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

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ABSTRACT - The influence of the local coordination on the Pb^{++} mobility has been studied by EXAFS in Lead-glaze systems with different modifier oxides. The interatomic distances and coordination numbers obtained are quite the same for all considered glazes. The different Pb^{++} mobilities cannot be related to different elastic stresses of the Pb-O bond.

INTRODUCTION

Lead-glazes are glassy systems of many oxide components mainly used for coating pottery [1,2]. The changes in composition influence particularly the stability of the Pb^{++} ions, that may be released by the glassy system when this one enters in touch with acid or basic substances. This effect may be related to various characteristic properties of single ions constituents of glazes. In particular dimensions, polarizability, electronic levels and ligand orbitals are to be carefully examined and experimentally tested.

Among the different network modifiers, the earth-alkaline cations are to be considered, as a first approximation, sufficiently defined and stable with respect to their coordination to oxygen atoms of the matrix. Zn^{++} and Pb^{++} are more "plastic", in the sense that they easily adapt themselves to different kinds of ligand fields.

A simple model for explaining the Pb^{++} mobility is to hypothesize an elastic stress at molecular network level, due to the different dimension of every specific cation.

It is reasonable to describe such network stress with 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 adjustments of particular atoms occur.

EXPERIMENTAL

The lead-glazes were prepared as indicated in previous works [1,2]

with compositions shown in table 1. In this work we analyze five different samples: A = crystalline red PbO as model compound; B = glaze with Na⁺ as alkaline cation; C = same as B with addition of 2% of CuO; D = glaze with Rb⁺ as alkaline cation; E = same as D with addition of 2% of CuO.

TABLE 1.

Normalized molar amounts of the cations present in the cited glazes. M⁺ is the symbol that indicates the specific alkaline ion.

Cat.	Si ⁴⁺	Al ³⁺	B ³⁺	Pb ²⁺	Zn ²⁺	Ca ²⁺	M ⁺
FBX	0.50755	0.11683	0.15590	0.05850	0.02961	0.07844	0.05317

For these glassy samples the Pb⁺⁺ release (measured following ASTM) is different: it changes from 16 ppm for glaze B to 60 ppm for glaze C and from 50 ppm for glaze D to 440 ppm for glaze E.

This difference may be related both to the ionic radius (0.97 Å for Na⁺ and 1.47 Å for Rb⁺) [3] and the polarizability of the alkaline ions (0.24 10⁻²⁴ cm³ for Na, 1.50 10⁻²⁴ cm³ for Rb) [4].

In order to check the hypothesized differences in coordination or in bond-length of the Pb⁺ ions EXAFS and XANES measurements were performed at the L₃ edge of Lead.

The samples were powdered and deposited on a Millipore filter in a conventional way.

The measurements were made at the Wiggler source of ADONE in Frascati. Red PbO was utilized as model compound: since the first coordination shell of Lead, formed by four oxygens symmetrically disposed at the basal vertices of a square-pyramid, is well defined, we could extract the experimental scattering phaseshift and amplitude for the Pb-O couple.

RESULTS

Experimental $K * X(k)$ signals for the measured samples are shown in figure 1. The EXAFS of the four glazes look very similar, with a single frequency and nearly equal amplitude. The Fourier transformed signals are shown in figure 2. The FT of PbO shows two different peaks, the first one corresponding to the Pb-O nearest distance of 2.32 Å the second one to the Pb-Pb and Pb-O distances for the other shells (there are 12 Pb atoms at distances varying from 3.69 Å to 3.98 Å). For the glazes, on the contrary, only the Pb-O peak is well defined, slightly lower than in the model compound. At higher distances from Pb the only significative structure is the peak centered at 3 Å present in both the glazes with Rb as alkaline cation, not detectable in other two samples. The height of this peak is anyway comparable with the background: any physical interpretation is thus not sure. The backtransformed signals of Pb-O first coordination shell have been analyzed by a standard bestfit procedure to extract more refined quantitative information. Results are summarized in table 2. A typical one-shell bestfit in the range 3.5 ÷ 10 Å⁻¹ is shown in figure 3.

The good reliability factor (last line in table 2.) for all the samples evidenciates the presence of a single distance Pb-O in the first coordination shell. Two-shells bestfits don't improve the reliability factor nor modify the results for any glaze. Note the small but progressive increase of the Pb-O distance from crystalline PbO to glazes with Na to glazes with Rb. The coordination number for the glazes is always lower than 3.5 (the small fluctuations are to be correlated with the fluctuations in the $\Delta\sigma^2$ values) with respect to N=4 of the model compound.

TABLE 2.

SAMPLE	B \Rightarrow Na	C \Rightarrow Na+2%CuO	D \Rightarrow Rb	E \Rightarrow Rb+2%CuO
N	3.4	3.2	3.1	3.4
r [Å]	2.34	2.34	2.36	2.36
$\Delta\sigma^2$	0.001	0.0005	0.0005	0.002
R%	1.7	2.3	3	2.5

DISCUSSION

In spite of the different Pb^{++} release ratios shown by these 4 glazes, the first coordination shells of Pb are nearly equal. This experimental result evidenciates that the differences in elastic stress hypothesized to explain the different Pb^{++} mobilities do not involve the nearest Pb-O bonds.

The coordination number lower than in PbO indicates that about 75% of Pb ions are threefold coordinated to oxygen. Assuming a hybridization sp^3 or sd^3 for the molecular orbitals, we may hypothesize a lone pair orbital at a vertex of a distorted tetrahedron. This orbital may be influenced by the presence of different modifier cations in the glazes. This may result in a general strenghtening or weakening of molecular bonds around the Pb.

A preliminary analysis of the XANES structures confirms the difference in coordination and symmetry between PbO and glazes, and the similarity of all the considered glazes.

Further EXAFS measurements on Cu and Zn edges are in progress aiming to evaluate the differences in the second coordination shell of Pb or, more generally, in the glass network .

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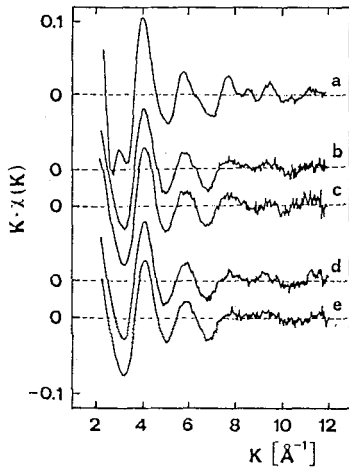


Fig.1 - Experimental EXAFS signals for:
 a) the model compound red PbO ;
 b) the glass with Na^+ alkaline cations;
 c) the same with 2% CuO ;
 d) the glass with Rb^+ alkaline cations;
 e) the same with 2% CuO .

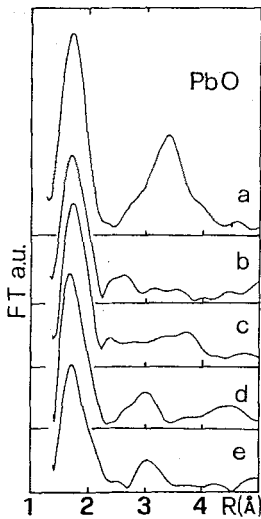


Fig.2 - Modulus of Fourier transform for:
 a) red PbO ; b) glass with Na^+ ;
 c) the same with 2% CuO ; d) glass with Rb^+ ;
 e) the same with 2% CuO .

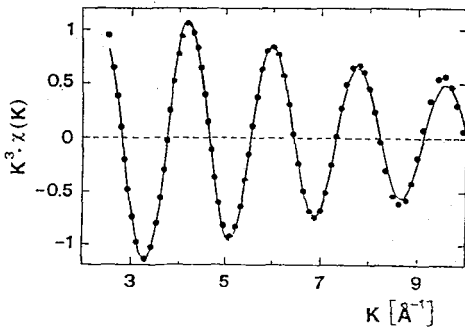


Fig.3 - EXAFS signal of the first coordination shell (continuous line) and best fit (dots) for the glass containing Na^+ alkaline cations.