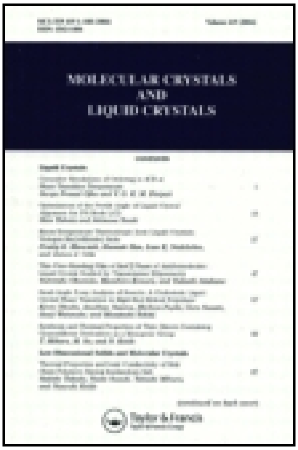

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BISMUTH(III) CHLORIDE GRAPHITE INTERCALATION COMPOUNDS: PREPARATION AND CHARACTERIZATION OF THE FIRST STAGE COMPOUND

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Abstract In dependence on the pressure of chlorine (1 to 14.5 bar) we prepared graphite intercalation compounds from $BiCl_3$ melts (T= 523K) The compounds were characterized by X-ray diffraction of the 00ℓ and hk0 pattern. We obtained first (identity period in c direction: 971 pm, a= 904 pm, b= 1935 pm, γ= 89.8°, δ_a= 28.3°) and second stage compounds. X-ray absorption measurements at the Bi-L_{III} edge showed a decrease in the Bi-Cl bond length from 250 pm to 245 pm. The edge is shifted about 0.8 eV to lower energies in comparison to pure $BiCl_3$.

INTRODUCTION

For a long while the intercalation of metal halides into graphite was performed in the presence of chlorine whereby a pressure of 1 bar is often sufficient to obtain a first stage graphite intercalation compound (GIC). However, the preparation of $BiCl_3$-GIC, stage 1, requires a chlorine pressure higher than 14 bar[1]. Further, we performed investigations concerning the reaction conditions, especially the chlorine pressure, which ranged from 1 to 14.5 bar. First structural studies on a $BiCl_3$-GIC, stage 1, were made by Lochte et al[2]. For the orthogonal in-plane lattice of the intercalated $BiCl_3$ in a first stage compound the following parameters were found: a= 926 pm, b= 2012 pm and γ= 90° . One of these lattice parameters (a= 926 pm) is found in the lattice of pure $BiCl_3$ (a= 917 pm) as well as in higher stage compounds[3]. In addition to X-ray diffraction methods, XAS-measurements clear up the low range order, particularly the coordination number, bond lengths and Debye-Waller factors can be determined.

EXPERIMENTAL

We used natural graphite flakes from Kropfmühl/Germany (diameter: 800-1000 µm) for XRD and graphite powder (<50 µm) for XAS measurements. Anhydrous $BiCl_3$ was purchased from Merck (Germany). To remove residual water and BiOCl the halide was vacuum heated and repeatedly sublimed. The reaction was carried out in sealed glass tubes containing condensed chlorine in such amount, that the calculated pressure yielded approximately 5 to 15 bar at room temperature. In this calculation the van der Waals equation was used (a= 6.493 (l^2atm mol^{-2}), b= 0.05622 (l mol^{-1}))[4]. These ampoules were inserted into a steel container and heated in a one temperature furnace (T=523K). The reaction conditions and the results are shown in Table 1. After the reaction was finished, the steel container was quenched in water and liquid nitrogen. The samples containing a chlorine pressure below 1 bar were prepared in the usual way. The $BiCl_3$ of the melting cake was extracted with diluted HCl. The flakes were washed with acetone and dried. Graphite flakes of the first stage compound showed a blue-black colour. The stage number of the samples were determined from 00ℓ diffractograms. The in-plane lattice of the intercalated $BiCl_3$ was obtained using the monochromatic Laue method (CuK_α - radiation). Considering the very large number of reflections, a computer aided evaluation method was developed. XAS measure-

TABLE 1 Experimental conditions and results (temperature of reaction: 523 K)

reaction time (days)	chlorine pressure• (bar)	graphite weight (mg)	GIC weight (mg)	stage number n	c(n) (pm)	c(1) (pm)
5	0.98	24.96	74.76	2.0	1305	970
5	4.69	25,00	71.65	2.0	1303	968
5	12.64	25.10	66.55	1.0	-	972
7⁺	13.70	49.20	101.98	1.0	-	970
3	7.96	50.32	197.91	1.0	-	971
				2.0	1303	968
3	7.87	50.37	143.95	2.0	1303	968
3	7.89	50.24	203.94	1.0	-	971
				2.0	1302	967
3	10.14	50.06	206.43	1.0	-	971
				2.0	1300	965
3	11.15	50.08	213.70	1.0	-	971
				2.0	1302	967
3	12.43	50.33	215.14	1.0	-	969
3	14.33	50.28	210.00	1.0	-	971

⁺Flake size: < 50µm •at T= 293 K

ments were performed at the RÖMO II beamline with a Si(311) double crystal monochromator at HASYLAB/DESY (Hamburg). The samples were sprinkled on capton foil in a glove box. The absorption spectra were measured at the Bi L_{III} edge (E= 13.426 keV). The energy of the Bi L_{III} edge was calibrated against the Br K edge (E= 13.470 keV). Conventional data evaluation procedures were applied to isolate the scattering phase and backscattering amplitude functions from pure $BiCl_3$.

RESULTS AND DISCUSSION

Second stage compounds of $BiCl_3$ are obtained for chlorine pressure up to 7.5 bar (see table 1). Above 12.5 bar only the first stage compound is formed. In the range from 7.5 to 12.5 bar first and second stage compounds appear side by side whereby the two stages can already be distingueshed by their colours. Mixed phases with stage disorder are not found. The enlarged interlayer spacing ($c^{(1)}$) comes up to 971 pm for $BiCl_3$-GIC stage 1, and 968 pm for the $BiCl_3$-GIC stage 2. Possibly this difference corresponds to the increased charge transfer for the first stage compound or to the changed geometrical surroundings.

TABLE 2 Lattice parameters for $BiCl_3$-GIC in-plane lattices and pure $BiCl_3$ (δ denotes the angles between the graphite and the intercalate axes)

	a (pm)	b (pm)	γ (deg)	δ_a(deg)	δ_b (deg)
stage 1	904	1935	89.8	28.3	1.9
stage 2	1424	1796	90.4	2.7	33.1
prist. $BiCl_3$	764	917	90.0	-	-

The decrease of the intercalate weight at constant reaction time and increasing chlorine pressure is an effect of the direct reaction of chlorine with graphite.

The parameters of the in-plane lattices are shown in Table 2. They were evaluated from the monochromatic Laue photographs of a first stage and second stage compound. In the sample prepared with a chlorine pressure of 7.89 bar first stage (Fig.1) and second stage lattices (Fig.2) coexist in different graphite flakes. The orthogonal in-plane lattice of the second stage compound has also been described by Behrens et al[3]. Similarities of the lattice of the first stage with that of the second stage are evident, indicating a slight but significant alteration of the in-plane structure during the transition from the second to the first stage.

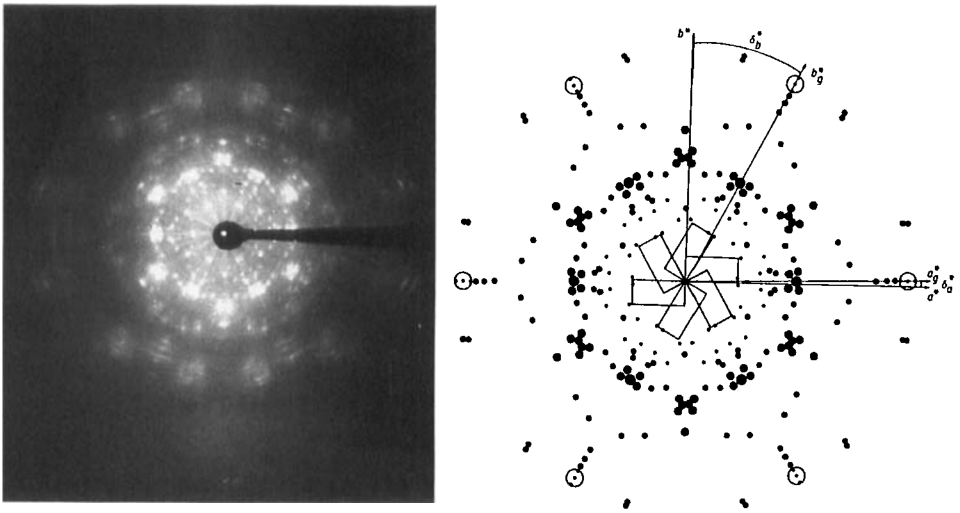

FIGURE 1 Monochromatic Laue pattern of the $BiCl_3$ -GIC, stage 1 (a), and (hk0)-diffraction pattern as evaluated from (a), one unit cell for each of the six possible rotational positions is depicted

The Fourier transforms (FTs) of the EXAFS at the Bi L_{III} edge of pure and intercalated $BiCl_3$ (stage 2) are very similar, as we reported in Ref 2 . No significant change is evident in the FT of $BiCl_3$-GIC, stage 1, as well (Fig. 3). The results of the best fit

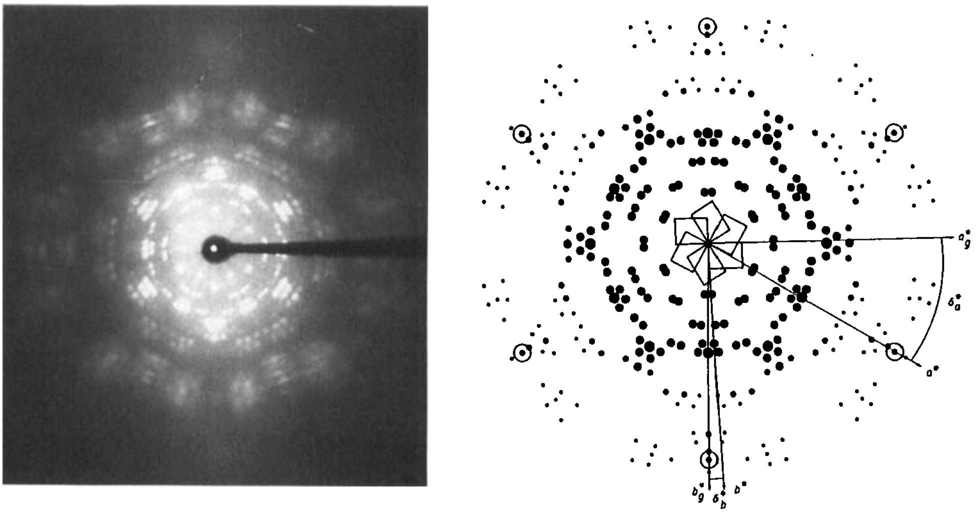

FIGURE 2 Monochromatic Laue pattern and the evaluated (hk0)-diffraction pattern of the second stage GIC

of the Fourier filtered first shell coordination from $BiCl_3$-GICs are listed in Table 3. Phase and amplitude functions were isolated from pure $BiCl_3$. R and N denote the coordination number of Bi and the Bi-Cl bond distance, respectively. In XAS measurements $\Delta\sigma^2$ describes the Debye-Waller factor relative to the reference sample. A noticeable decrease in Bi-Cl bond length and coordination number do probably not result from a serious short range distortion of the $BiCl_3$ molecules in the intercalated state, despite the transition from a 3-D to a 2-D order.

TABLE 3 Coordination number, Bi-Cl bond length and Debye-Waller factor obtained from the fit of the first shell of $BiCl_3$-GIC in comparison to pure $BiCl_3$

	N	R (pm)	$\Delta\sigma^2$ (pm^2)
BiCl3 (pristine)	3.0	250	0.0
BiCl3-GIC (stage 2)	2.5	246	1.0
BiCl3–GIC (stage 1)	2.3	245	1.6

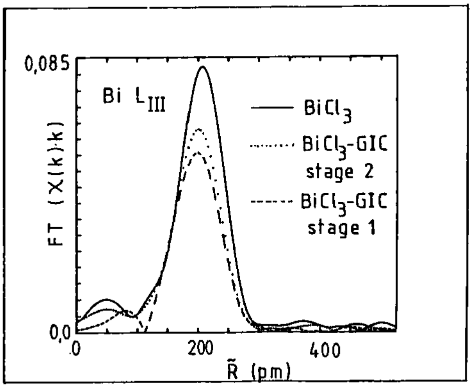

FIGURE 3 FTs of the EXAFS spectra (modified radial distribution function)

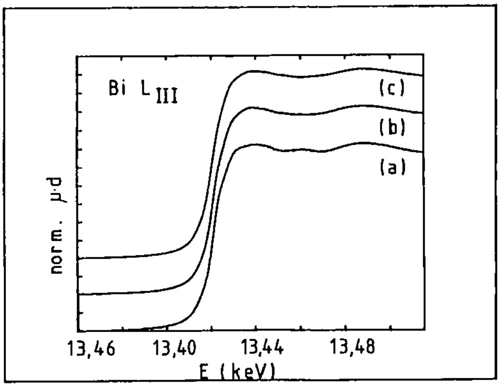

FIGURE 4 Normalized XANES spectra at the Bi L_{III} edge of a) $BiCl_3$, b) $BiCl_3$-GIC stage 2, and c) $BiCl_3$-GIC stage 1

The energy shift of the Bi L_{III} edge (see Fig.4) to lower energies was 0.3 eV for the second stage and 0.8 eV for the first stage (determined from a XANES fit). This points to a charge transfered to the Bi atom in the intercalate. In contrast to other acceptor compounds an increase in bond length connected with the charge transfer was not observed. In $BiCl_3$-GIC the decrease probably results from changes in the geometrical surroundings.

REFERENCES

1. V. A. Muchanov, V. V. Avdeev, and K. N. Semenenko, Vestnik Moskovskogo universiteta. Ser. Chimija, 25, 98 (1984)
2. K. Lochte, M. Fröba, F. Schulz, and W. Metz, Proc. 5th Int. Carbon Conf., Essen (Germany), 618 (1992)
3. P. Behrens, V. Woebs, K. Jopp, and W. Metz, Carbon, 26, 641 (1988)
4. Handbook of chemistry and physiks 70th Ed, edited by R. C. Weast, D. R. Lidi, M. J. Astle, and W. Beyer (CRC Press, Boca Raton, Florida), D-190