LEAD-CADMIUM OXYFLUORIDE GLASSES AND GLASS-CERAMICS

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1. Introduction

Oxyfluoride glasses are well known for many years, but our interest in this kind of material has grown after the demonstration in the literature [1] of the possibility of obtaining the so-called rare earth containing ultratransparent glass-ceramics. Besides the importance of oxyfluoride glasses and glass ceramics as technological materials, e.g. in photonics, a lack in systematic glass formation study, with the determination of vitreous domains, and structural studies, including spectroscopic techniques is observed. Moreover, there is the possibility to get hybrid materials displaying fluoride and/or oxide properties depending on the compositions, but the synergetic effects of these somewhat two phase materials are still a challenge to be explored in materials science.

This paper attempts to review our last woks in the synthesis, rare earth doping and structural and optical characterization of lead-cadmium oxyfluoride glasses and glass-ceramics [2-4]. Results from Differential Scanning Calorimetry (DSC), X-Ray Diffraction (XRD), Er3+ Luminescence and Extended X-ray Absorption Fine Structure (EXAFS) are reproduced here for glasses and glass-ceramics in the systems PbF2-CdF2-SiO2, PbF2-CdF2-B2O3 and PbF2-CdF2-TeO2. Glasses have been obtained by the conventional melting and casting glass techniques, in room atmosphere. In addition to the relatively simple preparation method and optical characteristics of rare earth (RE) doped samples, very interesting devitrification (glass crystallization) features are presented.
by these systems. For example, the PbF$_2$-CdF$_2$-SiO$_2$ and PbF$_2$-CdF$_2$-B$_2$O$_3$ glasses are characterised by the devitrification of the cubic form of lead fluoride, β-PbF$_2$, with the possibility of obtaining transparent glass-ceramics under controlled thermal treatments. Rare earth ions may concentrate in the crystalline phase and so their spectroscopic properties appear mainly with crystal-like features. Cd$_x$Pb$_{1-x}$F$_2$-type solid solutions where also identified in some devitrified samples. On the other hand, PbF$_2$-CdF$_2$-TeO$_2$ glass-crystallization leads to the formation of a transparent glass-ceramic, in which the first crystalline phase, the cubic lead tellurite PbTeO$_4$ decomposes into α-TeO$_2$ at higher temperature.

2. Experimental

Glasses were prepared by conventional melting and casting techniques. Starting materials were ground together and melted in open platinum crucibles in electric furnaces at temperatures ranging from 800-1100°C depending on the composition. Melts were quenched to room temperature between brass pieces. Glass formation was identified by considering together the visual inspection for crystalline-like phases, the amorphous character to the x-rays and the identification of glass transition temperature (Tg) followed by the crystallization of the supercooled liquid (Tx and Tp) in DSC curves.

Differential scanning calorimetry (DSC) curves were obtained from powdered samples in aluminum pans under N2 atmosphere in a TA equipment. Heating rate of 10°C/min was routinely used. X-ray diffractograms were obtained from powdered samples with a Siemens diffractometer with the Cu Kα line. A step mode (2θ) with integration time of 2s was used. X-ray absorption spectra were obtained at D44 beam line of LURE (France). EXAFS spectra were obtained at the Pb L$_{III}$-edge (13035 eV), Cd K-edge (26711 eV) and Te K-edge (31814 eV) in the transmission mode at liquid nitrogen temperature (77K). Details in the experimental set-ups during absorption spectra acquisition (monochromators, ionization chambers, time steps for acquisition) were described in previous papers [2-4].

X-ray absorption data have been analyzed by conventional methods including normalization, background removal and Fourier Transform. Data analysis was performed using the "EXAFS pour le Mac" simulation program [5]. To determine the structural parameters R, N and σ (absorbing atom's first neighbors distance, coordination numbers and Debye-Waller factors respectively) the filtered Fourier transformed EXAFS signal was treated as a sum of sinusoidal wave functions using the standard EXAFS equation:

$$k\chi(k) = S_0^2 \sum_i N_i e^{-2\lambda}\sigma^2 e^{-\frac{2\pi i}{\lambda}} f_i(\pi,k) \sin[2kR_i + \Phi_i(k)],$$  \hspace{1cm} (1)

where $\lambda(k)$ is the photoelectron mean free path ($\lambda=k\Gamma$), and $f_i(\pi,k)$ and $\Phi_i(k)$, the amplitude and the phase functions for this coordination shell, which have been tabulated by McKale [6] or obtained experimentally from standard compounds. In this case, starting reagents CdF$_2$ (cubic), β-PbF$_2$ (cubic), β-PbO (orthorhombic) and α-TeO$_2$ (tetragonal) were used during spectra analysis as reference compounds.

3. Results and discussions

With the criteria of glass formation listed above, vitreous domains with homogenous and clear samples could be identified for the investigated systems. Fig. 1 shows the resulting composition diagrams and Table 1 shows some values of characteristic temperatures obtained by DSC. Fig. 2 shows the X-ray diffraction spectra obtained for the glassy and glass ceramics samples of all systems. In the following sessions we show the main results obtained from each system separately. For a more detailed description of methods, results and discussions, we would like to send the reader to the main cited references.
positions agree with the obtained. These crystallization features, when erbium ions are present, indicate the important role of treatments at the $T_g$ and $T_\beta$ values raise significantly when Cd$^{2+}$ substitutes Pb$^{2+}$ (Table 1). We assume that Cd$^{2+}$ ions enter the vitreous network while Pb$^{2+}$ ions act mainly as modifiers.

All glasses obtained are amorphous under X-rays. Partially crystallized samples were obtained by submitting the glass of molar composition 30PbF$_2$-30CdF$_2$-40SiO$_2$ ("S" sample) and (PbF$_2$-CdF$_2$-SiO$_2$)$_{10}$ErF$_3$)$_{10}$ ("S\text{Er}" sample) to 30 (ST1 and S\text{Er}T1) and 60 (ST2 and S\text{Er}T2) minutes heat treatments at the $T_a$ temperatures obtained from DSC scans. Fig. 2 shows the X-ray diffraction spectra obtained for the samples.

Samples S and ST1 are amorphous. The ST2 sample, on the contrary, presents relatively intense peaks that could be easily assigned to the $\beta$-PbF$_2$ cubic phase ($a = 5.94$ Å). Some less intense peaks, marked with an asterisk in the Fig. 2, could be assigned to a solid solution of the type (Cd$_{1-x}$Pb$_x$)$_2$F$_4$. The cubic cell parameter obtained from the peak positions is $5.70 \pm 0.02$ Å.

For the sample S\text{Er} small diffraction peaks can be discerned from the base glass which positions agree with the $\beta$-PbF$_2$ pattern. With heat treatments (S\text{Er}T1 and S\text{Er}T2) only this phase can be identified. Peak positions however are shifted and a cubic cell parameter of $5.88 \pm 0.02$ Å is obtained. These crystallization features, when erbium ions are present, indicate the important role of
nucleating agent for the $\beta$-PbF$_2$ played by erbium, but also that the RE ions are present in the crystalline phase, reflected by the shift in the cubic cell parameter.

![Fig. 2. X-ray diffractograms of samples: (a) T; (b) TT1; (c) TT2; (d) TT3; (e) B; (f) BT1; (g) BT2; (h) BEr; (i) BErT1; (j) BErT2; (k) S; (l) ST1; (m) ST2; (n) SEr; (o) SErT1 and (p) SErT2. Stars indicate the Cd$_x$Pb$_{1-x}$F$_2$ solid solution related peaks in sample ST2.](image)

Fig. 3 presents the $|F(r)|$ curves obtained from EXAFS spectra at the Pb L$_{III}$ absorption edge for the samples studied. For samples S, ST1 and SEr only a first shell peak is observed at 1.6 Å with a clear shoulder at 2.0 Å. For samples ST2, SErT1 and SErT2 the main first peak appears shifted towards larger distances (at 2.1 Å) and a small peak is observed at 1.5 Å. Furthermore, a second broad and intense peak appears in the 4.0 to 4.9 Å range. All structural results obtained for the Pb$^{2+}$ L$_{III}$-edge are gathered in Table 2.

![Fig. 3. $|F(r)|$ curves obtained at the Pb L$_{III}$-edge for the samples: (a) S; (b) ST1; (c) ST2; (d) SEr; (e) SErT1 and (f) SErT2.](image)

A multi-shell fitting procedure was adopted for samples S, ST1 and SEr, with phase and amplitude functions obtained from McKale tables [6]. In the undoped glass, Pb$^{2+}$ ions are surrounded by a first shell with 4 to 5 first neighbor atoms located in 2 sub-shells at relatively short distances (2.3-2.4 Å). When Er$^{3+}$ ions are added (“SeR” glass), 2.3 atoms (at 2.3 Å) are obtained for the first sub-shell.
while 4.3 atoms (at 2.5 Å) are observed for the second sub-shell. This distance is also longer than the one observed for the “S” glass suggesting a more important contribution from F ions in the EXAFS signal.

Table 2. EXAFS results at the Pb L\textsubscript{III} edge on glasses and glass ceramics in the system PbF\textsubscript{2}-CdF\textsubscript{2}-SiO\textsubscript{2}.

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<td></td>
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<td>ST2 SeRT2</td>
</tr>
<tr>
<td>N</td>
<td>2.1 2.3 5.4 2.3 4.7 5.5</td>
<td>1.0(Cd) -</td>
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<tr>
<td>σ(Å)</td>
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<td>0.077 -</td>
</tr>
<tr>
<td>R(Å)</td>
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<td>4.03 -</td>
</tr>
<tr>
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<td>2.0 -</td>
</tr>
<tr>
<td>ρ(×10\textsuperscript{-4})</td>
<td>5.5 4.0 5.1 4.7 3.8 2.2</td>
<td>5.3 1.2</td>
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The main first peak of |F(r)| for the crystallized samples (ST2, SeRT1 and SeRT2), was simulated using phase and amplitude functions taken experimentally from β-PbF\textsubscript{2} (N = 8 and R = 2.57 Å). The numerical results indicate the crystallization of this cubic fluoride. Nevertheless, the small peak at the left side of the first peak for ST2, SeRT1 and SeRT2 indicates the presence of a second family of Pb\textsuperscript{2+} ions included in the glass network, probably surrounded by oxygen atoms. In fact that is the role suggested for Pb\textsuperscript{2+} ions in the non-crystallized samples S, ST1 and SeR.

The second main peak observed in the F(r) curves of the crystallized samples is related, in the β-PbF\textsubscript{2} structure, to the 12 Pb\textsuperscript{2+} atoms at 4.19Å and 24 F atoms at 4.91Å, at the second lead coordination shell. Table 2 shows a satisfactory result for sample SeRT2. As evidenced before from XRD results, a (Cd\textsubscript{8}Pb\textsubscript{12})F\textsubscript{2} solid solution was observed in the sample ST2, and no such a good fit could be obtained for this sample, considering only the Pb and F atoms in the second shell. Cadmium atoms were then included in the fitting procedure and an excellent fit was obtained. Cd\textsuperscript{2+} ions are located at about 4.03Å from the central Pb\textsuperscript{2+} atom in the average cubic cell. In such a (Cd\textsubscript{8}Pb\textsubscript{12})F\textsubscript{2} solid solution, the shortening of Pb-Cd distances (4.03Å) compared to Pb-Pb distances (4.19Å) is totally expected due to the smaller Cd\textsuperscript{2+} ionic radius (R\textsubscript{Cd}= 109 pm) compared to that of Pb\textsuperscript{2+} ions (R\textsubscript{Pb}= 133 pm).

Fig. 4 shows the Fourier transform |F(r)| curves of the EXAFS signal obtained for the samples at Cd K-edge. These |F(r)| curves, which express the short range ordering, do not show any structure indicating a medium or long range ordering. Quantitative simulation shows that either for the glasses or the glass-ceramics, the first Cd\textsuperscript{2+} ions coordination shell is composed of 4 atoms at about 2.26±0.02Å, distance significantly shorter than those found in cubic CdF\textsubscript{2} (8F at 2.33Å). One assumes that the change in Cd\textsuperscript{2+} environment between the crystalline starting materials and the glass should occur via a double decomposition in the melt, according to the general reaction:

\[
\text{SiO}_2+2\text{CdF}_2 \rightarrow \text{SiF}_4+2\text{CdO} \quad (2)
\]
These new [CdO₄] units formed in this way could enter the vitreous network structure constructed from the SiO₂ tetrahedra. This arrangement is likely to remain in the crystallized samples. Fig. 5 shows Er³⁺ emission spectra obtained under excitation at 378 nm (Er³⁺ ⁴I₁₃/₂→⁴I₅/₂ absorption transition). The ⁴I₁₃/₂→⁴I₅/₂ transition is observed with the typical inhomogeneously broadened spectrum, due to the statistical distribution of sites, for the base glass (Fig. 5(a)). After heat treatment well resolved lines are clearly observed (Fig. 5(b)). Fig. 5(c-d) show spectra obtained before in our laboratory for a lead-cadmium fluorogerminate transparent glass-ceramic [7] and the lead–cadmium fluoroborate glass-ceramic for comparison purposes. These results are in total agreement with the ones obtained by XRD and EXAFS, as the spectra from Fig. 5(b-d) could be assigned to Er³⁺ doped β-PbF₂ crystals [7].

3.2. PbF₂-CdF₂-B₂O₃

Very stable glasses could also be obtained in this system. As Table 1 shows, values around 160°C for the (T_c-T_g) parameter could be obtained. Structure and crystallization processes have been studied by X-ray diffraction and EXAFS analysis at the Pb L₃ and Cd K edges [3]. The structural
roles of these atoms are close to those of the system with SiO₂. But, under similar thermal conditions, the crystallization of β-PbF₂ in this system is less complete than the one on fluorostructure system, as concluded from the weak intensity of the XRD peaks (Fig. 2), and the amorphous character of the EXAFS spectra obtained at Pb LIII edge. Moreover, differently from the fluorostructure system, there is no evidence of formation of (Cd₃Pb₁₋ₓ)F₂ solid solutions during heating of the glass, and the optical properties of the erbium doped glass ceramics are those observed for a Er⁴⁺ doped β-PbF₂ crystals (Fig. 5).

### 3.3. PbF₂-CdF₂-TeO₂

Homogeneous, thin glassy samples, typically 1.0 mm in thickness, were obtained in the TeO₂ rich portion of the diagram. Fig. 6 shows a DSC thermogram for the glass of molar composition 10PbF₂-10CdF₂-80TeO₂, labeled “TT” sample [4]. The evolution of the glass transition temperature (Table 1) versus composition exemplifies the structural role of the modifiers compounds. The comparison of the Tg values for the TeO₂-PbF₂ glasses from this study and the TeO₂-PbO glasses reported previously [8] shows that the Tg drop is larger when PbF₂ is used, i.e. the “modifier” role played by PbF₂ is more pronounced that the one observed for PbO. This may be explained as it leads to a larger number of non-bridging anions. It is also more important than the effect induced by CdF₂ as it may be seen comparing 90TeO₂-10PbF₂ and 90TeO₂-10CdF₂ glasses.

![DSC thermogram of the “TT” sample](image)

**Fig. 6.** Differential scanning calorimetry thermogram of the “TT” sample, of composition (in mol%) 80TeO₂-10CdF₂-10PbF₂. Heating rate q=10°C.min⁻¹.

For the glass-ceramics preparation, heat treatments were performed as follow: sample "TT" was submitted to a heat treatment at 300°C for 30 minutes, which is just above the first crystallization peak observed in the DSC curve (Fig. 6). This heat treated sample will be called hereafter "TT1". The sample "TT" was also heat treated for 5 and 60 minutes at 400°C which is just before the second crystallization peak observed in Fig. 6. These two heat treated samples are called hereafter "TT2" and "TT3". Sample TT1 appears as a yellowish transparent block, with no visible crystallization. Sample TT2 displays crystallization at the surface and sample TT3 shows a completely white opaque body.

Fig. 7(a-d) shows the Raman spectra obtained for glassy samples 90TeO₂-10PbF₂, 70TeO₂-30PbF₂, 50TeO₂-50PbF₂ and also 80TeO₂-10PbF₂-10CdF₂. Fig. 7(e and f) shows the Raman spectrum obtained for the TT1 and TT3 samples, respectively. For the sake of comparison Fig. 7(g) shows the Raman spectrum obtained for the α-TeO₂. One can easily note the strong similarities between the spectrum obtained for sample TT3 and the one for the α-TeO₂. The bands centered at 450, 650 and 750 cm⁻¹ observed in Fig. 7 for the binary TeO₂-PbF₂ glasses have been assigned, respectively, to
the symmetric and antisymmetric vibrations of Te-O-Te linkages and to the stretching vibration between tellurium and non-bridging oxygen atoms like in TeO₃ tp or TeO₃+1 polyhedra [12]. Fig. 7 shows that, as PbF₂ content increases, the intensity of the bands located at 450 and 650 cm⁻¹ decreases, at the expenses of the relative increase in intensity of the band at 750 cm⁻¹. These results describe the changes in the tellurium coordination polyhedra from TeO₄ tp to TeO₃ tp with increasing lead/cadmium fluorides.

X-ray diffraction patterns obtained for these samples are shown in Fig. 2. As stated before, sample TT1 is completely transparent. However well defined diffraction peaks could be observed in DRX curves. The diffraction patterns were compared with data from JCPDF (Joint Commission on Powder Diffraction Files) and a good agreement was found between the diffractogram obtained for the transparent sample TT1 and the cubic (a = 5.650 Å) PbTe₂O₇ (File # 37-1392). This phase is described in the literature as an "antiglass" phase where order exists only at long distance and an important dispersion in the tellurium first neighbors distances is observed [9]. This "antiglass" character is in fact confirmed by the Raman spectrum presented in Fig. 7(e). The high frequency bands involving Te-O modes in the 550-850cm⁻¹ range, are inhomogenously broadened in the same way observed for the mother glass (Fig. 7(b)). Tetragonal form of tellurium oxide, α-TeO₂ (File#42-1365), was identified as the main crystalline phase in sample TT3. The increase in the temperature leads to the dissolution or decomposition of the cubic PbTe₂O₇ phase in the matrix, giving rise to tetragonal α-TeO₂.

![Raman spectra](image)

**Fig. 7.** Raman spectra for the samples: (a) 90TeO₂-10PbF₂; (b) sample "T" (80TeO₂-10CdF₂-10PbF₂); (c) 70TeO₂-30PbF₂; (d) 50TeO₂-50PbF₂; (e) sample "TT1" (300 °C / 30 minutes); (f) sample "TT3" (400°C/60 minutes); (g) α - TeO₂.

Fig. 8 shows the modulus of the Fourier Transform, |F(r)|, curves, not corrected for phase shift, obtained from EXAFS signals at the Te K-edge in samples T, TT1 and TT3, and reference α-TeO₂. The first peak, at about 1.46 Å, is relative to the first coordination shell around tellurium atoms, which is composed, in α-TeO₂, by the oxygen atoms in TeO₄ tpb units, i.e. two at 1.90 Å (equatorial position) and two at 2.08 Å (axial positions) [10]. The second peak, at about 3.57 Å corresponds to the second Te coordination shell, composed by four tellurium atoms at 3.74 Å, two at 3.83 Å and four at 4.07 Å. Simulations of the EXAFS signal relative to each shell were made using a multi-subshell fitting procedure. The first coordination sphere was better simulated considering two slightly different Te-first neighbors distances. For the second Tellurium coordination sphere a 3 sub-shells simulation was necessary. Table 3 gives the numerical results obtained from simulations, which describe the Te first shell environment as been close to the one found in reference paratellurite, in all samples. The same is observed for the second Te coordination shell in TT3 sample. This result is supported by X-ray diffraction observations. However, while vibrational spectroscopy shows a mixture of TeO₃ tpb and TeO₃ tp units, mainly in samples T and TT1, X-ray absorption indicates that TeO₃ tpb appears as a majority proportion. In fact, a mixture of entities must be considered since relative Raman Scattering cross-sections are not known for the two structures (if the force constant in the tp structure is very important, then a little fraction of tp unites can strongly interfere the Raman signal).
Cadmium K-edge EXAFS studies were performed in T, TT1 and TT3 samples. As in the precedent cases, with the fluorosilicate and fluoroborate systems, cadmium environment changes drastically by comparison to the cubic CdF$_2$ reference. Cd K-edge results indicate a diminution in the coordination number from 8 in the cubic CdF$_2$ cell to 4 in the samples. The asymmetry of peaks in the $|F(r)|$ curves reveals also the anionic distance distribution around cadmium atoms. Anion distributions are centered on mean distances varying between 2.27 and 2.29Å (samples T and TT1, respectively) and 2.35Å (sample TT3) [4]. As in the case of fluorosilicates and fluoroborates, these differences in the first coordination shell of samples and start compound CdF$_2$ could be well explained by the formation of [CdO$_4$] units, following the reaction:

$$\text{TeO}_2 + 2\text{CdF}_2 \rightarrow \text{TeF}_4 + 2\text{CdO}$$  \hspace{1cm} (3)

Lead L$_{III}$-edge EXAFS studies were also performed in T, TT1, TT2 and TT3. Asymmetric peaks were obtained in the $|F(r)|$ curves, reflecting the occurrence of a large atomic distance distribution in lead surroundings. Multi-shell fitting procedure was adopted and a two sub-shell environment for lead cations was found, in which anions are located around two main average distances, at about 2.3 and 2.5 Å. For the

### Table 3. EXAFS results at the Te K edge on glasses and glass ceramics in the system PbF$_2$-CdF$_2$-TeO$_2$.

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transparent glass-ceramic (sample TT1) we have assigned [4] a structure appearing around 3.49 Å (uncorrected for phase shift) to Te-Pb contribution from the PbTeO$_2$ phase. The structure of this kind of compound is characterized by Pb-Te interatomic distance of 3.7 Å and Pb-Pb distance of 3.9 Å [11].

4. Conclusions

New stable glasses have been synthesized in the PbF$_2$-CdF$_2$-MO systems. Lead-cadmium fluorosilicate glass ceramics have been obtained by annealing at 440°C, with β-PbF$_2$ and a solid solution with the formula Cd$_{1.8}$Pb$_{0.2}$F$_2$ as the main crystalline phases. For the three systems presented here, Cd K-edge EXAFS results showed lower coordination numbers and shorter first neighbor distances comparing with the CdF$_2$ precursor used. This result and the increase of the glass transition temperature observed when Cd$^{2+}$ substitutes for Pb$^{2+}$ suggest the role of glass former played by Cd$^{2+}$ ions and suggests that cadmium ions are preferentially surrounded by oxygen atoms although they were in a fluoride anion environment in the starting material. For fluorosilicate and fluoroborate samples, Pb L$_{III}$-edge EXAFS analysis suggests at least two families of sites for Pb$^{2+}$ ions. The first one observed for the mother glass with Pb$^{2+}$ coordination numbers and first nearest distances close to the values found for β-PbO. In crystallized samples this first family of sites is still present, but a fluoride containing first coordination shell is also observed. Crystallization experiments showed the inclusion of Er$^{3+}$ ions in the β-PbF$_2$ crystalline phase. From EXAFS and XRD results we could estimate the crystalline content to be from 30 to 40% of the initial Pb$^{2+}$ content in the fluorosilicate system [2]. No Pb-Cd solid solution could be observed in that case, suggesting the role of nucleation agent for the PbF$_2$ phase played by Er$^{3+}$ ions. Near infrared emission spectrums showed crystal-like spectra with the narrowing of the emission lines by comparing with the one observed for mother glass. Concerning the fluorotellurite system, Raman scattering results show the increase of the number of structural units described as [TeO$_3$] trigonal pyramids and [TeO$_4$]$^-$ polyhedra at the expense of the [TeO$_4$] trigonal bipyramids supposed to exist in the TeO$_2$ rich samples. Heat treatments performed at 300°C for the 10PbF$_2$-10CdF$_2$-80TeO$_2$ (mol%) sample reveal the possibility of obtaining transparent glass-ceramics in which the PbTeO$_2$ crystalline phase could be identified by x-ray diffraction and EXAFS measurements performed at the Te K, Cd K and Pb L$_{III}$ edges. Annealing at larger temperatures leads to the decomposition of this crystalline phase and the final material consists in a mixture of phases among which one of them could be identified as the α-TeO$_2$.

References