

COORDINATION ENVIRONMENT OF LEAD IN COLOURED GLAZES FROM ANCIENT TILES: AN EXAFS APPROACH THROUGH THE Pb L_3 -EDGE

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High-lead soda-lime glazes used to decorate ancient ceramic tiles (Portuguese manufacture, XVI-XIX centuries) incorporate a diversity of cations [1] that modify various fundamental properties of the glassy matrix, particularly transparency and coloring.

Lead has been studied in these materials by XANES at the L -edge to understand its role within the tetrahedral silica framework. The metal ion Pb^{2+} was found to be incorporated in the glassy matrix as a network modifier, whatever the glaze colour [2].

An EXAFS study at the Pb L_3 -edge was also undertaken to ascertain the coordination environment and mean Pb–O distances in those ancient tile glazes. Spectra were collected with synchrotron radiation using the instrumental set-up of beamline BM-29 at the ESRF, in Grenoble, dedicated to XAFS experiments. Irradiated samples were small tile glaze fragments (brown and yellow).

Collected data was deconvoluted with IFEFFIT program [3] and EXAFS spectra simulations were performed using the FEFF8 code [4].

The crystal structure of $PbTiO_3$ was used for the theoretical simulation of Pb L_3 -edge EXAFS spectra. Ideally, the cubic perovskite-type structure with space group $Pm\bar{3}m$ implies a cuboctahedral coordination (CN 12) of the large cation by oxygen and a regular octahedral coordination for the small cation; however, in the case of lead titanate, the crystal structure is distorted to tetragonal symmetry (space group $P4mm$) and the Pb^{2+} ion assumes a less regular environment, more favorable to accommodate the lone-pair of $6s^2$ electrons.

Fitting results corroborate a high coordination number for the first shell of oxygen atoms around Pb^{2+} ions in all studied glazes, with a good approximation to the distorted polyhedron observed for lead in the chosen model compound.

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