

Extended vs. Local Structure in Sb-Pyrochlores: An Illustration of the Valuable Interplay between Crystallography and XAFS

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Abstract. The convergence between extended structure provided by X-ray diffraction and local structure of antimony extracted from spectroscopic data is reached through an alternative crystallographic description for a Sb-pyrochlore arrangement within the same space group symmetry of pyrochlore structure-type. A full account on this description is presented, along with a calculated diffraction pattern matching experimental data and conforming to Sb 1s XANES data.

Keywords: Pyrochlore structure-type; antimony; XANES; cation disorder.

PACS: 61.10 Ht; 61.10 Nz; 61.50 Ah; 61.66 -f.

INTRODUCTION

Great interest has been focused on antimony oxides in the domain of ancient cultural materials because of metal speciation in relation to colour and its dependence on crystal structure [1]. Recently, very important ion exchange properties of Sb-pyrochlores were pointed out [2], turning Sb-oxides into a research target within materials in general.

Most of these oxides occur naturally as yellow minerals and display a variety of structural arrangements resulting from two stable Sb speciations: cervantite (orthorhombic) with Sb^{3+} in a pyramidal environment (coordination number, CN, 3) and Sb^{5+} in octahedral coordination; valentinite (orthorhombic but white) and the dimorphous mineral senarmontite (cubic, yellow), both also containing Sb^{3+} in pyramidal coordination, now with CN 4; finally, the very rare mineral stibiconite with octahedral Sb^{5+} ions within a pyrochlore-type atomic arrangement [3] and $\text{Sb}_3\text{O}_6\text{OH}$ as approximate chemical formula.

A recent Sb K-edge XANES study on from yellow glazes in majolica-type ancient tiles has disclosed the possibility of a Sb-pyrochlore alone being the ultimate responsible for colour [4], thus recalling the problem of antimony pyrochlores. An analysis is herein presented on the two possible crystallographic descriptions for a pyrochlore-type array under the usual cubic space group that could account for an anomalous increase in intensity of the 111 reflection

for a Sb-pyrochlore and simultaneously correlate very well with XANES data collected from the glaze.

The obtained results clearly emphasize the unique contribution of XAFS to the success of the crystallographic modelling in relation to the diffracting pyrochlore phase.

FUNDAMENTALS

The electron configuration of antimony favours two formal valences for Sb-ions, (3+) and (5+). The lone pair of strongly localized $5s^2$ electrons induces an asymmetric environment in Sb^{III} with unilateral positioning of ligands; conversely, a significant energy perturbation of $4d^{10}$ electrons may occur in Sb^{V} due to chemical bonding.

X-ray Absorption Near-Edge Structure of Sb 1s spectra is then expected to display energy shifts and post-edge details that will depend on the valence and bonding state(s) of antimony in the absorbing oxide material, as well as from the coordination environment (number of coordinating oxygen atoms and geometry of coordination polyhedron).

Therefore, XANES contributes a valuable clue towards interpreting antimony speciation in chemically complex materials as are the ancient glasses, glazes and enamels.

MATERIALS AND EXPERIMENTAL

Only non-destructive techniques were applied to study the glaze fragments: phase characterization by X-ray diffraction (XRD) using a laboratory Bragg-Brentano diffractometer, coupled with the assessment of chemical constitution by synchrotron radiation X-ray fluorescence (SRXRF spectra collected at the former LURE, Orsay/France) and element speciation by X-ray absorption spectroscopy.

Sb K-edge & Pb L₃-edge XANES spectra were collected at the ESRF/Grenoble using the instrumental set-up of beam line BM-29 operating in transmission mode. Small fragments of model minerals – cervantite, senarmontite and stibiconite (yellow) plus valentinite (white) – were directly irradiated, in this way keeping a sample format identical to the glaze fragments.

Simulation of Sb 1s absorption spectra of the model compounds (including stibiconite, Fig. 1) was performed through *ab initio* calculations based on the full multiple scattering approach using the FEFF8.10 code [5]. A full account on this study is found in [4].

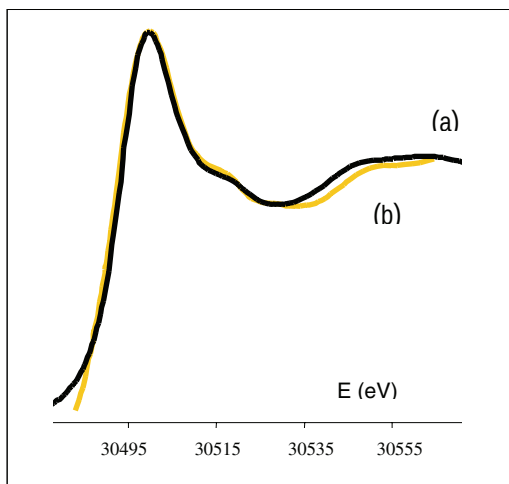


FIGURE 1. Sb K-edge XANES spectra: (a) stibiconite; (b) simulated for a cluster of 87 atoms in an ideal Sb-pyrochlore.

Simultaneously, Pb L₃-edge XANES spectra showed that lead remains hosted by the glassy matrix irrespective of the colour of the glaze or the period of its manufacture [6], thus ruling out the presence of a lead-containing phase – e.g. Pb₂Sb₂O₇, a yellow pigment used since the Egyptian Antiquity.

PYROCHLORE CRYSTAL STRUCTURE REVISITED

The search for an ideal array that could explain the anomalies in relative intensities of X-ray reflections noticed in the diffraction patterns of yellow glazes – in

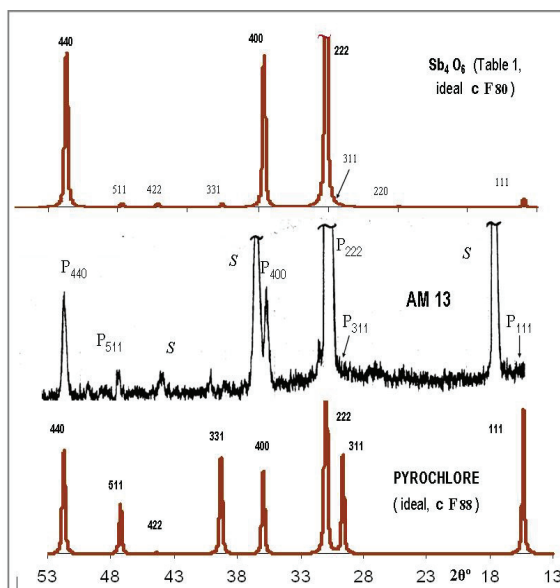


FIGURE 2. XRD pattern (Cu K α radiation) of a yellow glaze with reference AM13 (P - pyrochlore, S - spinel-type oxide), compared to calculated diffraction patterns assuming the same unit cell parameter for ideal structures.

particular, a very weak 111 reflection which is usually a very intense diffraction line for a face centered cubic crystal structure – required a critical reappraisal of the pyrochlore-type array.

Much has been written on this crystal structure type and its relatives [7]. Recalling the classification of structure types and nomenclature established by Lima-de-Faria & Figueiredo [8], pyrochlore derives from a super-structure of fluorite. This structure-type is based on a simple cubic packing (Qs) of oxygen anions with one vacant packing position (denoted $\square$) per eight packing sites; the cations fill half of the available ideally cubic (cb) interstices of this simple cubic anionic array, but due to the packing vacancies, half of the cations display six-fold coordination (Table 1).

The positional free parameter $\bar{x}$ of the oxygen site in the cubic pyrochlore structure described by space group (SG) $Fd\bar{3}m$ – equipoint (48 f) ($x\ 0\ 0$) with positional (site) symmetry mm – allows for a distortion of the bulk anionic array under the constraint of invariant positions for the cations, (16 c) $(1/8, 1/8, 1/8)$ plus (16 d) $(5/8, 5/8, 5/8)$, both with site symmetry $\bar{3}m$. The symmetry-allowed “distortion” of the anionic array promotes a quite regular octahedral coordination for the M' cations and a flattened 6-coordination plus two close neighbours for the M cations (Table 1).

Within the same space group, equivalent position (32 e) (xxx) $x=3/8$ or $7/8$, site symmetry $3m$, describes the unfilled sites in the fluorite superstructure. These ideally cubic interstices assume a 7-fold environment in pyrochlore due to the packing vacancies.

TABLE 1. Sb-oxides: the “pyrochlore” family of crystal structures.

Structural formula	$Fm\bar{3}m$ FLUORITE $\square^{cb}M^{cb}[X^t_2]^{Qs}$ $Fd\bar{3}m$ PYROCHLORE $\square_4^7M_2^{cb}M'_2{}^o[X^t_6X^t\square]^{<Qs>}$								
	Cryst. symbol	Latt. par. a (Å)	Colour	(32e) ^x $3m$	(16c) $\bar{3}m$	(16d) $\bar{3}m$	(48f) ^x mm	(8a) $\bar{4}3m$	(8b) $\bar{4}3m$
$\square_4M_2M'_2[O_7\square]^{Qs}$ Ideal pyrochlore	c F 88	~10.4	—	$\square$	M	M'	O $x = 1/4$	$\square$	O
$(Ca,Na)_2Sb_2O_6(F,OH)$ <i>romeite / atopite</i> [9]	c F 88	10.265	Honey yellow	—	Ca>Na	Sb ^V	O $x = 0.187$	—	F,OH
$Sb_{1.6}Cd_2(O_{6.9}OH_{0.1})$ [9]	c F 88	10.269	Yellow	—	Cd	Sb ^V	O,OH $x = 0.213$	—	O,OH
$Sb_2Pb_2O_7$ <i>Bindheimite</i> [9]	c F 88	10.70	Yellow	—	Sb ^{III}	Pb	O $x = 0.186$	—	O
$Sb_3O_{6.5}$ [1]	c F 88	10.303	Yellow	—	Sb ^{III} _{0.5}	Sb ^V	O $x = 0.18$	—	O _{0.5}
$\square_4(M,M')_4[O_7\square]^{Qs}$ Disordered pseudo pyrochlore	c F 88	~10.4	—	M,M' $x = 3/8$	—	—	O $x = 1/4$	—	O
Hypothetical Sb_4O_6	c F 80	~10.4	—	Sb ^{III}	—	—	O	—	—
$Sb_4O_6(OH)$ <i>Stibiconite</i> [9]	c F 88	11.152	Yellow	Sb ^{III,V} $x = 0.19$	—	—	O $x = 0.19$	—	OH

The flexibility of the anionic oxygen array in a disordered “pyrochlore”-type Sb-oxide would then allow to accommodate the $5s^2$ lone pair of Sb^{3+}/Sb^{III} cations in this equipoint.

The relative intensities of **hkl** reflections in the diffraction patterns of yellow glazes (Fig. 2) are accounted for when performing theoretical simulations with the program POWDER CELL [10], assuming an hypothetical “pyrochlore” Sb_4O_6 (cF80, Table 1).

CONCLUSIONS

The crystallographic approach and the search for a possible disordered pyrochlore-type array under space group $Fd\bar{3}m$ allowed for successfully simulating a diffraction pattern based on a Sb-O formulation.

Combined with this, XANES results confirm that the yellow colour of studied tile glazes is actually due to a neo-formed pyrochlore-type Sb-oxide that remains dispersed in the glassy matrix. The convergence between extended crystal structure provided by X-ray diffraction for the bulk material and local structure of antimony extracted from spectroscopic data configures a very relevant contribution to the non-destructive characterization of ancient cultural materials.

ACKNOWLEDGMENTS

The financial support of EU through *Improving Human Potential* Program is acknowledged. Thanks are due to Dr. S. Pascarelli (ESRF) and to J. Veiga, T. Silva and J. Mirão who participated in the experiments.

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