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Intercalation and formation of complexes in the system of lead(II) iodide–ammonia

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Abstract

Interaction between lead(II) iodide and ammonia was studied with the help of an X-ray in situ analysis, DTA-TG analysis, DSC measurements and IR spectroscopy. A two-stage mechanism of the reaction was defined. At the first stage of the reaction two phases with trigonal symmetry and a phase with monoclinic symmetry are developed. At the second stage of the reaction the structure changes lead to formation of a compound with orthorhombic symmetry. The results were discussed along with the data of thermal analysis and IR spectroscopy. The value of enthalpy of formation for the compound $PbI_2(NH_3)_4$ was determined.

Keywords: Lead(II) iodide; Ammonia; Intercalation; Complex

1. Introduction

Intercalation of various electron-donating molecules into interlayer of PbI_2 crystals having a layered structure has been studied widely in recent decades [1–16]. In particular, thermodynamics of forming intercalated compounds of PbI_2 [9,17,18], photochemical reactions of intercalated compounds and photolysis of PbI_2 sensitized by molecules of intercalates [17,19–21], as well as properties of intercalated phases of PbI_2 [8,18,22,23] were studied. There was shown the possibility of using PbI_2 for quantitative determination of amines in non-reducing media [19]. In this connection a study of PbI_2–intercalate systems, in which formation of several intercalated phases occurs, is of special interest. PbI_2–2-aminoethanol [8,20], PbI_2–pyridine [1,9,22], PbI_2–hexahydropyridine [1,14] and PbI_2–ammonia [12,20,21,23] are examples of such systems.

An X-ray analysis in situ was carried out for the system of PbI_2–NH_3 [24–26] and PbI_2–$C_5H_{11}N$ [14]. Changes of the unit-cell parameters of PbI_2 crystal matrix [24] and development of a metastable phase were determined [25,26]. Kinetics of the changes in diffraction patterns on incorporation of hexahydropyridine molecules into textured films of PbI_2 were studied [14].

In this paper, we speak about our study of consequent changes in crystal structure of lead iodide and in properties of intercalate during incorporating NH_3 molecules. Methods of an X-ray structure analysis in situ, DTA-TG analysis, differential scanning calorimetry (DSC) and infrared spectroscopy were used.

2. Experimental

The purity of PbI_2 powder was checked by an X-ray analysis and IR spectroscopy. The purity of gaseous NH_3 was checked by the IR spectroscopy method. An X-ray study was carried out with the help of two powder X-ray diffractometers using Cu$K\alpha$ radiation. The lattice parameters and their standard deviations were calculated using a dichotomy method [27] after least-squares refinement of peak positions. The profiles of the diffraction lines were fitted with a Pseudo-Voigt function. To index the powder diffraction patterns a DICVOL93 program (D. Louer and A. Boultif), to calculate the theoretical X-ray powder diffraction patterns a LAZYPULVERIX program (K. Yvon) and

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to fit the profiles of diffraction lines a DIFFRAC/AT program (SOCABIM) there were used.

A trigonal system and a $P\bar{3}ml$ space group for a pure PbI_2 powder with the hexagonal unit-cell parameters of $a = 4.5569(4)$ Å and $c = 6.9803(12)$ Å were revealed. The lattice parameters were in a good concordance with the data of the work [28] and corresponded to 2H polytype of PbI_2. After deammoniation a restoration of the PbI_2 structure was observed.

To perform an X-ray analysis in situ in course of interaction between PbI_2 and NH_3 the sample of PbI_2 powder was placed into a special vacuum chamber equipped with a valve, an inlet for gaseous ammonia supply and a gas-pressure-measuring system. At a lower temperature a decrease in the reaction rate occurs which made it possible to record the diffraction patterns at the intermediate stages of the reaction. Our X-ray diffraction experiments were performed at a temperature of 285 K. The previously evacuated chamber was filled with gaseous ammonia up to a pressure of about 760 Torr.

Calorimetric measurements were carried out by the DSC with the help of a diathermal-shell calorimeter. A sample was prepared in a small glass ampoule. The previously evacuated ampoule with PbI_2 powder was filled with gaseous ammonia up to a pressure of 760 Torr and maintained under that condition for 96 h. To avoid decomposition, the ampoule was cooled to the liquid nitrogen temperature and was immediately sealed. The exposure time of a PbI_2 sample in ammonia medium was chosen to be 96 h, since at the longer exposure times no changes in the diffraction patterns were observed. The heating rate of the sample was equal to 5 K min^{-1} during the DSC measurements.

Besides, the methods of differential thermal analysis (DTA) and thermogravimetric analysis (TG) in argon atmosphere employing a Paulic–Paulic–Erday thermoanalyser were used. The heating rate was equal to 5 K min^{-1}. A double-beam "Specord IR-75" spectrophotometer was used in an infrared study. PbI_2 powder of was put on a KBr plate. Then the sample was placed into a gas chamber equipped with an inlet for gaseous ammonia supply and a gas-pressure-measuring system.

3. Results and discussion

Fig. 1A shows a diffraction pattern of a pure PbI_2 sample. The several diffraction patterns that were obtained during an X-ray analysis in situ in the course of interaction between PbI_2 and ammonia at a temperature of 285 K are presented in Figs. 1B–E. Two stages of the reaction can be found. A decrease in pristine PbI_2 content, formation of the intercalated phases **I** and **II** and development of the phase **III** (Figs. 1B and C) were revealed at the first stage of the reaction. A decrease in peak intensity of pristine PbI_2, development of the double peak at $2\Theta_1^\circ = 11.60^\circ$ and $2\Theta_2^\circ = 11.81^\circ$ and an increase in peak intensity of the phase **III** lead to this conclusion.

The appearance of diffraction lines at lower angles is induced by the enlarged size of the unit cell in *c*-axis, which is a typical manifestation of incorporation of guest molecules into a host matrix [2,6]. Theoretical diffraction patterns for PbI_2 with the values $c_1 = 7.49$ Å (for $2\Theta_1^\circ$) and $c_2 = 7.62$ Å (for $2\Theta_2^\circ$) in $P\bar{3}ml$ space group were calculated and compared with the diffraction patterns obtained experimentally. A new parameter of the unit cell a_1 was selected using the most intensive lines from the (001), (011), (102), (012), (110), (103) and (201) planes. The value a_1 was found to be the same for the both values c_1 and c_2, which was equal to 4.92 Å. It exceeded the initial value for PbI_2 lattice by 0.38 Å.

Thus, at the first stage of the reaction the two kinds of the unit cells with enlarged hexagonal parameters $a_1 = 4.92$ Å, $c_1 = 7.62$ Å and $a_1 = 4.92$ Å, $c_2 = 7.49$ Å were formed—phases **I** and **II**, respectively. The enlarged size of the unit cell in *a*-axis by $0.2-0.4$ Å together with the enlarged size in *c*-axis by $5.8-14.1$ Å was also found [14] during hydrazine-intercalation of thin evaporated films and powdered single crystals of PbI_2 at a pressure of about 20 Torr.

Table 1 shows the X-ray diffraction data with assigned Miller indices for the phase **III**. Stoichiometry of the phases was determined by DTA–TG analysis and corresponded to the compound of $PbI_2(NH_3)_{2.47}$. The lattice parameters for the phase **III** were calculated: $a = 10.238(11)$ Å, $b = 12.061(8)$ Å, $c = 9.587(8)$ Å, $\beta = 107.73(7)^\circ$ and $V = 1127.54$ Å^3. The lattice symmetry of the phase **III** was found to be monoclinic.

A decrease in the phase **III** content and formation of the phase **IV** (Figs. 1D–E) were found at the second stage of the reaction. A decrease in the peak intensity of the phase **III** and an increase in the peak intensity of the phase **IV** supported the above conclusion. It was clear that the phase **IV** formed at this stage was not an intercalation compound but formation of the complex occurred. Stoichiometry of the phase **IV** was determined by DTA–TG analysis and corresponded to the compound of $PbI_2(NH_3)_4$.

Table 2 shows the X-ray diffraction data with assigned Miller indices for the phase **IV**. The lattice parameters for the phase **IV** were calculated: $a = 19.894(23)$ Å, $b = 9.345(27)$ Å, $c = 7.021(10)$ Å and $V = 1305.35$ Å^3. The lattice symmetry of the phase **IV** was found to be orthorhombic.

The thermal analysis data confirmed the existence of several compounds in the system of PbI_2–NH_3. The results of thermogravimetric study of the phase **IV** are shown in Fig. 2B and C. The weight loss was consistent with the formulation of the starting composition, i.e. the phase **IV**, of $PbI_2(NH_3)_4$. Decomposition began at the temperatures $T < T_0$ which was

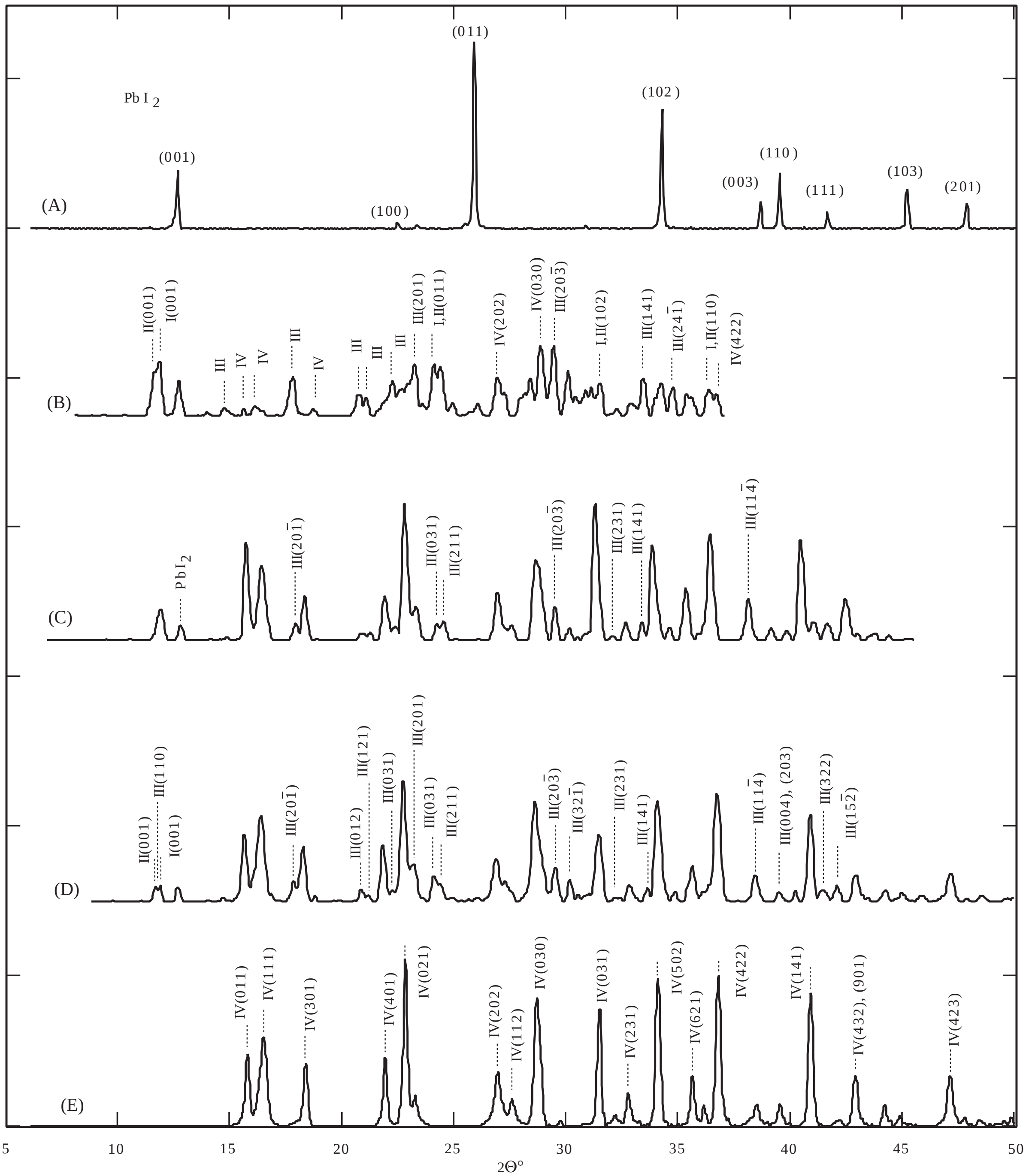

Fig. 1. X-ray diffraction patterns of PbI_2 powder sample at a temperature of 285 K before and after the beginning of the reaction between PbI_2 and NH_3: (A) pristine PbI_2; (B) 14 h, (C) 24 h, (D) 48 h; and (E) 72–96 h after the beginning of the reaction.

determined by instability of $PbI_2(NH_3)_4$ without ammonia medium. Fractions in the curve B (Fig. 2) occurred at temperatures of $T_2 = 359$ K, $T_3 = 393$ K and $T_4 = 423$ K. At the temperatures of T_2 and T_4 the rate of weight loss of the sample reached maximum values (Fig. 2C). So the point T_2 corresponded to a maximum temperature of decomposition of the phase **III**, and the point T_4 to a maximum temperature of decomposition of the phases **II** and **I**. The weight loss at the point T_2 was consistent with the formulation of the phase **III** of $PbI_2(NH_3)_{2.47}$; the weight loss at the point T_4 to with the formulation of the phases **II** and **I** of $PbI_2(NH_3)_{1.3}$. Probably the difference between the phases **II** and **I** was due to the orientation of the NH_3 molecules in the gallery space of the layered structure of PbI_2. The phase **III** differed from phases **I** and **II** in an

Table 1
X-ray data for the phase **III**—$PbI_2(NH_3)_{2.47}$

hkl	d_{OBS} (Å)	d_{CAL} (Å)	$d_{OBS} - d_{CAL}$ (Å)	I/I_0 (%)	$2\Theta^\circ_{OBS}$
1 1 0	7.557	7.58314	−0.02559	78.1	11.70
0 2 0	6.021	6.03066	−0.00941	15.7	14.70
2 0 $\bar{1}$	4.979	4.97658	0.00239	58.8	17.80
0 1 2	4.271	4.26993	0.00126	37.2	20.78
1 2 1	4.207	4.19422	0.01292	34.3	21.10
2 0 $\bar{2}$	3.995	3.99434	0.00142	62.7	22.23
2 0 1	3.834	3.84223	−0.00812	84.3	23.18
2 2 $\bar{1}$	—	3.83840	−0.00429	—	—
0 3 1	3.690	3.67957	0.01022	82.3	24.10
2 1 1	3.660	3.66096	−0.00109	76.5	24.30
1 3 $\bar{1}$	3.580	3.59128	−0.01119	23.5	24.85
2 0 $\bar{3}$	3.025	3.02942	−0.00391	78.1	29.50
0 3 2	—	3.01731	0.00819	—	—
3 2 $\bar{1}$	2.966	2.96678	−0.00023	77.5	30.10
2 1 $\bar{3}$	2.938	2.93816	−0.00021	40.2	30.40
2 3 1	2.778	2.77773	−0.00002	13.7	32.20
3 2 $\bar{2}$	—	2.78344	−0.00573	—	—
1 4 1	2.677	2.67899	−0.00228	58.8	33.45
2 4 $\bar{1}$	2.581	2.57888	0.00205	50	34.73
1 1 $\bar{4}$	2.342	2.34453	−0.00224	100.0	38.40
1 4 2	—	2.34304	−0.00076	—	—
1 5 0	—	2.34168	0.00061	—	—
0 0 4	2.285	2.28281	0.00230	87.5	39.40
2 0 3	—	2.28787	−0.00276	—	—
3 2 2	2.176	2.17620	0.00000	46.9	41.46
1 5 $\bar{2}$	2.148	2.14838	0.00011	50.0	42.02
1 0 4	2.086	2.08618	−0.00058	21.9	43.35

Table 2
X-ray data for the phase **IV**—$PbI_2(NH_3)_4$

hkl	d_{OBS} (Å)	d_{CAL} (Å)	$d_{OBS} - d_{CAL}$ (Å)	I/I_0 (%)	$2\Theta^\circ_{OBS}$
0 1 1	5.629	5.61348	0.01574	42.8	15.73
1 1 1	5.386	5.40252	−0.01647	53.3	16.45
3 0 1	4.836	4.82096	0.01523	36.8	18.33
4 0 1	4.062	4.05841	0.00322	40.4	21.86
0 2 1	3.903	3.89001	0.01254	100.0	22.77
2 0 2	3.310	3.31048	−0.00019	32.3	26.91
6 0 0	—	3.31560	−0.00532	—	—
1 1 2	3.239	3.24244	−0.00393	15.6	27.52
5 1 1	—	3.24605	−0.00753	—	—
0 3 0	3.115	3.11514	0.00029	77.5	28.63
2 1 2	—	3.12048	−0.00505	—	—
0 3 1	2.844	2.84747	−0.00322	70.0	31.43
7 0 0	—	2.84195	0.00230	—	—
2 3 1	2.735	2.73751	−0.00252	19.1	32.72
4 1 2	—	2.74185	−0.00687	—	—
2 2 2	2.695	2.70126	−0.00662	2.7	33.22
5 0 2	2.631	2.63240	−0.00142	89.2	34.05
7 0 1	—	2.63433	−0.00335	—	—
6 2 1	2.521	2.52337	−0.00266	30.2	35.59
8 0 0	2.487	2.48670	0.00036	12.2	36.08
4 2 2	2.444	2.44435	0.00005	90.4	36.74
1 4 1	2.207	2.20321	0.00355	79.9	40.86
9 0 0	—	2.21040	−0.00364	—	—
3 0 3	—	2.20699	−0.00022	—	—
3 4 0	—	2.20359	0.00318	—	—
7 0 2	—	2.20888	−0.00212	—	—
9 0 1	2.109	2.10839	0.00024	29.6	42.85
4 3 2	—	2.10998	−0.00135	—	—
2 2 3	2.049	2.04778	0.00082	12.2	44.17
4 2 3	1.929	1.92882	0.00007	30.1	47.07

increased ammonia content and another type of cell symmetry.

Endothermic effect was manifested during the outflow of ammonia from a sample, and on the DTA traces the maximums were fixed at the temperatures T_2 and T_4 (Fig. 2D). The temperature region $T_0 - T_2$ corresponds to the transition from the phase **IV** to the phase **III**, and the region $T_2 - T_4$ to the transition from the phase **III** to the phases **II** and **I**. In the temperature region $T_4 - T_5$ the transition to a pristine PbI_2 structure occurred.

Curve A shown in Fig. 2 was obtained during a differential scanning calorimetry (DSC) study of $PbI_2(NH_3)_4$ sample. In the curve there was a single endothermic peak at the temperature of $T_4 = 423\,K$ which indicated an deammoniation process in the sample. An absence of any peak at lower temperatures showed that ammonia molecules persisted in the sample at temperatures $T < T_3$. Evidently, at those temperatures the ammonia concentration in a sealed ampoule with the sample was higher than the threshold concentration of NH_3 at the beginning of decomposition. At a higher temperature an increase in the threshold concentration occurred. At temperatures $T > T_3$ the threshold concentration exceeded the ammonia concentration in the ampoule, and deammoniation process became possible. The intercalation threshold in PbI_2 for various amines

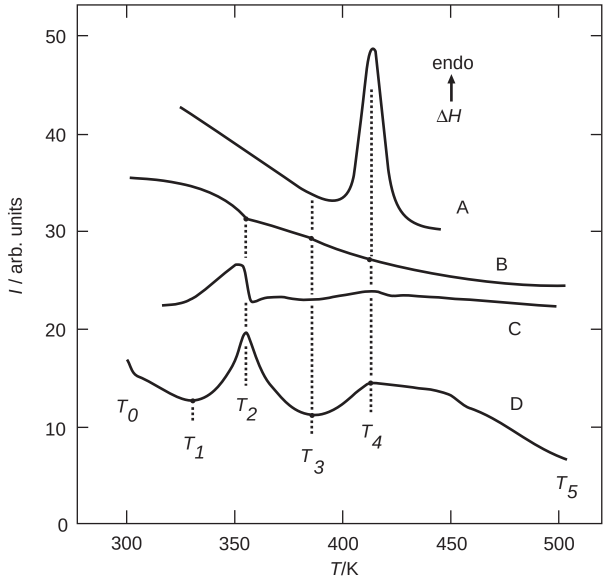

Fig. 2. Data of thermal analysis for the $PbI_2(NH_3)_4$ samples: (A) differential scanning calorimetric curve; (B) thermogravimetric curve; (C) derived from the slope of the curve B; and (D) DTA curve.

and the dependence of threshold on temperature were studied earlier [10,17].

An enthalpy (ΔH) of formation of $PbI_2(NH_3)_4$ was determined from the DSC data, and was equal to $20.8\,kJ\,mol^{-1}$. This value was close to that of other intercalated PbI_2 compounds [9,18].

To explore the changes of vibrational spectra of incorporated NH_3 molecules in NH_3–PbI_2 compounds, an IR spectroscopic study in the range of 400–4000 cm^{-1}, where the semiconductor matrix PbI_2 is transparent, was carried out. The changes of IR spectra of samples were recorded during deammoniation of $PbI_2(NH_3)_4$ at a temperature of 285 K. During transition from $PbI_2(NH_3)_4$ to the phase **III** the color of the sample changed from white to pale yellow. Parts of IR spectra of the $PbI_2(NH_3)_4$ and $PbI_2(NH_3)_{2.47}$ compounds during the deammoniation process are presented in Figs. 3A–C. Fig. 3D shows a part of IR spectra of gaseous NH_3 within the same region of wavenumbers. Symmetric ν_1(NH) and antisymmetric ν_3(NH) modes of the N–H bond of gaseous ammonia at 3333 and 3444 cm^{-1} were shifted: (i) to 3320 and 3433 cm^{-1} for $PbI_2(NH_3)_{2.47}$ and (ii) to 3307 and 3427 cm^{-1} for $PbI_2(NH_3)_4$, respectively. Observed changes for $PbI_2(NH_3)_{2.47}$ are in good agreement with the data of the work [12] for intercalated samples of textured thin films of PbI_2. These changes of vibrational spectra of incorporated amines were a typical manifestation of the fact of interaction between PbI_2 and amine intercalates [5,7,12,22]. In the works [5,7] the fact of charge transfer interaction between atom of Pb and free electron pair of nitrogen atom was ascertained for the compounds of PbI_2 intercalated by amines.

New modes at 3307 cm^{-1} for $PbI_2(NH_3)_{2.47}$ and at 3286 cm^{-1} for $PbI_2(NH_3)_4$ were found in the range of ν_3(NH). The H–N–H torsional mode at 628 cm^{-1} was slightly shifted to 624 cm^{-1} for $PbI_2(NH_3)_{2.47}$, and two new modes at 629 cm^{-1} and 611 cm^{-1} were found for $PbI_2(NH_3)_4$. The mode of NH^{4+} was not observed which was also pointed out in the work [12], where IR spectrum in the range of 400–4000 cm^{-1} was presented.

For $PbI_2(NH_3)_{2.47}$ and $PbI_2(NH_3)_4$ the values of the shift in absorption band of symmetric ν_1(NH) mode were essentially greater than those of the antisymmetric ν_3(NH) mode (Table 3). A similar effect was revealed during transition from gaseous to crystalline ammonia, when hydrogen bonds were formed by free electron pair of nitrogen atom and atom of hydrogen [29]. During selective adsorption of ammonia molecules on a surface [30], when the interaction between surface cations and free electron pair of nitrogen atom of NH_3 mostly occurred, an inverse effect was observed, namely, shift of ν_3(NH) mode exceeded shift of ν_1(NH) mode. A similar inverse effect was revealed earlier [9,22] during intercalation of PbI_2 by some amines: aniline, *p*-toluidine, hexylamine and *p*-nitroaniline (Table 4).

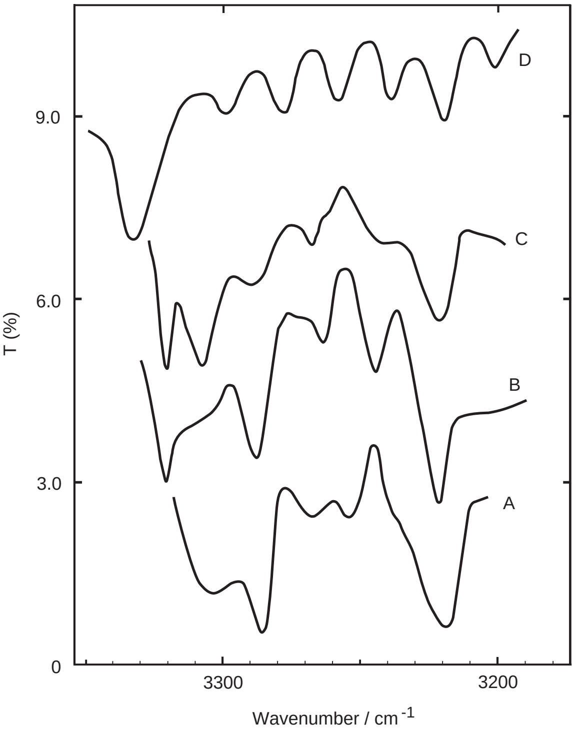

Fig. 3. Parts of infrared spectra: (A) of ammonia in the $PbI_2(NH_3)_4$ sample; (B) of ammonia in the sample during the transition from $PbI_2(NH_3)_4$ to $PbI_2(NH_3)_{2.47}$; (C) of ammonia in the $PbI_2(NH_3)_{2.47}$ sample; and (D) of gaseous ammonia.

Table 3
Changes in vibrational modes of NH_3 in the compounds with PbI_2 [this work] and in crystal NH_3 [29]

	ν_3 (cm^{-1})	$\Delta\nu_3$ (cm^{-1})	ν_1 (cm^{-1})	$\Delta\nu_1$ (cm^{-1})
Gaseous NH_3	3444		3333	
$PbI_2(NH_3)_{2.47}$	3433	11	3320	13
$PbI_2(NH_3)_4$	3427	17	3304	29
Gaseous NH_3 [29]	3444		3336	
Crystal NH_3 [29]	3378	66	3223	113

Table 4
Changes in vibrational modes of some amines in the compounds with PbI_2 [9,22]

	ν_3 (cm^{-1})	$\Delta\nu_3$ (cm^{-1})	ν_1 (cm^{-1})	$\Delta\nu_1$ (cm^{-1})
Aniline	3450		3375	
PbI_2–aniline	3320	130	3260	115
p-Toluidine	3420		3340	
PbI_2–*p*-toluidine	3300	120	3225	115
Hexylamine	3410		3320	
PbI_2–hexylamine	3320	90	3260	60
p-Nitroaniline	3480		3360	
PbI_2–*p*-nitroaniline	3285	195	3225	135

The anomalous shifts of ν_3(NH) and ν_1(NH) modes of ammonia in comparison with the shifts for other amines can be caused by the absence of radicals in the ammonia molecule, the radicals imposing steric restrictions on interaction between atom of hydrogen of the N–H bond and electron-donating atom of iodine.

The experimental results obtained can be explained by the existence of the interaction both between hydrogen atom of NH_3 and iodine atom as well as between Pb cation and nitrogen atom during the formation of the compounds PbI_2 with NH_3. That is in good agreement with the data of the works [10,11] where modelling the changes in the band structure of PbI_2 during intercalation resulted in the conclusion that interaction between the iodine $5p_z$ electron and intercalate substantially contributed to the changes in band structure of PbI_2.

4. Conclusions

The consequent changes in the crystal structure of PbI_2 during incorporating NH_3 molecules and the changes in vibrational spectra of incorporated NH_3 molecules during changing stoichiometry of the PbI_2–NH_3 complex were studied. The following four compounds were found: $PbI_2(NH_3)_{1.3}$ (**I** and **II**), $PbI_2(NH_3)_{2.47}$ (**III**) and $PbI_2(NH_3)_4$ (**IV**). Under the conditions of our experiment three phases $PbI_2(NH_3)_{1.3}$ (**I** and **II**) and $PbI_2(NH_3)_{2.47}$ were intermediated phases, and the phase $PbI_2(NH_3)_4$ in ammonia atmosphere at a pressure of 760 Torr and at room temperature was a thermodynamic stable phase. The formation of the complex compound $PbI_2(NH_3)_4$ passed through two stages. Two compounds $PbI_2(NH_3)_{1.3}$ with the lattice constants $a_1 = 4.92\,Å$, $c_1 = 7.62\,Å$ and $a_1 = 4.92\,Å$, $c_2 = 7.49\,Å$ in $P\bar{3}ml$ space group and the $PbI_2(NH_3)_{2.47}$ compound with the lattice constants $a = 10.238(11)\,Å$, $b = 12.061(8)\,Å$, $c = 9.587(8)\,Å$, $\beta = 107.73(7)^\circ$ in monoclinic system were formed at the first stage of the reaction. At the second stage of the reaction the $PbI_2(NH_3)_4$ compound with the lattice constants $a = 19.894(23)\,Å$, $b = 9.345(27)\,Å$, $c = 7.021(10)\,Å$ in orthorhombic system was formed. Anomalous shifts of symmetric ν_1(NH) and antisymmetric ν_3(NH) modes of the N–H bond of $PbI_2(NH_3)_{2.47}$ and $PbI_2(NH_3)_4$ in comparison with the shifts for other compounds PbI_2 with amines were found.

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