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2009 J. Phys.: Condens. Matter 21 285104

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Influence of AlN, TiN and SiC reduction on the structural environment of lead in waste cathode-ray tubes glass: an x-ray absorption spectroscopy study

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Received 19 November 2008, in final form 5 May 2009

Published 17 June 2009

Online at stacks.iop.org/JPhysCM/21/285104

Abstract

This paper reports an x-ray absorption spectroscopy (XAS) analysis of the local structure around lead contained in foam glasses prepared with waste funnel cathode-ray tube glasses (CRT) and three reducing agents AlN, TiN and SiC. The XAS data were collected at the Pb-L_{III} edge to measure the influence of the reducing agent concentration on the unreduced lead content present in the glass. XANES spectra have been demonstrated to be a linear combination of both pure metallic lead and funnel glass spectra, with a significant modification of the funnel spectra for the highest contents of reducing agent. We have shown that the average coordination number of lead decreases in the case of TiN and SiC but remains constant in the case of AlN. The coordination number was found to be more affected for TiN than for SiC. Nevertheless, Pb–O bond lengths were determined to be constant close to 2.23 Å whatever the reducing agent and its content.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Due to their specific and interesting properties, lead silicate glasses are used in a wide range of industrial applications [1]. They are thus encountered in electrical and electronic equipment (EEE) and, more precisely, in cathode-ray tubes (CRTs). CRTs, which are found in TV sets and computer monitors, are composed of three glass components [2]. Two of them are lead silicate glasses and they are hidden inside the monitor and thus called the funnel and the neck. In contrast, the third one constituting the screen (or panel) is a barium–strontium-containing glass. Funnel composition has been demonstrated to be close to 0.520 (wt%) SiO₂—0.220 (wt%) PbO—0.260 (wt%) other oxides which were alkaline (K₂O, Na₂O), alkaline earth (MgO, CaO, SrO, BaO) or metal oxides (Al₂O₃, TiO₂, Fe₂O₃, ZnO and Sb₂O₃). Lead represents an amount of 2–2.5 at.% and it is used to absorb x-rays

emitted by the electron gun. The role of lead in silicate glasses has been studied by various authors [3–11]. At low concentration, it has been established that lead is a network former. Recently, an XPS/XAS combined study on waste CRT glasses has confirmed the role of lead in these glasses with complex formulation. Its coordination number is almost three and Pb–O bond length close to 2.23(1) Å [12]. As funnel glasses contain lead, they present an environmental risk and thus should not be placed in landfill within the European Union. Re-use solutions have been investigated and recycling glasses in cellular materials has appeared to be a promising solution [13–18]. Foam glasses are then synthesized from powdered waste funnel cathode-ray tube glasses mixed with different amounts of reducing agent such as SiC and TiN. The mixture is heat-treated to obtain synthesis conditions dependent on the considered macro/mesoporous material [16, 17]. Previous investigations have shown that,

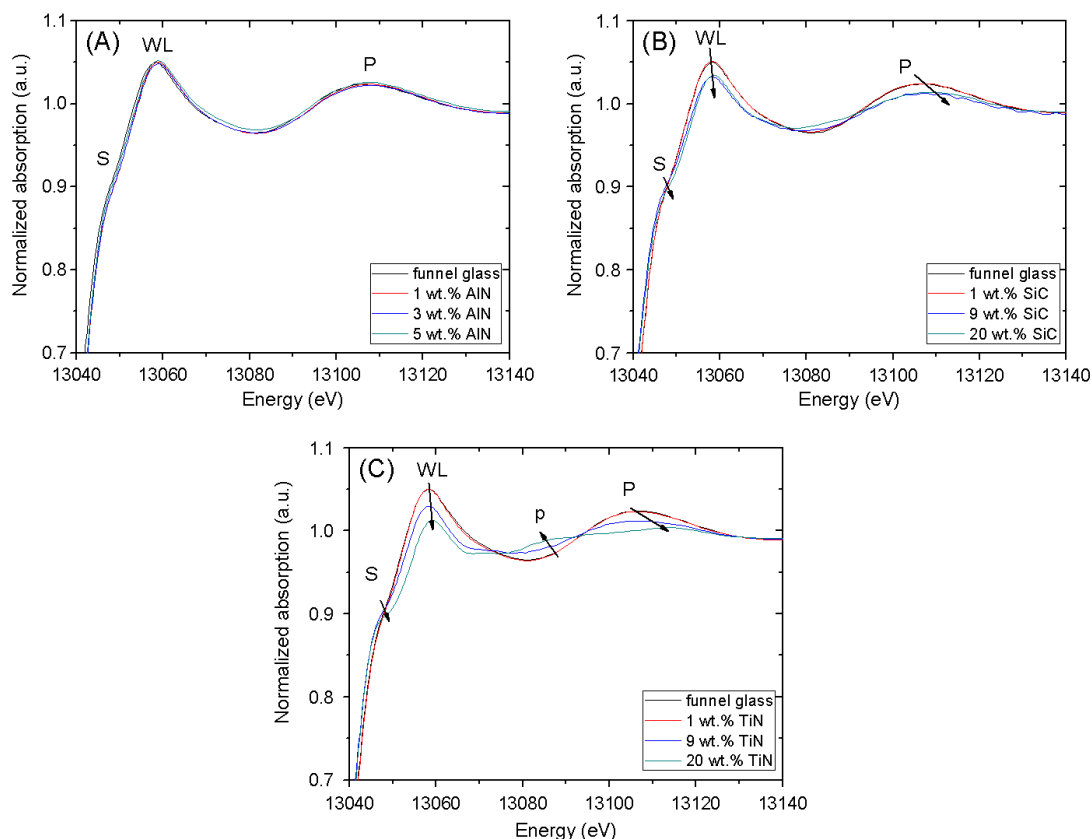


Figure 1. Normalized Pb-L_{III} XANES spectra for funnel glass and foam glasses elaborated with AlN (A), SiC (B) and TiN (C) compared to initial funnel glass [12].

in these systems, the reduction of lead(II) into metallic lead occurs as a result of the reaction between SiC, TiN and the lead oxide contained in the glass, generating carbon dioxide or nitrogen, respectively, within the framework [15]. Expansion is produced by gases (CO₂ or N₂) and a sample with cellular structure and metallic lead granules located on the pore (or cell) surfaces is obtained [17, 19]. Nevertheless, as far as we know, no particular work has been performed to study what occurs in the case of AlN. Méar *et al* has already shown that the reaction was less marked using AlN than using SiC or TiN [14]. For the first time, the influence of the reducing agent content on the local lead structure has been investigated by XPS [19]. This study has provided only trends concerning the local structure of nonreduced lead inside the foam glass. At this stage, the information available in the literature was rather scarce. Based on previous works of Witkowska *et al* [20, 21], XAS has been used to estimate the influence of the aforementioned reducing agent on the local structure around lead. The effect of both the nature of the reducing agent and its initial concentration on the local environment of lead is discussed in this paper.

2. Experimental details

Three different reducing agents (AlN, TiN or SiC) were used to prepare the foam glass specimen; three weight per cent contents were considered for the different reducing agents. The amount used were 1, 3 and 5 wt% AlN (Aldrich, 99%, particle

size $\leq 63 \mu\text{m}$) and 1, 9 and 20 wt% TiN (Alfa Aesar, 99.8%, particle size $\leq 10 \mu\text{m}$) and SiC (Aldrich, 99%, particle size $\leq 63 \mu\text{m}$). The funnel glasses used for the synthesis came from a Toshiba colour monitor whose composition was analysed previously [2]. The same glass has been used already to study the local structure around lead [12]. Funnel CRT glass powder with a defined granulometry ($\leq 65 \mu\text{m}$) was mixed with the reducing agents into a binder. Disc shape samples with a diameter of 40 mm and a thickness of 6 mm were prepared by uniaxial dry-pressing at room temperature into a steel die with a pressure of 5 tons. Expanded products in pebble form were obtained after a heat treatment at 850 °C for 60 min in an electrical furnace at air atmosphere. All samples were then removed from the furnace and were allowed to reach room temperature in ‘free fall’. The obtained samples were crushed and sifted to obtain another controlled particle size ($\leq 65 \mu\text{m}$) powder to carry out all the XAS measurements.

The x-ray absorption spectroscopy (XAS) data were recorded at the Dutch–Belgian beamline ‘DUBBLE’ (BM26A) at the European Synchrotron Radiation Facility (Grenoble, France). The electron beam energy of 6 GeV and an average beam current of 200 mA were used to record at least three numerical datasets for each sample. XAS spectra were recorded using the Pb-L_{III} (13 035 eV) in the transmission mode, with 0.04 Å⁻¹ steps in *k*-space using a double-crystal monochromator equipped with Si(111) crystals. The data acquisition time for one spectrum was about 40 min.

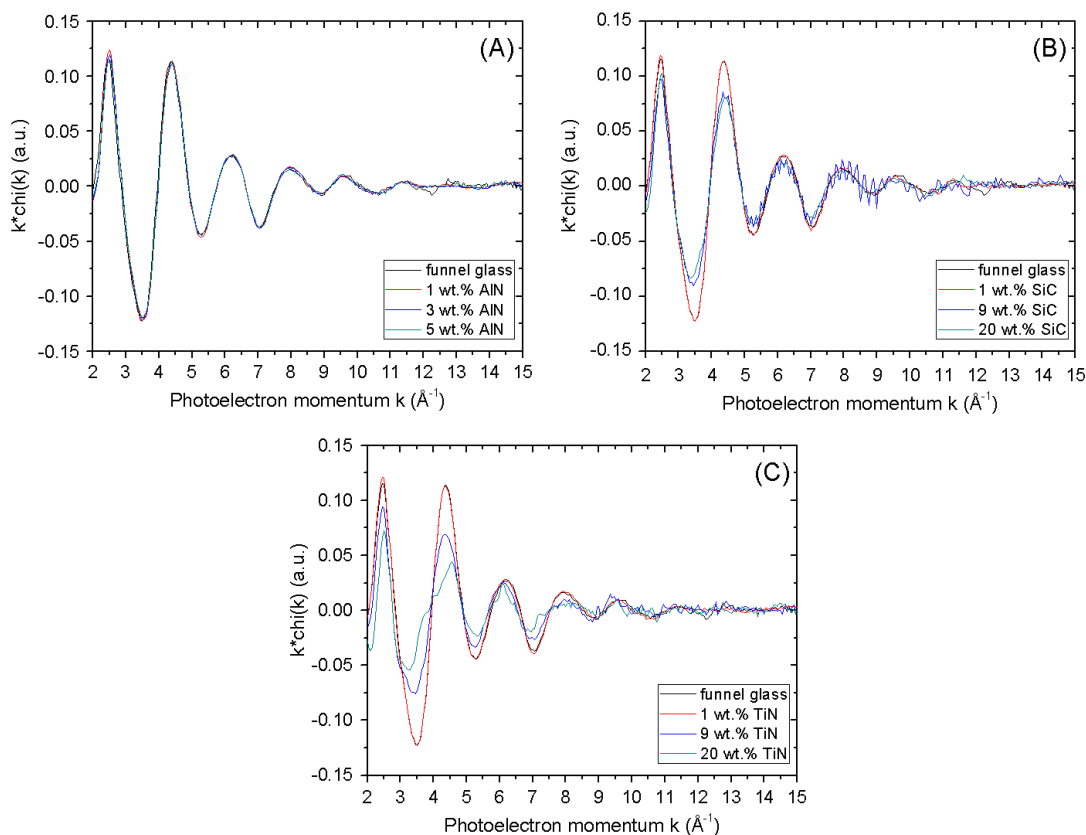


Figure 2. Typical $k \times \chi(k)$ obtained from Pb-L_{III} edges from AlN (A), SiC (A) and TiN (B) elaborated foam glasses.

All measurements were performed at room temperature on powdered samples conventionally mounted on thin tape.

In this work, the IFEFFIT [22, 23] package has been used to analyse the x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) parts of the spectra. XANES spectra were obtained using the Autobk algorithm [24] to remove the background and to normalize the absorption data while the energy of the absorption edge was calibrated to the atomic value of the edge, 13 035 eV. The k -weighted EXAFS oscillations were Fourier-transformed over the range of $2 \text{ \AA}^{-1} < k < 15 \text{ \AA}^{-1}$ and the phase shifts and amplitude functions were generated using the *ab initio* FEFF code [25–27].

3. Results and discussion

3.1. X-ray absorption near-edge structure

XAS spectra showing the influence of reducing agent content on the reduction process followed by the AlN (1, 3 and 5 wt%), SiC and TiN (1, 9 and 20 wt%) is presented in figure 1. To get a better overview of the reduction effect, each curve is compared to the one obtained in a previous work for the funnel glass used for the synthesis [12].

Some significant differences are observed for the three reducing agents. As can be observed, XANES fingerprints obtained in the case of the AlN-treated sample do not exhibit any significant deviations compared to those obtained for

Table 1. Relative positions of the peaks observed in XANES fingerprints for AlN-, SiC- and TiN-treated samples compared to pure funnel glass.

Compounds	Peak positions (eV)			
	S	WL	p	P
Funnel glass	13 047–13 048	13 058	—	13 105
AlN	13 047–13 048	13 058	—	13 105
SiC	13 047–13 048	13 058	—	13 105–13 113
TiN	13 047–13 049	13 058–13 059	13 088	13 105–13 120

funnel glass (figure 1(A)) whatever the aluminium nitride content. This first observation is then consistent with XRD measurements previously reported elsewhere [14]. In contrast with SiC and TiN, the spectra obtained for the glass structure are modified (figures 1(B) and (C)). The observed modifications are more important in the case of TiN than for SiC, as shown in figures 1(B) and (C). They correspond to some changes in the peak heights and positions depending on the silicon carbide and titanium nitride content. Table 1 summarizes the relative positions of the peaks observed on the XANES curves.

Increasing the concentration of SiC or TiN leads to the emergence of a shoulder (S in figure 1(C)) around 13 047 eV. The height of this shoulder is more important for TiN than for SiC and it is clearly linked to the metallic lead content since it is characteristic of the near-edge region of pure fcc lead. One can clearly see that the intensity of the ‘white line’

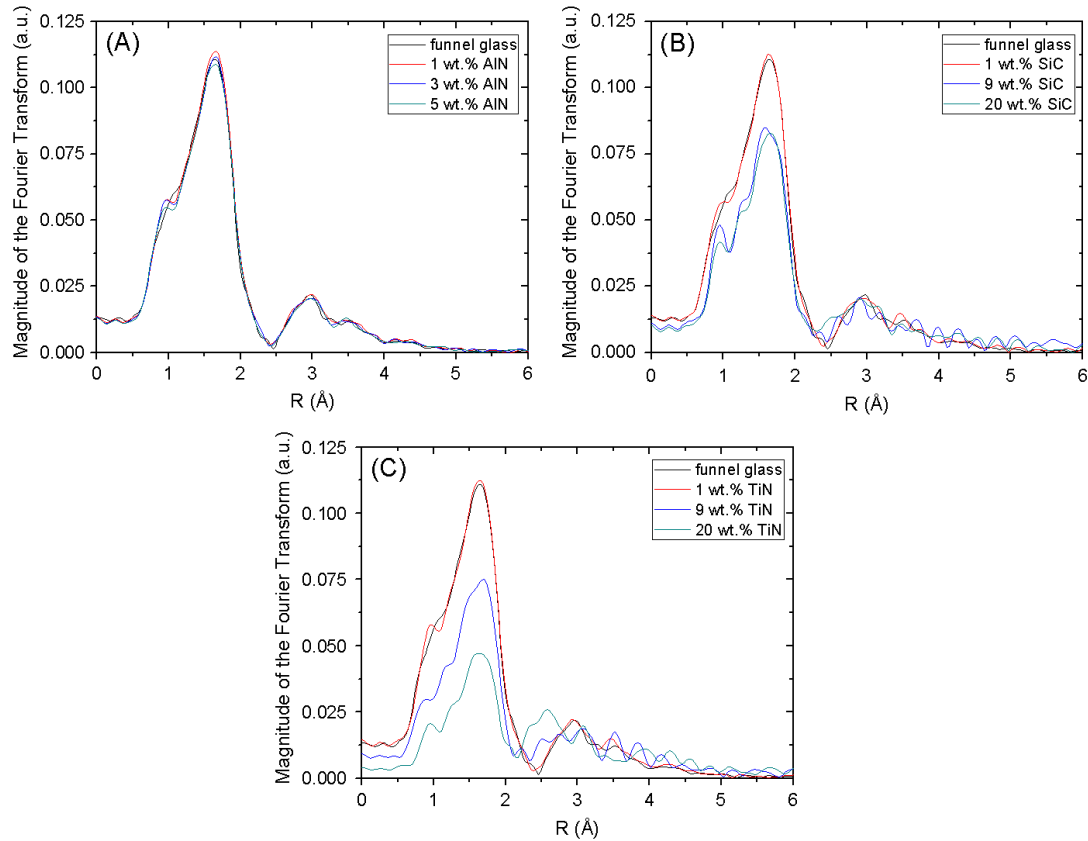


Figure 3. Magnitude of the Fourier transform (FT) of the k -weighted Pb–L_{III} edge $\chi(k)$ from AIN (A), SiC (B) and TiN (C) synthesized foam glasses.

Table 2. Results of the EXAFS fitting procedure for the funnel and the foam glass samples.

Compounds	$N \times S_0^2$	N (with $S_0^2 = 0.75$)	R (Å)	ΔE_0 (eV)	δR (Å)	σ^2 (Å ²)	r -factor
Funnel glass	2.25(1)	3.0(1)	2.23(1)	−0.86	0.0099	0.0060	0.014
AIN	1 wt%	2.27(1)	3.0(1)	2.23(1)	0.0081	0.0059	0.013
	3 wt%	2.26(1)	3.0(1)	2.24(1)	0.0174	0.0062	0.007
	5 wt%	2.22(1)	3.0(1)	2.23(1)	0.0131	0.0061	0.011
SiC	1 wt%	2.17(1)	2.9(1)	2.22(1)	−0.0032	0.0056	0.032
	9 wt%	1.72(1)	2.3(1)	2.23(1)	0.0112	0.0061	0.010
	20 wt%	1.58(1)	2.1(1)	2.23(1)	0.0061	0.0054	0.018
TiN	1 wt%	2.28(1)	3.0(1)	2.24(1)	0.0322	0.0062	0.011
	9 wt%	1.55(1)	2.1(1)	2.26(2)	0.0421	0.0059	0.006
	20 wt%	0.84(1)	1.1(1)	2.25(1)	0.0295	0.0048	0.038

(WL in figures 1(B) and (C)), decreases and shifts towards higher energies (≈ 1 – 2 eV) when the SiC and TiN content increases. Such behaviour has already been observed in the case of reduction of both Ag oxides [28, 29] and lead silicate glasses [20, 21]. In addition, the peak (P) is also affected by the reducing agent content that corresponds to a decrease in height and a shift towards the higher energies which gives flatter spectra. Moreover, for the higher content of TiN, we note the existence of an additional peak (p) in figure 1(C) in the energy range. Increasing the TiN content leads to a spectrum which resembles more and more the pure lead one. It can be observed from those observations that the reduction of lead(II) is more efficient for an SiC and TiN content higher than 1 wt%. Based on these conclusions, the increase of

the shoulder combined with the decrease of the ‘white line’ is the result of the reduction of lead(II) and, by the way, an increase of the lead(0) content inside the material. The same explanation could be given regarding the shift to higher energies of the third peak. These observations are in agreement with those previously made by Witkowska *et al* [20, 21]; where lead reduction by hydrogen was of interest.

3.2. Extended x-ray absorption fine structures

EXAFS analyses were performed to extract the interference function $\chi(k)$. Figure 2 shows the so-obtained $k \times \chi(k)$ for each sample.

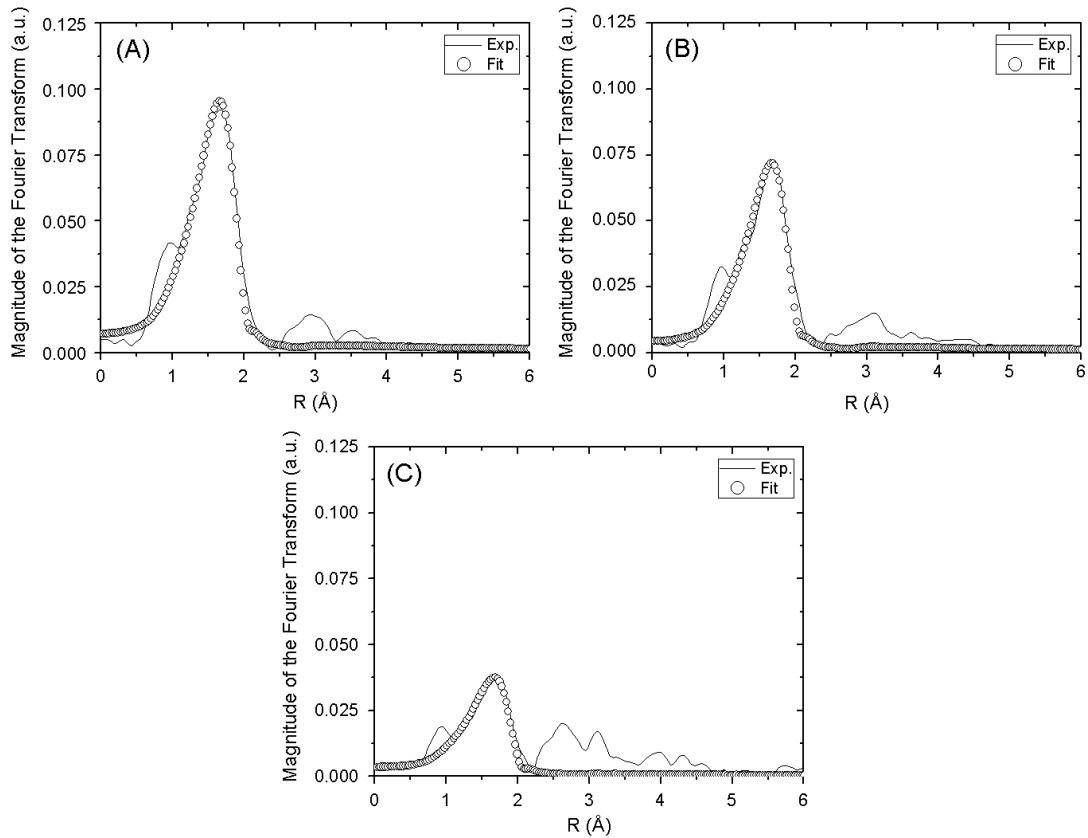


Figure 4. Magnitude of the Fourier transform (FT) (line) and result of the fit (circle) of the k -weighted Pb-L_{III} edge $\chi(k)$ from AlN 5 wt% (A), SiC 20 wt% (B) and TiN 20 wt% (C) synthesized foam glasses.

A significant modification of the interference functions appears for specimens prepared from SiC and TiN, whereas no changes are observed in the case of samples prepared with AlN. The extracted EXAFS interference functions were Fourier-transformed to extract the radial distribution functions (RDFs). Figure 3 shows the magnitude of the Fourier transforms of the EXAFS spectra for AlN-, SiC- and TiN-treated funnel glass.

The peaks in the RDFs correspond to the atoms surrounding lead. The first peak corresponds to the pair lead–oxygen. The low R shoulder appearing near 1 Å is a Fourier-transform artefact due to the EXAFS background removal procedure. A significant decrease of the height of the first peak of the RDF is observed in the case of SiC- and TiN-treated samples whereas its height remains constant in the case of AlN-treated samples. As the height of the peaks is directly proportional to the number of surrounding oxygen atoms, it suggests an important modification of the local structure around lead on increasing the reducing agent amount. The fitting procedure was performed in R -space using paths generated by FEFF. ΔE_0 was held constant in the fit and was previously determined from the fit of funnel glass. The fit is of good quality as can be seen in figure 4. The results of the fitting procedure are given in table 2.

One can clearly see that the average Pb–O distances (R) were found to be close to ≈ 2.24 Å, and are not affected by the reducing agent content (table 2). The lead–oxygen distances were found to be in the same range as those reported

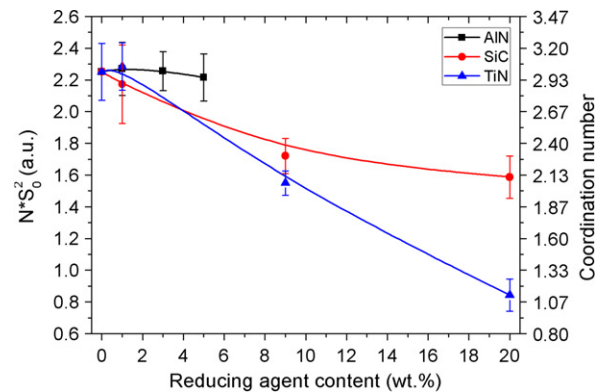


Figure 5. Evolution of the average coordination number of Pb–O as a function of the reducing agent content.

in our previous work carried out on funnel glass [12]. They are also close to the typical distance found in lead-containing glasses [30, 31]. Pb–Pb distances have been estimated close to 3.55(1) Å by fitting the RDF obtained for 20 wt% of TiN where a broad peak is present around 3 Å. The Debye–Waller factor (σ^2) was found to be constant (≈ 0.006 Å²) and close to the value found for the funnel glass. EXAFS amplitude is proportional to a product of the coordination number (N) and the amplitude reduction factor S_0^2 , which values are typically in the range 0.7–0.8 [32]. Hence, S_0^2 has been fixed at 0.75

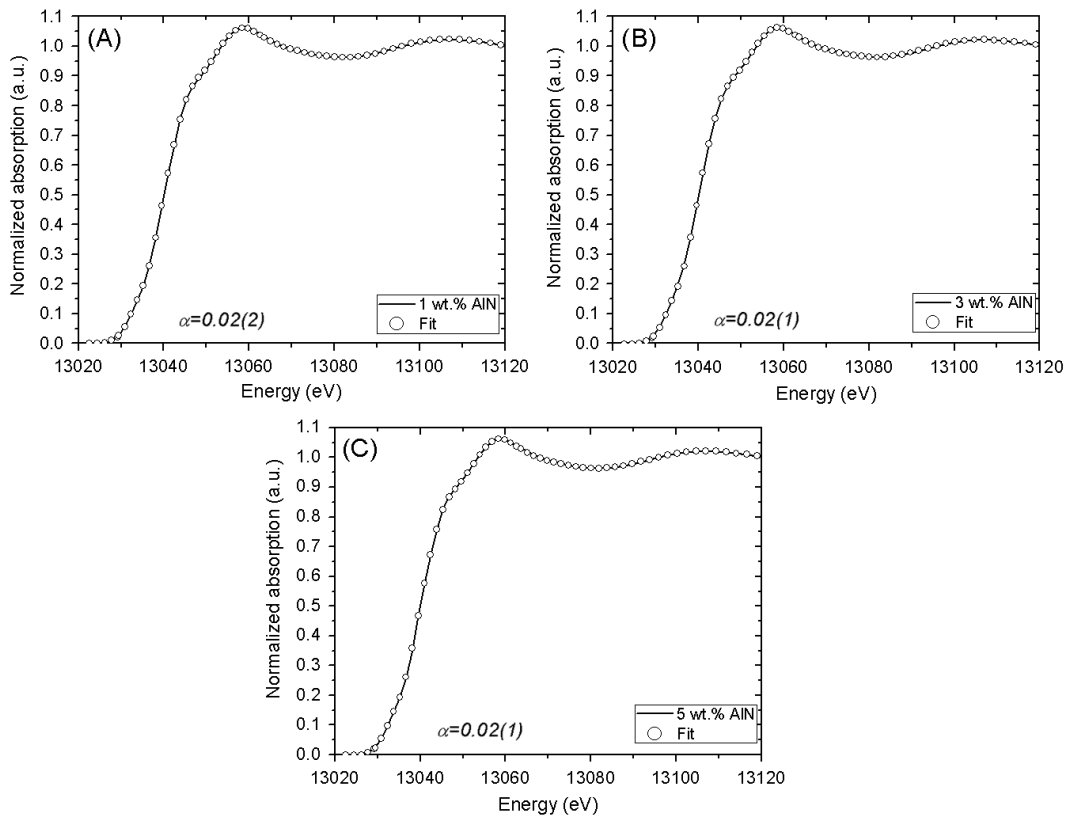


Figure 6. Results of the linear combination analysis for samples with various AlN contents (1 wt% (A), 3 wt% (B) and 5 wt% (C)).

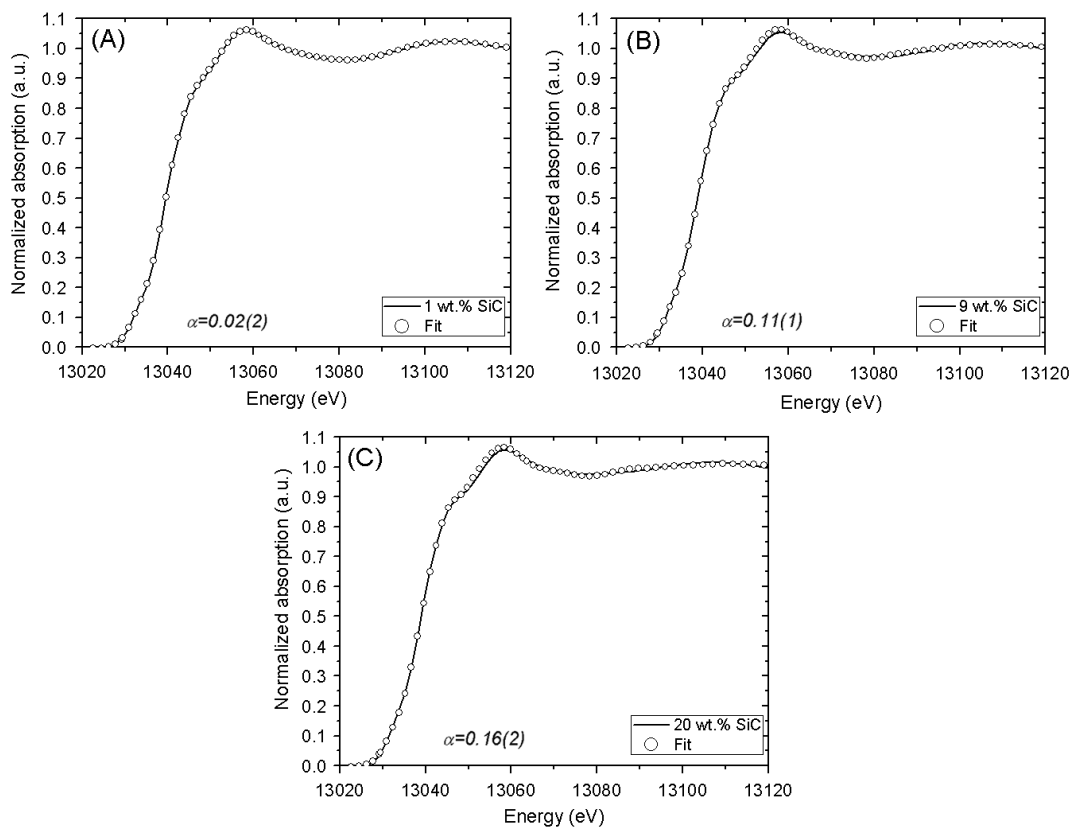


Figure 7. Results of the linear combination analysis for samples with various SiC contents (1 wt% (A), 9 wt% (B) and 20 wt% (C)).

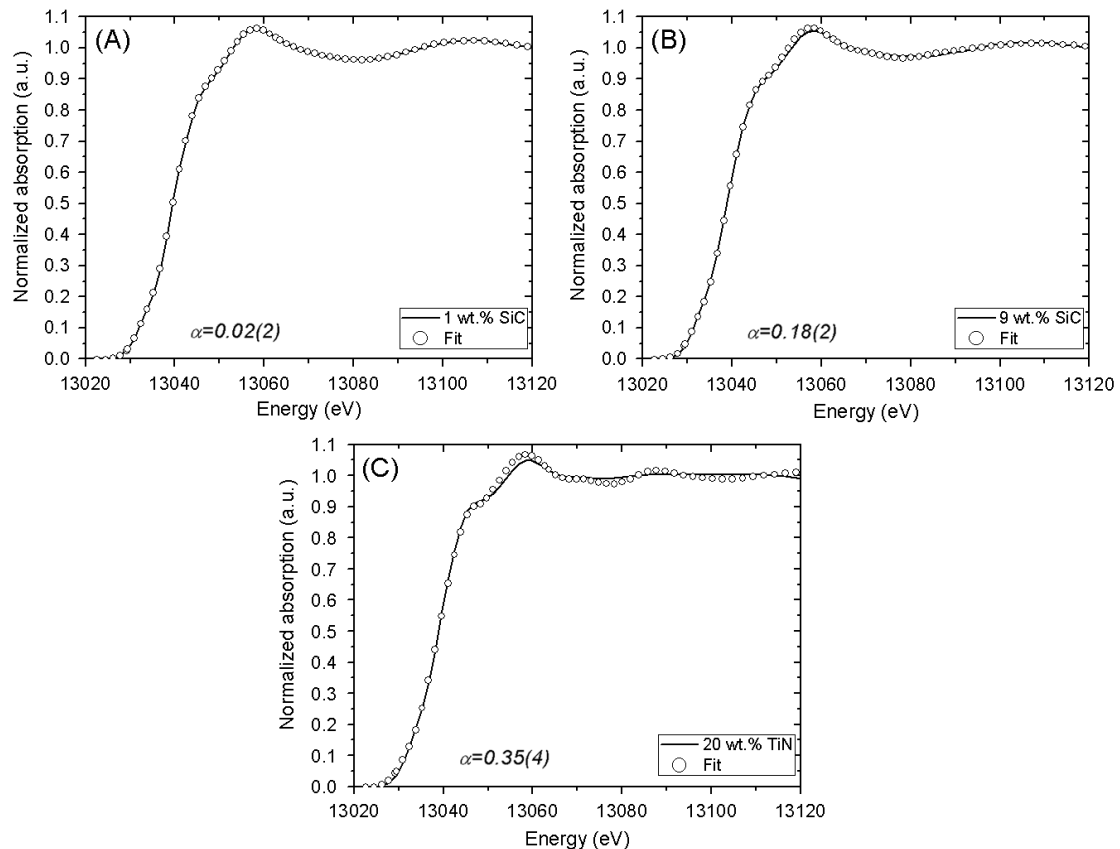


Figure 8. Results of the linear combination analysis for samples with various TiN contents (1 wt% (A), 9 wt% (B) and 20 wt% (C)).

and used to determine the coordination number. Figure 5 summarizes the evolution of the coordination number as a function of the reducing agent content.

The Pb–O partial coordination number was found to be around three and remained constant for the three AlN contents. A small amount of lead extracted from the glassy matrix is not enough to induce a change in the role of lead ions inside the unreduced glass. In contrast, the coordination number is strongly affected in the case of SiC and TiN. As can be seen, the coordination number is divided by two and near by three in the case of samples treated by SiC and TiN, respectively. As already observed by some authors in previous similar work [30, 31], this behaviour corresponds to a strong modification of the lead–oxygen unit inside the glass. This observation suggests that the PbO₃ units found in the initial funnel glass disappear for the high reducing agent contents. In a previous work, x-ray photoelectron spectroscopy has partially shown a possible modification of the local structure of unreduced lead inside similar materials [19]. EXAFS has demonstrated both the influence of lead reduction and extraction from the glass elaborated with SiC and TiN and the change of the role of the unreduced lead.

3.3. Discussion

As already mentioned, two phases were encountered in the samples: metallic lead granules and an unreduced lead-containing glassy phase. Hence, the absorption spectra

were supposed to be the result of two contributions: one corresponding to the absorption spectra of the unreduced lead inside the glass and the other one corresponding to the absorption spectra of the metallic lead inside the material [20]. These experimental spectra were fitted using a linear combination of metallic lead (obtained using the FEFF code) and an experimental funnel glass spectrum: $\mu(E) = \alpha \times \mu(E)_{\text{Pb}} + (1 - \alpha) \times \mu(E)_{\text{Funnel}}$ (α corresponding to the contribution of metallic lead spectrum). Figures 6, 7 and 8 show the fits of the experimental XANES curves obtained with the Athena linear combination analysis for the various reducing agents and contents.

Regarding the foam glasses synthesized with AlN, the obtained value of α was found to be constant and close to 0.02 (figures 6(A)–(C)). This result is then consistent with the EXAFS result and clearly emphasizes the nonreduction of lead and then the absence of modifications in the local structure around lead in this case: the coordination number remains close to three and Pb–O distance near 2.23 Å. Indeed, for SiC- and TiN-based foam glasses if the obtained fits in the case of 1 wt% are rather good and similar to those obtained previously in the case of AlN (figures 7(A) and 8(A)), showing then few modifications of the lead environment for the lowest contents of SiC and TiN, according to EXAFS results. On the difference, the fits carried out are not completely satisfactory and reveal some strong differences as is seen in the cases of 9 and 20 wt% for SiC and TiN (figures 7(B) and (C) and 8(B) and (C)).

As can be observed, the contribution of the lead spectrum (qualitatively given by the α value) increases with the reducing agent which reveals a lead extraction from the initial glass.

The small deviations in the XANES fitting could be explained taking into account three points: (i) the spectrum used for lead is a theoretical one calculated with FEFF; those observed should be more attributed to a strong modification of the photoabsorber neighbourhood; (ii) the metallic lead granules are finite (a few micrometres [15, 19]) and (iii) lead particles contained inside the foam glasses are located on the surface of the pores and then have oxygen atoms in their neighbourhood [21].

4. Conclusions

The aim of this work was to determine the influence of three reducing agents on the local structure around lead in waste funnel CRT glasses. X-ray absorption spectroscopy data were collected for various AlN, SiC and TiN contents. The changes in the XANES spectra have been demonstrated to be induced by the lead reduction by the different reducing agents. For all the studied cases, the average lead–oxygen bond length has been found to be close to 2.23(1) Å and not affected by the reaction of reduction. No changes in the Pb atoms' environment were observed with AlN-treated glass. The coordination was found to be almost three, similar in the initial funnel glass. In contrast, a significant decrease of the coordination number was found using SiC and TiN and thus the disappearance of PbO₃ units inside the unmodified glass component. The greater the reducing agent content is, the lower the lead oxygen average coordination number is and the greater the unreduced lead local environment is modified. This point emphasizes the change of role of lead inside the glassy matrix related to the decrease of its concentration.

Acknowledgments

Financial support from the French Ministry of 'Recherche et Technologie' and the French 'Association Nationale de la Recherche Technique' is gratefully acknowledged. The authors are grateful to IBM Corporation (Montpellier, France) and APF Industries (Montpellier, France) for their collaboration. Beamline BM26 'DUBBLE (Dutch–Belgian beamline)' at the European Synchrotron Radiation Facility in Grenoble (France) is acknowledged for allowing beam time. The authors greatly acknowledge also Drs A V Kolobov and P Fons (CAN-FOR, AIST Tsukuba, Japan) for useful discussions.

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