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Films and crystalline powder of BiI_3 intercalated with ammonia

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Abstract

Intercalation, i.e. the insertion of guest species in a crystalline layered structure, is an efficient route for generating new materials with novel properties. Thin films and crystalline powder of BiI_3 layered semiconductor were intercalated by exposure to ammonia vapors at room temperature. The intercalated compound was studied by thermo-gravimetric analysis, differential scanning calorimetry, X-ray diffraction, UV–vis optical absorption, FTIR spectroscopy and Raman scattering. After exposure of BiI_3 to ammonia the formation of a new phase, $BiI_3(NH_3)_{3.83}$, was evidenced by thermal analysis. The intercalation process leads to a blue shift of the BiI_3 optical absorption edge by 0.5 eV. The appearance of new Raman lines at 135 and 353 cm^{-1} in the Raman spectrum of intercalated BiI_3 is considered as an evidence of the chemical interaction between the ammonia molecules and BiI_3 lattice.

Keywords: Films; Spectroscopy; Optical properties; Thermal properties; BiI_3

1. Introduction

During the last years, the intercalation of organic/inorganic molecules in various layered materials such as graphite, clay minerals, metal dichalcogenides, layered double hydroxides, etc. has drawn the attention of the researchers at both fundamental and practical viewpoints. The intercalation process can modify the optical and electronic properties of the two components, the host layered material and the guest molecules; moreover, the properties of the intercalated material can be tuned by the proper choice of host–guest system. These features make possible to discuss the relationships between their structure, properties and applications. In this framework, intercalation compounds have been investigated for wider applications in areas such as: photoelectrochemistry, photodetection, photocatalysis, energy storage, nonlinear optics [1].

Due to their sandwiched layer structure, in which a plane of metal ions is surrounded by two planes of halogens ions, the crystalline layered semiconductors, as PbI_2, BiI_3 and CdI_2 are particularly interesting for intercalation with different molecules. The bonds within halogen–metal–halogen layer are strong while those between adjacent layers are weak, related to van der Waals type forces. As a result the insertion of guest molecules into the interlayer spaces is easy to achieve, leading to a change in many physical properties (optical, electrical, morphological, etc.) of the semiconductor layered crystal. In most cases, the works regarding the intercalation of layered metal iodides (PbI_2, BiI_3 and CdI_2) with different guest species were focused on PbI_2 as matrix [2–5].

BiI_3, a layered semiconductor with the band gap of ~2 eV, was found interesting especially as a material for nonlinear optics. The crystal structure of bismuth tri-iodide is rhombohedral with the *c*-axis perpendicular to the basal plane. Each bismuth ion is octahedrally coordinated with six iodine ions, and each structural layer consists in three I–Bi–I sheets. From a planar perspective along the *c*-axis, only two-thirds of the possible metal sites are occupied. Thus each anion is bound at two cations. According to the band structure calculations [6], the top of the valence band in bismuth tri-iodide is formed by an admixture of the $6s^2$ electrons in Bi^{3+} with $5p^6$ electrons of I^-. The lowest energy of the conduction band originates from the 6p state of Bi^{3+}. Thus the optical properties in BiI_3 bulk crystal are described by the cationic exciton model based on the intra-cation transitions from 6s to 6p states in Bi^{3+} ion [7]. It has to be mentioned that in the case of BiI_3 intercalated with hydrazine a shift of the cationic absorption band to higher energies was observed [8]. The process of intercalation may be accompanied by charge transfer, from the intercalate species to the host lattice. The most

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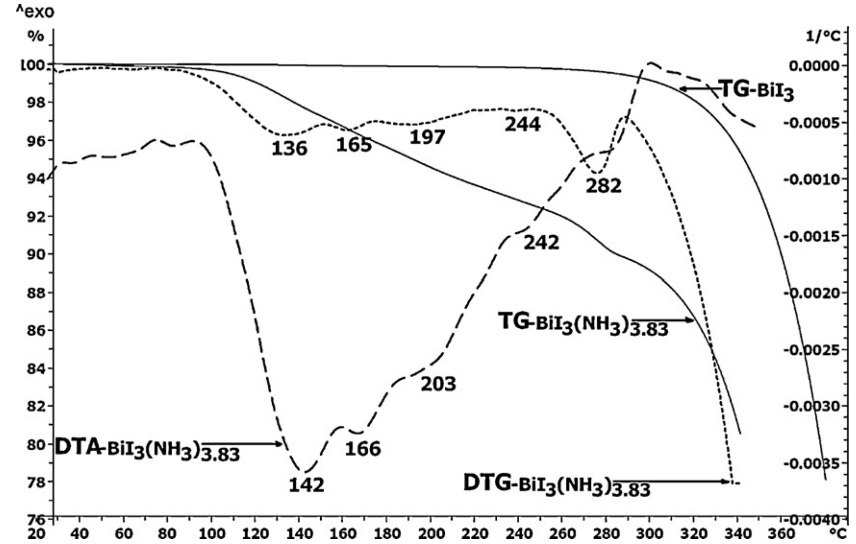

Fig. 1. Thermal analysis data (DTA–TG) for BiI_3 and $BiI_3(NH_3)_{3.83}$ powders. Heating rate: 10 °C/min.

papers taken into account the formation of the coordination complexes as result of the chemical interaction between BiI_3 and different organic molecules (tetramethylthiourea, pyridine, thiourea or triazole) [9–12].

Therefore, the aim of this paper is to supply further information about the intercalation of BiI_3, using ammonia, an inorganic nitrogen-containing molecule, as guest molecules. For this purpose, different techniques as thermo-gravimetric analysis, differential scanning calorimetry, X-ray diffraction, UV–vis optical absorption, FTIR spectroscopy and Raman scattering were used. Another goal of this work was to find an answer to a question which frequently arises in the context of any intercalation process, i.e.: what is the adsorption type of the guest molecules into the host matrix, a physical or a chemical one?

2. Experimental

Two kinds of samples were used in this work: micrometric crystalline powder and films of BiI_3. The crystalline powder was obtained by mechanical crumbling of a BiI_3 single crystal grown from melt by Bridgman method. The films of BiI_3, deposited on quartz substrates, were prepared by high vacuum thermal evaporation. Intercalation was achieved by exposing the samples (films and crystalline powder) to ammonia vapors at room temperature. It is interesting to notice a visual modification: as a consequence of ammonia molecules diffusion into both BiI_3 films and crystalline powder, the color of layered material is changed from black to reddish.

The thermal properties were studied with a Mettler Toledo TGA-SDTA 851^e equipment. The measurements were carried out in nonisothermal conditions, in the range of 25–390 °C with 10 °C/min heating rate. Two heating successive cycles with the intermediate cooling process (10 °C/min) were recorded.

The powder samples were characterized by X-ray diffraction (XRD) on a Bruker AXS D8 Advance instrument with Cu Kα radiation ($\lambda = 0.154$ nm) at room temperature.

Optical absorption spectra were obtained in the range of 200–800 nm using a Lambda 950 Perkin-Elmer spectrophotometer. All absorption measurements were made at room temperature and baseline corrected.

The infrared absorption spectra were recorded at room temperature with a Nicolet 6700 FTIR spectrometer in the range of 4000–400 cm^{-1}.

The Raman studies were performed at room temperature under 1064 nm excitation wavelength using a FT Raman Bruker RFS 100/S spectrometer.

3. Results and discussion

The thermal analysis data for the investigated powders are presented in Fig. 1 (DTA–TG – differential thermal analysis and thermal gravimetry analysis) and Fig. 2 (DSC – differential scanning calorimetry).

Pristine BiI_3 presents 0.52% weight loss up to 300 °C attributable especially to the adsorbed water. Above this temperature the slope of the curve changes indicating an accentuated weight loss (−21.8%) up to 390 °C. When BiI_3 is exposed to ammonia the thermal behavior changed. The weight loss took place in two stages: first, −9.95 wt%, in the range of 100–285 °C and the second, −9.55 wt%, starting from the inflection point up to 350 °C. We mention that the process is not finished in the investigated range of temperatures. The first loss is attributable to the release of ammonia from the powder. This observation is consistent with the thermal behavior of pristine BiI_3. The stoichiometry of the phase was determined by DTA–TG analysis and corresponds to the formula $BiI_3(NH_3)_{3.83}$. The first derivate of TG curve (DTG) presents some minima in this interval of temperatures which can be associated with the endothermic events recorded on the DTA curve: 142, 166, 203, 242 and 282 °C. The first four events can be associated with the elimination of the ammonia from the phase, depending on the bonding strength. Continuing to increase the temperature, a larger mass loss in TG curve (−9.5 wt% up to 340 °C) follows. This corresponds to

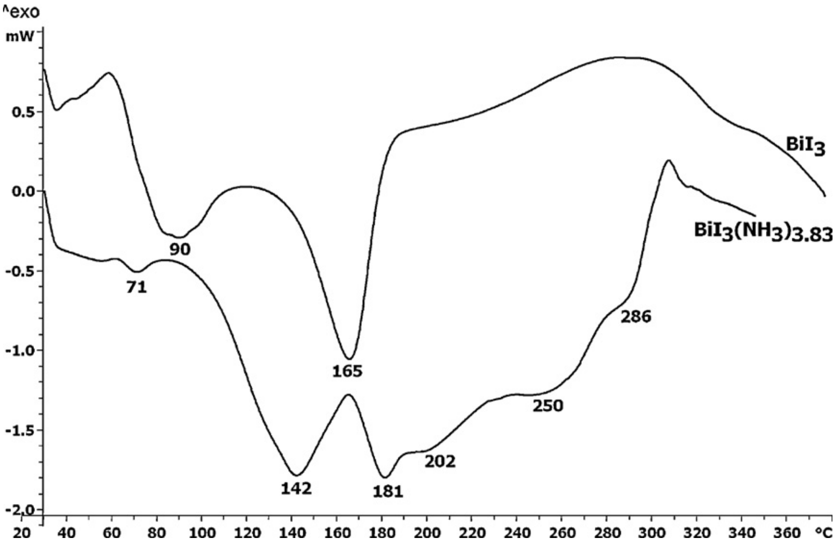

Fig. 2. Differential scanning calorimetry of BiI_3 and $BiI_3(NH_3)_{3.83}$ powders. Heating rate: 10 °C/min, in air.

iodine loses. The break of the Bi–I bond in the ammonia intercalated compound and the volatilization of I_2 from the sample demands a certain amount of energy, hence, this corresponds to an endothermic peak at 282 °C.

DSC results were corroborated with the phase diagram of Bi-I_2 system published in Ref. [13]. Fig. 2 shows two endothermic peaks at 90 and 165 °C, respectively, on DSC curve, the first one before the beginning of thermal decomposition of BiI_3. This endothermic event may be attributed to the structure rearrangement or to a possible phase transition ($\alpha \rightarrow \beta$) [13]. The second effect, observed also on the DTA curve, may be assigned to possible mixtures, ($BiI_3 + BiI$) or ($BiI_3 + I_2$), controlled by the system stoichiometry. The DSC curve of $BiI_3(NH_3)_{3.83}$ presents a different thermal behavior compared with BiI_3 suggesting the formation of a new structure. The small endothermic effect at 71 °C may be attributed to the adsorbed atmospheric water. The next endothermic events, signaled at 142, 181, 202, 250 and 286 °C respectively, correspond to the effects observed also on the DTA curve (Fig. 1). The first four events can be associated with the detachment and release of ammonia molecules from the phase, depending on the bonding type.

A structural information regarding the pristine BiI_3 and ammonia intercalated compound ($BiI_3(NH_3)_{3.83}$) is obtained from the XRD spectra (Fig. 3). It may be seen that the XRD spectrum of $BiI_3(NH_3)_{3.83}$ compound is totally changed from that of BiI_3. Thus, the intercalated compound belongs to a monoclinic system while the BiI_3 presents a hexagonal structure (JCPDS card no. 7-269). It is interesting to notice that a similar passage from hexagonal to monoclinic structure was signaled in the complexation process of BiI_3 with thiourea [11].

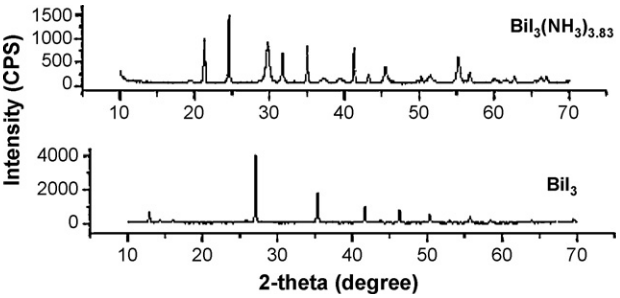

Fig. 3. X-ray diffraction patterns of BiI_3 before and after the reaction with NH_3.

In the following we present comparative data regarding the absorption properties of pristine BiI_3 and an ammonia intercalated compound.

Optical absorption spectra of BiI_3 film recorded at room temperature before and after intercalation are shown in Fig. 4A and B, respectively. In agreement with the literature data, the typical absorption spectrum of BiI_3 film consists in three peaks located at: 2.05 (the band edge), 2.67 and 3.25 eV [14]. After the exposure to ammonia vapors the texture of the initial film is partially disrupted, leading to a noticeable decrease of the absorbency (Fig. 4B). Another experimental visual detail which has to be notice is the color change of the BiI_3 film during intercalation, from black to reddish.

Upon 5 min exposure, the optical band edge of BiI_3 film blue shifts at about 2.42 eV (Fig. 4B solid line). Such a shift of the absorption band edge towards to higher energy was also observed in the case of BiI_3 intercalated with hydrazine [8] but its origin was uncertain. A chemical interaction between the guest nitrogen-containing molecules and the host lattice, having as result the change of BiI_3 electronic energy levels, could be an explanation. As we mentioned above, in the case of charge transfer complexes based on BiI_3 and different organic molecules, the modification of the pristine BiI_3 band gap have already been reported [12]. Also, a chemical interaction, leading to the formation of a coordination complex was observed in the intercalation of a kindred layered semiconductor, PbI_2, with pyridine [15].

In Fig. 4B with dotted line, the optical spectrum of the same BiI_3 film recorded 3 days after the removal from ammonia atmosphere is shown. Comparing the two curves, the main difference between them is a small red shift of the first peak from 2.42 to 2.30 eV. The shift indicates that a part of ammonia molecules was desorbed from the BiI_3 matrix during the 3 days when the film was stored in the air. The lost molecules are those bonded by weak forces into the host lattice. On the other hand, the gross similarity of the two absorption spectra in Fig. 4B suggests the formation of a stable intercalated compound involving ammonia molecules bonded by stronger forces. Based on these observations we can state that two adsorbed ammonia forms are presented in the crystalline lattice: a physisorbed one, featured by weak van der Waals type forces, and a chemisorbed one, involving stronger forces, probably originating in a charge transfer interaction between the lone electron pair of the nitrogen atom and the bismuth ions.

To explore the vibration properties of intercalated compound a FTIR spectroscopic study in the range of 4000–400 cm^{-1} was carried out (Fig. 5). The major difference of the two spectra (BiI_3 pristine and intercalated BiI_3) consists in the appearance of a sharp and intense band at 1402 cm^{-1} and two broad bands in the region 2900–3500 cm^{-1}. For these last bands symmetric ν_1(NH) and antisymmetric ν_3(NH) modes of the N–H bond of gaseous ammonia at 3333 and 3433 cm^{-1} were considered. It can be noticed a great shift of the symmetric mode to 3132 cm^{-1}. Similar changes of vibrational spectra were observed, also, in the case of PbI_2 intercalation with amines [16]. In our case the experimental results can be explained by the existence of the interaction between hydrogen atoms of ammonia and iodine atoms as well as between bismuth cations and nitrogen atoms during the formation of $BiI_3(NH_3)_{3.83}$. BiI_3 has a crystal structure very similar to PbI_2 except that one-third of the Pb^{2+} sites is vacant for BiI_3. We agree with Zhong et al. [11] that, as a consequence of different ionic radius, the ammonia molecules can only coordinate to the central metal ion through a donor atom with small dimension. This is why the nitrogen atom coordinates through the lone electron pair to the bismuth cation in the intercalated compound.

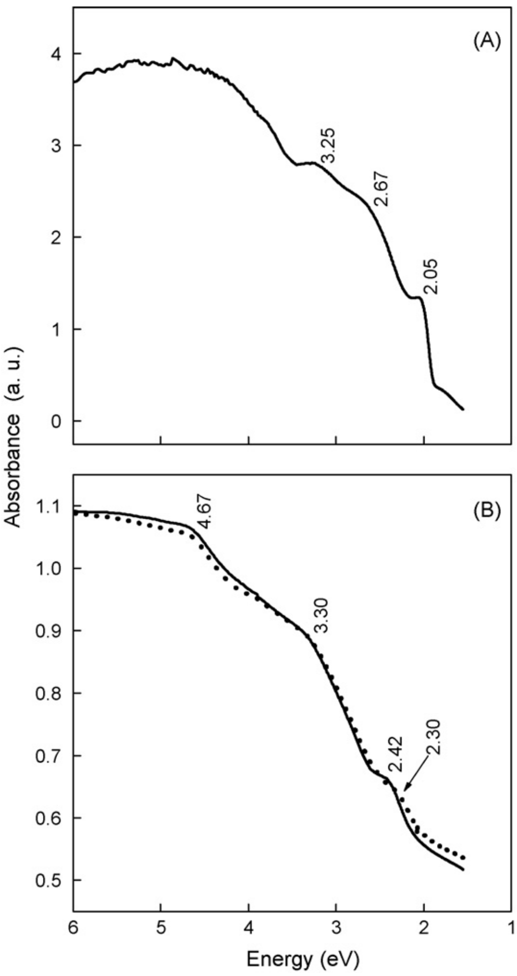

Fig. 4. The optical absorption spectra of thin BiI_3 film at room temperature before intercalation (A), after the exposure to ammonia vapor for 5 min (B, solid line) and recorded 3 days after the removal from ammonia atmosphere (B, dot line).

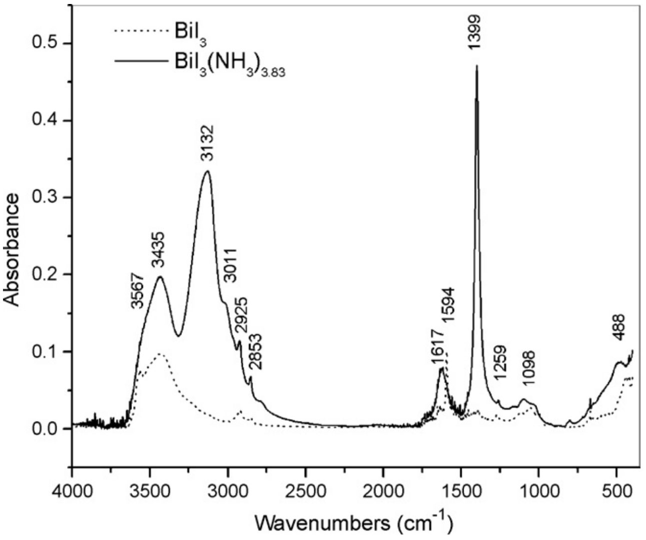

Fig. 5. FTIR spectra of BiI_3 and $BiI_3(NH_3)_{3.83}$ powders.

The adsorption type (physical or chemical) of the ammonia molecules into the BiI_3 lattice can be disclose by the Raman spectra. *A priori*, a physisorption leaves unchanged the spectra of the two components while a chemisorption modifies both Raman spectra, of the host and guest. Fig. 6 illustrates the Raman spectra recorded on pristine BiI_3 (Fig. 6A) and ammonia intercalated BiI_3 (Fig. 6B) powders. The Raman spectrum of pristine BiI_3 consists in two lines, a prominent one at 115 cm^{-1} and a weak one at 88 cm^{-1} attributed to E_g and A_g modes, respectively [17]. In the spectrum of the intercalated compound, an enhancement of the Raman line at 88 cm^{-1} and the appearance of new Raman bands situated at 135 and 353 cm^{-1} are observed. In our opinion, the enhancement of the line at 88 cm^{-1} is, in fact, the result of the superposition between the weak A_g vibration mode and a new vibration mode related to the stacking faults induced by the insertion of the ammonia molecules into the BiI_3 interlayer spaces. It has to be mentioned that such line, peaking in the 85–88 cm^{-1} range was observed for the intercalated PbI_2 with different guest molecules: ammonia, pyridine, polymers [4,5].

The new Raman lines at 135 and 353 cm^{-1} could originate from a chemical interaction between BiI_3 host lattice and ammonia guest molecules, through by the lone electron pair of the nitrogen atom. The hypothesis is sustained by the following: (i) a large number of infrared and Raman frequencies for ammine complexes of metal halides have been reported [18]

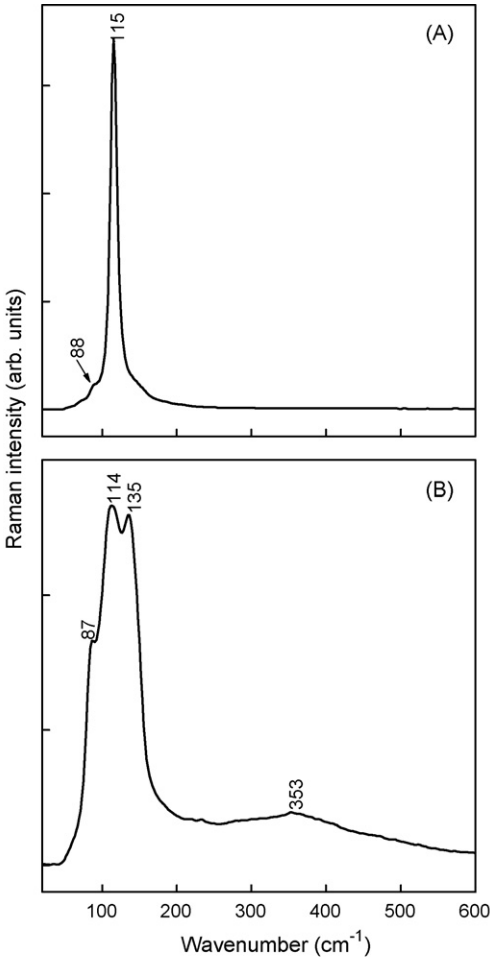

Fig. 6. Raman spectra of pristine BiI_3 (A) and ammonia intercalated BiI_3 (B) powders at 1064 nm excitation wavelength.

and in all cases the metal–nitrogen stretching frequencies are in the 243–545 cm^{-1} range; (ii) a Raman band at 322 cm^{-1} has already been assigned to Cd–N stretching in $[Cd(NH_3)_6]I_2$ [19] and to Pb–N bond in NH_3-intercalated PbI_2 [2] and (iii) a Raman band located at 135 cm^{-1} was identified in the Raman spectrum of PbI_2 intercalated with other nitrogen-containing molecules [4,5].

Concluding, the appearance of the lines 135 and 353 cm^{-1} in the Raman spectrum of the intercalated compound is considered as an evidence of the chemisorbed ammonia form into the BiI_3 lattice.

4. Conclusion

In this paper we have studied the intercalation of BiI_3 with ammonia by X-ray diffraction, thermal analysis, UV–vis optical absorption, FTIR spectroscopy and Raman scattering. After exposing BiI_3 to gaseous ammonia, the formation of a new phase, $BiI_3(NH_3)_{3.83}$, was evidenced. This phase is stable up to ~100 °C. In the 100–280 °C temperature range, the ammonia is released gradually as proved by thermo-gravimetric studies. The explanation resides in the different bonding type of the guest molecules to the host lattice. The experimental data sustain the presence of two adsorbed ammonia forms in the intercalated compound, a physisorbed one, featured by weak van der Waals type forces, and a chemisorbed one, involving stronger forces deriving from a charge transfer interaction between the two components.

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