Effect of Fluorine on the Structure and Properties of Some Silicate Glasses

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For alkali silicate glasses containing fluorine, the d.c. conductivity and density values decreased as fluorine subistitutes oxygen. The conductivity was attributed to ionic transport of alkali ion as well as electron hopping transport. The increase of non-bridging oxygen as fluorine content increases explains the decrease of density. However infrared absorption increased as fluorine content was increased. At higher fluorine concentrations, new bands appeared in infrared spectrum.

INTRODUCTION

The properties and structure of alkali silicate glasses have been studied in details.[1, 2] For glasses containing fluoride, the glass forming region showed phase separation at higher network former region[3, 4]. The action of modifier is to break up the continuous silica network by introducing *dangling* or non-bridging oxygen[5]. The non-bridging oxygen carry a single negative charge and are compensated by Na^+ ion nearby. In glasses containing transition metal elements, electronic conduction is mainly due to oxidation-reduction equilibrium[6]. At higher temperature, ionic conduction also dominates[7]. Introducing fluorine to amorphous silicon leads to materials with low conduction[8]. The density of silicate glasses and its relationship to composition was also studied[9]. Transition metal elements when introduce gives glasses of higher density values[10]. A model for describing the bridging to non-bridging oxygen ratio as a function of the glass composition was suggested.[11] Substitution of oxygen by fluorine ions, although they have the same size and the same low polarisability causes,[11] such as,

(a) Weakening of the glass structure

(b) The depolymerising action of fluorine in glass is that it enhances crystallization

(c) Fluorides decrease the viscosity of the glass melt.

Infrared of silicate glasses showed three bands: the first at 1100 cm^{-1} which is due to Si–O–Si vibration[12] and the second at 800 cm^{-1}, due to double S–O bonds[13] and the third at 468 cm^{-1}, due to S–O vibration[14]. Addition of Na_2O produce marked change in these bands. The intensity of the bands at 1100 cm^{-1} decreases while the bands at 950 cm^{-1} may be attributed to non-bridging oxygen Si–O and the band at 540 cm^{-1} is due to Si–O group[16]. Infrared spectrum for fluoride glasses was also studied[17].

So far not much work has been done to study the change in both structure and properties of alkali silicate glasses when fluorine is introduced replacing the oxygen ion. This because the materials are highly toxic and require special melting facilities. Most of the molten systems are very reactive with atomspheric water and oxygen[18] as well as with most conventional crucible materials[19]. The high vapour pressure prevents any consideration of vacuum melting[20]. This task was the aim of the present work to throw some light on the change in both structure and properties of such glasses when fluorine is introduced replacing the oxygen ion.

EXPERIMENTAL

On the basis of percentage molar composition, glass samples were made (Table 1) according to the formula:
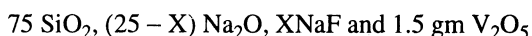
$$75 \ SiO_2, (25 - X) \ Na_2O, XNaF \text{ and } 1.5 \text{ gm } V_2O_5$$

TABLE 1

CHEMICAL COMPOSITIONS AND VALUES OF THE MOLAR VOLUME OF THE GLASSES CONTAINING SODIUM FLUORIDE

Glass	Glass composition				Molar volume
	Na_2O (mole per cent)	NaF (mole per cent)	SiO_2 (mole per cent)	V_2O_5 (gm)	
1.	25	0	75	1.5	26.28
2.	22.5	2.5	75	1.5	26.46
3.	20	5	75	1.5	26.51
4.	17.5	7.5	75	1.5	26.66
5.	15	10	75	1.5	26.79
6.	12.5	12.5	75	1.5	27.01
7.	10	15	75	1.5	27.74
8.	7.5	17.5	75	1.5	27.49
9.	5	20	75	1.5	27.68
10.	2.5	22.5	75	1.5	27.81
11.	0	25	75	1.5	28.21

(where X changes from 0 to 25). The raw materials used were of chemically pure grade. Silica was introduced in the form of finely pulverised and washed quartz containing 99.98% silica. Sodium oxide was introduced in the form of its respective carbonate. The melts were made in platinum crucibles in an electrically heated furance, under an air atmosphere. The temperature of melting ranged 1000°–1100°C for 5 h with the melt being poured onto a graphite mold. Since the mehtod operates in air, a partially oxidised glass is expected, which also contains some residual OH groups. Grinding and polishing were carried out in the usuall way with minimum amount of water and in the final stage of polishing paraffin oil was used.

For electrical conductivity measurements, disks of 2 cm diameter and 0.5 cm thickness were prepared. A thin layer of silver paste was used on each face to

ensure good electrical contacts. The current-voltage was investigated for these samples where a keithley 610C electrometer was used to detect the current. For adjusting temperatures, Oxford temperature stablizer DTC2 was used.

The density was determined by Archimedes method in which the glass sample was weighed both in air and when immersed in xylene as a liquid of known density. The density of the glass was then calculated from the formula:

$$d = \frac{a}{a-b} \times 0.86,$$

where d is the density of the glass, a is the weight of the sample in air, b is the weight of the sample in xylene; and 0.86 is the density of xylene. For molar volume calculations, the following formula was used:

$$V_m = \Sigma \frac{MW \times mole\ per\ cent}{\rho}$$

were V_m is the molar volume, MW is the molecular weight of the constituent oxides and the sodium halide introduced, mole per cent means the mole per cent composition of the different constituents; and ρ is the density of each glass sample.

Parts of the samples were crushed into power form and examined for molecular structure variation by infrared technique. IR spectrum were recorded on a fully automatic unicam SP 1100 infrared spectrophotometer.

RESULTS

The current-voltage characteristic curves showed an Ohmic behaviour up to 70 volts. The volume resistivity was measured in the temperature range from 30°–400°C. The resistivity values were plotted against reciprocal of absolute temperature as shown in Fig. 1 (a, b). All curves were found to be straight lines in the considered range of temperature, showing a sharp decrease in resistivities as the temperature was increased. The activation energy was calculated from the temperature dependence of the electrical conductivity assuming that the conductivities of the systems obey the Arrhenius equation:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{KT}\right)$$

where σ_0 is constant, E_a is the activation energy, T is the absolute temperature K is Boltzmann's constant. The values, calculated from the slopes of log. $\sigma - 1/T$, were plotted as a function of NaF content (Fig. 2). These values were found to increase from 0.65 eV at 2.5 mole % NaF to 0.80 eV at 25 mole % NaF. At different temperatures from 50–400°C, the resistivity was plotted against mole % NaF content, Fig. 3. This showed that for each temperature, two straight lines intersect at about (7.5–10) mole % NaF.

The density values were plotted against NaF content, Fig. 4. As shown, the density was decreased in a smooth curved manner from 2.40 g/cm³ at zero mole % NaF down to 2.23 g/cm³ at 25 mole % NaF. The insert of the graph shows the increase in the values of the molar volume as the composition (mole %) of sodium fluoride was increased.
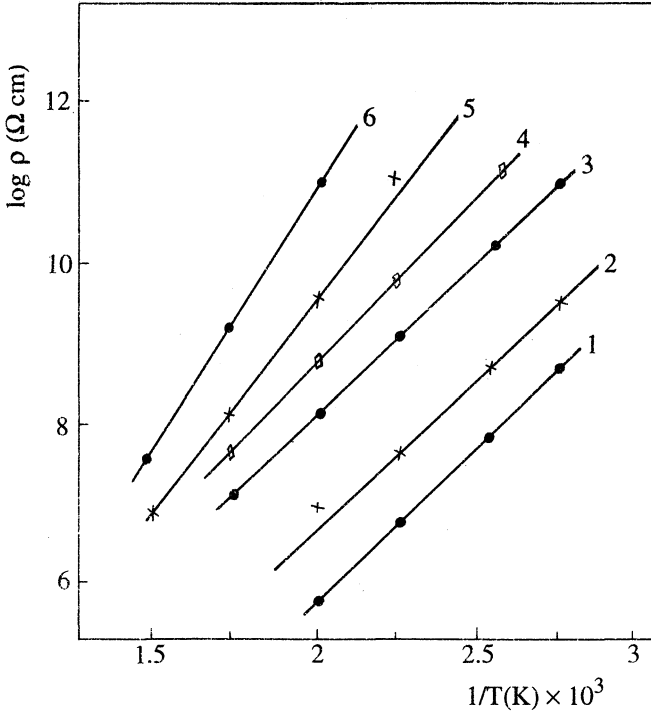
Fig. 1a   The relation between log resistivity and the resiprocal of absolute temperature for the system $Na_2O-NaF-SiO_2-V_2O_5$
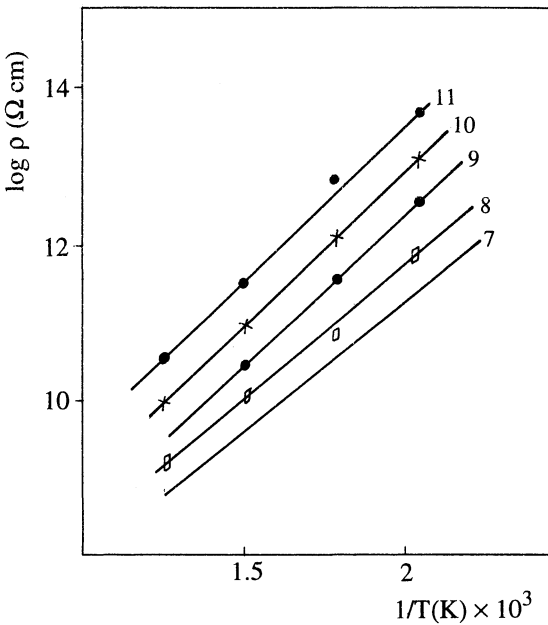
Fig. 1b   The relation between log resistivity and the resiprocal of absolute temperature for the system $Na_2O-NaF-SiO_2-V_2O_5$
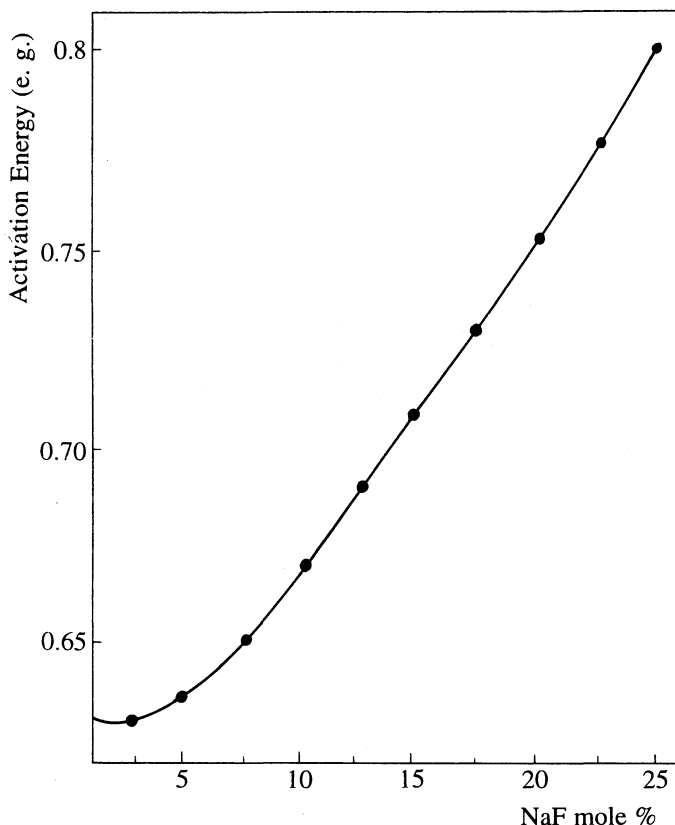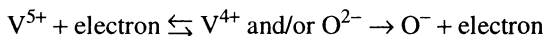
Fig. 2   The relation between activation energy and mole % NaF

The infrared absorption spectra of pure crystalline V_2O_5 showed two main absorption bands at 780 and 1020 cm^{-1}, the first is more intensive than the second, Fig. 5.

Five absorption bands at 700, 900, 960, 1000 and 1200 cm^{-1} were observed in glasses containing fluorine. The absorption intensity increased as the amount of NaF was increased.

DISCUSSION

The linear increase of the electrical conductivity (decrease of resistivity) with the increase of absolute temperature, Fig. 1 can be attributed to two main reasons: Firstly the increase in mobility sodium ions, as a mobile ions in the glass network structure (participation of fluorine for conduction is negligible[20]. Secondly the thermal energy which was contributed to the electron hopping process between cations of differnet valency in the form:

$$V^{5+} + electron \leftrightarrows V^{4+} \text{ and/or } O^{2-} \rightarrow O^- + electron$$

The addition of NaF increased the activation energy values, Fig. 2. This because as NaF content increase on the expenses of NaO, the electrically conductivity is
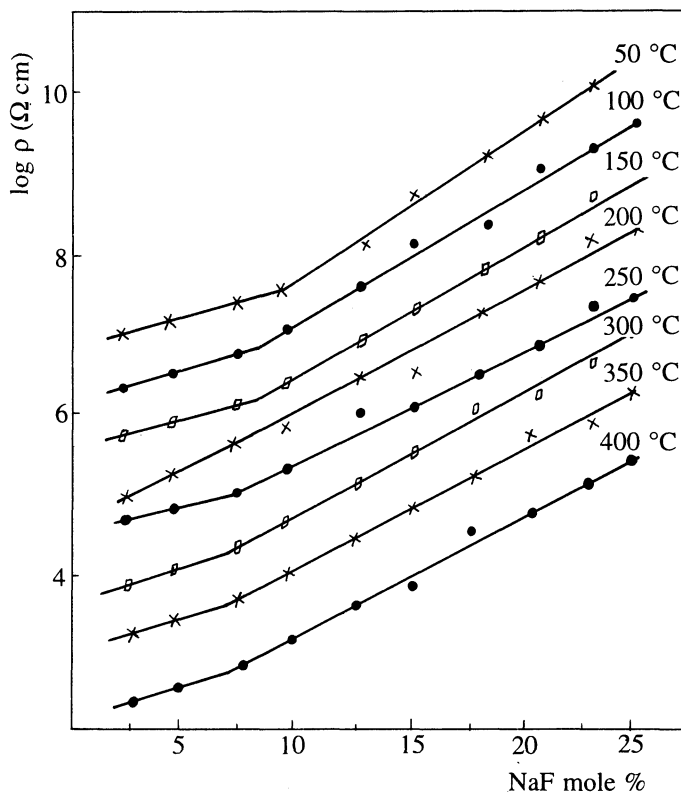
Fig. 3   The relation between log resistivity and mole % NaF at different temperatures.
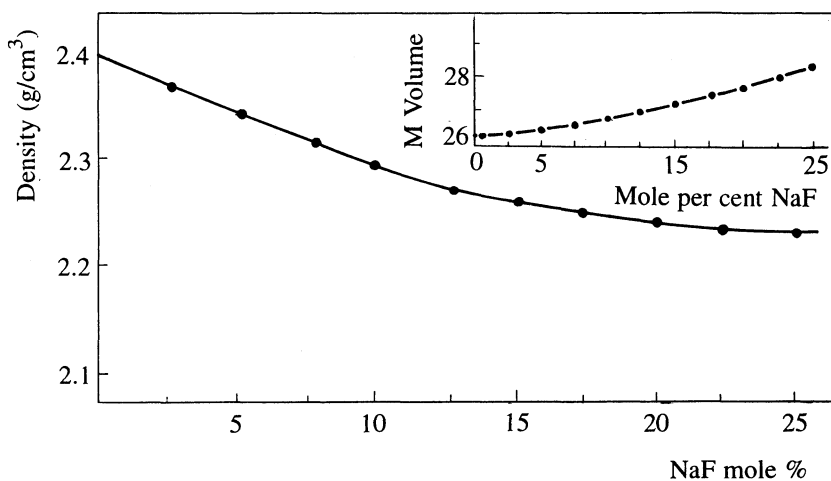

Fig. 4   The relation between density and mole % NaF.

reduced (the activation energy increased) in agreement with[7]. As can be seen in Fig. 3 the straight lines bending at about 7.5 mole % NaF. This indicates a reduction in ion mobility as NaF content is increased. The addition of NaF may produce smaller interstices and increase the forces exerted on the alkali ion which restrict the alkali ion migration. This also could be some formation between Na^+ and F^- ions.

The decrease in density values as NaF content was increased, (Fig. 4) because of an increase in the volume of the network. This is a consequent result for the increasing of non-bridging oxygen provided by NaF [21].

Infrared spectrum of samples without fluorine showed two broad bands at 700 cm^{-1} and 1200 cm^{-1} which are due to the normal vibration frequency of octahedral V–O bond[22] and band at 1000 cm^{-1} which is due to Si–O group[16]. The existence of absorption bands can be considered as an evidence that V^{5+} ion exists in the same coordination as in crystalline V_2O_5, i.e. in the octahedral configuration. As shown, Fig. 5, the intensity of the above mentioned bands were increased as the concentration of NaF increased up to 25 mole %. The new band appeared at 900

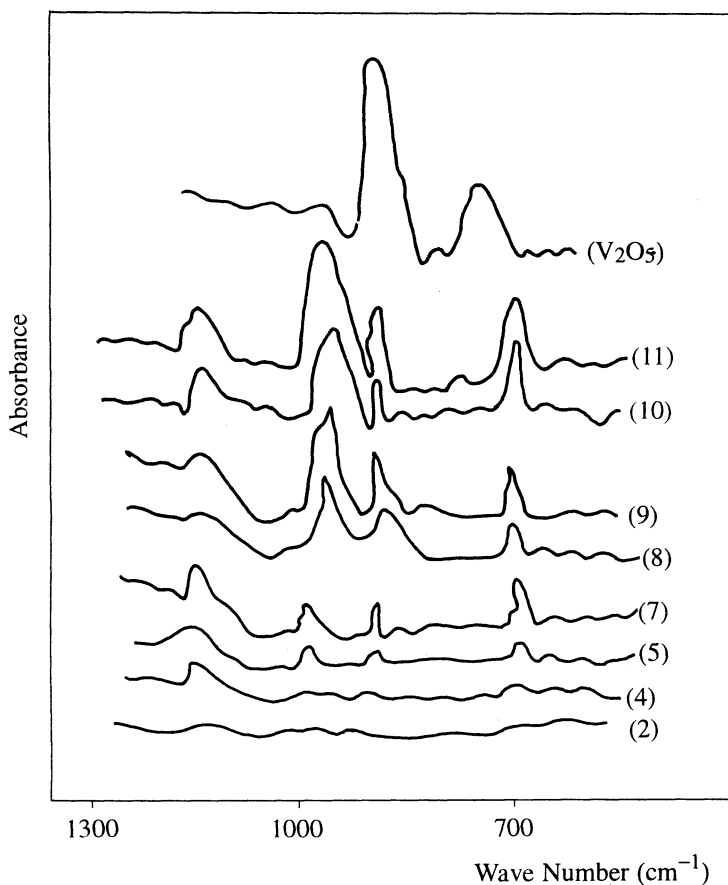Fig. 5 Infrared absorption of glass in the system (SiO_2–Na_2O–NaF–V_2O_5)

cm^{-1} is attributed to SiF_2 [23]. At high concentration of NaF, another new band appeared at 960 cm^{-1} which may be due to $Si-O^-$ group.

Finally it can be concluded that:

(1)   The structure of these glasses is composite interpenetrating structure and seems to confirm the dynamic liquid hypothesis of Weyl, and Marboe[22] with VO_6 group as the fundamental unit responsible for conduction.

(2)   The density of glasses decreases with the increase of fluorine on the expense of oxygen. This because of polarization, field strength and ionic radius of different cations introduced into the glass compositions.

(3)   The increase in the intensity of the absorption bands with the increase of NaF content may be attributed to the increase of V^{4+}/V^{5+} ratio. The broadness observed in the absorption bands at lower NaF concentrations may be due to the overlaping of individual absorption bands of Si–O and V–O bonds[24].

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