

## Changes in optical properties, structure and chemical composition of thin-film Ag–PbI<sub>2</sub> systems at intercalation of ammonia

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The results of optical, electron microscopic and electron diffraction studies of film PbI<sub>2</sub> and two-layer photosensitive Ag–PbI<sub>2</sub> systems and changes thereof under ammonia intercalation are reported. The effect of intercalation on the photographic characteristics of the samples (photosensitivity and contrast) has been established. The reversible changes in diffraction efficiency of photoinduced periodic structures have been revealed. The observed phenomena are discussed taking into account the concepts of the granular film optics and waveguide coatings, as well as of the chemical reaction kinetics.

Представлены результаты оптических, электронно-микроскопических и электронографических исследований пленок PbI<sub>2</sub> и двухслойных светочувствительных систем Ag–PbI<sub>2</sub> и их изменений при интеркаляции аммиака. Установлено влияние интеркаляции на фотографические характеристики образцов: светочувствительность и контрастность. Обнаружены обратимые изменения дифракционной эффективности фотоиндуцированных периодических структур. Наблюдаемые явления обсуждены с учетом представлений оптики гранулярных пленок и волноводных покрытий, закономерностей кинетики химических реакций.

The intercalation (IC) of layered crystals is known to be of interest in realization of structures with bidimensional electron spectra, in the studies on substance transfer in anisotropic media, the phase and structure transformation kinetics, etc. [1, 2]. The phenomenon can be used also to determine the organic molecules content in crystalline materials of layered structure (e.g., PbI<sub>2</sub>). The studies were carried out mainly using powders and single crystals. Of a great interest is no doubt to study the IC process in thin films, especially in connection with the known data [3] evidencing that layered compounds can take a photosensitivity when subjected to an intercalant action.

In this work, considered is the possibility to observe the IC process run using the diffraction efficiency  $\eta$  of periodic structures (PS). It has been found before [4–6]

that the photographic sensitivity effect is observed in two-layer systems on the basis of polycrystalline layers of some metals. This effect is due to photo-stimulated penetration (photo-diffusion) of the metal (Ag, Cu, etc.) into the polycrystal layer. That phenomenon is characterized by a number of simultaneous processes, in particular, by the formation and destruction of metal particles (granules) in the PbI<sub>2</sub> layer bulk, as well as appearance of new chemical compounds, including metastable ones. It has been revealed that conditions for excitation of waveguide modes and formation of diffraction periodic structures may arise when such film systems are exposed to one beam of monochromatic linearly polarized light [7, 8]. The processes mentioned are demonstrated themselves as various features, including reversible ones, in optical spectra of

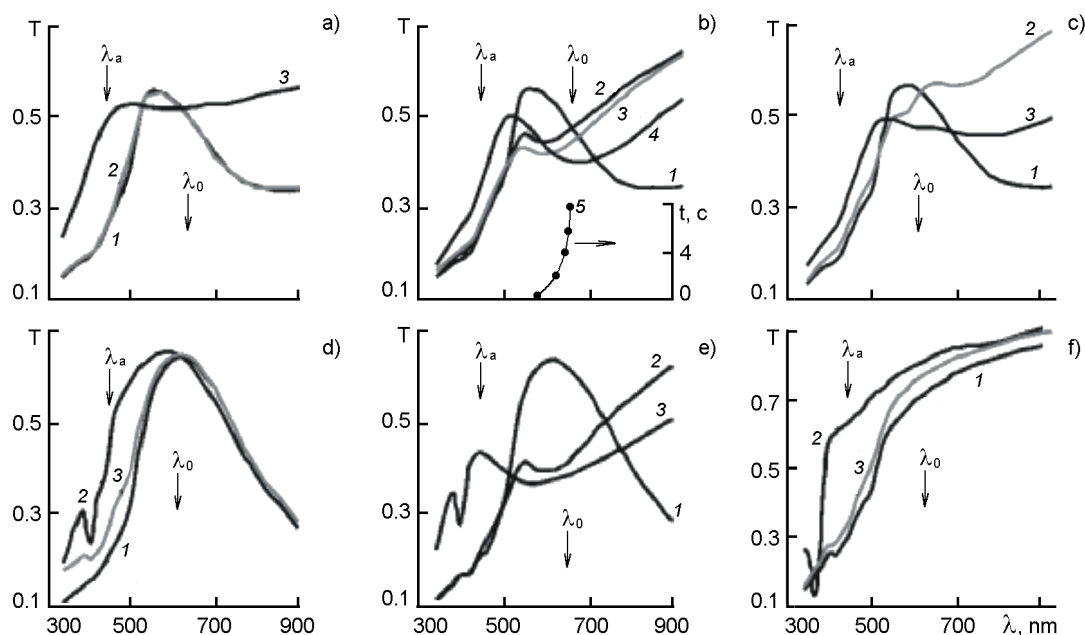


Fig. 1. Spectral dependences of optical transmission for a two-layer thin film Ag-PbI<sub>2</sub> system (a-e) and for a PbI<sub>2</sub> film (f). The layer thickness in the initial system: Ag, ~15 nm PbI<sub>2</sub>, ~30 nm. The curves 1 correspond to the freshly-prepared samples, the energy exposure at the irradiation  $H_e = 15 \text{ J/cm}^2$ . (a) after NH<sub>3</sub> exposure for 10 s (2) and 30 min (3); (b) irradiated at  $\lambda_a = 436 \text{ nm}$  (2); the same as (2) after NH<sub>3</sub> exposure for 1 s (3); the same as (2) after NH<sub>3</sub> exposure for 10 s (4); the  $\lambda_{min}$  wavelength as a function of NH<sub>3</sub> exposure duration (5); (c) irradiated at  $\lambda_0 = 633 \text{ nm}$  (2); the same as (2) after NH<sub>3</sub> exposure for 10 s (3); (d) a sample in NH<sub>3</sub> vapor (2) and after NH<sub>3</sub> removal (3); (e) irradiated at  $\lambda_a = 436 \text{ nm}$  (2) and after NH<sub>3</sub> removal (3); (f) a sample in NH<sub>3</sub> vapor (2) and one day after NH<sub>3</sub> removal (3).

thin film samples. The metal photo-diffusion mechanism into the polycrystal layers has been noted to be still not quite clear. There are essentially no data on the influence of some external factors on the processes in question, in particular, of the gas environment.

The two-layer samples to be studied were prepared by sequential deposition of the initial substances onto glass substrates at room temperature in vacuum ( $\sim 6.7 \cdot 10^{-3} \text{ Pa}$ ). The layer thickness during the deposition was monitored by photometry while the post-deposition thickness of individual layers and of the whole system was determined by multi-beam interferometry and found to be of 10 to 50 nm. Some structural and optical properties of the systems so obtained have been reported before [8]. The Ag metal films have an island-like (mosaic) structure (the particle size up to 100 nm, the filling factor  $q \sim 0.5$ ) while the PbI<sub>2</sub> layer is polycrystalline (the average crystallite size about 50 nm) and textured (the hexagonal axis predominant orientation is normal to the substrate). The samples were irradiated by laser beams at  $\lambda_a = 442 \text{ nm}$  and  $\lambda_0 = 633 \text{ nm}$  as well as by a mercury arc

lamp ( $\lambda_a = 436 \text{ nm}$ ) from both the sample free surface and the transparent substrate side. The optical properties of the thin film systems and the photo-induced changes therein were studied using the optical transmission  $T$  spectra in the 300 to 1000 nm wavelength range. Since the two-layer systems lose their photosensitivity in air rather fast (about 10 to 100 h), the freshly-prepared samples were examined.

A substrate with an Ag-PbI<sub>2</sub> or PbI<sub>2</sub> sample was placed into a chamber equipped with windows for laser beam input and output, means for NH<sub>3</sub> gas or ammonia-air mixture inlet and for the gas pressure control. Prior to the intercalant introduction, the chamber was partially evacuated or filled with atmospheric air. The ammonia content in the mixture was determined using the known chemical analysis technique including the titration [9]. The ammonia concentration was usually about 10 mg/L and its action on the samples was estimated basing on the residence time thereof in the gaseous medium.

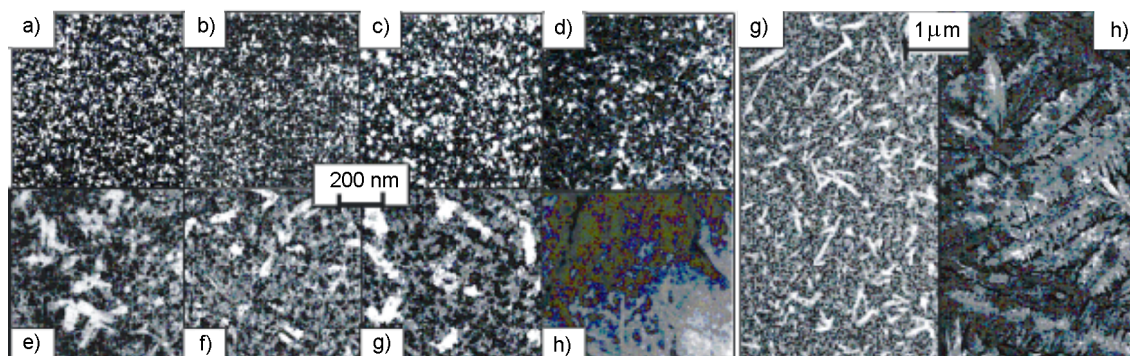


Fig. 2. Electron microscopic images of thin film Ag-PbI<sub>2</sub> system (a-c, e-g) and PbI<sub>2</sub> (d, h): (a-d), as-prepared samples; (e-h), NH<sub>3</sub> treated ones; (b, f) irradiated at  $\lambda_a = 436$  nm; (c, g) irradiated at  $\lambda_0 = 633$  nm. Energy exposure at the irradiation  $H_e = 15$  J/cm<sup>2</sup>. The NH<sub>3</sub> treatment duration 1 min under normal pressure.

Fig. 1 shows the experimental dependences of optical transmission  $T(\lambda)$  for the initial film systems irradiated with light of various spectral composition and exposed to ammonia; in Fig. 2, presented are the electron-microscopic (EM) images of the same systems. The spectra were measured both during the sample exposure in ammonia gas or air/ammonia mixture and after the sample removal out of the intercalant vapor where a fraction of intercalant is evaporated and only its equilibrium amount is remained in the film.

It follows from the transmission spectra shown in Fig. 1a–1c that a relatively short residence time of the freshly-prepared samples in ammonia medium results in insignificant changes in the spectra (curves 2, 3 and 3, respectively). At the same time, the feature (band) at 500 nm wavelength caused by the exciton state of PbI<sub>2</sub> disappears, thus evidencing its destruction. Considerable transformation in the transmission spectra take place under long-term intercalation (Fig. 1a–1c, curves 3, 4, 3, respectively). In the latter case, a considerable light scattering is observed, the samples are dispersed, that may result in the destruction thereof and separation from the substrate (Fig. 2h). The changes in spectra of Fig. 1d–1f (curves 2, 3, 2, respectively) are in general similar to those under long-term intercalation, but, in addition to the transmission edge shift to short-wavelength spectral region, narrow absorption bands are observed at 420 nm for silver-containing systems and at 360 nm for PbI<sub>2</sub>.

The changes in  $T(\lambda)$  dependences are obviously due to structural changes (Fig. 2e–2h) and in chemical compositions of two-layer systems, mainly in the PbI<sub>2</sub> layer.

This is evidenced by the results of NH<sub>3</sub> intercalation into a thin PbI<sub>2</sub> film (Fig. 1f), in particular, by the short-wave shift of the sample transmission edge.

The electronography results and the comparison thereof with the known X-ray diffraction data [9] prove the supposition that intercalation compounds of several types are formed in the thin film samples. Those are the intermediate PbI<sub>2</sub>(NH<sub>3</sub>)<sub>1.3</sub> phases having increased unit cell parameters as compared to those in the initial PbI<sub>2</sub> crystal (the I and II phases according to the classification [10]) as well as PbI<sub>2</sub>(NH<sub>3</sub>)<sub>2.47</sub> (III) and PbI<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub> (IV) phases.

The structural difference between the intercalated PbI<sub>2</sub> films and Ag-PbI<sub>2</sub> systems (Figs. 2e–2g and 2h) is connected likely with the presence of silver clusters (particles) in the Ag-PbI<sub>2</sub> samples, first of all in the locations of extended structure defects (dislocations, pores, etc.) where the intercalant molecules are fixed at penetration into the PbI<sub>2</sub> interlayer space. Moreover, hexagonal and cubic silver iodide phases are presented in the samples that arise during the partial penetration of silver into the PbI<sub>2</sub> at the sample preparation stages well during the irradiation with the  $\lambda_0$  light [7]. So, for example, the narrow absorption band in the Ag-PbI<sub>2</sub> spectrum (Figs. 1d, 1e, curves 2 and 3, respectively) at 420 nm may be due to the exciton state of  $\beta$ -AgI [11].

The optical radiation effect on the Ag-PbI<sub>2</sub> thin film systems results in changes in the transmission spectra thereof; that is typical of direct photographic recording in recording media based on photo-diffusion [4]. The irradiation of two-layer systems with the active light at  $\lambda_a = 442$  nm (or 436 nm) from the PbI<sub>2</sub> absorption edge (the

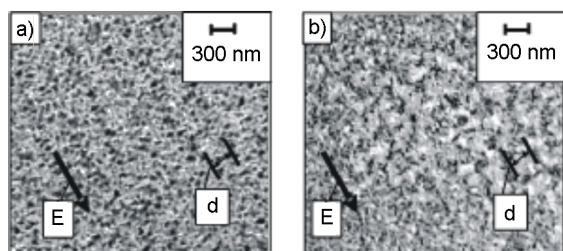


Fig. 3. Microphotos of a two-layer Ag-PbI<sub>2</sub> system sample: (a) irradiated at  $\lambda_0 = 633$  nm at  $H_e = 15$  J/cm<sup>2</sup>; (b) the same as (a) NH<sub>3</sub> treated for 1 min. The layer thickness in the initial system: Ag, ~15 nm PbI<sub>2</sub>, ~30 nm. **E**, the electric field strength of the light wave; **d**, the PS stroke spacing (period).

absorption coefficient  $\alpha \sim 2 \cdot 10^5$  cm<sup>-1</sup> [12] results in appearance of a band having the transmission minimum at  $\lambda \approx 620$  to 660 nm (Fig. 1b, curve 2). The band observed is due to the resonance absorption by silver particles appearing in the PbI<sub>2</sub> layer as a result of photo-diffusion caused by the irradiation [8]. The colloid band shift towards longer wavelengths under the sample intercalation (about 60 to 80 nm, see Fig. 1b, curves 3–5) may point to increasing dielectric constant of the medium surrounding the silver granules [13] connected with the formation of the intercalation-induced phases.

Under irradiation by  $\lambda_0 = 633$  nm from the PbI<sub>2</sub> transparency region [11], the transmission spectrum changes considerably but the colloid band is not appeared. The irradiation with linearly polarized light results in so-called photo-adaptation effect demonstrating itself as the transmission maximum

at the  $\lambda_0$  wavelength (Fig. 1c, curve 2). This singularity is a spectral sign of irregular PS photo-induced in the PbI<sub>2</sub> layer. The PS strokes are oriented predominantly in parallel to the light wave vector **E**, thus indicating the association thereof with the excitation of a waveguide mode TE<sub>0</sub> in the PbI<sub>2</sub> layer. The PS period **d** determined from the diffraction measurements agrees well with the electron microscopy data (Fig. 3a,  $d \approx 410$  nm). The small particles the PS are consisted of (evidently the silver metal granules) have a size of the order of few nanometers.

The action of ammonia medium on the irradiated samples causes a substantial transmission drop in the transparency region (Fig. 1c, curve 3). The observed transformations in optical spectra are due likely to the changes occurring in PS (Fig. 3b), where the strokes become disordered and the particles size increases; the dielectric surrounding thereof seems to be changed, too.

Thus, the study evidences that the ammonia IC into irradiated Ag-PbI<sub>2</sub> systems causes considerable changes in their transmission, that is, in the contrast of the optical image. An important feature of such a treatment is its selectivity demonstrated as different transmission changes in the irradiated and non-irradiated areas of the two-layer systems. The preliminary study show also that the sample exposure in ammonia atmosphere causes an enhanced light sensitivity thereof.

In this work, we have considered a possibility to monitor the IC process using the changes in the PS diffraction efficiency  $\eta$ . To that end, use was made of the optical

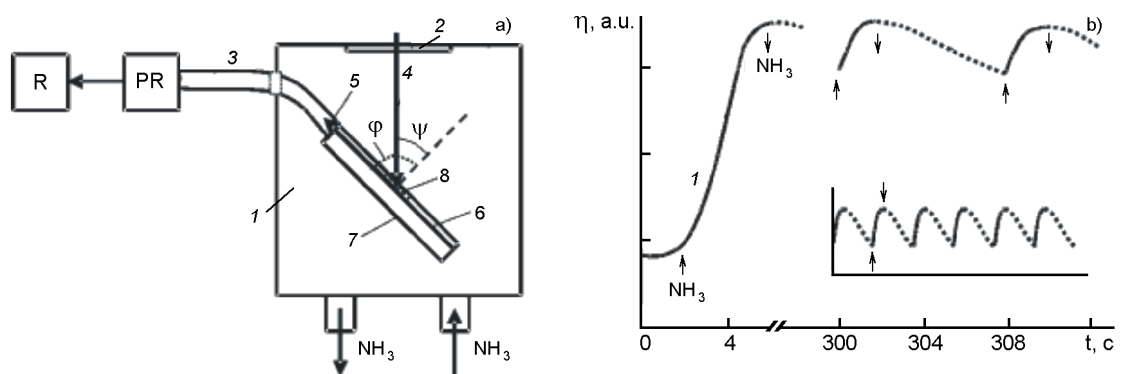


Fig. 4. Optical scheme for recording of beam diffracted on PS (a) and time dependences of the diffraction efficiency  $\eta$  (b): (a) 1, chamber; 2, transparent window; 3, fiber light guide; 4, incident laser beam; 5, diffracted beam; 6, Ag-PbI<sub>2</sub> film; 7, substrate; 8, the film area containing PS; PR, light receiver; R, recorder; (b) solid lines correspond to NH<sub>3</sub> introduction into the chamber, dashed ones, to NH<sub>3</sub> removal. Curve 1, the as-prepared sample; curve 2 and inset, subsequent reversible NH<sub>3</sub> introduction/removal cycles.

scheme for recording the beam diffracted on the PS (Fig. 4a) that, being propagated in the substrate, exits through its butt (only one diffraction reflection is observed). In Fig. 4b, shown are the time dependences of  $\eta$  changes (solid lines) during the air-ammonia mixture introduction into the chamber with the freshly prepared sample (curve 1), after the ammonia atmosphere removal (dashed lines) and during subsequent reversible cycles (more than 10) of the intercalant introduction/removal (curve 2, inset). It follows from the data obtained that the  $\text{NH}_3$  action results in increased intensity of the optical radiation diffracted on PS that may be due to the changes in dielectric surroundings of the metal granules as well as to enlargement thereof (Fig. 3b). For the as-prepared samples, the diffraction efficiency increases by about one decimal order, the kinetic curve in this case being S-shaped and having an inflection point (Fig. 4b, curve 1). The character of  $\eta(t)$  dependence changes in the subsequent cycles, the diffracted radiation intensity attaining a maximum value and then starts to decrease (Fig. 4b, curve 2).

The experimental  $\eta(t)$  curves can be described satisfactorily by a system of differential equations (1)–(3) typical of first order reactions including the formation of a metastable intermediate [2, 14]

$$C_0 = C_0^0 e^{-k_1 t}, \quad (1)$$

$$C_M = C_0^0 \frac{k_1}{k_1 - k_2} (e^{-k_2 t} - e^{-k_1 t}), \quad (2)$$

$$C_I = C_0^0 \left( 1 + \frac{1}{k_1 - k_2} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right), \quad (3)$$

where  $C_0$ ,  $C_M$ ,  $C_I$  are concentrations of the initial substance ( $\text{PbI}_2$ ), the intermediate and the final IC product, respectively;  $C_0^0 = C_0 + C_M + C_I = 1$ .

The calculated kinetic curves (Fig. 5, solid lines) for the intermediate (possibly metastable phases of  $\text{PbI}_2(\text{NH}_3)_{1.3}$ ,  $\text{PbI}_2(\text{NH}_3)_{2.47}$  phase [10]) and the final IC product ( $\text{PbI}_2(\text{NH}_3)_4$  [10]) are obtained for the values of the intermediate consumption constant  $k_1$  and formation one  $k_2$  of  $0.56 \text{ s}^{-1}$  and  $0.64 \text{ s}^{-1}$ , respectively.

The results obtained may be useful when studying the interaction regularities of optical radiation with thin film light-sensitive systems, in particular, the photo-stimulated

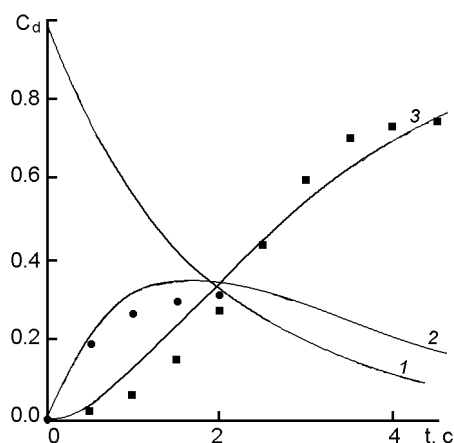


Fig. 5. Kinetic curves of ammonia intercalation. Solid lines calculated using Eqs. (1), (2) and (3); points denote experimental data.

diffusion mechanisms in polycrystalline semiconductor layers for technical photography, holography, integral optics, etc. The data on reversible changes of the PS diffraction efficiency may be of interest in the development of sensors for ammonia and its derivatives.

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## **Зміна оптичних властивостей, структури і хімічного складу тонкоплівкових систем Ag–PbI<sub>2</sub> при інтеркаляції аміаку**

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Представлено результати оптичних, електронно-мікроскопічних і електронографічних досліджень плівок PbI<sub>2</sub> та двошарових світлочутливих систем Ag–PbI<sub>2</sub> і їх змін за умови інтеркаляції аміаку. Встановлено вплив інтеркаляції на фотографічні характеристики зразків: світлочутливість і контрастність. Виявлено оборотні зміни дифракційної ефективності фотоіндукованих періодичних структур. Явища, які спостерігаються, обговорено з урахуванням концепцій оптики гранулярних плівок і хвилеводних покриттів, а також закономірностей кінетики хімічних реакцій.