

NOTIZEN

Excitonic Bands in the Optical Absorption Spectra of A_3MX_6 and $A_3M_2X_9$ ($A = \text{MeNH}_3, \text{Me}_2\text{NH}_2, \text{Me}_3\text{NH}, \text{Me}_4\text{N}$; $M = \text{Bi}, \text{Sb}$; $X = \text{Cl}, \text{Br}, \text{I}$)

G. C. Papavassiliou*, I. B. Koutselas

Theoretical and Physical Chemistry Institute,
National Hellenic Research Foundation, 48,
Vassileos Constantinou Ave., Athens 11635,
Greece

Z. Naturforsch. **49b**, 849–851 (1994);
received March 28, 1994

Main Group Metal Complexes,
Electronic Spectra, Excitons

The title compounds (natural low-dimensional semiconductors) show strong excitonic optical absorption bands in the UV-visible spectral region, because of the dielectric confinement of excitons, as in the cases of other similar systems based on PbX_3^{2-} , SnX_3^{2-} , $\text{Pt}^{\text{II}}\cdots\text{X}-\text{Pt}^{\text{IV}}-\text{X}$, Cd_4S_6 -clusters *etc.*

During the last twenty years a large number of artificial low-dimensional (LD) semiconductor systems have been fabricated and studied. They are characterized by enhanced excitonic binding energy, enhanced excitonic oscillator strength, and consequently enhanced optical nonlinearity, in comparison to the corresponding three-dimensional (3D) systems [1]. Similar effects have been observed in some natural two-dimensional (2D), one-dimensional (1D) and zero-dimensional (0D) semiconductor systems. Compounds of the formula A_2MX_4 (where A = alkylammonium, phenyl-alkylammonium *etc.*; $M = \text{Pb}, \text{Sn}$; $X = \text{Cl}, \text{Br}, \text{I}$) are 2D (natural quantum well) systems [2–6]. Compounds of the formula $M^{\text{II}}(\text{L}-\text{L})_2M^{\text{IV}}(\text{L}-\text{L})_2\text{X}_2(\text{ClO}_4)_4$ (where $M = \text{Pt}, \text{Pd}, \text{Ni}$; $\text{L}-\text{L}$ = diamine or $\text{L} = \text{NH}_3$; $X = \text{Cl}, \text{Br}, \text{I}$) are 1D (natural quantum wire) systems [5, 7, 8]. Compounds of the formula $M_xY_y(\text{SPh})_z$ (where $M = \text{Cd}, \text{Zn}$; $Y = \text{S}, \text{Se}, \text{Te}$) and the compound $(\text{MeNH}_3)_4\text{PbI}_6$ are 0D (natural quantum dot) systems [2, 5, 8, 9]. The spectra of these systems

exhibit strong excitonic bands in the UV-visible-near infrared spectral region [2–9]. Also, the crystal structures of some compounds of the formula A_3MX_6 and $A_3M_2X_9$ (where $A = \text{MeNH}_3, \text{Me}_2\text{NH}_2, \text{Me}_3\text{NH}, \text{Me}_4\text{N}$; $M = \text{Bi}, \text{Sb}$; $X = \text{Cl}, \text{Br}, \text{I}$) indicate LD semiconductor behaviour [10–16]. Crystals of $(\text{MeNH}_3)_3\text{M}_2\text{Br}_9$ consist of 2D layers of polyanions, while crystals of $(\text{Me}_3\text{NH})_3\text{Sb}_2\text{Cl}_9$ and $(\text{Me}_2\text{NH}_2)_3\text{Sb}_2\text{Cl}_9$ consist of 2D layers of SbCl_3 connected by Cl^- anions and sandwiched between alkylammonium cations (2D systems) [10, 11]. Crystals of $(\text{MeNH}_3)_3\text{M}_2\text{Cl}_9$ are built up of 1D double-chain polyanions and the alkylammonium cations surrounding them (1D systems) [11, 12]. Crystals of A_3MX_6 are built up of octahedral anions MX_6^{3-} , while crystals of $(\text{MeNH}_3)_3\text{M}_2\text{I}_9$, $(\text{Me}_2\text{NH}_2)_3\text{Bi}_2\text{I}_9$, $(\text{Me}_4\text{N})_3\text{M}_2\text{Br}_9$, and $(\text{Me}_4\text{N})_3\text{M}_2\text{Cl}_9$ are built up of bi-octahedral $\text{M}_2\text{X}_9^{3-}$ anions and the alkylammonium cations surrounding them (0D systems) [11–16].

In this paper we report results concerning the excitonic bands in the optical absorption (OA) spectra of A_3MX_6 and $A_3M_2X_9$ LD systems. When this work was in progress, preliminary results concerning optical absorption spectra in crystals of the 0D system $(\text{MeNH}_3)_3\text{Bi}_2\text{I}_9$ have been reported by others [17].

The compounds were prepared by methods described in the literature [10–17], and identified by elemental analyses and/or Weissenberg diagrams. Thin deposits of compounds on quartz plates were prepared by methods reported previously [4–7]. The optical absorption spectra were recorded at room temperature on a Varian 2390 model UV-visible spectrophotometer.

Figs 1–3 show the OA spectra of thin (solid) deposits of 0D systems, and Fig. 4 shows the spectra of some 1D and 2D systems. One can see that the position of excitonic band (which is the low frequency band close to the absorption edge) in the OA spectra is shifted to longer wavelengths in the order chlorides (310–332 nm) < bromides (360–409 nm) < iodides (457–500 nm). It occurs at intermediate positions for mixed halide compounds (*e.g.* Fig. 2d). The excitonic bands in the spectra of Sb-containing compounds occur at shorter wavelengths than those of the corresponding Bi-containing compounds as it is expected from the observed spectra of SbI_3 [18] and BiI_3 [19] crystals as well as from the spectra of SbX_6^{3-} and BiX_6^{3-} in solution [20], respectively. Also, one can see that the excitonic

* Reprint requests to Prof. G. C. Papavassiliou.

0932–0076/94/0600–0849 \$06.00

©Verlag der Zeitschrift für Naturforschung,
D-72072 Tübingen

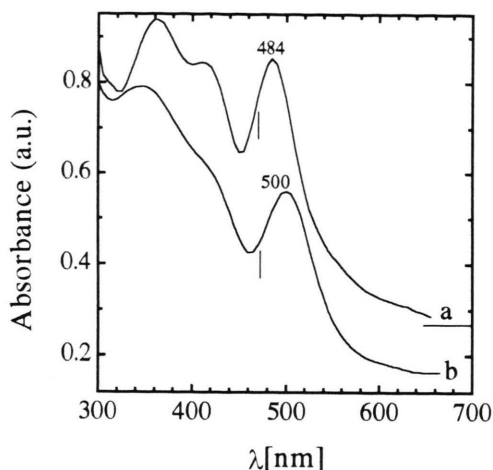


Fig. 1. OA spectra of $(\text{Me}_2\text{NH}_2)_3\text{BiI}_6$ (a) and $(\text{Me}_2\text{NH}_2)_3\text{Bi}_2\text{I}_9$ (b). The small vertical lines show the peak positions of the corresponding solutions in CH_3CN .

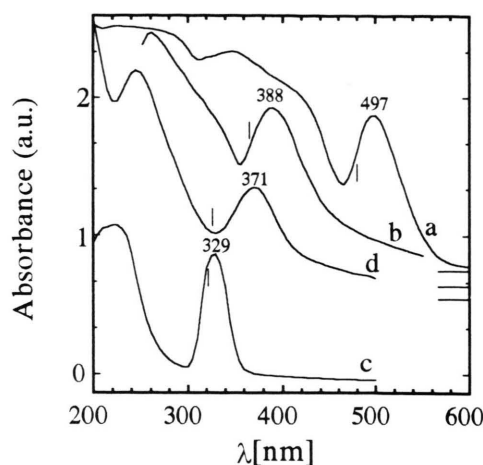


Fig. 2. Same as Fig. 1, but for $(\text{MeNH}_3)_3\text{Bi}_2\text{I}_9$ (a), $(\text{Me}_4\text{N})_3\text{Bi}_2\text{Br}_9$ (b), $(\text{Me}_4\text{N})_3\text{Bi}_2\text{Cl}_9$ (c) and $(\text{Me}_4\text{N})_3\text{Bi}_2\text{Br}_6\text{Cl}_3$ (d).

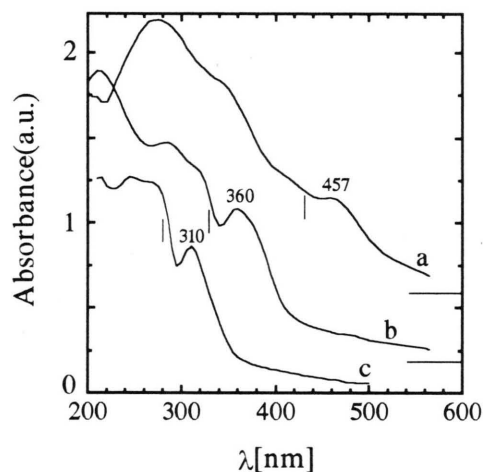


Fig. 3. Same as Fig. 1 but for $(\text{MeNH}_3)_3\text{Sb}_2\text{I}_9$ (a), $(\text{Me}_4\text{N})_3\text{Sb}_2\text{Br}_9$ (b) and $(\text{Me}_4\text{N})_3\text{Sb}_2\text{Cl}_9$ (c).

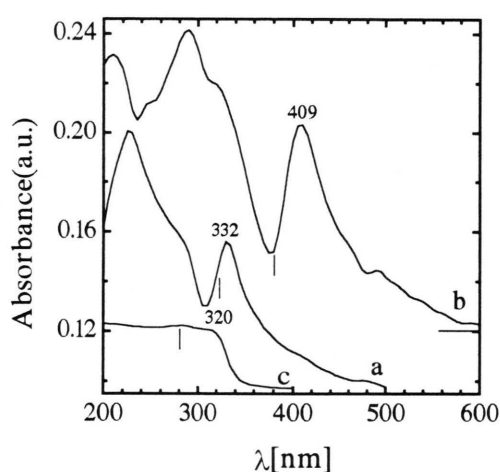


Fig. 4. Same as Fig. 1, but for $(\text{MeNH}_3)_3\text{Bi}_2\text{Cl}_9$ (a; 1D), $(\text{MeNH}_3)_3\text{Bi}_2\text{Br}_9$ (b; 2D) and $(\text{Me}_3\text{NH})_3\text{Sb}_2\text{Cl}_9$ (c; 2D).

bands of MX_6^{3-} , which are the smallest in size, occur at shorter wavelengths and are sharper than those of $\text{M}_2\text{X}_9^{3-}$, and the bands of the 0D systems occur at shorter wavelengths than those of the corresponding 1D and 2D systems. In the last two cases, the shifts of the excitonic bands are attributed to the different degree of confinement of the dots, wires and wells in the crystals. The bands in the OA spectra of (diluted) solutions in CH_3CN (see also [20]), of which the positions are shown by vertical lines in Figs 1–4, occur at shorter wavelengths and are broader than those of the corresponding solid deposits. Assuming that the continuum absorption

begins from the dip, which occurs close to the excitonic band, one can estimate the values of the excitonic binding energy (E_b) at room temperature. In $(\text{MeNH}_3)_3\text{Bi}_2\text{I}_9$, $(\text{Me}_4\text{N})_3\text{Bi}_2\text{Br}_9$, $(\text{Me}_4\text{N})_3\text{Bi}_2\text{Cl}_9$, $(\text{Me}_4\text{N})_3\text{Sb}_2\text{Cl}_9$, $(\text{MeNH}_3)_3\text{Bi}_2\text{Cl}_9$ and $(\text{MeNH}_3)_3\text{Bi}_2\text{Br}_9$, for example, one finds that E_b is $\geq 183, 306, 434, 203, 306$ and 274 meV, respectively. It has been observed that the low frequency band of $(\text{MeNH}_3)_3\text{Bi}_2\text{I}_9$ [17] becomes sharper at lower temperatures. This is an evidence of the excitonic nature of this band. E_b -Value has been accurately determined for low temperature ($E_b > 300$ meV at 4 K). Same results are expected for other com-

pounds. It should be noticed that the excitonic bands in the OA spectra of $(\text{BiI}_3)_1$ -clusters in zeolite [21], of $(\text{BiI}_3)_2$ -clusters in zeolite [21] and of the bulk BiI_3 [19] occur at *ca.* 468, 486 and 600 nm, respectively, and the E_b -value decreases as the size of the particles (clusters) increases [21]. This is a consequence of the quantum size effect (see for example [8]). The results reported above are similar to those obtained from other LD systems, such as A_2MX_4 (2D) [2–6], $\text{M}^{\text{II}}\cdots\text{X}-\text{M}^{\text{IV}}-\text{X}$ (1D) [5, 7, 8], A_4MX_6 (0D) [2], and $\text{M}_x\text{X}_y(\text{SPh})_z$ (0D) [5, 8, 9]. A_2PbI_4 (2D solid), for example, shows an OA excitonic band at *ca.* 512 nm [2–4], while PbI_6^{4-} (0D

solid) shows a band at *ca.* 362 nm (at 4 K) [2], the corresponding PbI_6^{4-} -solution in CH_3CN shows a band at *ca.* 376 nm and the PbI_4^{2-} -solution at *ca.* 361 nm (at room temperature) [22]. The OA spectrum of PbI_6^{4-} (solid) [2] is almost identical to that of very small PbI_2 -clusters in zeolite [21]. In all cases, it was found that the nature of the organic component (barrier) plays an important role in the intensity and the shape of the excitonic bands. However, details of this effect on the linear and nonlinear optical and related properties (photoluminescence, photoconductivity *etc.*) at room and lower temperatures will be reported elsewhere.

-
- [1] C. Weisbuch, B. Vinter, *Quantum Semiconductor Structures*, Acad. Press, London (1991).
 - [2] T. Ishihara, J. Lumin., in press, and refs. cited therein.
 - [3] C.-Q. Xu, S. Fukuta, H. Sakakura, T. Kondo, R. Ito, Y. Tokahashi, K. Kumata, *Sol. St. Commun.* **77**, 923 (1991).
 - [4] G. C. Papavassiliou, A. P. Patsis, D. J. Lagouvardos, I. B. Koutselas, *Synth. Metals* **57**, 3889 (1993).
 - [5] G. C. Papavassiliou, I. B. Koutselas, D. J. Lagouvardos, J. Kapoutsis, A. Terzis, G. J. Papaioannou, *Mol. Cryst. Liq. Cryst.*, in press.
 - [6] G. C. Papavassiliou, I. B. Koutselas, D. J. Lagouvardos, *Z. Naturforsch.* **48b**, 1013 (1993).
 - [7] G. C. Papavassiliou, R. Rapsomanikis, S. Mourikis, C. S. Jacobsen, *J. Chem. Soc., Faraday II* **78**, 17 (1982).
 - [8] G. C. Papavassiliou, in G. C. Hadjipanayis, R. W. Siegel (eds): *Nanophase Materials: Synthesis, Properties and Applications*, Kluwer Acad. Publ., The Netherlands, in press (1994).
 - [9] N. Herron, A. Suna, Y. Wang, *J. Chem. Soc., Dalton Trans.* **1992**, 2329.
 - [10] A. Kallel, J. W. Bats, *Acta Crystallogr.* **C41**, 1022 (1985).
 - [11] H. Ishihara, K. Watanabe, A. Iwata, K. Yamada, Y. Kinoshita, T. Okuda, V. Krishnan, S.-Q. Dou, A. Weiss, *Z. Naturforsch.* **47a**, 65 (1992).
 - [12] H. Ishihara, K. Yamada, T. Okuda, A. Weiss, *Bull. Chem. Soc. Jpn.* **66**, 380 (1993).
 - [13] M. Hall, M. Nunn, M. J. Begley, D. B. Sowerby, *J. Chem. Soc., Dalton Trans.* **1986**, 1231.
 - [14] M. Medyski, R. Jakubas, N. Pislewski, J. Lefebvre, *Z. Naturforsch.* **48a**, 748 (1993).
 - [15] R. Jakubas, J. Zaleski, L. Sooczyk, *Ferroelectrics* **108**, 109 (1990); J. Zaleski, R. Jakubas, L. Jobczyk, *Phase Trans.* **27**, 25 (1990).
 - [16] G. C. Papavassiliou, I. B. Koutselas, A. Terzis, to be published.
 - [17] T. Kawai, S. Shimanuki, *Phys. Stat. Sol.* **177b**, K43 (1993).
 - [18] A. D. Brothers, D. M. Wielczka, *Phys. Stat. Sol.* **80**, 201 (1977).
 - [19] Y. Kaitu, T. Komatsu, T. Aikami, *Nuovo Cimento* **338**, 449 (1977).
 - [20] K. Oldenburg, A. Vogler, *Z. Naturforsch.* **48b**, 1519 (1993) and refs. cited therein.
 - [21] Z. K. Tang, Y. Nozue, T. Goto, *J. Phys. Soc. Jpn.* **61**, 2943 (1992).
 - [22] G. C. Papavassiliou, unpublished results.