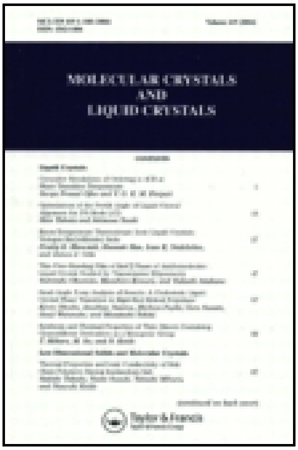

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XAS AND XRD STUDIES ON GRAPHITE INTERCALATION COMPOUNDS OF Re_2O_7

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Abstract Re_2O_7 was used as starting material for the preparation of pure low–stage graphite intercalation compounds (GICs). X–ray absorption measurements were carried out at the Re L_{III} and L_I absorption edges. The EXAFS analysis resulted in a coordination number of four and a Re–O bond length of 173.5 pm for the GICs. In the Re L_I XANES the analysis of the strong pre peak confirmed a slight distorted tetrahedral symmetry. Further XANES features indicated a variation of long–range order for the intercalate. Therefore the XAS measurements determined the tetrahedral perrhenate ion as the intercalated species. The majority of synthesized compounds showed sharp hk0 diffraction patterns. Only some compounds showed first diffuse rings and after several days sharp reflections of an ordered "in–plane" lattice. The analysis of the hk0 diffraction pattern yielded a lattice with the constants a = 652 pm, b = 764 pm, $\gamma = 100°$, $\delta_a = 0.6°$ and $\delta_b = 19.4°$.

INTRODUCTION

First investigations upon graphite intercalation compounds (GICs) of Re_2O_7 were carried out by Fuzellier.[1] He prepared the GICs from the oxide melt and from the vapour phase, but in both cases he could obtain only a low content of intercalate. Furthermore, he recognized the reduction of Re_2O_7 to ReO_3 due to the graphite which excludes a precise determination of the composition using chemical analysis. Seventeen years later the preparation conditions of the Re_2O_7 GICs were reinvestigated by Scharff et al.[2]. Besides the preferred formation of low–stage compounds at low temperatures, they could observe that the atmosphere in the reaction ampoules has no influence on the products.

Up to this time the main problem was the determination of the unknown intercalated species in the case of Re_2O_7 intercalation. The reason for this is the high sensitivity of Re_2O_7 to moisture. Therefore, it could not be excluded that the intercalated species is solid Re_2O_7 or hydrated Re_2O_7 or perrhenic acid. All previous analysis of the 00ℓ reflections could not give sufficient results about the "in–plane" structure of Re_2O_7 GICs. That is the reason why we used X–ray absorption spectroscopy (XAS) besides X–ray diffraction methods. XAS permits a direct determination of the short–range order around the central atom yielding bond lengths with high accuracy.

EXPERIMENTAL

Synthesis

For the synthesis of the GICs flakes of natural graphite (from Kropfmühl, Germany) with a diameter of 600–800 μm and powder graphite with a diameter of 50 μm were used. Commercial Re_2O_7 was taken, which was previously sublimed at 260° C under normal pressure. Comparison of Debye–Scherrer photographs before and after the sublimation could exclude decomposition of Re_2O_7. To avoid humidity all works were carried out under nitrogen atmosphere in a glove box. The GICs were prepared in sealed glass tubes placed vertically in a single–temperature furnace. Due to a spatial separation of graphite flakes from the Re_2O_7 besides a mixture of both, it was possible to carry out the synthesis from the oxide melt and the from vapour phase simultaneously. In every case we could confirm the result of Ref. 1, that the preparation from the vapour phase always yields GICs with a lower content of intercalate. Hence, we only used GICs prepared from the oxide melt for further investigations . The reactions were carried out in a temperature range of 250° – 285° C, and the reaction time varied between 45.5 hours and 73.5 hours. After quenching with compressed air the flakes were washed with small quantities of pyridine, water and acetone.[2]

X–ray absorption spectroscopy

The X–ray absorption spectra of the Re L_{III} and L_I edges were recorded in transmission mode at the DORIS III storage ring (HASYLAB/DESY, Hamburg, Germany) on the RÖMO II beamline. The synchrotron radiation was monochromatized by a silicon 311 double crystal monochromator. The samples were prepared as polyethylene pellets in a glove box. The energies of the Re L absorption edges were calibrated against the Pt L edges of platinum foil. The spectra of all componds were taken at room temperature, and those of the GICs were additionally measured at 77 K. In the EXAFS analysis the phase shift and backscattering amplitude for the first Re–O shell were extracted from XAS data of solid ReO_3.[3] As further reference compounds for EXAFS data analysis we used solid perrhenic acid monohydrate[4] $HReO_4 \cdot H_2O$ and commercial liquid perrhenic acid $HReO_4$. In the latter case the possible appearance of $Re_2O_7(OH_2)_2$ molecules in high concentrated aqueous solutions[5] could be excluded by analyzing IR and Raman spectra.

X–ray diffraction

The standard measurements of the 00ℓ reflections were carried out with a powder diffractometer in Bragg–Brentano geometry. The hk0 diffraction patterns were obtained using the monochromatic Laue method with a cylindrical camera. In both cases nickel–filtered Cu–Kα radiation was used.

RESULTS AND DISCUSSION

Contrarily to other synthesis[2] we could obtain pure low-stage GICs (see Figure 1). The preferred formation of low-stage compounds at lower temperature can be detected, but the lowest temperature for an extensive intercalation must be over is 250° C. Above 290° C one can only obtain high-stage compounds. The formation of a red coating on the surface of the flakes, probably due to the red ReO_3, is independent of the reaction temperature. Only the amount increases with increasing temperature. Due to this side reaction a precise analytical determination of the intercalate content is impossible.

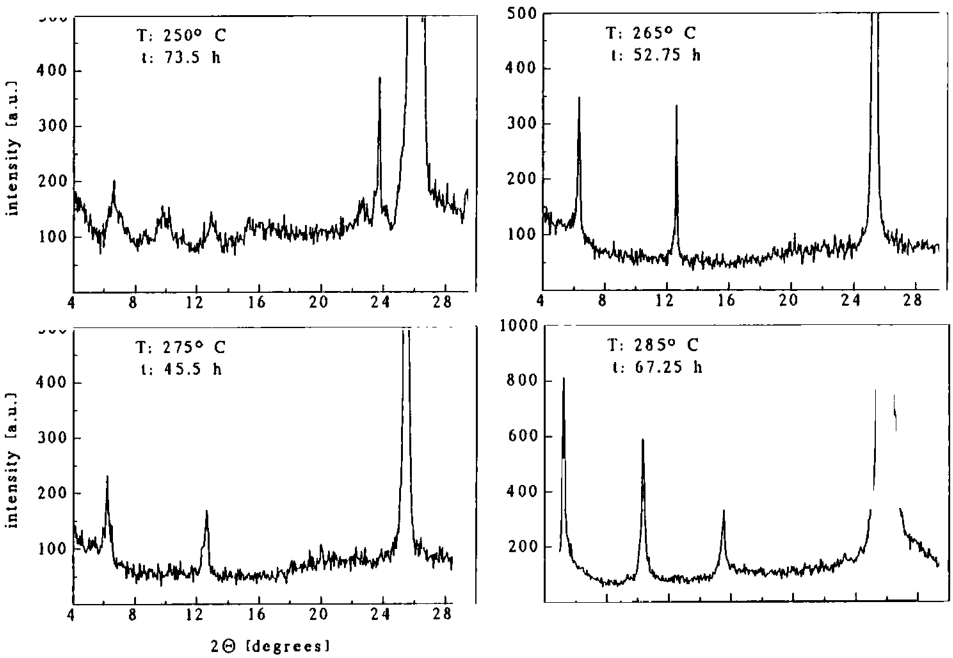

FIGURE 1 X-ray diffractograms of Re_2O_7 GICs prepared under various conditions.

The EXAFS analysis of the Re L_{III} edges yields for the Re_2O_7 GICs at 77 K and 298 K an average distance for the Re–O bond of 173.5 pm and a coordination number of four (see Table 1). The Debye-Waller factors show for both temperatures no significant difference which can be an indication for a rigid-body around the rhenium. The analysis of the reference compounds $HReO_4(l)$ and $HReO_4 \cdot H_2O(s)$ also result in the same bond lengths and coordination numbers. In case of solid perrhenic acid the Re–O bond length agrees very well with the value of 173.65 pm obtained from X-ray single crystal analysis.[4]

In polymeric Re_2O_7 [6] and dimeric $Re_2O_7(OH_2)_2$ [7] ReO_4 tetrahedrons exist besides ReO_6 octahedrons. Due to the fact that we cannot detect Re–O bond lengths higher than 190 pm (see Table 2) or an average value between 180–190 pm due to a superposition of the two shells we can exclude these compounds as intercalated species. Rather the XAS measurements determine the tetrahedral perrhenate ion as the intercalated compound.

TABLE 1 Coordination number N, Re–O bond length R, Debye–Waller factor $\Delta\sigma^2$ obtained from the fit of the first shell of Re_2O_7 GICs, liquid perrhenic acid and solid perrhenic acid monohydrate in comparison to solid ReO_3.

	N	R[pm]	$\Delta\sigma^2$ [pm^2]
ReO_3	6	187	–
GIC	4.04	173.57	-25.37
GIC (77K)	3.8	173.4	-29.91
$HReO_4(l)$	4.01	173.44	-32.4
$HReO_4 \cdot H_2O(s)$	3.69	173.9	-30.1

TABLE 2 The average $< Re - O >$ bond lengths in the polyhedrons of Re_2O_7 and $Re_2O_7(OH_2)_2$

Polyhedron	$< Re - O >$ [pm]	
	Re_2O_7	$Re_2O_7(OH_2)_2$
ReO_4	173.75	175.75
ReO_6	190.5	196

In the XANES of the Re L_I edges the following features can be detected.[8,9] First, all tetrahedral compounds exhibit a strong pre–peak (see Figure 2) caused by the 2s → 5d(Re) + 2p(O) transition.[10] Normally, the 2s→ 5d transition cannot be detected because it is not dipole allowed. However, in compounds without an inversion symmetry a stronger d-p orbital mixing and an overlap of metal d orbitals with ligand p orbitals results in a considerable transition probability and, accordingly, in an intensive pre–peak. Every distortion of the regular tetrahedral structure leads to a decrease of the intensity.[11] In case of the octahedral ReO_3 the pre–edge feature is observed only as a weak shoulder.

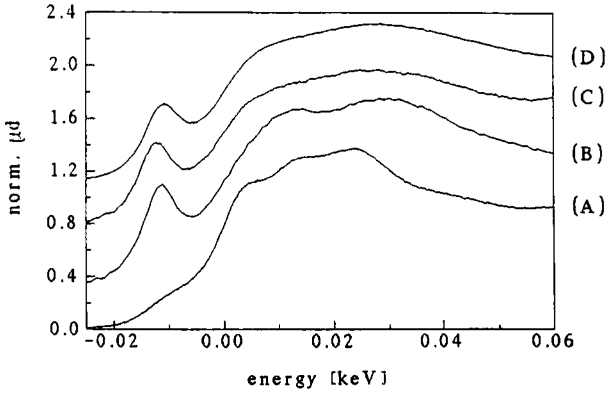

FIGURE 2 Re L_I absorption edges of (A) ReO_3, (B) $HReO_4 \cdot H_2O(s)$, (C) $HReO_4(l)$ and (D) graphite intercalation compound.

Besides the strong pre peak in the XANES of the tetrahedral compounds the solid $HReO_4 \cdot H_2O$ shows a peak at 12 eV which the Re_2O_7 GICs and the liquid perrhenic acid do not exhibit. This peak appears in several solid perrhenates and can be explained by scattering from more distant neighbours.[12] For a comparison between the solid $HReO_4$ with long range order, the high concentrated liquid $HReO_4$ and some GICs, we fitted the normalized Re L_I edges with three symmetric Gaussian functions and one arctangent. All fitting parameters were kept free. The intensities (FWHM × height) of the first and second peak are shown in Table 3.

TABLE 3 The intensities I_1 and I_2 (arbitrary units) of the first and the second peak of the normalized Re L_I edges for different tetrahedral compounds.

	I_1	I_2
GIC1	8.656	0.426
GIC2	8.413	0.579
GIC3	8.199	0.732
$HReO_4(l)$	8.831	0.777
$HReO_4 \cdot H_2O(s)$	10.725	4.384

In case of the GICs the lower intensity of the first peak indicates a slight distortion of the tetrahedral symmetry compared with the liquid and solid perrhenic acid. The second intensity is quite different between the solid perrhenic acid and the other compounds. The lower intensities are a proof for the alteration of long range order in the liquid and the GICs. The differences in the peak areas point to a variation in arrangement of the tetrahedrons.

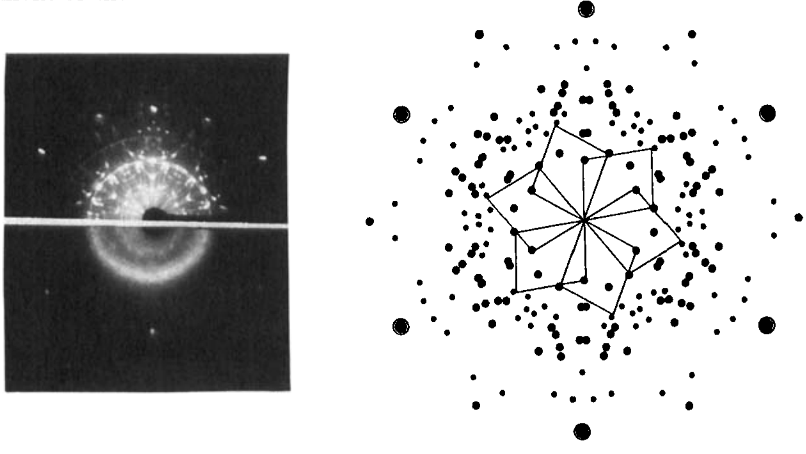

FIGURE 3 Left: Monochromatic Laue pattern (hk0 plane) of the Re_2O_7 GIC, (bottom: just after preparation, top: after several days). Right: The "in plane" lattice. The unit cells for each of the six rotational positions are depicted.

The analysis of the hk0 reflection patterns yield for the majority of synthesized GICs a sharp "in-plane" lattice (see Figure 3 left/top) with the constants a = 652 pm,

$b = 764$ pm, $\gamma = 100°$, $\delta_a = 0.6°$ and $\delta_b = 19.4°$. The values for δ_a and δ_b constitute the angles between the corresponding axes of the intercalate and the graphite lattice. This lattice includes all strong reflections. Also the weak reflections can be explained by a lattice with the same angle, but with lengths three and two times higher than the smaller lattice. Additionally to earlier results[13] we also found some compounds, which showed first diffuse rings (see Figure 3 left/bottom) and after several days sharp reflections of an ordered "in-plane" lattice. The inner ring includes d values in the range of 645–765 pm and the second circle between 355 pm and 425 pm.

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