SOME NATURAL THREE- AND LOWER-DIMENSIONAL SEMICONDUCTOR SYSTEMS WITH METAL-HALIDE UNITS

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ABSTRACT

The structural, optical and related properties (i.e. photoluminescence, photoconductivity etc.) of some natural three- and lower-dimensional semiconductor systems based on metal halides are briefly reviewed and some new results are reported. A blue shift of the excitonic bands was observed by decreasing the dimensionality or the size of the materials active part. The results are similar to those obtained from conventional semiconductor systems (e.g. GaAs, CdS, PbI_2) by decreasing artificially the dimensionality or decreasing the size.

INTRODUCTION

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 and enhanced excitonic oscillator strength with the possibility of enhanced excitonic nonlinearities and enhanced efficiency of light emission, 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 based on single- or mixed-valence metal chalcogenides (see[2,3]), metal oxides (see[3]), and metal-halides (see[4-44] and refs cited therein).

There is a large number of single-valence metal-halide complexes with the general formulas $Z_xM_zX_{z+x}$ [where M=Ga(I), In(I), Tl(I); Cu(I), Ag(I), Au(I); Z=K, Rb, Cs, $MeNH_3$etc.; x=0,1,2....; z=1,2,3...;X=F,Cl,Br,I], $Z_xA_yM_zX_{2z+x+y}$ or $Z_x M_{z+w}X_{2z+x}X'_{2w}$ or $Z_xM_zM'_wX_{2z+2w+x}$[where A=(amine-H) or (diamine-2H)$_{0.5}$; M, M'=Ge(II), Sn(II), Pb(II), Zn(II), Cd(II), Hg(II); Cu(II), Ni(II), Co(II), Fe(II), Mn(II) etc, y=0,1,2,3....., w=1,2,3....] and $Z_xA_yM_zX_{3z+y+x}$ [where M=As(III), Sb(III), Bi(III); Ga (III), In(III), Tl(III)] . In this paper the structural, optical and related properties of some 3D and LD systems based on single-valence metal-halides are briefly reviewed and some new results are reported. The room temperature (RT) results are mainly discussed.

EXPERIMENTAL

Single-valence metal-halide complexes were prepared from the corresponding simple halides according to the following chemical reactions:

1) $xZX+zMX \rightarrow Z_xM_zX_{z+x}$

2) $xZX+yAX+zMX_2 \rightarrow Z_xA_yM_zX_{2z+x+y}$ or $xZX+zMX_2+wMX'_2 \rightarrow Z_xM_{z+w}X_{2z+x}X'_{2w}$ or $xZX+zMX_2+wM'X_2 \rightarrow Z_xM_zM'_wX_{2z+2w+x}$

3) $xZX+yAX+zMX_3 \rightarrow Z_xA_yM_zX_{3z+y+x}$.

Optical absorption (OA) or reflectance, photoluminescence (PL), photoluminescence excitation (PLE), and photoconductivity (PC) spectra were recorded by methods reported in [5-9].

RESULTS AND DISCUSSION

Compounds of the formula ZMX_3 (M=Pb, Sn, Ge) have cubic-perovskite structures as it is shown in Fig. 1a for $MeNH_3PbI_3$. Some of them were found to be 3D semiconductors [4-10, 14, 18-30] . Compounds of the formula A_2MX_4 (A=alkylamine-H, phenylethylamine-H etc; M=Pb, Sn, Cu, Cd, Mn etc) have layered-perovskite structures as it is shown in Fig. 1b for $(C_9H_{19}NH_3)_2PbI_4$. Some of them (mainly those with M=Pb, Sn) were found to be 2D semiconductor (: quantum-well) systems [4-19]. Compounds of the formula $Z'PbI_3$ (where Z'=piperidinium-, quinolinium-ion) consist of infinite PbI_3-chains as it is shown in Fig. 1c for (piperidinium)PbI_3 [5,19] , while the compound ET_2PbBr_3 (where ET=bis-ethylenedithio-tetrathiafulvalene) consists of infinite $PbBr_3$-chains [20]. These compounds were found to be 1D semiconductor (: quantum - wire) systems. Compounds of the formulas $(MeNH_3)_4PbI_6.2H_2O$ or Cs_4PbX_6[31] and Et_4NMX_3 (M=Pb, Sn)[32,38] consist of isolated PbX_6 units, as it is shown in Fig. 1d for $(MeNH_3)_4PbI_6.2$ H_2O and isolated PbX_3 units [32], respectively. They were found to be 0D semiconductor (: quantum dot) systems. In all cases, the inorganic part (:metal-halide) is the active part of the system, while the organic part (amine-H, or Cs and H_2O) plays the role of barrier.
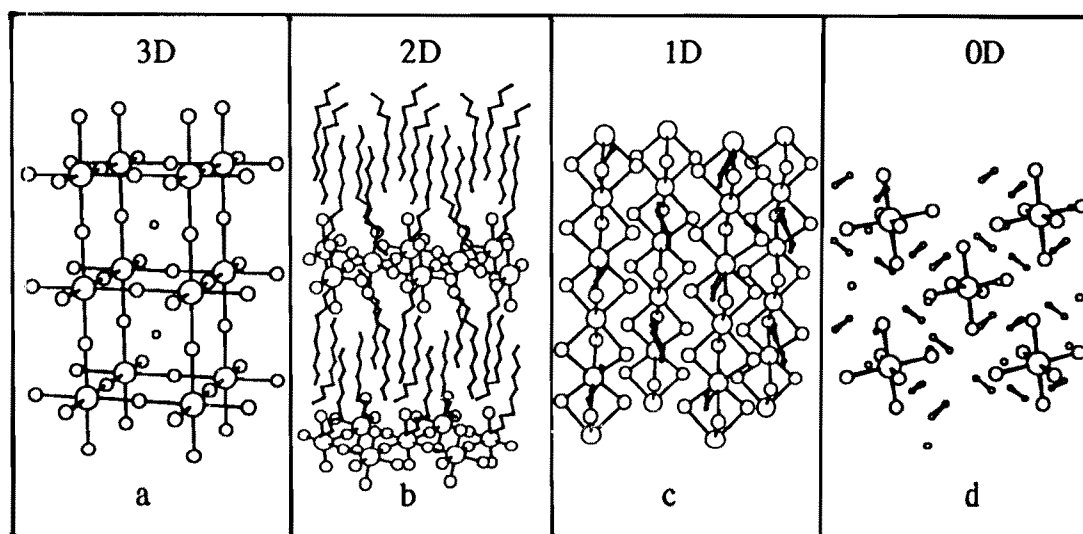

Fig. 1. Crystal structures of $MeNH_3PbI_3$(a), $(C_9H_{19}NH_3)_2PbI_4$(b) , (piperidinium)PbI_3(c), and $(MeNH_3)_4PbI_6.2$ H_2O (d): where large spheres= Pb atoms, medium spheres=I atoms, and small spheres =O,N,C atoms.

Fig. 2 shows the absorption coefficient vs. wavelength (λ) obtained from Kramers-Kronig transformation of the corresponding reflectance spectra of $MeNH_3PbI_3$ (3D), $(C_9H_{19}NH_3)_2PbI_4$ (2D)[19], (piperidinium)PbI_3(1D)[19] and $(MeNH_3)_4PbI_6.2H_2O$(0D). One can see that by decreasing the dimensionality (3D→ 2D→ 1D →0D) the low ener
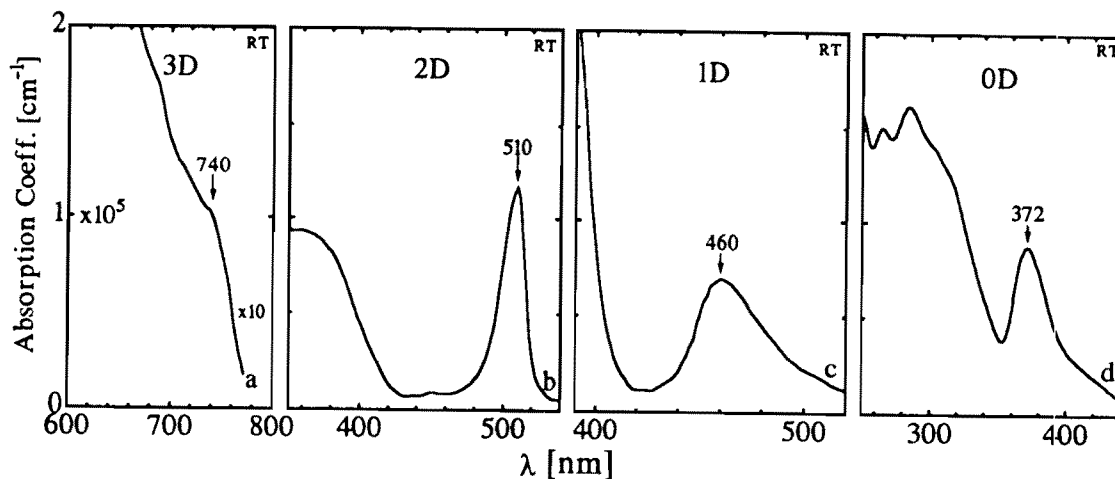
Fig. 2. Absorption coefficient vs. λ of $MeNH_3PbI_3(a)$, $(C_9H_{19}NH_3)_2PbI_4(b)$, (pipe-ridinium)$PbI_3(c)$, and $(MeNH_3)_4PbI_6.2\ H_2O$ (d).

gy peaks, which correspond to the lowest (free) excitonic states, are shifted to high energies (i.e. shorter wavelengths).

As it is shown in Fig.3, the OA spectrum of $(MeNH_3)_4PbI_6.2H_2O$ (0D) (see also [16] for low temperature results) is almost the same as the OA spectra of $(Et_4N)PbI_3$ [32],$(C_6H_5CH_2CH_2NH_3)_2$ PbI_4 in CH_3CN-solution and PbI_2 colloidal solution in CH_3CN [34]. It is similar to the spectrum of $(PbI_2)_1$ -clusters in zeolite [33]. The excitonic peaks of these compounds occur at higher energies than that of PbI_2 (see Fig. 4a'). The excitonic peak of PbI_2 small particles (4-6 nm) [35,36] and that of PbI_2-aniline intercalated compound [37] occur at intermediate positions. Compounds of the formula $Z_{n-1}A_2M_nI_{3n+1}$ (with M=Pb, Sn and n=1,2,3...) are monolayer (n=1), bilayer (n=2), trilayer (n=3) and multilayer (n>3), semiconductor (quantum-well) systems. Compounds with $n \geq 3$ can not be isolated in a pure form. Fig.4 shows the OA spectra of $(C_9H_{19}NH_3)_2\ PbI_4$, $(MeNH_3)\ (C_9H_{19}NH_3)_2Pb_2I_7$, $(MeNH_3)_{n-1}(C_9H_{19}NH_3)_2Pb_nI_{3n+1}$
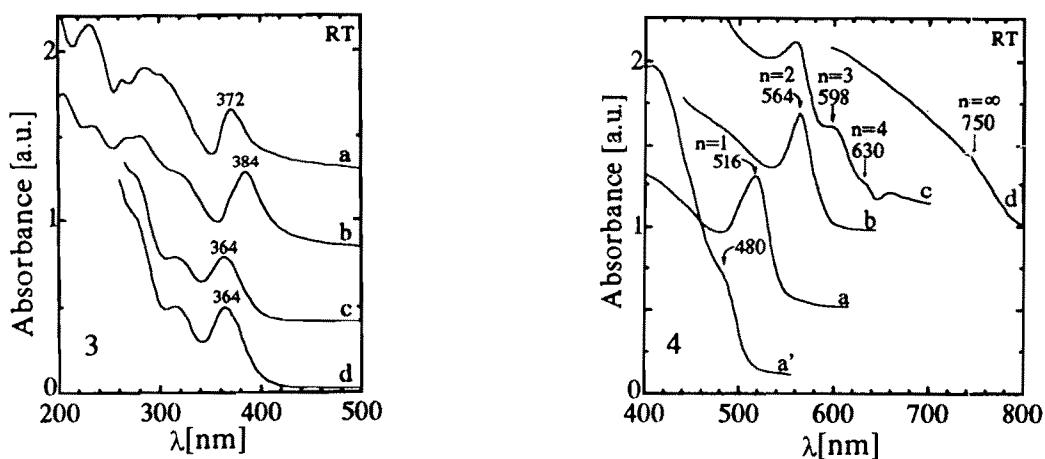
Fig.3.OA spectra of $(MeNH_3)_4PbI_6.2H_2O$(a), $(Et_4N)PbI_3$(b), $(C_6H_5CH_2CH_2NH_3)_2$ PbI_4 in CH_3CN -solution (c), and PbI_2 colloidal solution in CH_3CN (d).

Fig.4. OA spectra of PbI_2(a'),$(C_9H_{19}NH_3)_2$ PbI_4 (a), $(MeNH_3)(C_9H_{19}NH_3)_2Pb_2I_7$ (b), $(MeNH_3)_{n-1}(C_9H_{19}NH_3)_2Pb_nI_{3n+1}$ (n $\geq$ 3, c) and $MeNH_3PbI_3$ (d) deposits.

($n \geq 3$),MeNH$_3$ PbI$_3$ and the OA spectrum of PbI$_2$ for comparison. One can see that the excitonic peaks are shifted to lower energies (larger wavelengths) as the layer-thickness increases ($n=1\rightarrow2\rightarrow3....$).The excitonic peak of PbI$_2$ is weaker than that of A$_2$PbI$_4$ and ZA$_2$Pb$_2$I$_7$ because of the interlayer interactions in the PbI$_2$ crystals.

Similar results have been observed in the PL, PLE, and PC spectra of PbI containing complexes as well as in the spectra of complexes with PbBr, PbCl, SnI and SnBr units [5-18] . Fig.5 shows the PL, PLE and PC spectra of some materials with PbI units, in comparison to the corresponding absorption spectra. One can see that the absorption spectra are almost the same as the PLE spectrum. Also, it has been found that the PL spectrum is the same as the electroluminescence spectrum [11]. Fig. 6 shows the OA spectra of three samples (MeNH$_3$)$_{n-1}$ (C$_9$H$_{19}$NH$_3$)$_2$Pb$_n$Br$_{3n+1}$ (2D) obtained by
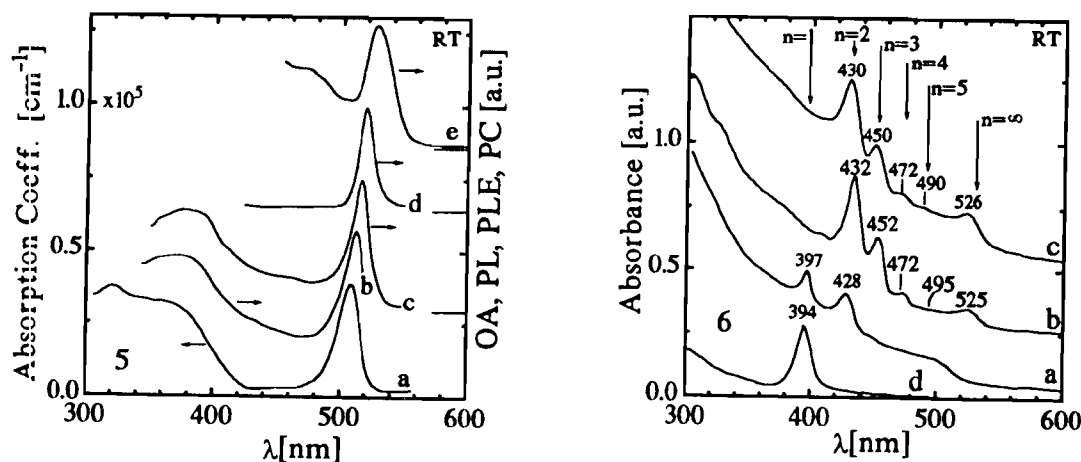
Fig.5.Absorption coefficient of (C$_9$H$_{19}$NH$_3$)$_2$PbI$_4$(a), PLE(b), OA(c), PL(d) and PC(e) spectra of (C$_6$H$_5$CH$_2$CH$_2$NH$_3$)$_2$ PbI$_4$.

Fig. 6.OA spectra of three samples (a,b,c) of (MeNH$_3$)$_{n-1}$ (C$_9$H$_{19}$NH$_3$)$_2$Pb$_n$Br$_{3n+1}$ thin deposits and OA spectrum of pure (C$_9$H$_{19}$NH$_3$)$_2$PbBr$_4$ (d).

addition of several amounts of MeNH$_3$Br in a solution of (C$_9$H$_{19}$NH$_3$)$_2$PbBr$_4$. The peak with $n=\infty$ corresponds to the excitonic peak of CH$_3$NH$_3$PbBr$_3$ (3D). One can see that, as in the case of iodides, the excitonic peaks are shifted to lower energies as n increases. For all 3D and LD systems, it was found that the excitonic peaks of bromides occur at shorter wavelengths than those of the corresponding iodides and the peaks of chlorides at shorter wavelengths than those of bromides. Also, the excitonic peaks of plumbates occur at shorter wavelengths than those of the corresponding stannates. Figs. 2-6 show that the binding energy values (E$_b$) and the intensity values (i.e. oscillator strength) of excitonic peaks in LD systems are higher than those of the corresponding 3D systems. Employing the variational method used in ref. [11] for some materials of Pb and Sn, one finds that the calculated E$_b$ values are close to the experimental values. The results are listed in Table I, along with the corresponding parameters used for calculations.The E$_b$ values decrease as in increases. Also, E$_b$-values of stannates are smaller than those of the corresponding plumbates. By changing the amine (A) the E$_b$ value is changed, because of the difference in the dielectric confinement (see [11,16]).

The OA spectra of compounds based on Bi and Sb [39] (dielectric materials) show large E$_b$-values, but in these cases the (free) excitonic luminescence peaks are weak and

Table I. E_b- and α-values of some 2D systems

Compound	Parameters				Theor. α (Å)	Theor. E_b(meV)	Exp. E_b(meV)
	ε_w	ε_b	L_w(Å)	μ(m_o)			
$(C_9H_{19}NH_3)_2PbI_4$	6.1	2.40	6.36	0.09	15.5	309	330
$(C_{10}H_{21}NH_3)_2PbI_4$	6.1	2.44	6.36	0.09	17.12[17.0]*	304[315]*	320
$(C_{6-2})_2PbI_4$	6.1	3.32	6.36	0.09	17.12[17.0]*	216[230]*	220
$(MeNH_3)(C_{6-2})_2Pb_2I_7$	6.1	3.32	12.72	0.09	20.7 [20.5]*	167[175]*	170
$(MeNH_3)_2(C_{6-2})_2Pb_3I_{10}$	6.1	3.32	19.08	0.09	23.5	140	
$(C_{10}H_{21}NH_3)_2SnI_4$	4.0	2.44	6.29	0.049	20.3	255	230-240
$(C_{6-2})_2SnI_4$	4.0	3.32	6.29	0.049	23.4	168	160-190
$(MeNH_3)(C_{6-2})_2Sn_2I_7$	4.0	3.32	12.58	0.049	26.6	146	130
$(MeNH_3)_2(C_{6-2})_2Sn_3I_{10}$	4.0	3.32	18.87	0.049	29.4	129	

C_{6-2}= $(C_6H_5CH_2CH_2NH_3)$, ε_w and ε_b = the dielectric constant of the well and barrier, respectively; L_w =the well-thickness, μ=the reduced electron-hole mass, m_o=the free electron mass, α=Bohr exciton radius; *values from ref. [11].

difficult to be observed at room temperature. Instead, broad luminescence bands are observed at low frequencies which could be attributed to trapped excitons. Also, OA spectra of some other metal-halide complexes based on Tl [41],Cu [42],Mn[43], Cd[44] etc.(ferroelectric or magnetic materials) have been reported, but their line-intensities are weak. So, compounds based on Sn,Pb, and Bi seem to be the most important for further investigations and possible applications as optoelectronic materials [12,18].

The results reported above, especially for compounds based on Pb and Sn, are similar to those obtained from LD systems based on conventional semiconductors, i.e. quantum structures based, for example,on the GaAs/GaAlAs artificial systems [1]. The effects in the optical and related properties of 0D metal-halide complexes are similar to those of CdS [2,7], PbI$_2$ (33-36)], BiI$_3$ [33,39]etc small particles or Cd$_x$S$_y$(SPh)$_z$ clusters [2,7].

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