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Structure and properties of glasses with a low amount of SiO_2 in a quaternary system of Al_2O_3–SiO_2–CaO–MgO

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Abstract

This study concerns the determination of the compositions of glasses in the quaternary system Al_2O_3–SiO_2–CaO–MgO for SiO_2 concentrations ranging from 4 to 10 mol.%, and the investigation of their structure and properties. The selected compositions were characterised by melting temperatures below 1500 °C. The glasses obtained were investigated by X-ray diffraction, thermal analysis and IR spectroscopy in order to determine their structures and some important properties, namely, refractive index, density, glass transition temperature and crystallisation temperature.

INTRODUCTION

Studies in the field of glass formation for systems like CaO–Al_2O_3–SiO_2 and CaO–MgO–Al_2O_3–SiO_2 have shown that aluminium ions may be considered as formators if they are found in a tetrahedral coordination [1]. Data published elsewhere [2] show that glasses from calcium aluminate, because of their high tendency to crystallise, can be obtained in small amounts by fast cooling. Larger amounts may be obtained only if the initial composition contains a small amount of SiO_2. Glasses made from aluminates are known to possess useful and interesting properties such as high elasticity and good IR transmittance [3,4]. These glasses can also be used to produce glass fibres (tow).

There seems to be a lack of information for quaternary glass systems such as Al_2O_3–SiO_2–CaO–MgO that are obtained from recycled raw materials [5,6]. There is also a lack of data for glasses with low levels of SiO_2.

This paper presents the results from the investigation of a range of glasses which belong to the quaternary system Al_2O_3–SiO_2–CaO–MgO, with an SiO_2 molar content of less than 10%. The structure and properties of the glasses investigated are discussed from the point of view of their

TABLE 1

Molar percentages of the constituents of the glasses

Glass no.	Composition (mol.%)			
	CaO	MgO	Al_2O_3	SiO_2
2	50	10	30	10
3	56	10	30	4
4	55	5	30	10
5	45	15	30	10
7	58	8	30	4
8	61	5	30	4
9	58	5	30	7
10	55	8	30	7
11	53	10	30	7

change in composition, the Al_2O_3 content being kept at 30 mol.% and the concentrations of SiO_2, CaO and MgO being varied.

EXPERIMENTAL

The following raw materials were used to synthesise the glasses: Al_2O_3, SiO_2, $CaCO_3$ and MgO. They were melted in an oven with silite bars in platinium crucibles, at a temperature range of 1430–1470 ° C and a melting time of 2–4 h. All the compositions were homogeneous.

The glasses were subsequently baked; the parameters of this treatment were according to the results obtained from the dilatometric and thermal investigations. The compositions, in molar percentages, of the glasses are given in Table 1. The purity of the raw materials was assessed by spectrographic analysis and by atomic adsorption spectroscopy. The results are given in Table 2.

The refractive indices of the glasses were measured at room temperature on Pulfrich equipment using a wavelength corresponding to the D band of sodium. The visible transmission of the glasses was measured with M40,

TABLE 2

The impurities in the raw materials

Impurity	SiO_2	Al_2O_3	MgO	$CaCO_3$
Fe_2O_3	0.013	0.25	0.007	0.007
Cr_2O_3	0.01	0.1	0.01	-
Co_3O_4	–	0.043	0.0043	0.0027
CuO	0.0015	0.015	0.0015	0.0006
NiO	0.0045	0.0127	0.008	0.0005
MnO_2	0.025	0.0187	–	0.0007

TABLE 3
The dependence of the refractive index on the composition of the glasses

Glass no.	Composition (mol.%)				Refraction index, n_D
	Al_2O_3	SiO_2	CaO	MgO	
3	30	4	56	10	1.66954
7	30	4	58	8	1.67037
8	30	4	61	5	1.67177
11	30	7	53	10	1.65994
10	30	7	55	8	1.66104
9	30	7	58	5	1.66302
5	30	10	45	15	1.64930
2	30	10	50	10	1.65332
4	30	10	55	5	1.65505

61NIR and M80 equipment manufactured by Karl Zeiss Jena, using samples of 2 mm and 1 mm thick.

The IR transmission in the range 1600–400 cm^{-1} was measured with an M80 (Karl Zeiss Jena) instrument, using KBr pellets. The density of glasses was measured by weighing the samples in air and xylene.

The crystallinity of the glasses was investigated by X-ray diffraction using a URD-6 equipment with 2θ in the range 17–47 deg.

The thermal analysis of the glasses was performed using a Derivatograph C, with alumina as reference, air atmosphere, platinium crucibles, in a temperature range 20–1000 °C, a heating rate of 10 K min^{-1} and with a sample grain-size of 56–71 mesh.

RESULTS AND DISCUSSION

Refraction index

The glasses investigated have indices within the range 1.65–1.67. The effect of the composition on the refraction index is given in Table 3 and the influence of the CaO and MgO contents on n_D may be followed.

It can be seen that n_D increases when the concentration of CaO increases which suggests that the internal structure of the glasses changes with even small changes in CaO level. The same conclusion may be obtained when two sets of samples with constant levels of Al_2O_3 and MgO are observed, see Table 4.

Molar refraction

The coordination state of aluminium ions in the system Al_2O_3–SiO_2–CaO–MgO with 30% Al_2O_3, was investigated by molecular refraction,

TABLE 4

The dependence of the refractive index on the amount of CaO in the glasses

Glass No.	Constant concentrations of MgO and Al_2O_3	
	10% MgO, 30% Al_2O_3	5% MgO, 30% Al_2O_3
2	1.65332	
11	1.65994	
3	1.66954	
4		1.65505
9		1.66302
8		1.67177

computed by the Lorentz–Lorenz equation [7]. Safford and Silverman [8] have published the results for the contribution of Al_2O_3 when the aluminium ions are in tetrahedral and octohedral coordinations, as 12.3 and 10.5 cm^3 mol^{-1}, respectively. Our results are given in Table 5. The data for Al_2O_3 are computed by subtraction, taking the literature values 7.5 cm^3 mol^{-1} for CaO, 7.43 cm^3 mol^{-1} for SiO_2 and 4.9 cm^3 mol^{-1} for MgO [9].

The results in Table 5 suggest that the AlO_4 group in the glasses is deformed to varying extents.

Visible transmission

Although no chromophore had been introduced, all the glasses were differently coloured ranging from yellow to brown. We assume that this is the result of impurities in the raw materials (see Table 2), mainly introduced with alumina. The presence of Fe^{3+} ions is confirmed by a band at about 28 600 cm^{-1} (for glass no. 9); Cr^{3+} ions are less evident than Fe^{3+} ions, being indicated by a change in the slope of the transmission curve in

TABLE 5

Determination of the molar refraction of Al_2O_3

Glass no.	Density ($g\ cm^{-3}$)	Molar refraction of glass (cm^3 mol^{-1})	Molar refraction of Al_2O_3 (cm^3 mol^{-1})
2	2.9189	86.0678	12.24
3	2.9296	215.5124	12.36
4	2.9186	174.4533	12.21
5	2.9049	85.0580	12.32
7	2.9353	218.6029	12.54
8	2.9237	221.3655	12.66
9	2.9290	151.8908	12.53
10	2.9407	123.1028	12.57
11	2.9117	124.2674	12.49

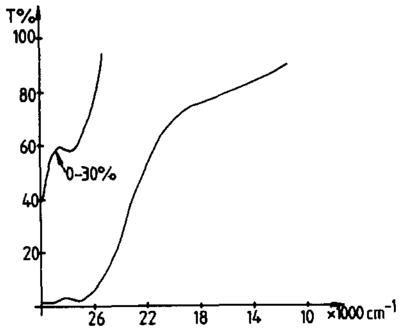

Fig. 1. Visible transmission curve of glass no. 9.

the range 500–600 nm. Figure 1 also shows an increased absorption beyond the visible range.

IR transmission

Figure 2 shows a transmission curve for a 2 mm thick sample recorded in the range 13 000–3000 cm^{-1} on a Specord 61NIR instrument. There is also a strong absorption close to 3400 cm^{-1}, the peak area being influenced by the SiO_2 content; the smaller the amount of SiO_2, the greater the area.

IR spectral data

The structure of the glasses was investigated on an M80 instrument, in the range 1600–400 cm^{-1}. The spectra obtained vary as a function of composition, as follows.

Glasses 3, 7 and 8

Figure 3 shows the three spectra obtained. Two strong absorption bands at 700–800 and 420–440 cm^{-1} respectively may be observed for all three

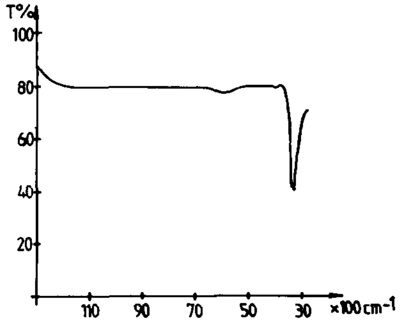

Fig. 2. IR transmission curve of glass no. 2.

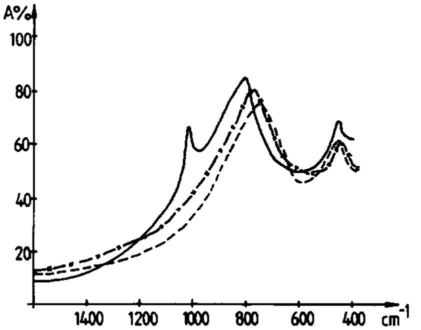

Fig. 3. IR absorption curves for glasses: no. 3, - - - - - ; no. 7, ——— ; and no. 8, ×—×.

glasses. Glass no. 7 has an additional peak at 1015 cm^{-1}. Table 6 gives the characteristic frequencies of AlO_n coordinated groups as obtained from the literature [10].

According to the literature, the 1015 cm^{-1} peak is due to the vibration of Si–O–Al bonds. The band at 760–800 cm^{-1} is considered to be due to AlO_4 groups. The relationship between the frequencies of vibration and the coordination number is an approximate one as there are influences from the neighbouring groups, the deformation of coordinated groups and the presence of "condensed" or "isolated" groups [10].

Glasses 9, 10 and 11

These glasses have absorption bands in the ranges 985–1015, 780–810 and 420–440 cm^{-1}. The height of the first peak at 1000 cm^{-1} increases as SiO_2 increases.

Glasses 2, 4 and 5

The first and strongest absorption peak lies in the range of 990–1020 cm^{-1}.

X-ray diffraction

An URD-6 X-ray diffractometer was used to identify the compounds that crystallised during the thermal treatment. All the glass samples were first subjected to thermal analysis and were analysed by X-ray diffracto-

TABLE 6

Bond vibration frequency (cm^{-1}) of Al–O

	AlO_4 tetrahedral	AlO_6 octahedral
Condensed	900–700	680–500
Isolated	800–650	530–400

TABLE 7

X-ray data for glass no. 11

Line no.	Angle (deg)	d (nm)	I (%)	Phase	d (nm)	I (%)
1	18.06	0.4907	100	$12CaO \cdot 7Al_2O_3$	0.4892	95
2	23.44	0.3793	17.3		0.3791	16
3	27.80	0.3206	16.3		0.3704	25
4	28.57	0.3121	7.9		0.2992	45
5	29.76	0.3000	31.0		0.2680	100
6	33.38	0.2682	80.2		0.2556	18
7	35.06	0.2557	15.7		0.2447	50
8	35.54	0.2524	11.0		0.2440	35
9	36.69	0.2448	34.7		0.2350	10
10	41.20	0.2189	27.3		0.2189	40
11	46.68	0.1944	22.5		0.1945	30

metry after the exothermal effect. The dimensions of the basic cells were computed and the influence of the modifier oxides was determined. In all cases, only $12CaO \cdot 7Al_2O_3$ was identified: Table 7 gives the results for glass no. 11.

Table 8 shows the basic cell dimensions of glass no. 11, calculated using a computer program. The value of a agrees well with the ASTM data for $12CaO \cdot 7Al_2O_3$ ($a = 1.1982$ nm).

The same compound was obtained for the other samples although the cell parameters were considerably modified. Sample 8, for example, has $a = 1.518023$ and sample 4 has $a = 1.51002$. These values imply a more stratified lattice than was expected for these glasses.

Thermal analysis

A MOM derivatograph C (Budapest), with air atmosphere, alumina reference, a temperature range of 20–1000 °C and a heating rate of 10 K min^{-1} was used. The recorded curves (DTG, TG, DTA and T) for glass no.

TABLE 8

Lattice constants

	Value	Standard dev.	Confidence interval
a (nm)	1.197121	0.000374	1.196235–1.198006
b (nm)	1.197121	0.000374	1.196235–1.198006
c (nm)	1.197121	0.000374	1.196235–1.198006
α (deg)	90	0	90.000–90.000
β (deg)	90	0	90.000–90.000
γ (deg)	90	0	90.000–90.000

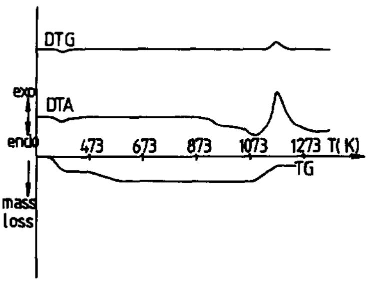

Fig. 4. DTA, TG, DTG and T curves for glass no. 7.

7 are shown in Fig. 4. There are endothermal effects due to glass transition at 733 and 779 °C, respectively, and an exothermal effect at 899 °C accompanied by an increase in weight.

The curves recorded for all the other samples have similar characteristics, but the effects have different temperature ranges. The weight increase is about 0.7–1, depending on the composition. It is assumed that the gain in mass is due to the reaction [11]

$$12CaO \cdot 7Al_2O_3 + H_2O \rightarrow Ca_{12}Al_{14}O_{32}(OH)_2$$

Table 9 gives the temperatures of the maximum for the second glass transition effect and for the exothermal effect. The high temperatures of the glass transition indicate that these glasses may be used in a high-temperature environment.

The activation energy of the exothermal effect for glass no. 7, at heating rates of 5, 7.5, 10 and 15 K min^{-1} was calculated [12] to be 25.6 kcal mol^{-1}.

TABLE 9

Temperatures of the endo- and exothermal effects

Glass no.	Endothermal effect (°C)	Exothermal effect (°C)
2	788	980
3	760	968
4	798	1000
5	780	1000
7	779	899
8	740	938
9	780	928
10	743	1000
11		977

CONCLUSIONS

The present work demonstrates the compositional range of the glasses formed in the quaternary system Al_2O_3–SiO_2–CaO–MgO with SiO_2 levels in the range 4–10 mol.% and with a constant Al_2O_3 composition of 30 mol.%. The change in the quantities of CaO and MgO, when Al_2O_3 and SiO_2 are kept constant, indicates the influence of these modifier oxides on the properties of the glasses.

The results of the analyses suggest that the structure of these glasses is composed of AlO_4 tetrahedra in which there are Al–O–Si bonds and two AlO_4 tetrahedra associated with each Ca^{2+} ion.

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