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Properties of YIG-based magnetic glass–ceramics with different nucleating agents

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The effect of bismuth, silver oxide and palladium on the crystallization of yttrium iron garnet in Na_2O–SiO_2–Y_2O_3–Fe_2O_3 glass–ceramics has been investigated by X-ray diffraction thermal analysis, magnetic measurements and optical microscopy. It is found that the magnetic properties of these glass–ceramics can be altered significantly by a change in the nucleating agents and the heat treatment schedule. This behaviour is explained on the basis of the microstructure and the volume fraction of the different magnetic phases crystallized within the glasses.

1. Introduction

Glass–ceramics with suitable magnetic phases have been investigated extensively in recent years [1–7]. Of late, the effect of nucleating agents on the crystallization kinetics of the precipitated magnetic phases has been studied [7–9]. While characterizing the various yttrium iron garnet-based (YIG-based) magnetic glass–ceramics developed in our laboratory we have found that the magnetic properties of these materials can be altered significantly by a change of nucleating agent and heat treatment schedule. In this paper, we report the results on YIG based glass–ceramics with bismuth oxide, silver oxide and metallic palladium as the nucleating agents respectively.

2. Experimental procedure

The glass compositions investigated are given in Table I. The glasses were prepared from reagent grade chemicals by melting the mixture in alumina crucibles in an electrically heated furnace between 1300 to 1450° C. Glass plates were cast by pouring the melt on an aluminium mould. In the case of palladium containing glasses, 0.05 wt % of palladium was added through a complex salt $Pd(Py)_2(SCN)_2$. The glass transition temperatures (T_g) and crystallization temperatures (T_c) were estimated from differential thermal analysis (DTA) analysis using a MOM Hungary, Derivatograph. DTA plots for all the compositions are given in Fig. 1. For composition C1, DTA has already been reported by us [8]. Heat treatments, based on DTA analysis, and the detailed sample codes are given in Table II. X-ray powder diffraction patterns of ceramized glasses were recorded with a Rich and Seifert Iso-Debyeflex 2002 diffractometer. Magnetization measurements were carried out with a PAR vibrating sample magnetometer (model 150A) in conjunction with a varian 9″ magnet (model V-7200). The variation of magnetization with temperature was studied with the help of a high temperature oven assembly (model 151). The optical micrographs were taken with a Zeiss optical microscope.

3. Results and discussion

The X-ray diffractograms of all the two stage heat treated samples show the lines characteristic of two magnetic phases YIG and iron oxide. The volume fraction of the crystalline phases depends on the composition and the heat treatment of the different glasses. In our earlier report [8], we have mentioned that 1015 and 1055 K are the most favourable nucleation and growth temperatures respectively for the crystallization of YIG phase for composition C1. For C1, we have now varied the nucleation and growth times to find out their effects on the microstructure and magnetic properties.

The plot of magnetization against temperature for some of the glass–ceramic samples are given in Fig. 2. The data refer to values measured at a field of 6 kG. All the samples except C21 show two transition temperatures. The first transition around 550 K is typical of YIG. There is a wide variation in the second transition temperature. The sample C21, on the other hand, shows essentially one transition which is around 650 K. Fig. 3 shows the hysteresis loops for the different glass–ceramic samples at room temperature. All the samples show hysteresis. However, most of them do not show complete saturation upto a field of 10 kG. Also, it is seen that the coercivity is a strong function of heat treatment and composition. Table III summarizes all these magnetic data for the various

TABLE I Chemical compositions of glasses investigated

Glass	Compositions (%)			
–	C1	C2	C3	C4
SiO_2	48	49.6	48	48
Na_2O	26	33.6	26	26
Y_2O_3	9	5.9	9	9
Fe_2O_3	15	10.1	16	17
Bi_2O_3	2	0.8	–	–
Ag_2O	–	–	0.5	–
As_2O_3	–	–	0.5	–

In C4 0.05 wt % of paladium is added through a complex salt $Pd(PY)_2(SCN)_2$.

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TABLE II Sample label and heat treatments given to different glass compositions

Composition	Heat treatment	Label	Heat treatment	Label	Heat treatment	Label
C1	1015/2 h + 1055/24 h	C11	1015/5 h + 1055/24 h	C12	1015/2 h + 1055/2 h	C13*
C2	895/2 h + 990/20 h	C21				
C3	1000/2 h + 1095/2 h	C31	1000/2 h + 1095/24 h	C32	1000/5 h + 1095/24 h	C33
C4	1070/2 h + 1105/2 h	C41	1070/2 h + 1105/24 h	C42	1070/5 h + 1105/24 h	C43

Note: temperatures are given in Kelvin.
*This composition has already been reported by us [8].

compositions. The simultaneous presence of large coercive field and the absence of complete saturation is not common and it indicates the presence of at least two phases. This is supported by X-ray diffraction results and the magnetization data where two transitions are observed. One of these phases obviously shows saturation and hysteresis whereas the other is probably in a superparamagnetic state and is responsible for the absence of complete saturation. Optical micrographs also exhibit the presence of at least two phases. A typical set of micrographs for composition C31, C33 and C41 are given in Fig. 4a, b and c, respectively. The most prominent phase for sample C41 has essentially an acicular microstructure which is similar to that reported for the composition C1 [8]. The average length and width of the acicular particles for C41 are 3 and 0.3 μm, respectively. A similar structure is also exhibited by C33. The average length and width of these particles are 3 and 0.4 μm, respectively. The acicular particles have been identified as Fe_2O_3 by selected area electron diffraction. The volume fraction of these particles is $\sim 60\%$ for the sample C41 which also exhibits the highest coercivity (~ 2000 Oe) in the series of magnetic glass–ceramics prepared in this study. The sample C33, on the other hand, has a small volume fraction %) of acicular particles and shows a coercivity of the order of 200 Oe. The selected area diffraction of finer particles in all these samples revealed the presence of YIG phases. A typical electron micrograph of the area where YIG phase is predominant for the sample C33 is shown in Fig. 5a. The corresponding electron diffraction pattern is shown in Fig. 5b. The diffraction spots have been identified to be characteristic of YIG phase. The presence of the fine particles of YIG is evident from the micrograph. These YIG crystallites have dimensions varying between less than 0.01 to 0.5 μm. The sample C31 which does not contain acicular particles gives a coercive field of the order of 100 Oe. It is interesting that we obtain large variation in coercivity and other magnetic properties (Table III) and it is a strong function of heat treatment and composition. The shape anisotropy of acicular particles is known to impart a large coercivity [10]. The surface spins may get pinned or assume non-collinear spin configuration which could also add to the anisotropy [11–13]. In the present set of samples, large impediments are expected on account of grain boundaries and surface structure of fine particles.

The transition temperature estimated for sample C21 is around 650 K. There is no indication of YIG phase in this sample for which the transition is expected around 550 K. The X-ray diffraction data also indicate that this sample is least favourable for YIG. It is possible that the volume fraction of YIG phase in this sample is very small. All other samples, on the other hand, show two transitions. One at around 550 K is for YIG phase whereas the other varies between 650 and 900 K. The variation in the second transition temperature between 650 and 900 K is typical of heat treatment and compositions. From X-ray diffraction studies, it is indicated that besides YIG phase, iron oxides in α- or γ-forms coexist in most of the samples. Secondly, their volume concentrations vary considerably in different samples as is evident from X-ray

TABLE III Summary of magnetization data for different compositions

Composition	Magnetization at 9 K gauss (emu g^{-1})	Coercive field (Oe)	Transition temperature (K)
C11	0.3	800	550 800
C12	0.3	1000	550 750
C13*	9.0	100	550 850
C21	5.8	400	650
C31	1.5	100	550 875
C32	0.5	200	550 900
C33	–	200	550 900
C41	1.8	2000	550 800
C42	0.4	800	550 850
C43	0.5	200	500 875

*The data for this composition has already been reported by us [8]

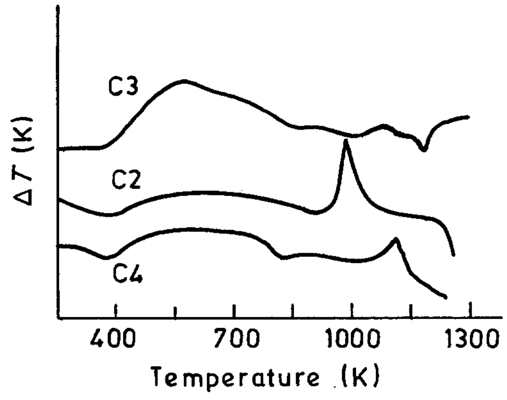

Figure 1 DTA plot for various as-prepared compositions.

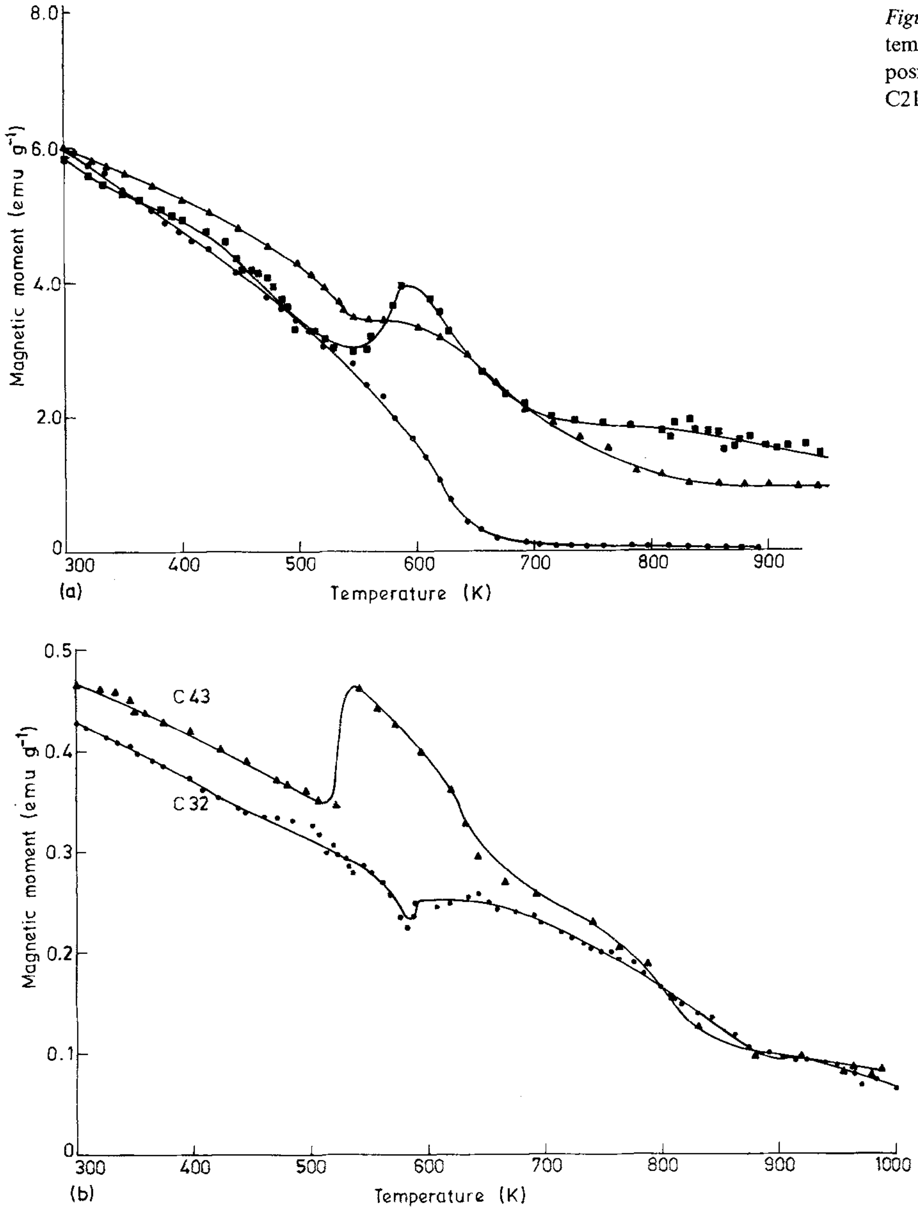

Figure 2 Plot of magnetization against temperature for typical samples of composition C1 to C4 (a) (▲) C11, (■) C12, (●) C21, (b) (▲) C43, (●) C32.

diffraction data. In fact, simultaneous presence of different phases of iron oxides and their easy conversion into each other in slightly different condition is a common occurrence [14, 15]. In the present set of samples, the variation in the second transition temperature could therefore be ascribed to the interconversion of various forms of iron oxide. The variations in volume fraction of the different forms of iron oxide is also evident from X-ray and electron diffraction data.

It is interesting that the sample C41 shows complete saturation, a coercive field of the order of 2000 Oe and Mr/Ms value ~ 0.55, where Mr is the remanence magnetization and Ms is the saturation magnetization. It is to be noted that by just varying the nucleation and growth times for composition C4, the magnetic properties could be varied considerably. For example, coercivity for sample C43 is 200 Oe whereas for C41, it is 2000 Oe. There is evidence that highest coercivities can be achieved when a magnetic phase in the form of acicular particles is distributed in a non-magnetic matrix [16]. In the glass–ceramic route, this is one of the advantages.

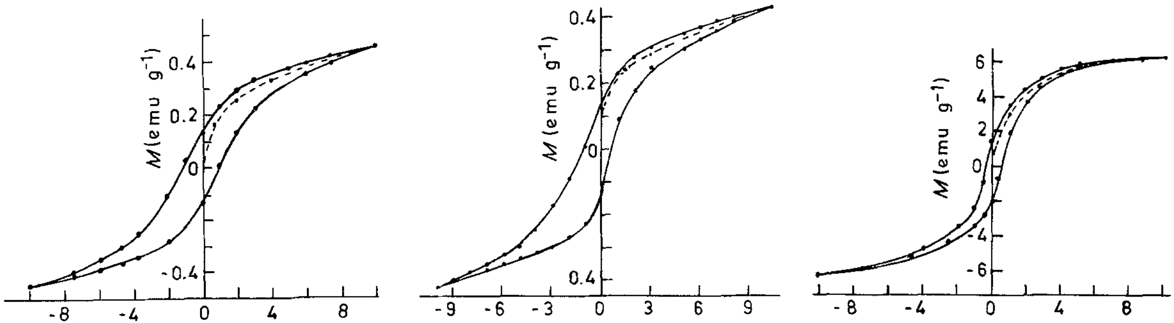

Figure 3 Hysteresis plots for samples of composition (a) C12, (b) C11, (c) C21, (d) C33, (e) C43, (f) C42, (g) C41.

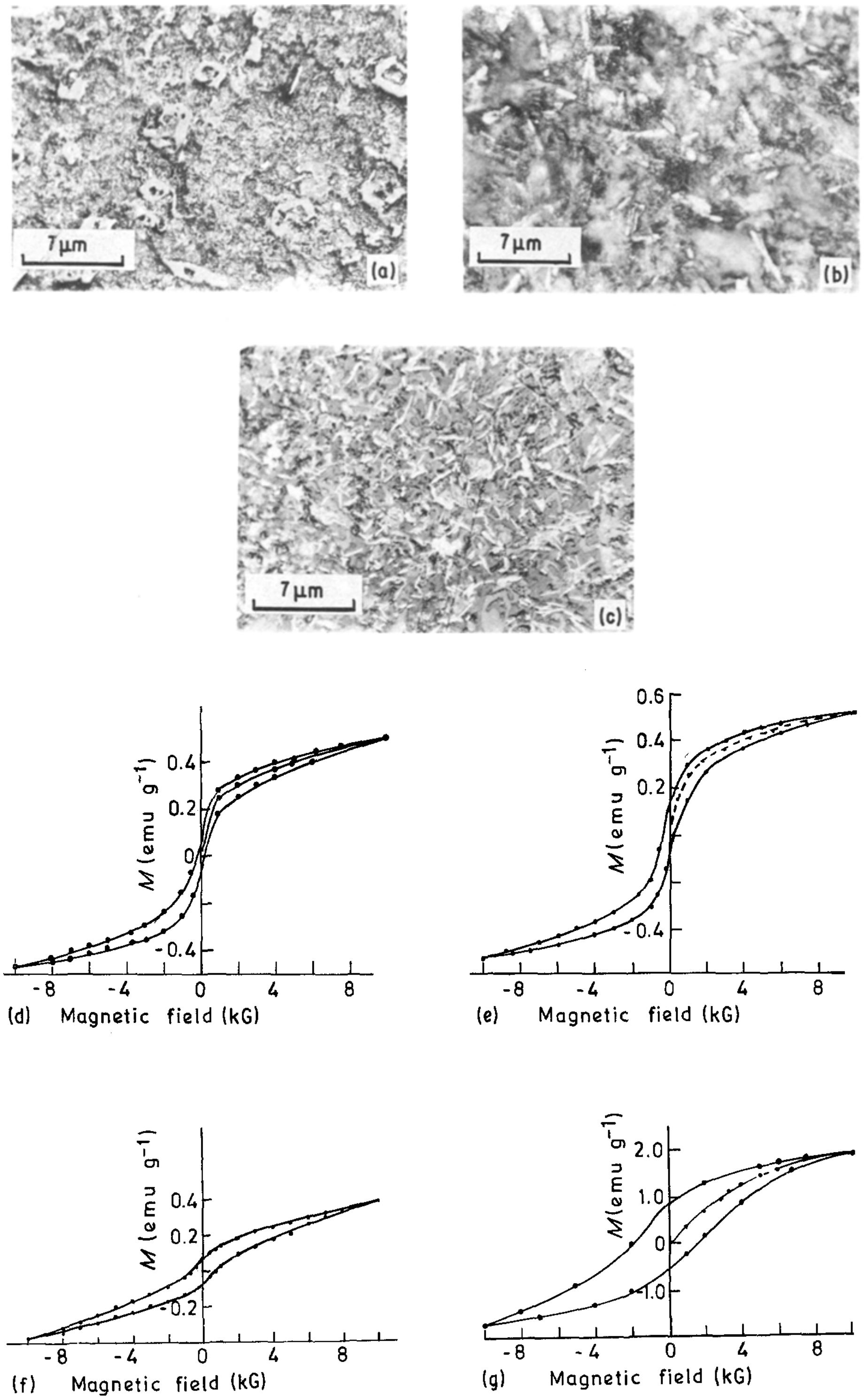

Figure 4 A typical set of optical micrographs for samples (a) C31, (b) C33 and (c) C41.

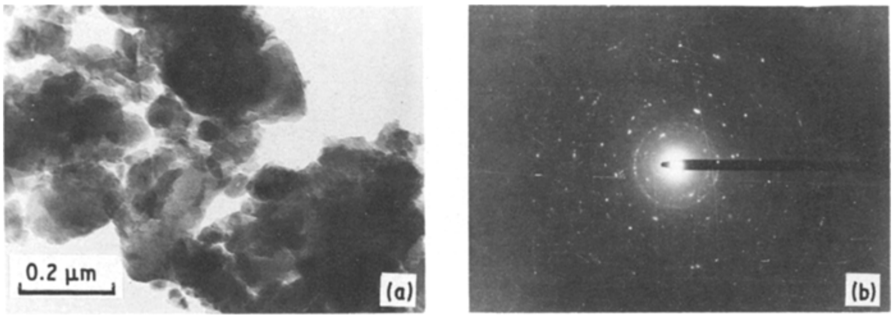

Figure 5 (a) A typical electron micrograph for sample C33. (b) This shows the corresponding electron diffraction.

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