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Mössbauer study of crystallization of glasses in the system K_2O–Na_2O–CaO–MgO–Al_2O_3–SiO_2

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Mössbauer spectroscopy has been used to study several glasses and glass ceramics based on the system K_2O–Na_2O–CaO–MgO–Al_2O_3–SiO_2 with additions of Fe_2O_3, Fe_3O_4 and P_2O_5. The change of co-ordination and proportion of $Fe^{2+}$and Fe^{3+} occurring during the transformation from glass to glass ceramic was studied. By means of the nuclear magnetic hyperfine splitting effect Fe_3O_4 was found in glass ceramics with more than 2% of P_2O_5. The amount of Fe_3O_4 formed was found to increase with P_2O_5 addition, but Fe_3O_4 was not identified in the glass with no P_2O_5 addition.

1. Introduction

Mössbauer resonance occurs when recoil-free source γ-rays are resonantly absorbed by nuclei (identical with those which give rise to those source γ-rays) that are present in a separate absorber sample. Resonance can normally only occur when the nuclear-level separation corresponding to the γ-ray transition in both the source and absorber are identical to within the nuclear line width. Absorber nuclear levels are, however, sensitive to the nuclear environment as they are modified by the nuclear hyperfine interactions characteristic of that particular environment. Thus if the level separation is different in source and absorber nuclei, the source γ-ray energy must be modified in order to restore resonance. Such a modification may be attained simply by moving the source bodily with respect to the absorber sample, thus using the Doppler effect to change the γ-ray energy (by a fractional amount $\delta E/E = v/c$) as seen by the stationary absorber nuclei. To obtain a Mössbauer absorption spectrum, therefore, it is simply necessary to record the intensity of γ-rays transmitted through an absorber as a function or relative velocity between source and absorber. The magnitude of the energy-level changes arising from the hyperfine interactions experienced by the absorber nuclei typically require measurements over a velocity range of within just a few mm s^{-1}. For a fuller account of the Mössbauer effect and the relevant nuclear hyperfine interactions see Williams [1].

To study particular absorber sample nuclei, the appropriate corresponding source nucleus must therefore be chosen. ^{57}Fe is one of the strongest resonances known and so a study of iron nuclei is easily achieved, despite the fact that natural iron contains only approximately 2% ^{57}Fe, the rest being ^{56}Fe. In this investigation therefore a ^{57}Co source was used as this is the parent nucleus for decay to ^{57}Fe. The three relevant nuclear hyperfine interactions which may be observed and measured in this way are:

(i) the isomer or centreshift (CS), which arises from the different s-electron density seen at a nucleus when in different chemical or valence states;
(ii) the quadrupole splitting (QS), which is a measure of the deviation from spherical symmetry of the electron cloud around the nucleus;
(iii) the magnetic splitting arising when probe atoms experience a magnetic field, as they do for example when the absorber atoms are magnetic.

All three interactions can occur together, and the particular combination of individual hyperfine values obtained provides a clear ‘fingerprint’ of the environment of the iron atoms in the glass or ceramic absorber materials being studied. Generally, by comparing the three hyperfine parameters, we can obtain information on the atomic state, co-ordination and concentration of ions such as Fe^{2+} and Fe^{3+}. For a ^{57}Co source the CS values for Fe^{2+} ions are around 1.0 and 1.2 mm s^{-1} for tetrahedral and octahedral oxygen co-ordination respectively [2]. Trivalent Fe^{3+} gives values of around 0.3 and 0.5 mm s^{-1} in tetrahedral and octahedral co-ordinations. The QS for Fe^{2+}, normally about 2–3 mm s^{-1}, is due to the *d* electron outside the half-filled shell. As a result of the spherically symmetrical charge distribution of the Fe^{3+} ion, quadrupole splitting in the trivalent ion is mainly due to the crystal-field effects and is thus a measure of its asymmetry. Thus the value is very small. In the presence of either an internal or external magnetic field, due to the removal of the degeneracy of both the ground and excited nuclear levels, a six-line split hyperfine (Hfs) spectrum is obtained, corresponding to the allowed absorption transitions in such a magnetic absorber environment.

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2. Experimental procedure

As explained above, the energy of the γ-ray incident upon the absorber in a Mössbauer spectrometer is usually modulated by applying a Doppler velocity to the source. In our case this was achieved by mounting the radioactive source firmly onto a constant acceleration drive unit which moves back and forth cyclically, spending equal times at each velocity increment. These energy-modulated γ-rays impinge on the absorber (the sample under investigation) and those transmitted are detected by a proportional counter. The detector signal is amplified and the pulses corresponding to the 14.4 kev γ-ray are stored in a multichannel analyser operating in the multiscaling time mode. In this way a Mössbauer absorption spectrum is built up over a period of several hours. A schematic diagram of our spectrometer is shown by Williams [1].

The source used was 25 m Curie ^{57}Co in a rhodium matrix. The rhodium matrix provides a cubic, non-magnetic environment for the source nuclei, and due to the consequent absence of quadrupole and magnetic splitting, such a source provides monochromatic γ-rays. The absorbers were prepared by sandwiching fine powders of glass or glass ceramics of interest between plastic discs bound together with glue. The glasses were made by melting at 1450 °C for 5 h, followed by annealing at 600 °C for 1 h. The glass ceramics received isothermal treatments as stated below.

Low-temperature spectra were recorded using a continuous flow helium cryostat for cooling of the absorber samples. Temperatures could be varied between room temperature (RT) and the boiling point of liquid helium (4.2 K). Data processing involved folding, calibrating and analysing the recorded spectra. These spectra were fitted using a least squares method which uses, as parameters, the hyperfine shifts and splittings. Details of this procedure are given by Alhasan [3]. In addition to the hyperfine parameters, the fitting procedure also gives the relative concentrations of the individual Fe sites through the relative areas of the corresponding absorption peaks concerned. This assumes that the recoil-free fraction is the same for each iron site. For ^{57}Fe this is a reasonable approximation in these absorber materials.

3. Results and discussion

Firstly, it is useful to have a survey of the compositions of the glasses studied. All glasses were derived from base glass B which has the composition given in Table I. Glass BF(3)5 has 5 mol % Fe_2O_3 added to glass B. Based on glass BF(3)5, glasses containing P_2O_5 were derived, i.e. BP1F(3)5, BP2F(3)5 and BP4F(3)5, by adding a further 1, 2 and 4 mol % of P_2O_5 respectively. A further glass ceramic BF(5)5 with 5 mol % Fe_3O_4 added in glass B was also studied. Mössbauer spectra were recorded for the following samples:

Glasses BP2F(3)5, BF(3)5 as annealed;
Glass ceramics BF(3)5, BF(5)5, BP1F(3)5, BP2F(3)5 and BP4F(3)5 obtained from a heat-treatment schedule of 18 h at 680 °C and 23 h at 950 °C. After such heat treatments, the samples were almost completely crystalline as indicated by X-ray diffraction (XRD), and the effect of the small amount of residual glassy phase could be ignored. The same type of main crystal phase fassaite, which is the solid solution of diopside, was found for BF(3)5, BP1F(3)5, BP2F(3)5 and BP4F(3)5 by XRD. In external appearance, the latter two are black and the former two are brownish.

3.1. Glasses BF(3)5 and BP2F(3)5

The room-temperature Mössbauer spectra for glasses BF(3)5 and BP2F(3)5 are shown in Fig. 1, and the results are analysed in Table II. From the above lists we can see that for both glasses, Fe^{2+} and Fe^{3+} are in tetrahedral sites. The large values of QS for Fe^{3+} reflect the highly asymmetrical electronic configuration of Fe^{3+}. As a result, the tetrahedral sites are highly distorted in the two glasses. The QS values for Fe^{2+} are within the normal range of 2–3 mm s^{-1} and are small. The large QS value for Fe^{3+} can be explained by the repulsive or polarization effects of Na^+ or K^+ which is required for coupling with Fe^{3+} to maintain electronic neutrality when Si^{4+} is replaced by Fe^{3+}. Again, greater QS values can be observed for Fe^{2+} and this is assumed to be due to distorted tetrahedral sites.

TABLE I The chemical compositions of glass B.

Glass		K_2O	Na_2O	CaO	MgO	Al_2O_3	SiO_2
Glass B	mol %	2.5	2.5	22	12	8	53
	wt %	3.86	2.54	20.20	7.92	13.35	52.13

TABLE II Mössbauer analysis for glasses BF(3)5 and BP2F(3)5.

Sample	Site	Content (mol %)	H	CS (mm s^{-1})	QS (mm s^{-1})	State	CN
BF(3)5	1	13	–	1.02	2.03	Fe^{2+}	4
	2	87	–	0.31	1.2	Fe^{3+}	4
BP2F(3)5	1	18	–	0.97	2.0	Fe^{2+}	4
	2	82	–	0.24	1.2	Fe^{3+}	4

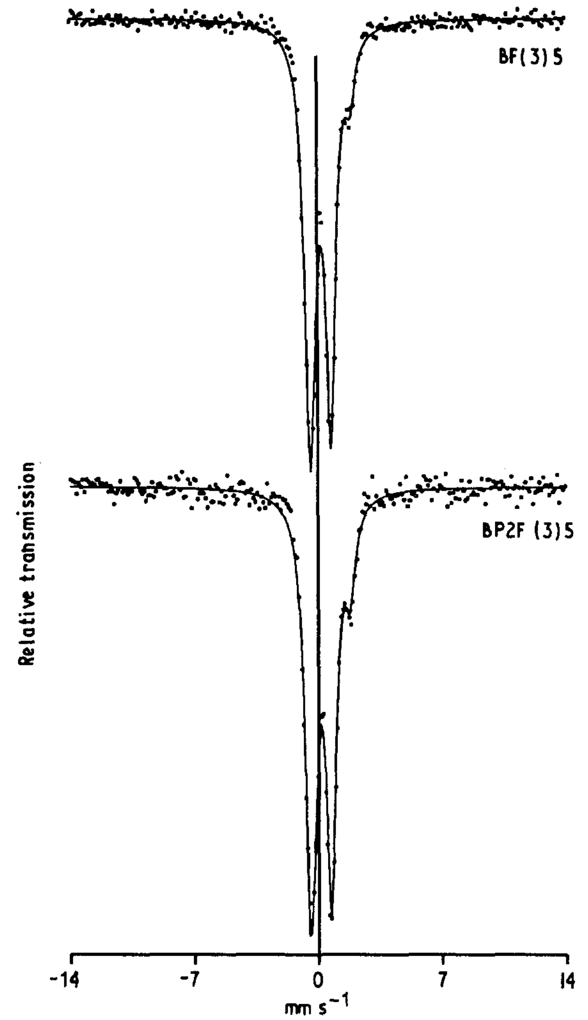

Figure 1 Mössbauer spectra for glasses.

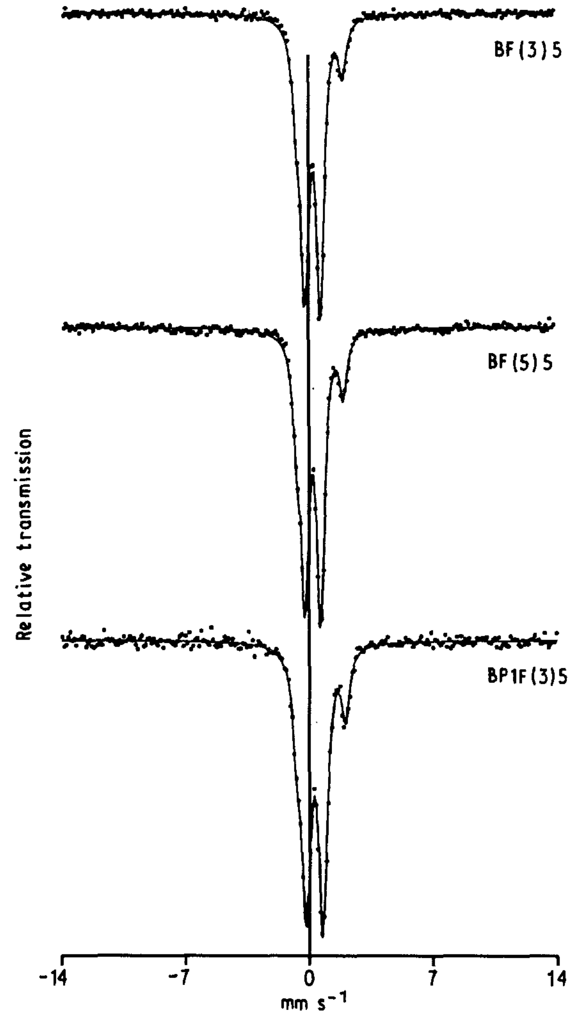

Figure 2 Mössbauer spectra for glass ceramics.

TABLE III Mössbauer analysis for glass ceramics

Sample	Site	Content (mol %)	H	CS (mm s^{-1})	QS (mm s^{-1})	State	CN
BF(3)5	1	65	–	0.36	0.94	Fe^{3+}	6
	2	15	–	1.1	1.98	Fe^{2+}	4, 6
	3	20	–	0.083	1.21	Fe^{3+}	4
BF(5)5	1	60	–	0.32	0.88	Fe^{3+}	6
	2	16	–	1.1	2.0	Fe^{2+}	4, 6
	3	24	–	0.2	1.48	Fe^{3+}	4
BP1F(3)5	1	58	–	0.37	0.93	Fe^{3+}	6
	2	18	–	1.16	2.02	Fe^{2+}	4, 6
	3	24	–	0.24	1.62	Fe^{3+}	4

3.2. Glass ceramics BF(3)5, BF(5)5 and BP1F(3)5

No Fe_3O_4 was observed by XRD in any of the three samples. The Mössbauer spectra are shown in Fig. 2 and the absence of any magnetic hyperfine components confirms the lack of Fe_3O_4. The spectra for the three samples look almost the same. As shown in Table III, three types of site were detected. The first type is occupied by Fe^{3+} ions: the most abundant type with about 60% of the Fe atoms. The second type of site is occupied by Fe^{2+}, the concentration of which is ~ 16 %. Because the CS value is about 1.1, between 1.0 and 1.2 for four-fold and six-fold co-ordinations, it is difficult to judge the co-ordination type. It is highly probable that a mixture of tetrahedral and octahedral sites of Fe^{2+} exist. The remaining 24 % is Fe^{3+} in tetrahedral co-ordination.

We thus see two types of site for Fe^{3+}, the first type having a higher CS value than the third. Although these values are near the lower limit of the CS range for Fe^{3+} (0.3–0.5 mm s^{-1}), thus predicting tetrahedral sites, we suspect that as $CS_{(\text{tetrahedral})} < CS_{(\text{octahedral})}$, and observing the structure of diopside, the first type Fe^{3+} ions (1) are in octahedral sites and the other Fe^{3+} ions (3) are in tetrahedral sites. The chemical formula for diopside is $CaMgSi_2O_6$, which is the basic structure unit for fassaite solid solution. The co-ordination numbers (CN) for Ca^{2+}, Mg^{2+} and Si^{4+} are 8, 6 and 4, respectively. Thus we predict that the first type of Fe^{3+} ions replace Mg^{2+} ions and remain as octahedrally co-ordinated, and the third type of Fe^{3+} replaces Si^{4+} in tetrahedral sites. For Fe^{2+} in the second type of site, both tetrahedral and octahedral co-ordination are possible. Although we assumed 100% transformation of the glass to ceramics, it is unavoidable that some glassy phase remains. Based on this thought, it is also possible for some Fe^{3+} to retain tetrahedral sites in the residual glass.

3.3. Glass ceramics BP2F(3)5 and BP4F(3)5

For these two samples, which were very dark coloured, Fe_3O_4 was positively identified by XRD and electron diffraction. The room temperature Mössbauer spectra for the two samples are shown in Fig. 3. Also shown in Fig. 3 is the Mössbauer spectrum for BP2F(3)5 recorded at 10 K. Table IV shows the analysed results. As already mentioned these samples have a different appearance from those not containing P_2O_5, being black as opposed to brown. The Mössbauer analysis also confirms the existence of Fe_3O_4 in these samples through the appearance of clear magnetic hyperfine components corresponding to an effective magnetic field of around 450–510 kgauss, and the absence of any quadrupole splitting.

As discussed in the previous section, apart from the formation of Fe_3O_4, Fe^{3+} now predominantly enters octahedral sites replacing Mg^{2+}, whereas Fe^{2+} is capable of substituting for both Si^{4+} and Mg^{2+} sites. In the case of glass ceramics containing P_2O_5, Fe^{3+} no longer replaces Si^{4+}, or the replacement is too small to be detected. Besides, the low-temperature experiment (which is theoretically more accurate than tests performed at higher temperatures) in which the CS value was 0.5 for such Fe^{3+} ions fully supports the previous analysis that Fe^{3+} mainly replaces Mg^{2+} in octahedral sites. We also saw a higher amount of Fe_3O_4 formation when P_2O_5 addition is increased. If Fe^{3+} ions were to replace Si^{4+} in the case of glass ceramic containing 4% P_2O_5, the amount would be far less than in the case of BP2F(3)5, because much more Fe_3O_4 was formed with 4% P_2O_5. So Fe^{3+} (with a proper amount of Fe^{2+}) first of all forms Fe_3O_4, then the rest is substituted for Mg^{2+}.

Finally, in order to clarify the process of crystallization and the effect of P_2O_5 addition on crystallization, we have assembled some of those typical Mössbauer spectra for glasses and glass ceramics in Fig. 4. Other studies to be reported elsewhere have shown that nucleation of the main phase occurs

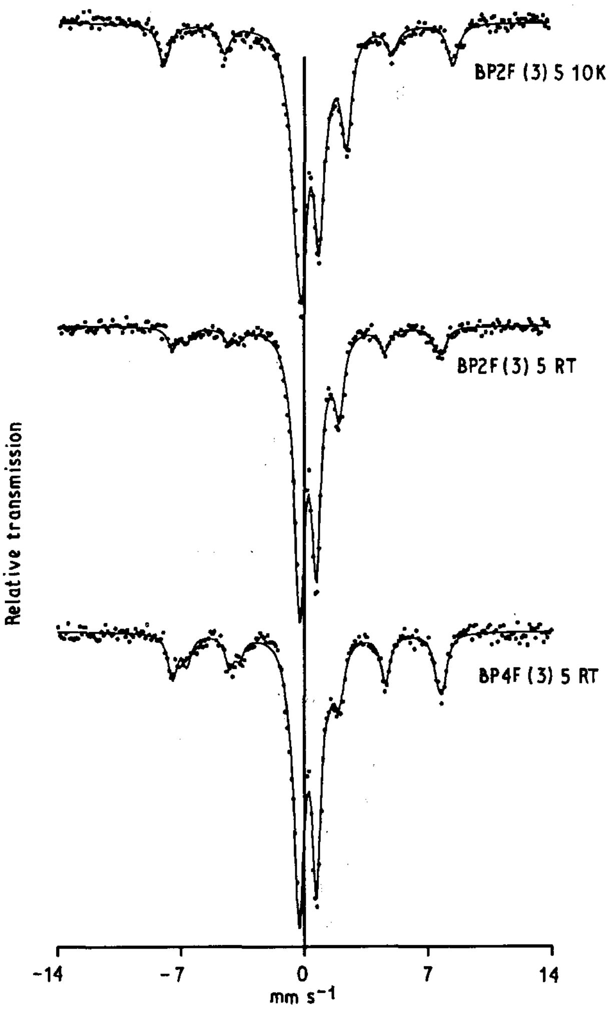

Figure 3 Mössbauer spectra for glass ceramics.

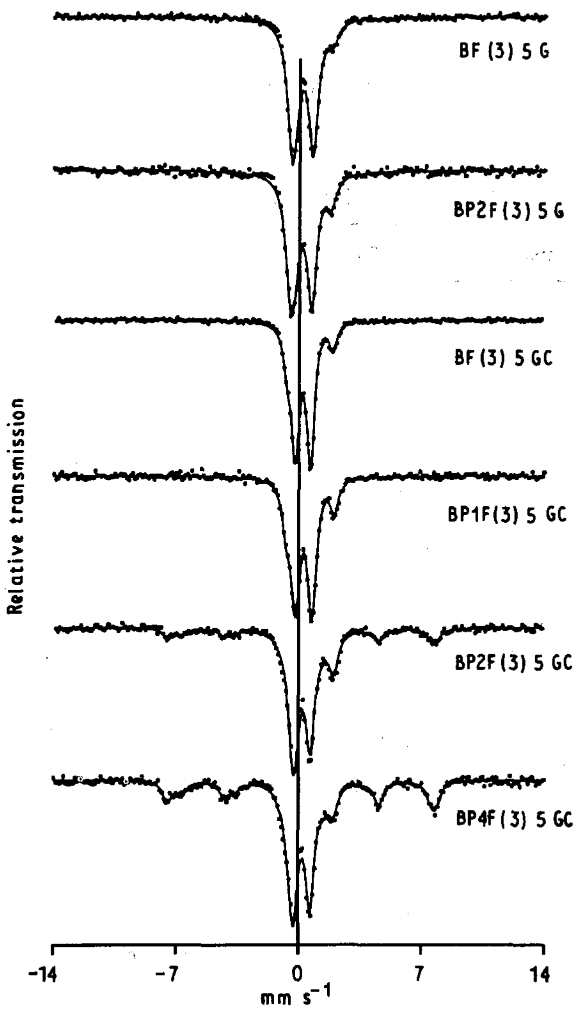

Figure 4 Mössbauer spectra for glass–glass ceramics.

TABLE IV Mössbauer analysis for P_2O_5-containing glass ceramics

Sample	Site	Content (mol %)	H	CS (mm s^{-1})	QS (mm s^{-1})	State	CN
BP2F(3)5	1	11	479	0.32	0	Fe_3O_4	4, 6
RT	2	8	443	0.53	0		
	3	21	–	1.10	2.05	Fe^{2+}	4, 6
	4	60	–	0.33	1.00	Fe^{3+}	6
BP2F(3)5	1, 2	22	513	0.36	0	Fe_3O_4	4, 6
10K	3	29	–	1.09	2.84	Fe^{2+}	4, 6
	4	49	–	0.5	0.96	Fe^{3+}	6
BP4F(3)5	1	21	480	0.30	0	Fe_3O_4	4, 6
RT	2	13	445	0.56	0		
	3	12	–	1.09	2.07	Fe^{2+}	4, 6
	4	54	–	0.32	1.02	Fe^{3+}	6

homogeneously in the glasses with no P_2O_5 but addition of more than about 2 % P_2O_5, which causes the formation of Fe_3O_4, also brings a change to heterogeneous nucleation of the main crystal phase. From these spectra, we can clearly see that with the increase of P_2O_5 the amount of Fe_3O_4 produced also tends to increase, i.e. from homogeneous nucleation to heterogeneous nucleation.

4. Conclusions

1. In glasses BF(3)5 and BP2F(3)5, both Fe^{2+} and Fe^{3+} are in tetrahedral sites replacing Si^{4+}.

2. After Fe_2O_3 induced volume crystallization, very probably homogeneous Fe^{2+} retained both tetrahedral and octahedral sites. Fe^{3+} predominantly enters octahedral sites but also partly replaces Si^{4+} in tetrahedral sites.

3. When P_2O_5 addition was increased beyond a certain limit, Fe_3O_4 formed on heat treatment. The precipitation of Fe_3O_4 increased with the increase of P_2O_5. In such cases, in addition to the Fe consumption for Fe_3O_4 formation, Fe^{3+} enters octahedral sites replacing Mg^{2+} and Fe^{2+} for Si^{4+} or Mg^{2+} in both tetrahedral and octahedral sites.

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