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EXAFS AND EDGE STRUCTURES ; APPLICATION TO NUCLEATION IN OXIDE GLASSES

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Abstract - Results and problems of X-ray absorption spectroscopy in oxide glasses are briefly overviewed. The complementarity between EXAFS and fine edge structures is described about several examples. For network modifying elements information is limited in general to the coordination atomic shell, when, for network formers and "intermediate" elements, pieces of information can be obtained concerning the next nearest neighbours of the absorbing atom. They offer the possibility to study structural changes induced either by composition or by thermal treatments as in nucleation processes.

I - INTRODUCTION

EXAFS has now become a method currently used for investigating the atomic scale structure of amorphous materials. It has been recognized as very useful in those materials because it is insensitive to long range order and it has given rise to many studies in metallic and covalent glasses (1). The amount of results in oxide glasses is much smaller, although the atomic selectivity is particularly attractive in them because they are generally multicomponent.

More recently it appeared that, with the same experimental approach but at the price of an effort towards a good energy resolution, the edge fine structure within 10-20eV around the threshold energy also contains precious information. That is especially true in insulating materials because the transitions from core levels to the first empty states which are localized, are strongly dependent upon the chemical and geometrical state of the absorbing atom. The intermediate energy range (from 5-10eV to 70-100eV above the threshold), where multiple scattering processes have to be taken into account, receives now quantitative interpretation. We choose to name this part of the spectra XANES (X-ray Absorption Near Edge Structure), when this term has generally been used before to describe together the edge structure and the near edge range. It potentially contains information "beyond radial distribution" and it is an exciting domain for the near future. It can already be used by approximate methods in complex systems.

X-ray Absorption Spectroscopy (XAS) in general offers various pieces of information. XANES is at its early beginning, but edge structure and EXAFS have
already taken advantage of being used together for their complementarity. Their information content will therefore be gathered in this paper.

**What information does EXAFS give access to in oxide glasses?**

As an EXAFS spectrum provides a partial radial distribution function, the ideal situation is reached when the distributions relative to each atomic species can be joined up. This situation is often encountered in amorphous metallic, metal-metalloid or chalcogenide compounds and has led to important results. The oxide glasses case is less propitious: EXAFS have never been measured at the K-edge of oxygen because of the difficulty to collect extended spectra at low energy thresholds; the oxygen K-edge structure is however accessible to measurement in a limited energy range. In any case the oxygen environment is not of an unique type as soon as the glass is not a pure oxide and it would be probably difficult to distinguish the various oxygen environments in the overall EXAFS information, should it have been possible to collect the data. EXAFS information is therefore limited to the cations environments. The difficulties encountered for low energies also prevents from reaching boron environment and has limited to a very few the number of studies on other light network former and modifier elements such as silicon, aluminum or sodium.

On the other hand only atoms in the near vicinity of the absorbing atom contributes to the EXAFS spectra because of the small photoelectron mean free path. In glasses, the structural information is thus actually limited to the nearest and next nearest neighbours.

The fine structures of the absorption edges are very useful in being able to give directly the cations coordination number. As it has been recognized a long time ago, the edge also provides an indication of the oxidation numbers, by the "chemical shift" effect, but generally this is not the major information, as the oxidation state is usually known in these materials. On the contrary the coordination number is one of the main questions for many important components of oxide glasses.

Problems relative to network former and to modifier elements do not arise in the same terms. The unsolved questions about forming elements concern mainly the middle range order, the first shell organization being little affected by changes in the composition or in the preparation method. On the contrary, the nearest neighbour organization is often unknown around modifier elements and is the first important question we must answer to, especially when they are present at a low concentration. The degree of order in the next nearest environment is the second object concerning network modifiers. It characterizes their purely modifying or "intermediate" role in the structure of the glass. It is also the key question for understanding the early stages of crystalline nucleation.

This paper would provide a brief overview of results and would try to give a realistic idea of the possibilities and limitations of XAS. We first deal with the nearest neighbour atomic shell, around network formers, modifiers and "intermediate" components; we then discuss results about next nearest environments and especially relative to nucleation problems.

II - NEAREST NEIGHBOURS: THE COORDINATION ATOMIC SHELL

II.1 - Network forming elements  
The rigidity of the coordination tetrahedron is maintained in the glass and allows any change in site geometry (metal-oxygen distances or coordination number) to be detected. Two ways may be used independently to follow some eventual coordination changes as a function of chemical composition or thermal treatment: edge structure and EXAFS. The former was used to study aluminum in alumino-silicate glasses, because viscosity or density data indicate some Al to be 6-fold coordinated in peraluminous compositions (2). The Figure 1 shows the evolution of the edge structure as a function of the coordination number of Al in some reference compounds: as for the spectra of other elements (3) a marked change is observed between 4-fold and 6-fold coordination as in crystalline aluminum silicate polymorphs. The edges recorded in the glasses do not show any significant evolution when the ratio Al/Na varies: this indicates that -as in feldspar glasses
Figure 1 - Aluminum K-edge fine structure in several glasses and crystalline reference compounds. (x represents the Al/Na ratio. From (2)).

(where Na/Al=1) - Al remains in a network forming position. EXAFS study at the germanium K-edge in alkali germanate glasses (4,5) revealed an increase of Ge-O distances with alkali concentration and was interpreted as arising from the presence of a minor quantity of 6-fold coordinated Ge. This interpretation confirms previous experiments on these glasses, pointing out an anomaly in the GeO2-Na2O system at high alkali content. A similar hypothesis was drawn out on Ga/Al, Ge/Si feldspar glasses (6) on the basis of the observed increase of Ge-O and Ga-O distances; as a 3-dimensional structure is expected for these glasses, this could be better interpreted as a disorder effect.

II.2 - Network modifiers
Few data are available for experimental limitations as the usual modifiers require relatively low energies which are more difficult to get on conventional storage rings. Recent experiments were made on Na and Ca in various silicate and alumino-silicate glasses. Sodium does not exhibit any significant change with glass composition, but strong disorder effects are to be taken into account (7): the obtained mean distance and coordination number are not significantly different from their values in the crystals. Furthermore in a strongly distorted environment, only the shortest distances are sensed as was observed in crystalline nepheline and probably also in glasses. The same type of comparison between crystal and glass was made for calcium (8): the same type of local structures are found around calcium in CaMgSi2O6 and CaAlSi2O8 glasses, although the corresponding crystals have distinct structures and different oxygen environments around Ca. In that case, glasses exhibit greater Ca-O distances than crystals.

II.3 - "Intermediate" elements
This group comprises the elements which do not play a so contrasted role in the glassy structure as the ones studied above. In fact the local structure is very variable, from strongly covalent internal bonds as in vanadate, vanadyl (9) or uranyl groups to ions with a generally regular coordination shell as transition d elements. The latter, though less covalent than the previous ones are also less ionic in character than the pure modifiers. Several other elements have been the subject of EXAFS or edge studies, as silver in borate glasses (10) or technetium in borosilicate glasses (11).
Zirconium.

Zirconium, for which a large coordination number is expected from the structures of crystalline compounds, has been the subject of several studies (12,13). Its environment seems similar in various silicate glasses. Different models of the nearest neighbours shell were tried (13), but none of them gave fits significantly better than a one shell model (6 oxygens within a shell of 0.1-0.15 broadness). It is not possible to exclude the presence of some more oxygens aside from this main part of the distribution. However the fact that the Zr-O measured distance is equal to what is usually found in crystals is a strong argument in favour of this value. It is important to notice that independent determinations of the neighbours numbers and of the radial distances are necessary to obtain reliable results, so that the obtainment of accurate experimental amplitudes is essential. Finally, it must be pointed out that no significant changes are observed in the first shell during nucleation processes, although the second shell is strongly affected (see below).

Uranium.

Hexavalent uranium is part of a rigid uranyl complex in glasses; beyond the two covalently bonded oxygen atoms which are confirmed by EXAFS, five next nearest oxygen atoms are measured at a shorter distance than the usual one in other uranyl compounds. This tendency towards a shortening of metal-oxygen distances when going from the crystal to a glass of similar composition will be confirmed with the 3d elements (see below): in this respect, the uranyl group behaves as an isolated ion.

3d- elements.

Various 3d elements have been studied as minor or major components of oxide glasses. The K-edge structures of these elements have a rich information content because they contain transitions to localized 3d states, which are partially allowed through a d-p mixing. The intensity of this "pre-edge" is thus relatively sensitive to the coordination number. Analysis of the oxygen shell contribution to

Figure 2 - Decomposition of the pre-edge peak into lorentzian components for Fe(III) crystalline compounds (1: 6-fold coordinated; 2: 4-fold) and a silicate glass (70% 4-fold). In the right, the corresponding transitions for 6-fold (a) and 4-fold (b) coordinations.
EXAFS confirms these results and completes them in giving the coordination distance which is generally short. It seems important to point out that the direct determination of the coordination number by the edge structure ensures that this distance measurement is not affected by disordered effects, but actually describes a polyhedron with narrow radial distribution.

A study of the preedge was undertaken in Fe-containing silicate glasses and reference compounds in which ferric or ferrous ions have a well-defined coordination number (14). After subtracting an arctangent baseline, these prepeaks may be decomposed into lorentzian components which were shown to correspond to transitions to crystal-field type levels (Fig. 2). The use of references allow to measure the proportion of 4-fold and 6-fold coordinated ions. Such a study is very promising as it gives informations which can be directly compared to the more classical spectroscopic techniques.

In tetravalent titanium, such a change is also observed and ascribed to a coordination change from a 4-fold coordinated ion, which gives rise to an intense absorption of lorentzian shape, to a 6-fold coordination which gives a much weaker complex structure. This coordination change is observed as a function of composition, as in TiO2-SiO2 glasses (15) and in TiO2-SiO2 sol-gel glasses (16). It is also observed during the nucleation processes of Mg- and Li-aluminosilicates (17-18). In the Figure 3 is reported such an evolution, which describes the progressive incorporation of titanium into crystalline phases since the first steps of the process: these data are confirmed by a subsequent increase of Ti-O distances measured by EXAFS. The study of the second shell is also consistent with this analysis (see below).

Manganese-containing silicoaluminate glasses were studied to see the role played by an element as a function of its concentration, with values ranging from 12 to 50 MnO moles%. The edges do not vary in the glasses and are -once more- different from those of the corresponding crystalline phases. Whatever the manganese content is, the coordination number remains equal to six. On the other hand the Mn-O distances are significantly shorter than for 6-fold coordinated Mn and they increase with decreasing manganese concentration in the glass composition: the shortening of the Mn-O distances in glasses vs crystals goes from .05Å in concentrated glasses to .10Å in the most concentrated ones.
III - NEXT NEAREST ENVIRONMENT

III.1 - Network forming elements.
For monoxide glasses, as pure GeO₂, X-ray or neutron diffraction and EXAFS give information of equal quality about the coordination tetrahedron, but diffraction methods act clearly better for further atomic shells, the weakness of EXAFS lying in the lack of meaningful information at low momentum transfer. Taking again the example of GeO₂, the amplitude of the second neighbours contribution can be expressed as the percentage of Ge-O-Ge angles which lie in a range of 5 to 7 degrees around the mean value (130°); no information is obtained about the radial distribution "tails" corresponding to Ge-O-Ge angles values outside this range. The relation between the order of the second shell and the metal-oxygen distances in the coordination shell have recently been demonstrated in glasses of the SiO₂-SiO system (19). The more random is the second shell, the larger are the Si-Si distances and the shorter the Si-O bond length.

However the advantage of looking directly at a partial pair correlation function becomes obvious for binary glasses, such as the so important GeO₂-SiO₂ system which has been the subject of two studies (5-20). Both of them, made at germanium K-edge, suggest a random solution of GeO₄ and SiO₄ tetrahedra, with no clustering of GeO₂ up to a concentration of 25wt% of GeO₂. This result is inferred from the amplitude of the second neighbours contribution which is very low by comparison to the case of pure GeO₂ and which is very sensitive to clustering for atomic species having large weight differences. The same type of information, relative to the changes appearing in the network of GeO₄ tetrahedra when the composition becomes complex, has been obtained in various glasses of the system SiO₂-GeO₂-B₂O₃-Na₂O. The weakness of this work is that it has only been done at the Germanium edge, for the reasons given before. The measurements, made at the silicon K-edge in several silicate glasses by Greaves et al. at LURE-ACO, have remained for several years the only work on light network forming elements (21). The existence of a second shell contribution to the glasses spectra is not obvious, when it is present and analyzed in the quartz spectrum taken as a reference.

III.2 - Network modifier and "intermediate" elements.
Their considerable influence over mechanical, optical, electrical and other properties of the glasses has been recognized, studied and used for a long time. However, if various spectroscopic techniques, including EXAFS of the first atomic shell and fine edge structure, inform about their chemical and coordination state in many cases, their situations relative to the network are unaccessible by diffraction methods as soon as the complexity of composition prevents from the discrimination of partial radial distributions. As a consequence, EXAFS information concerning the next nearest atomic shell surrounding a selected modifier element is very precious, although rather poor. It is especially interesting when comparisons can be made at different stages of an evolution or for different concentrations.

For Mn, Fe, Co and Ni at low concentrations in silicate and borate glasses, no contribution from a second shell generally emerges from the data, apart from a broad range of non-zero amplitude usually found in radial distributions of borate glasses and unexplained at that time. This lack of any middle range order, in the sense that EXAFS gives to this concept, could be interpreted as characteristic of a modifying role. The situations for Mn or Fe, when they are major components, are more diversified; second atomic shells are sometimes put in evidence but with an amplitude which makes their interpretation difficult.

We measured EXAFS at the zirconium K-edge in various silicate and borosilicate glasses where its concentration lies in the 1% range. The results are very similar in showing a small contribution from second neighbours, behind the first oxygen shell. This is directly visible in the EXAFS signal $\chi(k)$ (Fig.4a) which does not look like a simple damped sinusoidal function. The Fourier transform of $\chi(k)$ (Fig.4b) puts in evidence a two shell distribution and clearly indicates that it is not possible to make independent fits for these two shells. Parts c and d of the figure 4 show the two successive fits obtained by first back transforming the only first shell and secondly by transforming together the two shells and making a fit with two subshells. This last fit reproduces quite well the experimental spectrum and corresponds to 2.5 silicon atoms. The conclusion should be given in
the same terms as for the germanium case: the SiO₄ tetrahedra are linked by corners to the ZrO₆ polyhedra with a non random angular distribution; EXAFS gives the central part of this distribution.

By the same type of analysis, titanium and zinc are shown to occupy in aluminosilicate glasses the centers of tetrahedra linked by corners to SiO₄ tetrahedra. However the Ti-O-Si angle (130°) and Zn-O-Si angle (115°) mean values are significantly different from the usual value for Si-O-Si angle in silica glass (152°).

III.3 - Environment of nucleating elements.

Results concerning changes in the environment of titanium, zirconium and zinc during crystalline nucleation processes will be described with some details. The precise role of each nucleating element can only be understood by investigating the very first stages of the nucleation process with a strictly local structural probe having atomic selectivity. XAS presents these characteristics and gives original information, interpretation of which has to be ensured by the simultaneous use of methods having access to different scales of observation (electron microscopy, small angle X-ray or neutron scattering etc.).

The first approach of nucleation by EXAFS spectroscopy has concerned the role of zirconium in a glass of the MgO-Al₂O₃-SiO₂ system (12). The growing up of tetragonal zirconia during the crystallization step was recognized together with an ordering of the first oxygen shell during the nucleation process.

We have investigated the role of zirconium, and also those of titanium and zinc in glasses of the same system, with a special attention to the very early stages of the nucleation process (17-18-22). Glasses of the Li₂O-Al₂O₃-SiO₂ system, known for their capability to give very fine glass-ceramics are also studied now; first results concerning this system are presented in this book and we will focus this paper on the first system.

In the case of titanium, it has already been said that the pre-edge structure clearly indicates a progressive change from a 4-fold coordination to a 6-fold one.
Analysis of the oxygen peak in EXAFS spectra is consistent with this direct information, showing an increase in the amplitude together with an increase in the mean Ti-O distance which becomes larger than any Ti-O distance in 4-fold coordination. More significant is the change in the next nearest environment. It is shown in Fig.5 by the successive Fourier transforms for the initial glass and at three stages of the nucleation process. The second peak (A), corresponding to the linking of Ti04 and Si04 tetrahedra by corners is progressively replaced by the peak B.

Figure 5 - Change in the Ti environment during the nucleation of a Mg-alumino-silicate glass (9 wt.% TiO2).

a: EXAFS signal; b: Fourier transform; c: backscattering amplitudes of the glass-constituting atoms.

At this point of the discussion, it seems necessary to precise the analysis that can be made of such a peak in a multicomponent material. The corresponding interatomic distance and the nature of the backscattering atom are correlated because the phase shift occurring in the scattering process (which shifts the peak in the apparent radial distribution from the actual atomic position) is atomic number dependent. It is then clear that an EXAFS contribution can be a priori interpreted by several "scatterer species + interatomic distance" hypothesis. Irrealistic distances often allow to exclude some solutions. Major help for making an unambiguous choice is brought up by the fact that the backscattering amplitudes also vary significantly along the periodic table. For titanium, at the last stages of the nucleation process, that insures the fact that second neighbours are light atoms (Al, Mg or Si). Joined to the distance information it gives a crystalline A12Ti05 phase as the most probable.

When the titanium environment seems to change directly from its situation in the glass to its crystalline final phase, the zirconium environment, on the contrary, shows a more complex evolution characterized by an intermediate stage before the final formation of tetragonal zirconia. In this latter stage zirconium atoms remain...
6-fold coordinated. The oxygen polyhedra share edges with SiO$_4$ tetrahedra (or AlO$_4$) and are thus in a situation similar to the empty sites forming channels in the "high -quartz" structure, which is the main phase observed in the further crystallization stages. This may be explained by the structural rearrangement of the glass caused by diffusion processes which occur during heating. The specific role of zirconium put in evidence by EXAFS consists in the formation of transient sites. These sites could induce the further crystallization of high-quartz. Zirconium atoms are finally found in tetragonal zirconia crystals and MET shows that these crystals grow without any definite structural relations with "high-quartz" crystals (18-22).

IV - DISCUSSION

X-ray absorption spectroscopy has two attractive qualities for the local atomic structure investigation of oxide (or halide, or nitride) glasses. The first one is its perfect atomic selectivity which makes it a tool exactly as performant, or not very performant, for the study of a given environment in a multicomponent glass or in a single-oxide glass. This remark remains true down to concentrations in the range 0.01 - 1.at.% depending on the relative atomic weights of the element under study and of the other components of the glass. This characteristic is very precious in those materials whose properties and applications generally lie on the keen influence of various atomic components present at relatively small concentrations and therefore inaccessible by non selective methods.

The second point lies in the complementary information that the near edge structure (XANES) may provide to the EXAFS analysis, particularly in insulating compounds, either crystalline or amorphous. The structures of the different parts of the edge region can be considered as probes of the chemical and structural state. They have principally been used with an empirical approach lying upon comparisons with known situations but theoretical treatments are now appearing. Examples have been given above and we only recall the typical points concerning the features which may exist at energy lower than the absorption jump, in the region of the absorption maximum or within a range of 50-100eV above the edge. At the K-edges of the 3d-transition elements the most informative edge feature is generally the "pre-edge" structure due to 1s (3d, p) transitions and which is well separated from the main absorption jump. It is very sensitive to the site geometry by crystal field effects and make available the determination of the coordination number, the regularity of the site etc.; for example the percentage of atoms of the absorbing species having two different coordination numbers can be measured due to the simply additive contributions of each type of environment to the "pre-edge" structure. The shape of the absorption maximum can also depend strongly on the type of coordination; this has provided the identification of 4-fold or 6-fold coordinated aluminum in a series of silicoaluminate glasses. The first calculations of the "near edge structures" up to about 100ev after the edge, taking account of the successive orders of multiple scattering processes are very promising, giving access to a partial information "beyond the radial distribution". It has been shown for example that the oxygen K-edge in the region of the absorption maximum is very sensitive to the angle between the two bonds of oxygen with its neighbours.

The joint measurements of absorption edges corresponding to different electronic transitions, such as the K- and L-edges of silver or the L- and M-edges of uranium may bring valuable precisions upon the electronic and structural state.

To come back to EXAFS and, now, to its limitations, the main problem arises from the intricate effects of high radial disorder which are mainly due to the absence of "pure EXAFS" information for low momentum photoelectrons. "Pure EXAFS" designs the structures which lead to a partial radial distribution by a Fourier analysis. High radial disorder means a radial distribution of such a broadness that scattering atoms, lying in different parts of this distribution, may give opposite contributions to the spectrum in its most significative parts and then may be completely lost in the experimental information. When this phenomena has a chance to occur, it is necessary to get accurate amplitudes of the EXAFS
oscillations in order to associate a measured number of scattering atoms to each absorber-scatterer distance determined by phase analysis. The number of atoms having given a contribution to EXAFS oscillations may represent only a part of the coordination shell. This EXAFS limitation shows clearly the advantage that can be taken from the edge structure examination when it leads to a direct and independent determination of the coordination number and therefore "controls" the EXAFS information.

As a direct consequence of the radial disorder effect the partial radial distribution given by EXAFS in oxide glasses is limited to the nearest plus, in good cases, a partial insight into the next nearest neighbours organization. In crystals it can go up to the third or fourth atomic shell, the limitation being then given by the small mean free path of the photoelectron.

The consequence of these qualities and limitations is that X-ray absorption spectroscopy is principally useful in multicomponent glasses to gain selective information relative to the various elements, information which is obviously imperfect but unapproachable by any other method. This has already been demonstrated in several cases. A striking result is the rather narrow radial distribution of the oxygen nearest neighbours around the elements playing an "intermediate" role such as transition elements. Original information of the organization around modifying elements have been obtained concerning sodium and calcium. The role of the nucleating elements at the early stages of crystalline nucleation have been partly understood in an alumino-silicate glass.

These studies have been very few until now; they are likely to be developed and to provide valuable information by taking advantage of the complementarity between the different parts of the absorption spectra and on the condition that the intrinsic limitations are properly taken into account.

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