

Mössbauer studies of the effect of nucleating agents on the crystallization of YIG in the $\text{Na}_2\text{O}-\text{SiO}_2-\text{Y}_2\text{O}_3-\text{Fe}_2\text{O}_3$ glass system

A. PRASAD, R. M. SINGRU, D. BAHADUR*

*Department of Physics and *Advanced Centre for Materials Science, Indian Institute of Technology, Kanpur 208016, India*

D. CHAKRAVORTY

Central Glass and Ceramics Research Institute, Jadavpur, Calcutta 700032, India

The effect of 2 mol % of P_2O_5 or TiO_2 on the crystallization of yttrium-iron-garnet (YIG) in $\text{Na}_2\text{O}-\text{SiO}_2-\text{Y}_2\text{O}_3-\text{Fe}_2\text{O}_3$ glass ceramics has been investigated by X-ray and Mössbauer spectroscopic studies. These studies indicate that the glass ceramics containing P_2O_5 are more favourable for the crystallization of YIG. Analysis of the results suggest that an optimum growth temperature for crystallization of the YIG phase is 800°C in the sample with P_2O_5 as the nucleating agent. The sample heat-treated at the growth temperature for 40 h is not as favourable for crystallization of the YIG phase as the sample which is given a two-stage heat-treatment.

1. Introduction

In recent years considerable interest has grown in the development of glass ceramics containing magnetic phases, such as lithium ferrite, barium hexaferrite, nickel ferrite and manganese ferrite [1-5]. A glass composition in the system $\text{Na}_2\text{O}-\text{SiO}_2-\text{Fe}_2\text{O}_3-\text{Y}_2\text{O}_3$ in which yttrium-iron-garnet (YIG) can be precipitated by a suitable heat-treatment has recently been developed in this laboratory [6, 7]. It has been shown that the crystallization kinetics of the YIG phase can be enhanced by using suitable nucleating agents such as the oxides P_2O_5 or TiO_2 [8]. It was observed that P_2O_5 acts as a better nucleating agent than TiO_2 and the magnetic properties of the glass ceramic containing P_2O_5 are superior.

The effect of the above nucleating agents on the crystallization of the YIG phase in the $\text{Na}_2\text{O}-\text{SiO}_2-\text{Y}_2\text{O}_3-\text{Fe}_2\text{O}_3$ glass system has been studied using a Mössbauer spectroscopic technique which has already demonstrated its usefulness for such studies [9-11]. X-ray and related measurements have also been carried out to support the results obtained by Mössbauer studies. These results are presented and discussed in this report.

2. Experimental details

The glass compositions investigated are given in Table I along with the labels used in the text for discussing the various samples. The glass samples were prepared from reagent grade chemicals by melting the mixture in an alumina crucible between 1200 and 1400°C in an electrically heated furnace. Glass plates were cast by pouring the melt onto an aluminium mould. The glass transition temperature (T_g) and crystallization temperature (T_c) were estimated from DTA analysis using a MOM Hungary Derivatograph [8]. The estimated values of T_g and T_c for different compositions were found to be nearly same. Based on this result, all the samples were given a two-stage heat-treatment at $T_g = 720^\circ\text{C}$ and $T_c = 820^\circ\text{C}$ for a duration of two hours each. Since the Y9P glass was found to be the most favourable for the crystallization of YIG, we gave a number of different heat-treatments to this sample according to the following schedules to find out the right growth temperature for the garnet phase: (1) $720^\circ\text{C} + 750^\circ\text{C}$ for 2 h each; (2) $720^\circ\text{C} + 775^\circ\text{C}$ for 2 h each; (3) $720^\circ\text{C} + 800^\circ\text{C}$ for 2 h each; (4) $720^\circ\text{C} + 820^\circ\text{C}$ for 2 h each; and (5) 800°C for 40 h.

TABLE I Composition of the glasses studied (values are given in mol%)

Glass	SiO ₂	Na ₂ O	Y ₂ O ₃	Fe ₂ O ₃	P ₂ O ₅	TiO ₂
Y9	50	26	9	15	—	—
Y6P	48	34	6	10	2	—
Y9T	48	26	9	15	—	2
Y9P	48	26	9	15	2	—

X-ray powder diffraction patterns for glass ceramic samples were recorded by a Rich and Seifert Iso-Debyeflex 2002 diffractometer with CrK α target. Mössbauer spectra were recorded at room temperature (r.t.) with a constant acceleration (linear mode) Mössbauer spectrometer coupled to a multichannel analyser. The source used was radioactive ⁵⁷Co in rhodium matrix obtained from New England Nuclear Inc. USA. The spectrometer was calibrated by using a natural iron absorber [7]. The glass samples were powdered and approximately 50 mg of the powder was spread uniformly over an area of 1 cm in diameter between two layers of sellotape. A least-squares curve-fitting computer program was used to determine the Mössbauer parameters. Standard errors in these parameters were calculated by the usual methods [12].

3. Results and discussion

The results of the X-ray diffractograms for all the two-stage heat-treated samples show lines due to the YIG phase. In addition lines due to different oxidation products of iron which could be either γ -Fe₂O₃, or its derivative, or α -Fe₂O₃ are also observed. X-ray diffraction for the Y9P sample indicated that this particular glass composition is the most favourable for crystallization of the YIG phase. The lines due to the YIG phase are much weaker in Y9, Y6P and Y9T. X-ray diffraction data for the Y9P glass are given in Table II where the X-ray data for YIG is also given for comparison. The lattice constant of this crystallized YIG phase (Table II) is found to be 1.231 nm. The magnetization measurements for the two-stage heat-treated samples Y9, Y9T and Y9P have been reported by Bahadur *et al.* [8]. Their results indicate the presence of two magnetic phases by a clear break near the Curie temperature (280° C) of YIG [8]. It should be pointed out that this break is most obvious in samples containing P₂O₅ as nucleating agent. For the other phase, the Curie temperature appears to be around 475° C.

Mössbauer spectra of all the as-prepared samples (Y9, Y6P, Y9T and Y9P) taken at room temperature are shown in Fig. 1 and they all display quad-

TABLE II X-ray diffraction data for the heat-treated sample Y9P

Sample heated at 720 + 820° C for 2 h each			Sample heated at 800° C for 40 h			YIG		
<i>d</i> (nm)	Intensity	<i>hkl</i>	<i>d</i> (nm)	Intensity	<i>hkl</i>	<i>d</i> (nm)	Intensity	<i>hkl</i>
			0.4007	VS	—			
			0.3656	M	012			
0.3042	S	400	0.3036	M	400	0.3088	S	400
			0.2954	W	220			
0.2634	VS	420	0.2724	S	420	0.2764	VS	420
			0.2679	VS	104			
0.2640	S	—						
0.2503	S	422	0.2508	S	422	0.2517	S	422
0.2239	W	521				0.2251	W	521
			0.2204	M	113			
			0.2052	W	202			
0.1916	M	—	0.1915	W	—			
			0.1837	M	024			
0.1811	W	444	0.1805	W	444	0.1779	M	444
			0.1713	VW	640	0.1710	S	640
0.1698	W	640	0.1691	M	640			
0.1644	W	642	0.1641	W	642	0.1647	S	642
			0.1625	VW	211	0.1542	W	800
0.1479	W	—	0.1485	W	214			
			0.1453	VW	300			
						0.1378	W	840
						0.1347	W	842

VS = very strong; S = strong; M = medium; W = weak; VW = very weak.

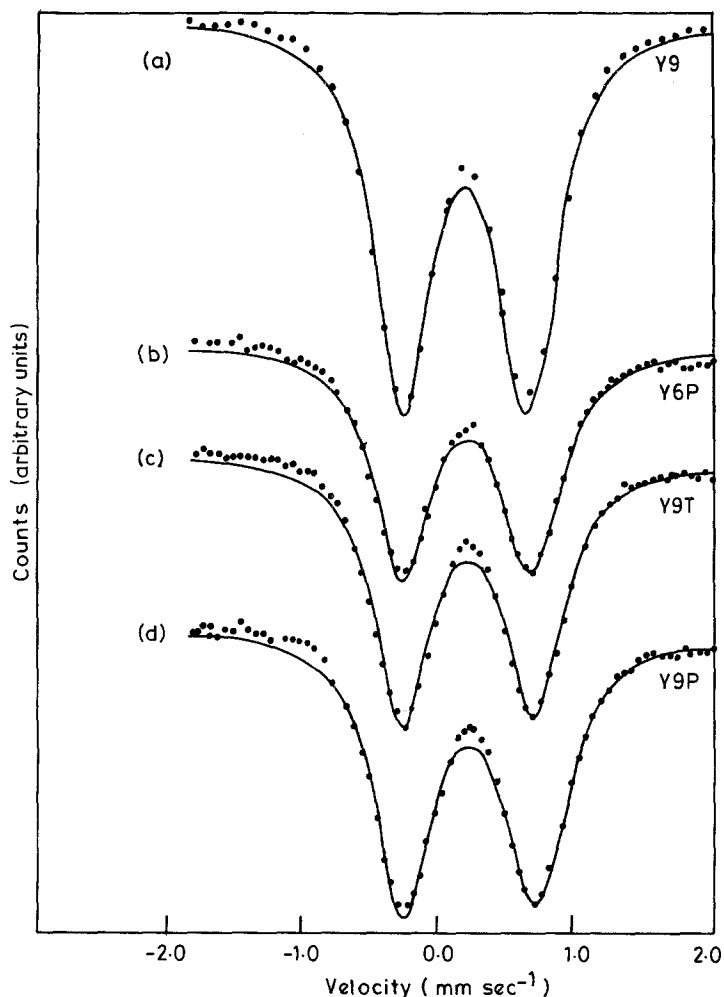


Figure 1 Room temperature Mössbauer spectra of as-prepared samples (a) Y9; (b) Y6P; (c) Y9T; and (d) Y9P. The zero of the velocity scale refers to the zero of the Mössbauer spectrum of natural iron.

rupole splitting. The values of the corresponding Mössbauer parameters (isomer shift, IS, and the quadrupole splitting, ΔE) are given in Table III. Similarly, the Mössbauer spectra and the various parameters for the samples Y9, Y6P and Y9T heat-treated at $(720 + 820^\circ \text{C})$ for 2 h each and Y9P heat-treated at 800°C for 40 h are given in Fig. 2 and Table IV. All these spectra show magnetic hyperfine splitting. Fig. 3 shows the Mössbauer spectra for the Y9P sample heat-treated for 2 h

each at temperatures $(720 + 750^\circ \text{C})$, $(720 + 775^\circ \text{C})$, $(720 + 800^\circ \text{C})$ and $(720 + 820^\circ \text{C})$.

The values of the isomer shift (IS) of all the as-prepared samples (with respect to $\alpha\text{-Fe}$) is in the range $(+0.209$ and $+0.242)$ mm sec^{-1} and is characteristic of Fe^{3+} mostly in tetrahedral coordination [11]. The sample Y9P demonstrates the largest IS value, indicating a certain concentration of Fe^{3+} in octahedral coordination. The linewidth of the individual peak in the doublet

TABLE III Mössbauer parameters for the as-prepared samples

Sample	IS* (mm sec^{-1})	ΔE (mm sec^{-1})	Peak width (mm sec^{-1})	
			I	II
Y9	0.209 ± 0.008	0.900 ± 0.006	0.49 ± 0.01	0.49 ± 0.01
Y6P	0.217 ± 0.008	0.960 ± 0.008	0.49 ± 0.01	0.54 ± 0.01
Y9T	0.232 ± 0.008	0.978 ± 0.008	0.48 ± 0.01	0.53 ± 0.01
Y9P	0.242 ± 0.008	0.991 ± 0.008	0.50 ± 0.01	0.57 ± 0.01

*Values with respect to $\alpha\text{-Fe}$.

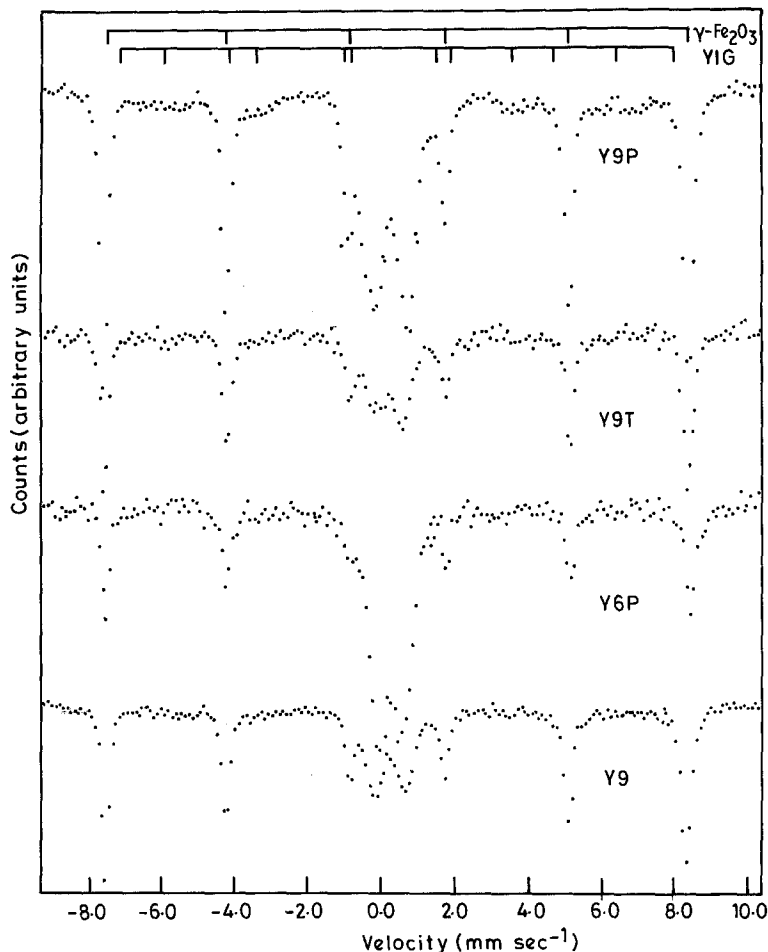


Figure 2 Room temperature Mössbauer spectra of samples Y9, Y6P, Y9T heat-treated at 720 and 820° C for 2 h each and Y9P at 800° C for 40 h. The peak positions for the YIG phase and $\gamma\text{-Fe}_2\text{O}_3$ are shown at the top. The zero of the velocity scale is the same as in Fig. 1.

spectra is 0.50 mm sec^{-1} which is above the average linewidth usually observed. The linewidth is again largest for sample Y9P which supports the above conclusion. In order to investigate the reason for this rather large linewidth these spectra were analysed with the help of a computer program to obtain the EFG distribution ($p|V|$). The

results of such an analysis [13] indicate a broad width (FWHM) for the ($p|V|$) distribution of about 0.44 mm sec^{-1} which is larger than that obtained in case of single iron site for sodium nitroprusside (FWHM = 0.20 mm sec^{-1}) [13]. These results indicate that the large peak width could be due to the presence of two sites for ^{57}Fe . However,

TABLE IV Mössbauer parameters for two-stage heat-treatment at temperatures 720 + 820° C for 2 h each

Sample	Quadruple splitting		Peak widths		Magnetic hyperfine splitting	
	IS* (mm sec ⁻¹)	ΔE (mm sec ⁻¹)	I (mm sec ⁻¹)	II (mm sec ⁻¹)	IS* (mm sec ⁻¹)	H_{int} (kOe)
Y9	0.25 ± 0.02	0.83 ± 0.02	0.57 ± 0.04	0.55 ± 0.04	0.44 ± 0.01	509 ± 5
Y6P	0.23 ± 0.02	0.63 ± 0.02	0.57 ± 0.02	0.56 ± 0.03	0.43 ± 0.02	508 ± 5
Y9T	0.16 ± 0.03	0.72 ± 0.05	0.85 ± 0.14	0.54 ± 0.07	0.39 ± 0.02	507 ± 5
Y9P	0.32 ± 0.02	0.92 ± 0.01	0.57 ± 0.01	0.56 ± 0.01	0.49 ± 0.04	446 ± 20
					0.23 ± 0.04	414 ± 20
					0.52 ± 0.05	431 ± 20
					0.35 ± 0.05	250 ± 20
Y9P [†]	0.29 ± 0.02	0.92 ± 0.02	0.73 ± 0.03	0.50 ± 0.03	0.45 ± 0.05	514 ± 5

*Values with respect to $\alpha\text{-Fe}$.

[†]Heat-treatment given to the sample is at 800° C for 40 h.

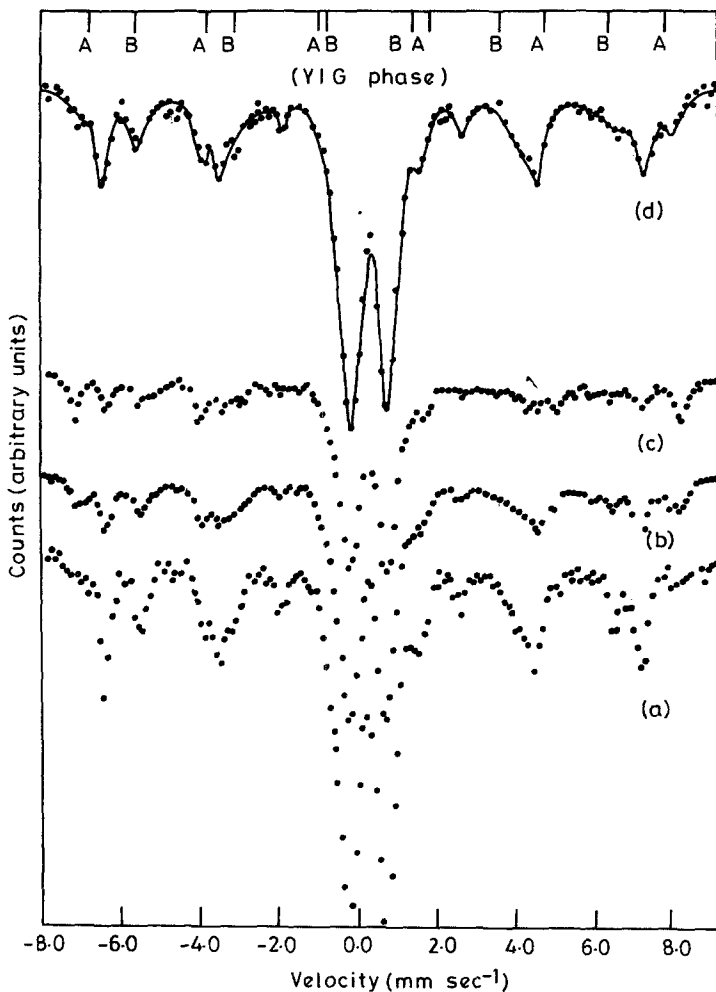


Figure 3 Room temperature Mössbauer spectra for sample Y9P heat-treated for 2 h each at (a) 720 + 750° C; (b) 720 + 775° C; (c) 720 + 800° C; and (d) 720 + 820° C. The peak positions for the YIG phase are shown at the top. The zero of the velocity scale is the same as in Fig. 1.

the difference in these could be small because of the amorphous nature of glass.

The value of the quadrupole splitting for the as-prepared samples are all above $\Delta E = +0.90 \text{ mm sec}^{-1}$ and the value of ΔE decreases in samples subjected to a two-stage heat-treatment. Similar behaviour was observed by the authors recently in a different glass system [7]. Kamatsu and Soga [2] have reported a similar decrease in the ΔE values for silicate glasses upon heat-treatment. The variation in ΔE appears to be determined by the mole percentage of the nucleating agent and the presence of the nucleating agent seems to raise the ΔE values. This behaviour could arise due to the lowering of symmetry in the presence of the nucleating agents. The limited ability of Ti^{4+} or P^{5+} ion to participate in tetrahedral networks and their respective tendencies to attract non-bridging oxygen ions or form double bonds may cause lowering in symmetry.

In the case of all the four samples (Y9, Y6P, Y9T, and Y9P) heat-treated by a two-stage process at 720 and 820° C for 2 h each, the Mössbauer spectra show magnetic hyperfine splitting in addition to quadrupole splitting. Examination of the IS values determined from the doublet peaks of these spectra show that for each sample (except Y9T) the IS value for the heat-treated sample is higher than that for the as-prepared sample. This indicates that the coordination number increases after the heat-treatment.

It is observed that while the Mössbauer spectra of the heat-treated samples Y9, Y6P and Y9T can be resolved into one doublet and one sextet, the Mössbauer spectrum for the heat-treated sample Y9P is quite complex and it has to be resolved into one doublet and four sextets. The values of the relevant Mössbauer parameters, determined from this analysis, are given in Table IV.

The X-ray diffractograms for the two-stage

TABLE V Intensities of the outer peaks of the sextet at the two sites A and B for the two magnetic phases precipitated in the Y9P sample after different heat-treatments.

Temperature of heat-treatment (° C) for 2 h each	YIG phase		Unknown phase (%)	
	Site A (%)	Site B (%)		
720 + 750	0.3	0.9	1.5	0.6
720 + 775	0.55	0.7	1.0	0.36
720 + 800	1.1	0.7	0.8	0.04
720 + 820	0.38	1.4	1.1	0.4

heat-treated samples Y9, Y6P, Y9T and Y9P showed lines due to the yttrium-iron-garnet (YIG) phase. However, the lines due to this phase are much stronger in Y9P than the other three samples. Besides this, some other diffraction lines due to phases such as $\gamma\text{-Fe}_2\text{O}_3$ or its derivative and $\alpha\text{-Fe}_2\text{O}_3$ are also present. The Mössbauer spectra observed for two-stage heat-treated samples Y9, Y6P and Y9T do not show evidence of YIG. This behaviour is attributed to the possibility that although the YIG phase is precipitated in these samples, the amount formed is small and the corresponding hyperfine field is smeared out. This is supported by X-ray diffraction data for which the lines due to YIG phase are much lower in intensity compared to the other lines. The observed Mössbauer spectra for these samples, however, show lines which could be due to either $\alpha\text{-Fe}_2\text{O}_3$ or $\gamma\text{-Fe}_2\text{O}_3$ phase in agreement with the X-ray data.

The Mössbauer spectra for Y9P (two-stage heat-treated) gives one quadrupole splitting and four magnetic hyperfine splittings. Out of these, the two magnetic hyperfine splittings correspond to the two (A and B) sites of the YIG phase with the IS values as $0.49 \pm 0.04 \text{ mm sec}^{-1}$ and $0.23 \pm 0.04 \text{ mm sec}^{-1}$ and the H_{int} values as $446 \pm 20 \text{ kOe}$ and $414 \pm 20 \text{ kOe}$, respectively, as determined from the spectra shown in Fig. 3d. In order to confirm this assignment, a Mössbauer spectrum was recorded of polycrystalline YIG sample at room temperature and the values of IS for site A and B were measured to be $0.50 \pm 0.03 \text{ mm sec}^{-1}$ and $0.22 \pm 0.03 \text{ mm sec}^{-1}$ and $H_{\text{int}} = 469 \pm 15 \text{ kOe}$ and $405 \pm 15 \text{ kOe}$, respectively. The slight discrepancy in the internal field could be due to variation in the composition and particle size. The other two hyperfine splittings observed in this sample (Fig. 3d) appear to have IS values of $0.52 \pm 0.05 \text{ mm sec}^{-1}$ and $0.35 \pm 0.07 \text{ mm sec}^{-1}$ and H_{int} values of $431 \pm 40 \text{ kOe}$ and $250 \pm 40 \text{ kOe}$, respectively. These two could be due to the precipitation of some spinel

phases such as a derivative of $\gamma\text{-Fe}_2\text{O}_3$. From the above observations it is concluded that the volume fraction of the YIG phase precipitated in the samples subjected to a two-stage heat-treatment is largest for the Y9P sample.

In order to investigate the precipitation of the YIG phase in the Y9P sample in detail the sample was subjected to a two-stage heat-treatment at different growth temperatures of 750, 775 and 800°C keeping the nucleation temperature constant at 720°C . The Mössbauer spectra (at room temperature) for these samples are shown in Figs. 3a, b and c respectively. In Table V are shown the intensities of the outer peaks of the sextet at the two sites A and B for each magnetic phase precipitated in these samples. The results for the sample heat-treated at $720 + 800^\circ\text{C}$ give the ratio of peaks corresponding to the sites A and B of YIG phase to be 3:2 as required [14]. It is therefore concluded that 800°C is the optimum growth temperature for the most efficient crystallization of the YIG phase in the glass ceramic sample Y9P. Further, the Mössbauer spectrum for the sample Y9P heat-treated at 800°C for 40 h shows the presence of a small volume fraction of YIG and a larger fraction of the oxidation products of iron or their derivatives.

As mentioned earlier the main interest in this work was to study the crystallization of the YIG phase in different glass ceramics. However, the observed variation in the pattern of Mössbauer spectra, X-ray and other data indicates the presence of other magnetic phases besides YIG in the system. These could be different oxidation products of iron. A comment on this effect will be in order. It is well known that the different oxidation products of iron are interconvertible into one another under slightly different conditions [14]. It is, therefore, possible that more than one oxidation product of iron or its derivative is present in the different glass ceramic samples

studied. It is further possible that the relative concentration of these products (or their derivatives) may also vary from sample to sample depending on the degree of the concentration of the constituents, the heat-treatment conditions or the presence of hydrogen ions. These oxidation products and their derivatives can be modified to α -Fe₂O₃ (more favourably in a dry atmosphere) [14]. However, it does not rule out the possibility of coexistence of the spinel and hexagonal phase of α -Fe₂O₃. In fact the coexistence of these two oxidation products of iron is quite common.

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