Functional Materials 6, No.1 (1999)

Intercalation compounds formation process (X-ray examination in situ)

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Received July 9, 1998

The process of equilibrium intercalation compounds formation based on layered inorganic crystal by organic molecules introduction into interlayer gaps has been first studied. Using the X-ray analysis in situ, the equilibruim intercalation phase has been shown to be formed via a series consecutive structure-chemical transformations. The intermediate states are a set of variuos long-periodic structures. In the course of intercalation, the initial textured film of the layered crystal undergo dispersion forming fragments of scale-like shape having characteristic dimension of several tens of Angstroms.

Впервые исследован процесс образования равновесных интеркаляционных соединений на основе неорганического кристалла слоистой структуры при внедрении в межслоевые промежутки органических молекул. С использованием рентгенографического анализа in situ показано, что образование равновесной интеркаляционной фазы происходит через ряд последовательных структурно-химических трансформаций. Промежуточные состояния представляют собой набор различных длиннопериодных структур. В процессе интеркаляции исходная текстурированная пленка слоистого кристалла диспергируется так, что фрагменты имеют форму чешуйки, а их характерные размеры составляют несколько десятков ангстрем.

We have given reasons before [1] for why the intercalation, i.e. the introduction process of atoms, ions or molecules into layered crystalline structures as well as the equilibrium result of that process, is of both purely scientific and technologic interest. We have pointed in the cited work that while thermodynamics and electronic properties of equilibrium intercalation compounds have been studied in sufficient details, the formation process of intercalation phases and its kinetics remain still inadequately researched. It has been shown on the qualitative level [2] that the intercalation process is a fast non-diffusional spreading of the intercalation phase along the initial matrix layers.

In [1], that process was studied quantitatively using texturized films of PbI_2 layered crystal. The process occurs at a speed of an express train, of course on the atomic scale (10^{-4} cm/s), thus exceeding the rate of any conceivable solid-phase diffusion processes. It has been revealed [1, 2] that the intercalation front displacement is accompanied by cracks propagation and the crystal matrix dispersion. The intercalation process,independent of its peculiarities, results in formation of an equilibrium intercalation phase with an ordered distribution of intercalated molecules in the matrix interlayer gaps.

How the phase transformation proceeds? What is sequence of the crystal structure transformations during the intercalation? This paper is aimed at elucidation of those questions. To that end, structure measurements in situ were to be carries out.

The experiment was realized as follows. PbI_2 films were prepared by vacuum evaporation according to the procedure described

in [1]*). The samples were placed into a special chamber provided with thin polyethylene windows transparent for X-rays and the chamber was put into a X-ray apparatus. The chamber was connected through a valve with a vessel containing liquid piperidine ($C_5H_{11}N$). Molecules of this compound have been shown to be capable of penetration into layered PbI_2 matrix forming an intercalation compound [3]. The opening moment of the valve connecting the vessel and the chamber containing PbI_2 film corresponded to the start of the intercalation reaction. The evolution of diffraction patterns allowed to trace the phase composition dynamics of the layered crystal being subjected to intercalation.

X-ray diffraction studies were carried out using a DRON-3K unit in CuK_α emission, the angular range was from 4 to 14 deg and the scanning time about 4 min. Since the typical duration of the complete film intercalation amounted three or four hours, we have obtained an instantaneous image of the sample structure state at each X-ray scanning. The total number of diffraction patterns taken during the process was from 12 to 19. Just this number of experimental points is presented on kinetic curves below. During the intercalation interlayer gaps are increased according to the size of intercalating molecules [3], therefore, the use of small angles 2θ, in X-ray examinations is of particular importance. In this angular range, however, a fraction of the primary beam fall on the receiver thus causing a background increasing in intensity as the angle diminishes. A collimator was placed before the counter to reduce that background.

The diffraction pattern of the initial PbI_2 film is presented in Fig.1. The line $2\theta = 12.67°$ is attributed to reflection from (*001*) planes of the haxagonal lattice while the increased intensity at small angles (inset in Fig.1) is the above-mentioned instrumental background due to the primary beam (1) influence. All diffraction pattern as well as results of their processing presented in what follows are corrected by the instrumental background substraction from the total reflected intensity at all angles.

The diffraction pattern is seen to undergo transformations in the course of intercalation. The intensity of the pure PbI_2 line at $2\theta = 12.67°$ decreases and drops from 10^4 to

*Texturized film samples were obtained under participation of N.V.Tkachenko

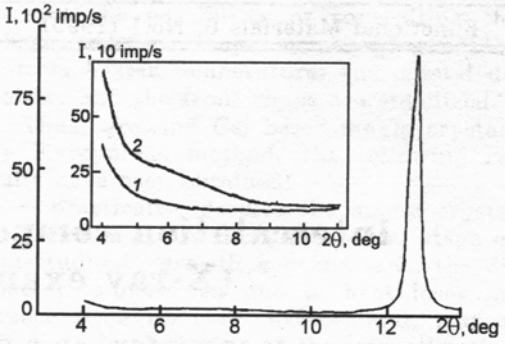

Fig.1. Diffraction pattern of the initial PbI_2 film. Inset: angular dependence of the background for the film (instrument noise) (1) and for the same film after the initial intercalation stage (exposure in piperidine vapor for 20 min) (2).

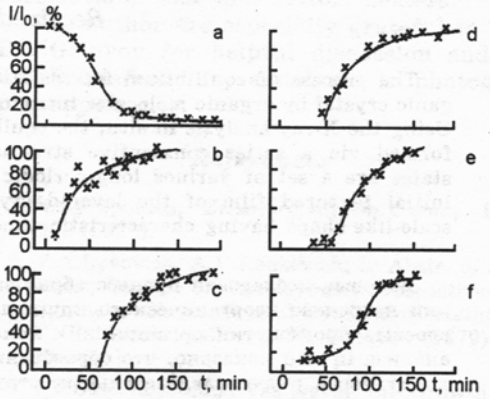

Fig.2. Time dependence of normalized intensity of X-ray, reflections: the 12.67° reflection (pure PbI_2) (a); integral reflection intensity in angular range 4–9° (b); integral intensity of band A (c); that of band B (d); intensity in the maximum of C line (e); that of D one (f). Notations A, B, C, D see in Fig.3. I_0 is the maximum intensity value for each curve.

40 pulse/s already at an exposure about 120 min. This evidences an essentially complete intercalation of the initial layered matrix. The intensity of that line was determined by its value at the maximum. Its variation kinetics is shown in Fig.2a.

Simultaneously with intensity reduction of that line, a background in the angular range 4–9° appears already at the initial intercalation stage and then its intensity increases progressively (inset in Fig.1, curve 2). In what follows, the word "background" will be used to denote the reflection intensity in the small angular range

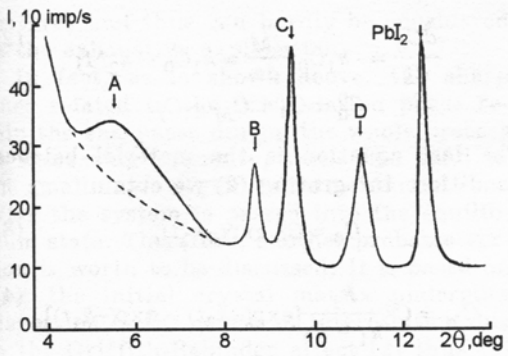

Fig.3. Diffraction pattern for PbI_2 film exposed in piperidine vapor during 120 min.

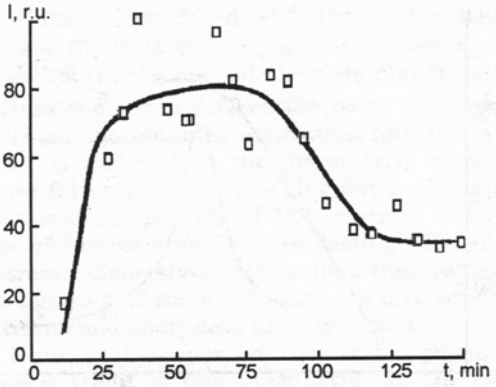

Fig.4. Time dependence of integral intensity of the structureless X-ray background in 2θ range from 4 to 9°.

where the instrumental background due to illumination by the primary beam is eliminated. The curve 2 in Fig.1 characterizes the angular dependence of the reflection intensity 20 min after the intercalation start. As the process continues, three narrow lines (B, C, D) appear with half-widths almost unchanged in time (Fig.3). The line B (8.73°) is formed in the region of the intercalation-induced background. After a time, another very diffuse band A with a maximum about 6° appears also within that region (see Fig.3).

Fig.2 presents dependences of A, B, C and D lines intensities on the exposure time in piperidine vapor. The intensity of sharp lines (C, D) was determined by their height. Since their half-widths are essentially independent of the intercalation time, those can be considered as instrumental constants. As to the line A with a great half-width that "grows out" of the background as well as to the narrower band B, their intensities were determined by integration over the angular range where these lines are visible (with substraction of the background that was interpolated as is shown in Fig.3). All four kinetic curves (Fig.2) turned out to be identical; their half-growth times as well as characteristic saturation ones (120–130 min) and latent periods (about 30 min) are essentially the same. Thus, all four X-ray reflections are evidenced to be related to the same phase arosen due to intercalation.

In the same time, the half-width of reflections changes in different manners at the same integral intensity kinetics for all lines related to the equilibrium intercalation phase. Two of four reflections (C and D) are revealed in the angular range where the intercalation-induced background does not appear while two others (A and B) are formed in the region of X-ray background arising in the course of intercalation at small angles of X-ray scattering. We estimated the integral intensity of X-ray reflection in the 2θ range from 4 to 9°. Its variation with time is presented in Fig.2b. The X-ray background caused by intercalation is seen to appear earlier (already after 20 min exposure) than pronounced Bragg reflection can be revealed. The time dependence of this integral intensity is strictly antibate to that for PbI_2 phase intensity (Fig.2a,b). It is apparent that the small-angle background is due to superposition of various long-periodic, very weakly ordered states arosen from PbI_2 in the course of intercalation. We determined the integral intensity of the continuous background in the 2θ region from 4 to 9° minus the intensity of formed A and B reflections. Fig.4 presents the time dependence of this structureless background intensity. The solid curve is the approximation of the experimental dependence by a 6th order polynom using the least square method. This dependence can be stated with assurance to pass a maximum. In the exposure time range 40–80 min, so considerable fluctuations are revealed both in Fig.2b and in Fig.4 that it seems to be quite likely that the system evolution is characterized by two maxima corresponding to weakly structurized intermediate states. The question on their origin will be discussed later, but no matter what it is, the integral background intensity characterizes a certain structure state of the intercalant-matrix system.

A more detailed analysis based on the integral intensity determination in angular ranges 4–5° and 5–9° within the time inter-

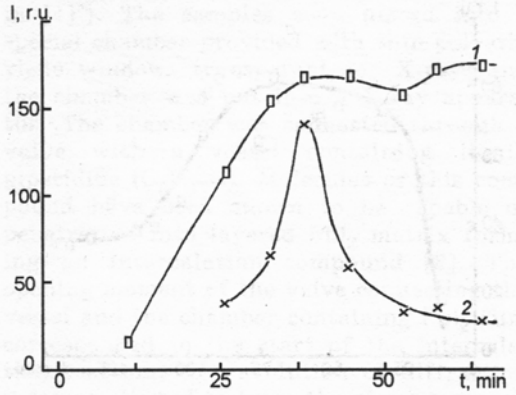

Fig.5. Dependences of the X-ray reflection intensity on the exposure time in piperidine vapor for angular ranges 5–9° (1) and 4–5° (2).

val up to 65 min has given the result presented in Fig.5. It is obvious that it is just the small-angle reflection that is responsible for the presence of the maximum shown in Fig.5 at short exposure durations. Thus, the long-periodic states are intermediate unstable ones in the kinetic of the stable intercalation phase formation. Consequently, this structure state is the intermediate stage of the formation reaction of the intercalation compound on the basis of the layered crystal matrix.

In fact, since the PbI_2 film was subjected to intercalation at open surface, the entering of intercalant molecules occurs homogeneously on the whole film surface in sites of its morphologic defects (see [1]). Therefore, the process kinetics is independent of space coordinates of a particular point on the film and the process rates are defined only by concentration ratios of corresponding structure states in the course of their transformations.

It is not difficult to describe the revealed processes in a general form. Let C_0, C_I and C_M be concentrations of the initial layered substance PbI_2, equilibrium intercalation phase INT and intermediate structure state M, respectively. The intercalation phase is supposed to be formed from the initial one according to consecutive reactions

$$PbI_2 + (pp) \xrightarrow{k_1} M \xrightarrow{k_2} INT, \qquad (1)$$

where k_1 and k_2 are rate constants of the corresponding reactions. The kinetics of such consecutive reactions is described by a system of equations (see e.g.[4])

$$\frac{dC_0}{dt} = -k_1 C_0; \frac{dM}{dt} = k_1 C_0 - k_2 M; \qquad (2)$$
$$C_0^0 = C_0 + C_M + C_I.$$

The last equation is the material balance condition. Integrating (2) we obtain

$$C_0 = C_0^0 \exp(-k_1 t), \qquad (3)$$

$$C_M = C_0^0 \frac{k_1}{k_1 - k_2}[\exp(-k_2 t) - \exp(-k_1 t)], \qquad (4)$$

$$C_I = C_0^0 \{1 + \frac{1}{k_1 - k_2} \times \qquad (5)$$
$$\times [k_2 \exp(-k_1 t) + k_1 \exp(-k_2 t)]\}.$$

It is seen from (3) that C_0 is diminished monotonously while according to (5), C_I increases monotonously approaching the complete transformation of the initial substance into the reaction product, in agreement with real data (Fig.2). At last, C_M pass a maximum [5] in the time moment

$$t = \alpha Ln\left(\frac{C_M^{(max)}}{k_2}\right), \qquad (6)$$

where C_M^{max} is the highest concentration value of the intermediate state and α characterizes the rate of the intercalant arrival to the matrix. It is just this behaviour that the intermediate state exhibits (Fig.5).

The equation (3) is seen to describe quite adequately the consequence of PbI_2 structure transformations during the intercalation process. What is the nature of the intermediate structure state ?

There are two likely reasons for such a great half-width of the A band ($\delta(2\theta) \approx 2\div3°$). The first might consist in that a considerable number of various matrix-intercalant structures is formed at the intermediate intercalation stage: those structures differ in interplane distances which are of course not eqiulibrium ones. By the completion of the process, equilibrium values of the intercalated crystal lattice parameters become established. This interpretation agrees with that the backround starts to increase before sharp B, C and D lines can be distinguished in diffraction patterns. The following analysis evidences, however, that the above interpretation, though being looking as a plausible one, does not describe adequately other process

features and thus can hardly be considered as the exhaustive explanation.

In fact, as is shown above, the sharp lines related to the intercalation phase retain the sharpness during the whole process at increasing intensity, while the band in the small-angle region remains blurred even after the system is passed into the equilibrium state. Therefore, another probable version is worth to be discussed. It is based on that the initial crystal matrix undergoes dispersion in the course of intercalation due to the Griffith-Rebinder effect [2] thus resulting in a broadening of diffraction lines. Using the Selyakov-Scherer formula [6], the mean size of the crystallite reflecting X-rays coherently can be estimated:

$$\delta = \frac{\lambda}{L \cos\theta}, \qquad (7)$$

where δ is the line angular width, λ is the X-ray wavelength, L, the crystallite dimension in the specific crystallographic direction, θ, the angle characterizing the diffraction maximum position.

Using data of Fig.3, let the characteristic crystallite size be estimated along the direction corresponding the maximum X-ray interferention at the diffraction angle 5–7°. It amounts from 30 to 100 Å, agreeing well with theoretical and experimental estimations of linear size of the layered matrix fragment after intercalation (see [3]). How the strange fact can be interpreted that the line A is very diffuse while lines B, C and D related to the same phase turn out to be very sharp with half-width not exceeding the instrumental reflection width? This fact, however, invokes a clear explanation. It is shown [2, 3], entering of molecules into interlayer gaps of layered matrices results in formation of crystalline fragments with dimensions limited just along the cleavage planes. Thus, if B, C, D lines corresponds to (00l) reflections, the crystallite size does not affect the line width. If, however, the interferention of reflections is associated with (h, k, l) planes (h, $k \neq 0$), it is the dispersivity along h, k direction (in the crystal cleavage plane) that defines the X-ray diffraction band width, δ.

Thus, the obtained estimation (30–100 Å) is to be assigned to the dispersivity of the phase forming due to breaking-down of quasi bidimensional packets of PbI_2 matrix. In the case of intercalation, we are dealing with anisotropic dispersivity. It is just that causes the blurring of some reflections in diffraction patterns and sharpness of others ones.

Note that dispersed matrix fragments show a trend to recrystallization in the atmosphere of intercalant substance vapors [7], thus, the band A is to be expected to become narrower at a further exposure of the film, however, this requires a considerably longer relaxation period.

Thus, the formation of intercalation compounds occurs by consecutive structure-chemical transformations. Intermediate states in this multistage process are strongly dispersed anisotropic formations including a wide set of long-periodic inequilibrium structures forming, in the end, the equilibrium intercalation phase.

This research had been supported in part by Ministry of the Science of Ukraine.

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Процес утворення інтеркаляційних сполук (рентгенографія in situ)

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Вперше досліджено процес утворення рівноважних інтеркаляційних сполук на основі неорганічного кристалу шаруватої структури при входженні органічних молекул у міжшарові проміжки. З використанням техніки рентгенографічного аналізу in situ показано, що утворення рівноважної інтеркаляційної фази протікає через низку послідовних структурно-хімічних перетворень. Проміжні стани являють собою низку різних довгоперіодних структур. У процесі інтеркаляції початкова текстурована плівка шаруватого кристалу диспергується, утворюючи фрагменти лускоподібної форми з характерними розмірами у кілька десятків ангстрем.