Laboratori Nazionali di Frascati

LNF-87/69

G. Dalba, P. Fornasini, F. Rocca, A. Krajewski, A. Ravaglioli and E. Burattini:
XAS STUDIES ON THE ROLE OF THE ALKALINE ION IN A LEAD-GLAZE SYSTEM

Estratto da:
SIF - Conf. Proc. "Synchrotron Radiation at Frascati" Vol. 5, 119 (1986)

Servizio Documentazione
dei Laboratori Nazionali di Frascati
P.O. Box, 13 - 00044 Frascati (Italy)

XAS STUDIES ON THE ROLE OF THE ALKALINE ION IN A LEAD-GLAZE SYSTEM

G.Dalba[xo], P.Fornasini[xo], F.Rocca[o], A.Krajewski[+], A.Ravaglioli[+] and E.Burattini[*]

(x) Dip. di Fisica, Universitã di Trento, 38050 Povo, Italy
(o) Centro CNR di Fisica degli Stati Aggregati e Impianto Ionico, 38050 Povo, Italy
(+) Istituto di Ricerche Tecnologiche per la Ceramica del CNR, 48018 Faenza, Italy
(*) INFN, Laboratori Nazionali di Frascati, 00044 Frascati, Italy

Introduction

Lead-glazes are glassy systems of many oxide components (SiO_2, Al_2O_3, ZnO, CaO, B_2O_3, PbO and M_2O, where M^+ is an alkaline cation), mainly used for coating pottery[1,2].

The main problem is that of the Pb^{++} stability, since it may be released by the glassy system when this one enters in touch with acid or basic substances.

It was experimented in the past that changing the type of the alkaline cation the amount of Pb^{++} released (following ASTM) changed. This was attributed to the formation of an elastic stress at molecular network level, due to the different dimension of every specific cation. It was hypothesized that such stress would involve mainly the network modifiers (Zn^{++}, Pb^{++}, Ca^{++}, M^+). The coordination field involving oxygen atoms of alkaline and earth-alkaline cations (Ca^{++}, M^+) was considered, as a first approximation, sufficiently defined and stable with respect to the other two. Zn and Pb may be considered as more "plastic", in the sense that they easily adapt themselves to different kinds of ligand fields. It is reasonable to ascribe the network stress to modifications of the lengths and angles in the cation-oxygen bonds. Furthermore such stress may consist in rearrangements of bridging and non-bridging oxygen atoms in order to give rise to useful connections when changes in coordination number and/or steric adjustements of particular atoms occur. In this work these atoms are Rb^+ and Na^+.

Moreover it has been measured that tha Pb^{++} release increases by doping the glazes with few percent of an oxyde cromophore like CuO, or Cr_2O_3

In view of the high number of different components, XAS is particularly suited to study the environments of selected atomic species.

The measurements have been performed at the wiggler facility in Frascati. Room temperature EXAFS spectra at the L_3 edge of Pb and at the K edge of Zn have been measured on four different glasses containing as modifier oxides respectively Na_2O, Na_2O and CuO, Rb_2O, Rb_{20} and CuO.

Results and discussions

In this work we present preliminary results of EXAFS analysis at the L_3 edge of lead utilizing PbO (red) as model compound. In PbO (red), lead has 4 oxygen atoms as nearest-neighbours at the same distance: so we have been able to extract the experimental phaseshift and amplitude for the Pb-O coordination without multiple shell components.

Experimental $K^* \chi(k)$ signals for the measured samples are shown in Fig. 1.

The Fourier transform analysis of the EXAFS spectrum of the PbO (red) shows two well defined peaks corresponding to the Pb-O shell (with 4 oxygens at 2.32 Å) and to the Pb-Pb shell (with 12 Pb atoms at distances varying from 3.69 Å to 3.98 Å).

For the glasses,on the other hand, only the Pb-O peak is well defined. At the higher distances it is possible to evidenciate some differences between the glasses containing Rb_2O and those containing Na_2O.

A more accurate quantitative analysis is in progress.

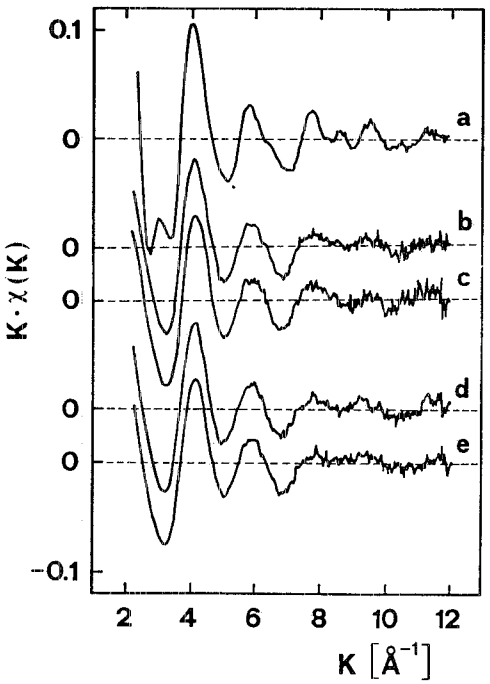

Fig. 1 - Experimental EXAFS signal of red PbO(a) and glasses with different modifier oxides: Na_2O(b), Na_2O and CuO(c), Rb_2O(d), Rb_2O and CuO.

In order to check the differences in the first coordination shell of Pb due to the change of the modifier oxide we have analysed the back-transformed signal by a standard fitting procedure.

A typical one-shell bestfit, having a reliability factor $R < 3\%$, is shown in Fig. 2 for the glass containing Na_2O as modifier (glass FB4 in ref.(1)).

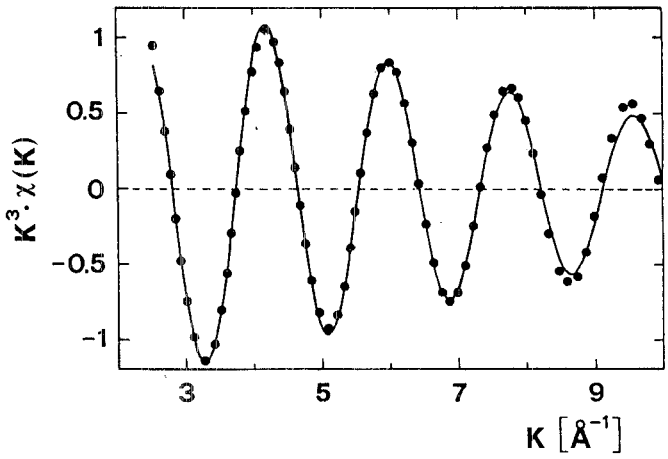

Fig. 2 - Bestfit of backtransformed EXAFS signal for glass with Na_2O as modifier oxide.

The Pb-O distance for the four glasses examined is 0.02-0.04 Å greater than for PbO.

The coordination numbers vary from 2.8 to 3.2, indicating that the average first shell number of oxygen atoms is lower in the glasses than in PbO.

The study is in progress in order to correlate this low coordination number with structural models[2,3] that hypothesize modifications of the Pb-O bonds when changing the oxide modificators.

Further EXAFS measurements on the K edges of Zn and Cu should be performed, aiming to analyse the coordination of as many atoms as possible for a more general comprehension of this complex system.

References:

(1) C.B.Azzoni, G.L.Del Nero, A.Krajewski and A.Ravaglioli, J. Mat. 15, 646 (1980).
(2) C.B.Azzoni, G.L.Del Nero, A.Krajewski and A.Ravaglioli, J. Mat. Sci. 16, 1081 (1981).
(3) C.H.L.Goodman, Phys. and Chem. of Glasses 26, 1 (1985).