Disorder and optical spectroscopy of Cr^{3+}-errors in the nature and structure of an alkali/alkaline earth fluoride glass (comment)

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COMMENT

Disorder and optical spectroscopy of Cr^{3+}—errors in the nature and structure of an alkali/alkaline earth fluoride glass

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Abstract. Recently reported optical properties of Cr^{3+} in several glasses included descriptions of structures of alkali/alkaline earth fluoride glasses. This comment amplifies and clarifies the presently known structural evidence for one of these glasses.

In a paper by Rasheed and co-workers (Rasheed *et al* 1991), there appear several errors concerning the composition and structure of an alkali/alkaline earth aluminium fluoride glass, (G8197 in their paper).

In table 1 (p 3826), the glass G8197 should have the molar composition given in table 1 of this comment. On p 3835 appears the statement: 'In constructing table 4 the molar volume of O^{2-} is assumed to be twice that of F^-'. This is incorrect. Effectively the charge carried on one oxide ion substitutes for, or is equivalent to, the charge carried by two fluoride ions. In table 4, p 3836, the glass G8197 is described as a lithium tin fluoride glass. It should be described as an alkali/alkaline aluminium fluoride glass. Column 4 of that table should be headed 'amount of former −mol.%' *not* modifier. Table 2 of this

Table 1. Composition of glass G8197.

Item	Mol. %	Mol. wt	wt (g)	wt in 1 cm^3	Moles in 1 cm^3 ($\times 10^{-3}$)
MgF_2	8.40	62.30	523.32	0.2481	2.688
AlF_3	17.00	83.98	1427.66	0.6769	8.060
Al_2O_3	2.70	101.96 }	428.23	0.2030	1.991
Al_2O_3	1.50	101.96 }			
P_2O_5	1.50	141.95	212.92	0.1009	0.711
SrF_2	13.75	125.62	1727.27	0.8190	6.520
LiF	37.60	25.94	975.34	0.4625	17.830
BaF_2	5.10	175.83	894.18	0.4240	2.418
CaF_2	12.5	78.08	976.00	0.4628	5.927
CrF_3	0.05	109.00	5.45	0.0026	0.024
			7170.53	3.3998	46.169

We note that $Al(PO_3)_3 \rightarrow \frac{1}{2}Al_2O_3 + \frac{3}{2}P_2O_5$.

Table 2. Fluoride equivalent content of glass G8197.

Item	Moles of fluoride compound in 1 cm^3	Moles of F^- ion in 1 cm^3 ($\times 10^{-3}$)
MgF_2	2.688	$2 \times 2.688 = 5.376$
AlF_3	8060	$3 \times 8.060 = 24.180$
Al_2O_3	1.991	$2 \times 3 \times 1.991 = 11.946$
P_2O_5	0.711	$2 \times 5 \times 0.711 = 7.110$
SrF_2	6.520	$2 \times 6.520 = 13.040$
LiF	17.830	$1 \times 17.830 = 17.830$
BaF_2	2.418	$2 \times 2.418 = 4.836$
CrF_2	5.927	$2 \times 5.927 = 11.854$
CrF_3	0.024	$3 \times 0.024 = 0.072$
Total fluoride ion equivalent		= 96.244
Total oxide ion equivalent		= 48.122

comment shows how the corrected values of the fluoride ion content was calculated for G8197, from the quantities shown in table 1 of this comment. The equivalent oxide content would be half the equivalent fluoride ion content. From the literature (Matecki and Poulain 1983, Khaliber *et al* 1983, Tick 1983, Kumar and Harris 1984, Comyns 1990), we estimate a density in between 3.2 and 3.7, and *assume* for this study a value of 3.4. In constructing table 2 of this comment, we bear in mind that the number of oxide ions in a glass is treated as equivalent to twice that number of fluoride ions on account of their relative electronic charges.

For glass G8197, the phosphorus and aluminium clearly act as formers, and the alkaline earths as modifiers. However, the position of the lithium and magnesium is less clear. If these are treated as modifiers, then the value of 34 mol.% modifier ions (expressed as their fluoride compound) appears in table 4 of Rasheed *et al* (1991). However, if both the lithium and magnesium are 4-coordinated, and treated as formers, the figure rises to 60%, more in line with the other glasses and their Dq/B values. However, the spectroscopic and structural data to justify such an assumption are not known to the authors at this time.

Since these revised values do not greatly alter table 4 of Rasheed *et al* (1991), their conclusions remain unaffected.

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