

Intercalation of Layered Metal Iodides with Pyridine Evidenced by Raman Spectroscopy

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PbI₂, BiI₃, CdI₂ and AgI crystalline samples intercalated with pyridine have been studied by Raman spectroscopy. Comparing the Raman spectra of pristine metal iodides with those of intercalated samples we have shown the coexistence, in the host crystalline lattice, of two adsorbed forms: a physisorbed one, featured by weak forces of van der Waals type and a chemisorbed one, involving stronger forces related to an electrostatic interaction. The physisorbed form is consistent with the molecules inserted into the interlayer spaces while the chemisorbed form is represented by the molecules forming coordination complexes with the crystalline lattice cations. The crucial role in the formation of such complexes is played by the lone pair of nitrogen atom belonging to the molecules.

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1. Introduction

Due to their sandwiched layer structure, in which a sheet of metal ions is surrounded by two sheets of iodine ions, the semiconductor metal iodides are particularly interesting for intercalation with different molecules. Bonding within iodine-metal-iodine layer is strong, while adjacent layers are keeping together by van der Waals forces. Such a packing, involving weak forces, is susceptible to permit an easy insertion of different guest molecules into the interlayer spaces, leading to a change in the optical, electrical, etc. properties of the host crystal. Until now, the most papers regarding the intercalation of layered metal iodides have been focused on PbI₂ as host matrix and ammonia as guest molecule [1–3]. Therefore, the aim of this paper is to extend the intercalation studies to other layered metal iodides (BiI₃, CdI₂ and AgI), using pyridine as guest molecule. The intercalated compounds have been characterized by the Raman spectroscopy.

2. Experimental

Intercalation was achieved by exposing the crystalline powders of layered metal iodides (LMI) to pyridine (PY) vapors at room temperature. The crystalline powders of PbI₂, BiI₃, CdI₂ and AgI were obtained by mechanical crumbling of melt grown single crystals. After exposure to PY vapors, the color of PbI₂, BiI₃ and CdI₂ crystalline powders changes from orange, black and light brown in yellow, reddish and white, respectively. Interestingly, in

the case of AgI the yellow color of pristine powder remains unchanged. 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 discussions

Photographs of PbI₂ crystal, before and after one day exposure to PY vapors, are shown in Fig. 1a, b. The crystal (Fig. 1a) presents a quite noticeable expansion of the lattice along the *c*-axis (Fig. 1b), suggesting the adsorption of the PY molecules into the host interlayer spaces.

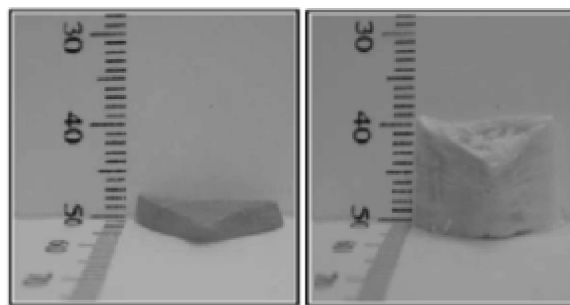


Fig. 1. Photographs of PbI₂ crystal before (left) and after (right) intercalation with pyridine.

In the following, comparing the Raman spectra obtained for the host layered material, the guest molecule and the intercalated compound we have tried to elucidate if the adsorption of PY molecules into LMI is a physical or a chemical one. Finding an answer to the question regarding the type of the host-guest interaction (physical

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or chemical) is a challenging topic in the context of any intercalation process.

The Raman spectrum of PbI_2 crystalline powder (Fig. 2a) covering the 50–200 cm^{-1} range reveals four lines at 75, 96, 112 and 164 cm^{-1} attributed to E_2^1 , A_1^1 , A_1^2 and $2E_2^1$ vibration modes, respectively [4]. In the Raman spectrum of the intercalated compound (Fig. 2c₁), the lines at 76, 98 and 119 cm^{-1} are, in fact, less and more up-shifted Raman lines observed in the spectrum of pristine PbI_2 . Besides these three lines, having a correspondence in the Raman spectrum of PbI_2 , two new lines at 88 and 135 cm^{-1} are also observed. We relate the Raman line at 88 cm^{-1} to the interface modes activated by the insertion of PY molecules into the PbI_2 interlayer spaces. It has to be noticed that a similar interpretation was given in Ref. [5]. for a line arising at 83 cm^{-1} in the Raman spectrum of a PbI_2 crystal having stacking faults induced by laser irradiation. In our case such stacking faults can appear as result of PY molecules insertion into the host lattice. We refer to the less bonded molecules, lying between PbI_2 layers, as physisorbed form of PY. The weak forces featuring this PY form are of van der Waals type.

For the appearance of the Raman line at 135 cm^{-1} we invoke a chemical interaction between PY molecules and cations, leading to the formation of coordination complexes. In this case, stronger forces related to an electrostatic interaction between lead ions and the lone pair of nitrogen atom belonging to the PY molecules are involved. Evidently, just PY molecules situated closer to the metallic ions can be implied in the appearance of the coordination complexes. In the following we refer to these molecules as chemisorbed form of PY.

If such a chemical interaction occurs, it should be also observed in the Raman region where the PY molecules are active. Indeed, the main Raman lines of PY (Fig. 2b) associated with ring deformation (605–654 cm^{-1}), ring breathing (992 cm^{-1}), trigonal ring breathing (1032 cm^{-1}), C–N in plane (1069 cm^{-1}), C–H deformation (1149–1218 cm^{-1}), (C–C + C–N) (1484 cm^{-1}), ring stretching C–C (1574–1582–1598 cm^{-1}) and C–H stretching (3023–3057–3090 cm^{-1}) vibration modes [6] appear drastically changed in the spectrum of the intercalated compound (see Fig. 2c₂). The modifications observed in the 600–3200 cm^{-1} Raman region for intercalated PbI_2 compound may be summarized as follows: (i) a relative increased intensity of the Raman lines at 605–654, 1032, 1067, 1149–1218, 1484, 1574–1598 cm^{-1} ; (ii) the disappearance of the Raman line at 1582 cm^{-1} that is accompanied by a down-shift of the Raman line at 1598 to 1592 cm^{-1} ; (iii) an enhancement of the Raman line situated in the spectral range 990–1040 cm^{-1} accompanied by an up-shift of the line at 992 to 1004 cm^{-1} ; (iv) the decrease of the Raman line intensity at 3057 cm^{-1} accompanied by the appearance of the new Raman lines at 747 and 3066 cm^{-1} . A special attention must be paid to the PY Raman line situated at 992 cm^{-1} , this being extremely sensitive to the nature of

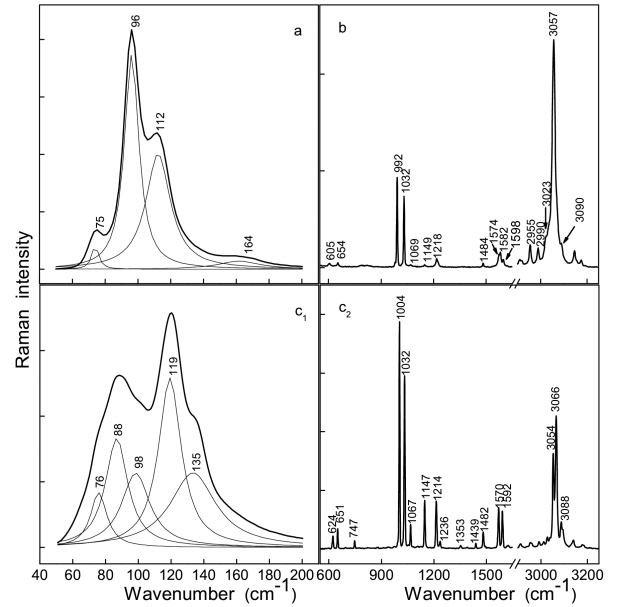


Fig. 2. Raman spectra at 1064 nm excitation wavelength of PbI_2 crystalline powder (a), pyridine alone (b) and pyridine intercalated PbI_2 compound ((c₁) and (c₂)).

interaction of the molecule with the environment. Based on Ref. [6], the up-shift of the Raman line from 992 cm^{-1} to 1004 cm^{-1} is considered as an evidence for the presence in the intercalated compound of chemisorbed form of PY.

Into similar manner with that used in the PbI_2 case, the vibrational spectra of the other metal iodides (BiI_3 , CdI_2 and AgI) intercalated with PY are discussed in two Raman domains: 50–200 cm^{-1} where the LMI lattice vibrations occur and 600–3200 cm^{-1} where the PY vibrations modes are observed.

The Raman spectra of the three LMI crystalline powders are presented with dot lines in Fig. 3a₁ (BiI_3), Fig. 3b₁ (CdI_2) and Fig. 3c₁ (AgI). According with Ref. [7, 8], the lines at 88 cm^{-1} (BiI_3) and 87 cm^{-1} (AgI) correspond to E_g mode while the Raman lines at 115 cm^{-1} (BiI_3), 112 cm^{-1} (CdI_2) and 108 cm^{-1} (AgI) are assigned to A_g mode.

The Raman spectrum of PY intercalated BiI_3 (Fig. 3a₁ — solid line) shows: (i) the enhancement of Raman lines situated at 88 cm^{-1} accompanied by an up-shift of the 115 cm^{-1} line to 125 cm^{-1} and (ii) the appearance of the new Raman lines at 137 and 160 cm^{-1} . In the Raman spectrum of PY intercalated CdI_2 (Fig. 3a₂ — solid line) new lines at 87 and 133 cm^{-1} are observed. A new Raman line at 135 cm^{-1} is also disclosed in the Raman spectrum of PY intercalated AgI (Fig. 3a₃ — solid line). As in the case of intercalated PbI_2 , the appearance or the enhancement of the line at about 88 cm^{-1} confirms the presence of the physisorbed PY form into the crystal lattice while the Raman line at about 135 cm^{-1} repre-

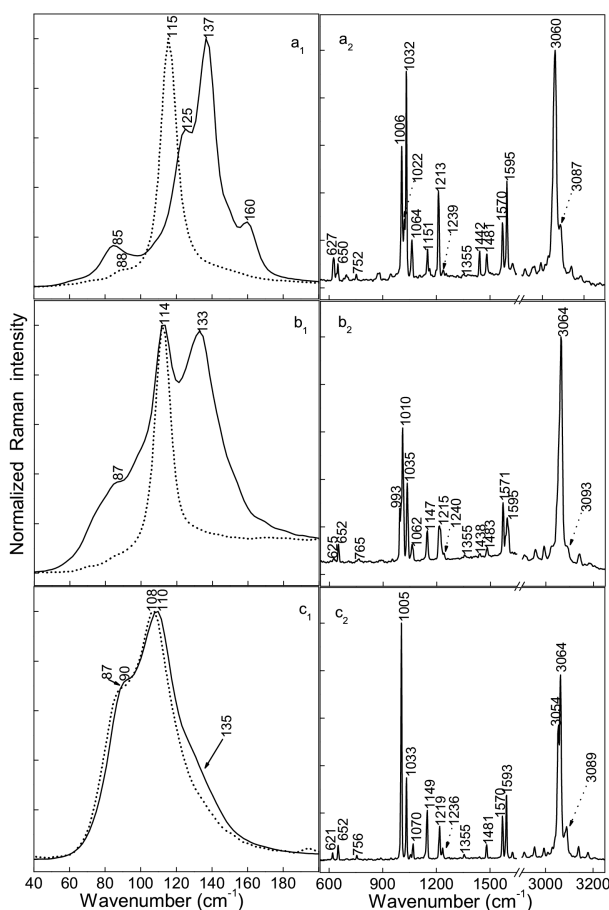


Fig. 3. Raman spectra at 1064 nm excitation wavelength of BiI_3 (a_1), CdI_2 (b_1) and AgI (c_1) crystalline powders (dot lines) and pyridine intercalated compounds: BiI_3 (a_1 , a_2), CdI_2 (b_1 , b_2) and AgI (c_1 , c_2) (solid lines).

sents the signature of the chemical interaction between LMI and PY guest molecules.

The Raman spectra of PY intercalated LMI, recorded in the 600–3200 cm^{-1} region, are presented in Fig. 3 a_2 (BiI_3), Fig. 3 b_2 (CdI_2) and Fig. 3 c_2 (AgI). For all three intercalated LMI, the Raman spectra reveal almost the same modifications with those observed in the Raman spectrum of PY intercalated PbI_2 (Fig. 2 c_2). The Raman region, where the ring breathing mode is active, shows the existence of the chemisorbed PY form by the up-shift of the Raman line from 992 cm^{-1} to 1006 (BiI_3), 1010 (CdI_2) and 1005 (AgI) cm^{-1} .

Therefore, we may conclude that two forms of PY molecules (physisorbed and chemisorbed) can be found in the intercalated LMI. The physisorbed molecules are

bonded in the crystalline lattice by weak forces, of van der Waals type. The chemisorbed molecules are bonded by stronger forces originating in the electrostatic interaction between the cations and the lone electron pair of nitrogen atom of pyridine.

4. Conclusions

Several layered metal iodides (PbI_2 , BiI_3 , CdI_2 , and AgI) intercalated with pyridine molecules were investigated by the Raman spectroscopy. Two adsorbed PY forms were put in evidence: a physisorbed one, involving weak forces of van der Waals type and a chemisorbed one, involving stronger forces related to an electrostatic interaction. The physisorbed PY form is revealed by the appearance or the enhancement of the Raman line at about 88 cm^{-1} observed in the spectra of all four intercalated materials. The appearance of new Raman lines at 135 cm^{-1} (for all investigated compounds) and the up-shift of the Raman line of PY from 992 cm^{-1} to 1004 (PbI_2), 1006 (BiI_3), 1010 (CdI_2) and 1005 (AgI) cm^{-1} are considered as evidences of the chemisorbed PY molecules into the host crystalline lattice. The presence of PY molecules under chemisorbed form is consistent with the formation of coordination complexes through the lone electron pair of nitrogen atom.

Acknowledgments

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