

LOCAL STRUCTURES ABOUT SOME TRANSITION ELEMENTS IN OXIDE GLASSES USING X-RAY ABSORPTION SPECTROSCOPY

J. Petiau⁺ and G. Calas*Laboratoire de Minéralogie-Cristallographie, Universités Paris VI et VII, 75230 Paris, France et L.U.R.E., 91405 Orsay, France**⁺ et Ecole Normale Supérieure J.F., Montrouge, France*

Résumé.— La structure locale autour de certains métaux de transition (Cr-Fe-Co-Ni) présents dans des verres silicatés ou boratés est étudiée à partir des résultats de la spectrométrie d'absorption X. La complémentarité des informations qui peuvent être obtenues à partir des oscillations "EXAFS" (distance des atomes voisins) et de la structure du seuil (symétrie, état chimique) est mise en évidence.

Abstract.— Absorption X-ray spectroscopy is used to study the local structure around transition elements (Cr-Fe-Co-Ni) in silicate and borate glasses. The complementarity of EXAFS, giving the neighbour distances, and of the near edge structure giving informations about symmetry and chemical state is emphasized.

X-Ray absorption spectroscopy is an adequate method for studying local structure about one definite element in multicomponent glasses if one uses its two complementary aspects, XANES (X-Ray Absorption Near Edge Structure) and EXAFS (Extended X-Ray Absorption Fine Structure). The former gives the same type of informations as the other spectroscopic techniques : with the same atomic selectivity, it informs about local symmetry and chemical effects. On the other hand, EXAFS is more similar to diffraction methods but its atomic selectivity is a clear advantage and allows to get informations on short range order around minor components of complex glasses. Some results are presented as an illustration of the various kinds of informations that can be obtained using XANES and EXAFS. The measurements are made using the synchrotron radiation of LURE-DCI (Orsay) at the K-edges of chromium, iron, cobalt and nickel, present as minor components (one to several Wt%) in silicate and borate glasses.

1.- Near-edge structure (XANES) . It extends from the beginning of the edge to several tens electron-volts above. The successive increases of the absorbance in the K-shell ionization threshold region correspond to transitions of an ls electron to a more or less bound empty level. The shape and position of the absorption edge are determined by the oxidation-state of the studied element ("chemical-shift"), the metal-oxygen covalency and the local symmetry (including the site distortion). In fact things are far more complicated than this over simple presentation : many body problems, multiple scattering have important effects which are not always completely understood.

1.1.- Oxidation state : About a 6 eV shift between iron K-edge in glasses containing either purely divalent or purely trivalent iron has already been described (1). In cases of mixing of both oxidation states, the shift of the main part of the edge follow their respective proportion ; taking into account the influence of other parameters on the shape of the edge, it is nevertheless probably impossible to attain a precision better than twenty per-cent.

1.2.- Site symmetry : The effect of the distortion of the site is clearly shown on Fig. 1 by the splitting of the upper part of the edge.

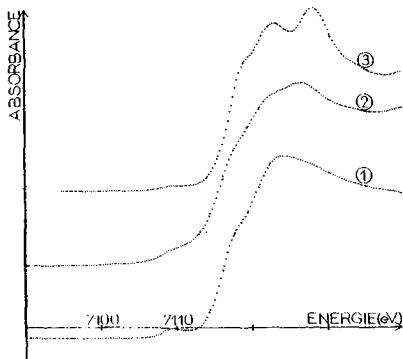


Fig. 1 : Fe(II) in octahedral environment

- 1) Glass (pyroxene composition)
0.5 FeO, 1.5 MgO, 2SiO₂
- 2) Oxide Fe O_{1-x}
quasi regular octahedron
- 3) Crystalline pyroxene
0.5 FeO, 1.5 MgO, 2SiO₂
Distorted site (C_{2v}).

In the case of a crystalline pyroxene of metasilicate composition, ferrous ions are in a strongly distorted site ; in the contrary the site is a nearly regular octahedron in ferrous oxide. The curve relative to the glass is almost featureless indicating an apparently regular site. This fact is observed in most cases and gives limitations on structural models to be chosen for these ions in glasses.

1.3.- M-O Covalency : In oxide systems the pre-edge region corresponds to forbidden dipolar transitions from 1s to 3d partially empty levels of the transition element ; its intensity is then usually very weak and is only enhanced by the 3d metal-2p oxygen orbitals mixing (quadrupolar transitions giving scarcely several % of the total absorption).

Three examples of this effect are presented :

- ferric ions in glasses always exhibit a strongly marked pre-edge peak conforing the model of a 4-fold coordination (Fig. 2).

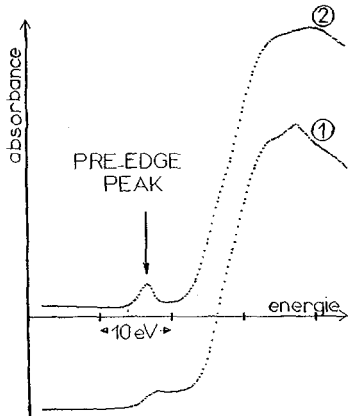


Fig. 2 : Enhancement of the pre-edge peak of Fe(III) K-edge in sodium disilicate glass (2) v^s crystalline ferric oxide (1).

- in well-known cobalt containing alkali-borate glasses it is possible to follow the coordination change of cobalt as a function of the alkalinity of the system by looking at the pre-edge peak amplitude. The same effect, though less pronounced, is observed in nickel corresponding glasses.

- in cases of an extremal oxidation state, as in the molecular complex CrO₄²⁻, the pre-edge peak is very intense ; the transition is favoured by the important mixing of the chromium-3d orbitals with the oxygen-2p orbitals having the T₂ symmetry (2). The amplitude of this pre-peak in a glass allows to confirm the presence of discrete molecular complexes very similar to those observed in crystals. The identity of the the two spectra (Fig. 3) clearly show that in this

sodium borate glass chromium is mainly in hexavalent state.

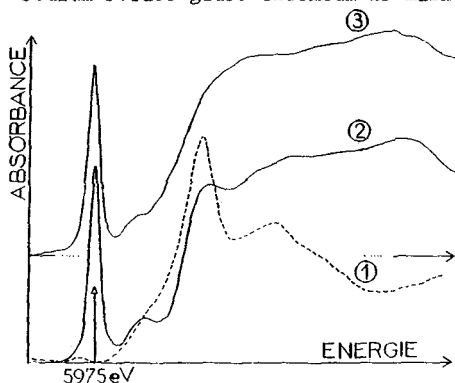


Fig. 3 : K-shell threshold of chromium in :

- 1.- chromic oxide (Cr_2O_3)
- 2.- potassium chromate (K_2CrO_4)
- 3.- sodium diborate glass (3 wt% Cr).

2.- EXAFS.- From EXAFS oscillations which

extend up to several hundred eV above the edge, it is possible to extract information about the successive atomic shells surrounding the observed element. In the case of a transition element in oxide glasses, it seems only possible to measure the M-O distance (3) and to get qualitative indications concerning intermediate range order. The development of the method has led to a better comprehension of its possibilities but also of its limits, in particular concerning the direct determination of coordination numbers using EXAFS amplitudes.

Metal-oxygen distances are calculated by Fourier filtering on both glasses and reference crystalline compounds, using theoretical phase-shifts (4). Typical Fourier transforms are shown on Fig. 4 for some Co-containing glasses. The main contribution is given by the metal-oxygen peak, which is the only significant feature in many oxide glasses, especially in iron case (5). On Fig. 4, further peaks can be seen at larger distances, indicating a small intermediate range order. In silicate glasses, this peak corresponds to characteristic cobalt-cation distances observed in crystalline silicates. In borate glasses, the interpretation of the broad peaks at large distance (4-5 Å) is not clear ; this feature is also present in Ni-borate glasses and remains stable when changing Fourier transform conditions.

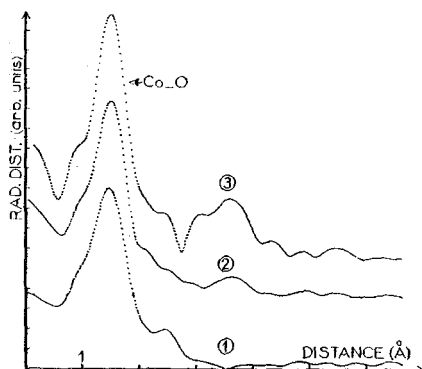


Fig. 4 : Radial distribution around cobalt in three glasses :

- 1) $\text{CaO}, \text{MgO}, 25\text{SiO}_2$
 - 2) 27 wt% $\text{Na}_2\text{O}, \text{B}_2\text{O}_3$
 - 3) 7 wt% $\text{Na}_2\text{O}, \text{B}_2\text{O}_3$
- } 4 wt% Co

The measured distances can be used to discuss the structural models of transition metals ions in oxide glasses.

If compared to octahedral case in crystals, we observed always a shortening of the metal-oxygen distance (Table 1). In the case of ferric ion, in sodium silicate glasses, it corresponds to the predominance of tetrahedral site which is coherent with the pre-edge peak amplitude. In cobalt- and nickel-containing borate glasses the shortening of the distance with the increasing of alkalinity confirms

the well-known coordination change. The distance measured in silicate glasses indicate a rather tetrahedral coordination, being similar to those observed in Na-rich borate glasses.

TABLE 1

	GLASS		CRYSTAL	
	Composition	Observed M-O distance	Type of site	Corresponding distance
II Fe	reduced sodium silicate (3wt% Fe)	2.07	octahedral site	2.15
III	oxidized sodium silicate (3wt% Fe)	1.91	octahedral site tetrahedral site	2.00 1.89
Co II	CaO, MgO, 2SiO ₂)	1.98	octahedral site	2.13
	27wt% Na ₂ O, B ₂ O ₃) 4wt% Co			
	7wt% Na ₂ O, B ₂ O ₃)			
Ni II	CaO, MgO, 2SiO ₂)	2.00	octahedral site	2.09
	27wt% Na ₂ O, BiO ₃) 4wt% Ni			
	7wt% Na ₂ O, BiO ₂)			

However the measurement, by EXAFS, of a short M-O distance is not, by itself, a direct proof of the coordination change ; radial distribution effect may led to the same result since it is now known that EXAFS give preferential information on shortest distances. This effect was verified in the case of Fe(II) in the strongly distorted sites of the pyroxenes, but in this case the distance distribution is also put in evidence in the edge structure, as opposed to the edge shapes in glasses presented above.

References

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