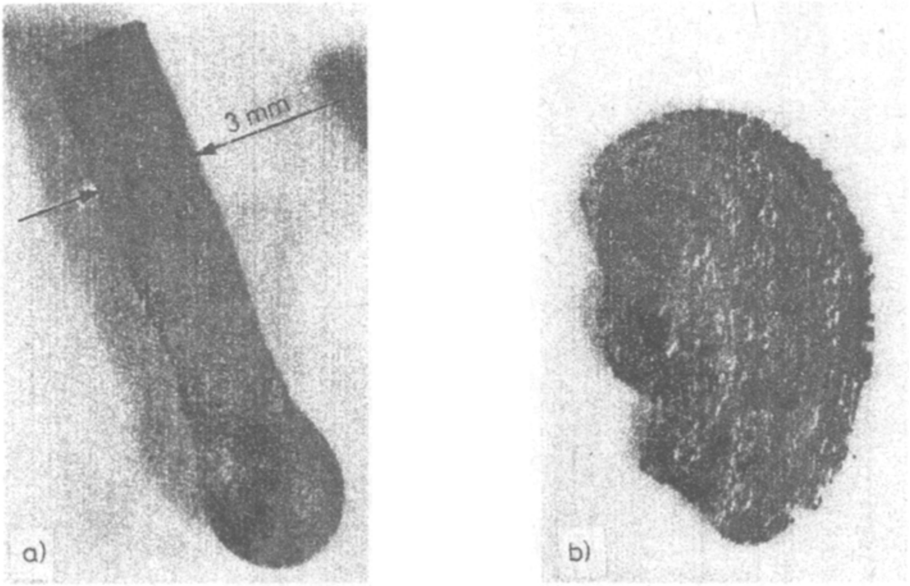

Fig. 3 Detailed view of the sample rod (a) with a solidified drop of the laser-melted system of $Fe_{0.5}Mn_{0.5}BiO_3$ and (b) its splatted specimen after application of the quenching equipment shown in Fig. 2

Discussion

The substitution of Bi_2O_3 for B_2O_3 increases the upper limit of Fe_2O_3 content to above 20 mol% (e.g. 30 mol% for $Fe_2O_3 \cdot Bi_2O_3 \cdot B_2O_3$ formed at 10^2–10^3 deg s^{-1}). In contrast with the simple (Fe, Mn)–B–O, the substitution of Fe by Mn in a Bi_2O_3-rich matrix does not improve the glass formation, but decreases the Curie temperature. The end composition $FeBiO_3$ requires quenching rates as high as about 10^4–10^5 deg s^{-1}. At lower cooling rates, the crystalline phases Fe_2O_3, $Fe_4Bi_2O_9$ and $FeBiO_3$ precipitate, disappearing in the given sequence if the quenching rate increases from 10^2 through 10^3 to 10^4 deg s^{-1} for single, double copper plates and pendant drop pressing, respectively. Substitution of B for Bi in $FeBiO_3$ changes the phase relations substantially. Besides the above-mentioned phases, a series of borates occurs and the magnetic moment of the (remaining) crystalline phases is increased. The temperature-dependence of the matrix magnetic susceptibility provides evidence of interactions of antiferromagnetic type involving moments of the order of 10^2 K (Fig. 4). The composition containing not only Bi, but also B, exhibits Curie–Weiss behaviour. Samples with Bi and Mn probably

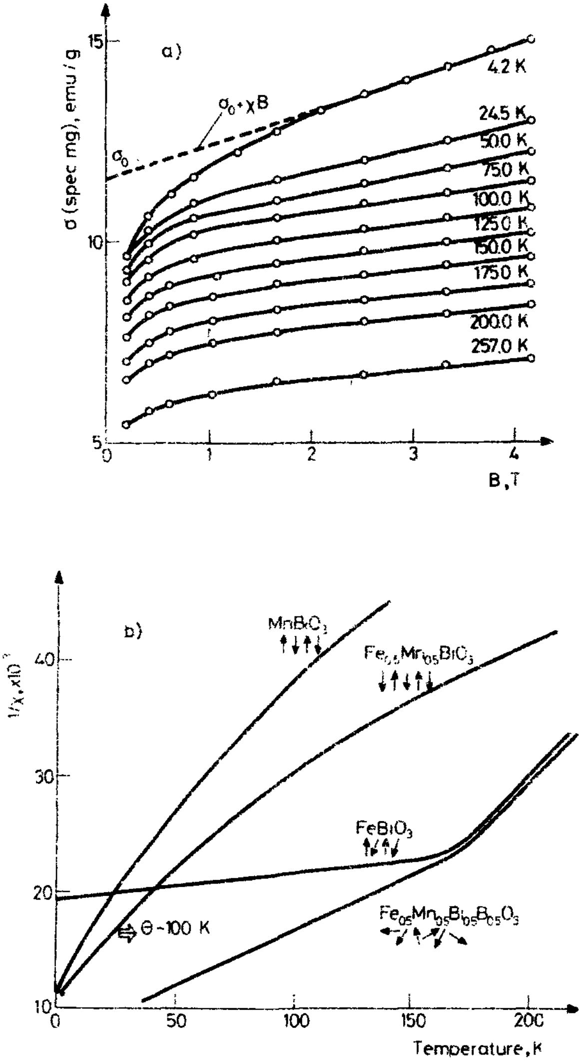

Fig. 4 (a) Magnetization curves of the as-quenched glass; (b) temperature-dependences of reciprocal specific magnetic susceptibility $1/\chi$ for the series of glassy samples investigated. The magnetic behaviour changes from paramagnetic ($Fe_{0.5}Mn_{0.5}Bi_{0.5}B_{0.5}O_3$) to a mixture of paramagnetic and antiferromagnetic ($MnBiO_3$ and $Fe_{0.5}Mn_{0.5}BiO_3$) phases exhibiting a Néel temperature θ in the order of 100 K. The $FeBiO_3$ phase displays antiferromagnetic behaviour with not completely compensated moment orientation, as illustrated by the arrows for each composition.

contain ions as a result of their broad distribution, showing their incorporation into the glass network. Only $FeBiO_3$ provides magnetic measurements explainable on the basis of weak ferromagnetism, probably caused by canted spins in the antiferromagnetic sublattice, long ago suggested in [9], but so far not proved.

The type of incorporation of either Mn or (less probably) Fe ions into the glass network affects the resulting magnetic moment of the glass. The number of ions incorporated will be given by transition metal (M) equilibria of the following type [3, 10]:

$$2\,M^{3+}+3\,O^{2-} = 2\,M^{+''}+2\,O''+2\,O^{2-} = 2\,M'''+3\,O''$$

where the number of primes denotes the multiplicity of the bond of the given atom in the network and for the free ions. Bi_2O_3 added to the B_2O_3 matrix presumably prefers to undergo incorporation in the form of BiO_3^{3-} groups, their negative charge being compensated by bonding transition metal into the network. Thus the concentration of bridging oxygens is decreased, i.e. the equilibria are shifted to the right. This effect is similar to that caused by Al_2O_3, but stronger, due to the higher deformability of the larger Bi ions.

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Zusammenfassung — Vorgesinterte Stäbe von Oxidmischungen des Systems $(Fe, Mn)^2O_3$–$(Bi, B)_2O_3$ wurden mit einem Laser in einem Rhodiumdraht-Mikroofen tiegelfrei geschmolzen. Der Schmelztropfen wurden durch Pressen zwischen zwei Kupferplatten an den Enden einer Zange innerhalb des kugelförmigen Strahlungsreflektors abgeschreckt. Mit zunehmender Abkühlungsgeschwindigkeit von 10^2 bis (geschätzt) 10^4 K s^{-1} verschwanden nacheinander die kristallinen Phasen Fe_2O_3, $Fe_4Bi_2O_9$ und $FeBiO_3$. Substitution von Bi und B und von Fe durch Mn verändert die Phasenzusammensetzung und erleichtert die Glasbildung. Die Gläser zeigen antiferroelektrische Wechselwirkungen; beim $FeBiO_3$ sind die magnetischen Messungen auf der Grundlage eines schwachen Ferromagnetismus zu erklären, der wahrscheinlich durch die gekippten Spins der antiferromagnetischen Teilgitter verursacht ist.

Резюме — Предварительно подвергнутые спеканию стержни оксидной смеси в системе $(\mathrm{Fe, Mn})_2\mathrm{O}_3$–$(\mathrm{Bi, B})_2\mathrm{O}_3$, с помощью лазера были расплавлены в подвешенном состоянии в родиево-проволочном микронагревателе. Расплавленная висячая капля была затем резко охлаждена путем прессования ее между двумя небольшими медными пластинками, смонтированными на кончиках пинцетов с внутренней стороны сферического отражателя. Установлено, что кристаллические фазы $\mathrm{Fe_2O_3}$, $\mathrm{Fe_4Bi_2O_9}$ и $\mathrm{FeBiO_3}$ непрерывло исчезают с увеличением скорости охлаждения от 10^2 град·сек$^{-1}$ до максимально предельного значения 10^4 град·сек$^{-1}$. Замещение висмута на бор и железа на марганец, в значительной степени изменяет сотношение фаз и способствует стеклообразованию. Такие стекла обладают магнитными свойствами типа антиферромагнетиков. Только $\mathrm{FeBiO_3}$ проявляет магнетизм, объяснимый на основе слабого ферромагнетизма, возможно обусловленного скошенными спинами антиферромагнитной подрешетки.