Synthesis, Structure, and Luminescence of 2D-Dilute Magnetic Semiconductors: $Zn_{1-x}Mn_xSe{\cdot}0.5L$ (L = Diamines)

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The two-dimension dilute magnetic semiconductors (2D-DMS) $Zn_{1-x}Mn_xSe{\cdot}0.5L$ (L = ethylenediamine or en, 1,3-propanediamine or pda, 1,4-butanediamine or bda, and 1,6-hexanediamine or hda) and their host compounds ZnSe·0.5L were prepared by solvothermal reaction in solvent L at 190 °C. The powder X-ray diffraction patterns of ZnSe·0.5L are indexed as isomorphous orthorhombic lattices, whose constants *c* increase monotonically from L = en to L = hda. The orthorhombic lattice in *ab* plane of ZnSe·0.5en is a shrunken 2D superlattice ($\sqrt{3}a\times c$) of the (110) plane of hexagonal ZnSe. When Zn^{2+} is partly substituted by Mn^{2+}, $Zn_{1-x}Mn_xSe{\cdot}0.5L$ become 2D-DMS. Their photoluminescence (PL) spectra show strong Mn^{2+}-related emission peaks at 2.07 eV (600 nm). The Mn content dependence of PL intensity of $Zn_{1-x}Mn_xSe{\cdot}0.5$hda is especially studied, and high intensities are obtained when $x < 0.2$. For $x \approx 0.2$, the PL intensities of $Zn_{1-x}Mn_xSe{\cdot}0.5L$ increase from L = en to L = hda, which can be attributed to the formation of Zn/Mn−N bonds and the effective energy transfer routes and radiative recombination of the 3d electron of Mn^{2+} within the 2D $[Zn_{1-x}Mn_xSe]$ layers.

1. Introduction

Mn-based II−VI group compounds have been extensively studied as typical diluted magnetic semiconductors (DMS). They have wide direct gaps and outstanding magnetooptical properties such as strong Faraday rotation and giant exciton Zeeman splitting,[1−3] which originate from the s,p-d exchange interaction between band electron/hole and Mn^{2+} $3d^5$ electron.[4−7] These properties make it possible to fabricate high performance microstructures of optoelectronic devices. In the past two decades, the optical properties of 2D $Zn_{1-x}Mn_xSe$ quantum wells and superlattices grown by molecular beam epitaxy (MBE) have been researched.[8−11] Recently, the Mn^{2+}-related emission ($^4T_1 \rightarrow {}^6A_1$) with high quantum efficiency was obtained in $Zn_{1-x}Mn_xSe$ nanocrystals and quantum dots.[12, 13]

Inorganic/organic (I/O) hybrid compounds have novel properties due to the combination of inorganic components and organic molecules. The diamine-intercalated layered compounds, ZnE·0.5L, MnSe·0.5L and $Zn_{1-x}Mn_xSe{\cdot}0.5L$ (E = Se, Te, and L = en, pda), which were solvothermally syntheisized,[14] are a novel type of the I/O hybrid structures. Optical absorption measurements show that the band gaps of ZnSe·0.5L and $Zn_{1-x}Mn_x$-Se·0.5L have large blue shifts (1.4∼1.5 eV) compared with that of ZnSe,[15,16] which are attributed to the quantum confinement effect of the $[Zn_{1-x}Mn_xSe]$ layers.

In this study, ZnSe·0.5L and 2D-DMS $Zn_{1-x}Mn_xSe{\cdot}0.5L$ (L = en, pda, bda, and hda) were synthesized by solvothermal reaction in solvent L at 190 °C. The indexing of the powder XRD patterns of ZnSe·0.5L indicates that they are isomorphous crystals. The structural relationship between ZnSe·0.5en and hexagonal ZnSe are revealed. In the PL spectra, $Zn_{1-x}Mn_xSe{\cdot}0.5L$ shows strong Mn^{2+}-related emission at 2.07 eV (600 nm). The high PL intensities can be obtained when the Mn content (*x*) is less than 0.2 according to the Mn content dependence of the PL intensity of $Zn_{1-x}Mn_xSe{\cdot}0.5$hda. For $Zn_{1-x}Mn_xSe{\cdot}0.5L$ ($x \approx 0.2$), the luminescence-enhancement effect is observed.

2. Experimental Section

2.1. Synthesis. 1,3-Propanediamine (pda, 99%) and 1,4-butanedimine (bda, 98%) were purchased from Fluka Chemicals Co. Ltd. Other chemicals were of analytical grade purity and were purchased from Shanghai Chemical Reagent Co. Ltd.

ZnSe·0.5L (L= en, pda, bda, and hda) were solvothermally synthesized as follows. A 5 mmol sample of $Zn(CH_3CO_2)_2{\cdot}2H_2O$ and 5 mmol of selenium were dissolved into 50 mL of solvent L. The mixture was sealed into a 60 mL Teflon-lined stainless steel autoclave, heated at 190 °C for 7 days, and then cooled naturally. The products were washed with distilled water and absolute ethanol and then dried in a vacuum at 70 °C for 2 h. $Zn_{1-x}Mn_xSe{\cdot}0.5L$ were prepared in a similar procedure with different molar ratios of Zn^{2+}:Mn^{2+} ($Mn(CH_3CO_2)_2{\cdot}4H_2O$ as Mn source).

2.2. Component Analysis. Elemental analysis of C, H, and N weight percentages of ZnSe·0.5L (using a Perkin-Elmer 2400 elemental analyzer) are listed in Table 1. It can be seen that the obtained data of H and N are consistent with the calculated values in the range of experimental error (±0.5%), As for C, however, the slightly greater experimental values probably resulted from the carbon contamination of sample surfaces. Therefore, the chemical stoichiometry of ZnSe·0.5L can be regarded as accurate.

Inductively coupled plasma-atomic emission spectra (ICP-AES, using an Atomscan Advantage Spectrometer, Therma Jarrell Ash Corp.) were used to determine the Mn contents of $Zn_{1-x}Mn_xSe{\cdot}0.5L$. For L = hda, Zn^{2+}:Mn^{2+} = 19:1, 9:1, 7:3, 3:2, 2:3, and 1:4, the determined Mn contents are $x = 0.046$, 0.0829, 0.279, 0.390, 0.581, and 0.779, respectively. For Zn^{2+}:

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TABLE 1: Analysis Results of C, H, and N Contents of ZnSe·0.5L

	C, H, N (wt %)			
	L = en	L = pda	L = bda	L = hda
calcd	9.42, 3.16, 10.99	9.93, 2.778, 7.721	12.75, 3.206, 7.433	17.80, 3.978, 6.918
found	9.77, 3.02, 11.10	11.35, 2.791, 7.995	13.66, 3.254, 7.409	18.57, 3.980, 6.902.

TABLE 2: Indexing Results of Powder X-ray Diffraction of ZnSe·0.5L

L	cryst syst	*a* (Å)	*b* (Å)	*c* (Å)	vol (Å^3)	program	FOM
en	ortho	6.634	6.459	17.360	743.91	ITO15	$M_{20} = 26.0$
pda	ortho	6.638	6.450	20.010	856.72	ITO15	$M_{20} = 58.9$
bda	ortho	6.610	6.446	22.188	945.39	DICVOL91	$F_{19} = 8.8$
hda	ortho	6.616	6.449	27.116	1156.85	DICVOL91	$F_{24} = 16.6$

Mn^{2+} = 4:1 with different L, the determined Mn contents are $x = 0.159$ (L = en), $x = 0.173$ (L = pda), $x = 0.205$ (L = bda), and $x = 0.195$ (L = hda), respectively. Therefore, the synthetic reactions for Zn^{2+}:Mn^{2+} varying from 19:1 to 1:4 can be regarded as quantitative.

2.3. Indexing of Powder XRD Patterns of ZnSe·0.5L. The powder XRD patterns of ZnSe·0.5L (2θ: 5.00−65.00°) were collected using a MAX 18 AHF X-ray diffractometer (MAC Science Co. Ltd., Cu Kα_1, $\lambda = 1.54056$ Å, scanning rate 8.0000° min^{-1}). Indexing and lattice constant refinements were carried out by three PC software programs ITO15,[17] TRERRO90,[18,19] and DICVOL91,[20,21]and the 2θ values of selected well-defined diffraction peaks were used as input data. The results are compared and the most reliable ones are listed in Table 2, which give consistent orthorhombic lattices with good figures of merit (FOM, M_N and F_N, simplified criteria for the reliability of a powder diffraction indexing[22−24]). The indexed constants of ZnSe·0.5en and ZnSe·0.5pda are consistent with the reported values,[15] those of ZnSe·0.5bda and ZnSe·0.5hda are not reported previously. It can be seen that the indexed constants *a* and *b* in all of the four compounds are almost identical, which implies that the 2D [ZnSe] layer structure in L = en and pda[15] is preserved in L = bda and hda. The increase of the *c* axis from L = en (17.360 Å) to L = hda (27.116 Å) is reasonably parallel with the lengthening of diamine molecules from en to hda.

2.4. Photoluminescence Measurement. The PL emission and excitation spectra of $Zn_{1-x}Mn_xSe$·0.5L were recorded at room temperature with a Hitachi 850 fluorescence spectrophotometer. The measurement conditions were identical in all cases and therefore relative intensities can be compared.

3. Results and Discussion

3.1. Structural Relationship of ZnSe·0.5en and Hexagonal ZnSe. Comparing with hexagonal ZnSe, one finds that the size of the orthorhombic lattice in the *ab* plane of ZnSe·0.5en (6.633 × 6.463 Å) is close to that of the $\sqrt{3}a \times c$ orthorhombic lattice (6.921 × 6.53 Å) in the (110) plane of hexagonal ZnSe (JCPDS, PDF, 15-105). Therefore, the unit cell in the *ab* plane of ZnSe·0.5en can be viewed as a shrunken $\sqrt{3}a \times c$ 2D superlattice of the (110) plane of hexagonal ZnSe. It can be expected that the coordination of Zn^{2+} in ZnSe·0.5en should be similar to the $ZnSe_4$ tetrahedra in hexagonal ZnSe. This has been verified by the crystallographic analysis of ZnSe·0.5en polycrystals and its isomorphous one-MnSe·0.5en single crystal.[15] The structure of ZnSe·0.5en is shown in Figure 1 where the $ZnNSe_3$ coordination tetrahedra are revealed. On the other hand, when ethylenediamine molecules are removed from ZnSe·0.5en by acid washing or annealing at elevated temperature,[25] lamellar hexagonal ZnSe crystallites with (110) orientation are obtained. Taking the above analyses into consideration, this deintercalation reaction can be described as follows, when diamine molecules leave the lattice, Zn−N bonds are broken, 2D [ZnSe] monolayers collapse along the *c* axis, and the fourth Zn−Se bonds form, which result in hexagonal ZnSe crystallites with (110) cleavage. Therefore, it can be concluded that the deintercalation reaction is topochemical. Because ZnSe·0.5en and MnSe·0.5en are isomorphous crystals, their solid solution of $Zn_{1-x}Mn_xSe$·0.5L can be consequently regarded as 2D-DMS.

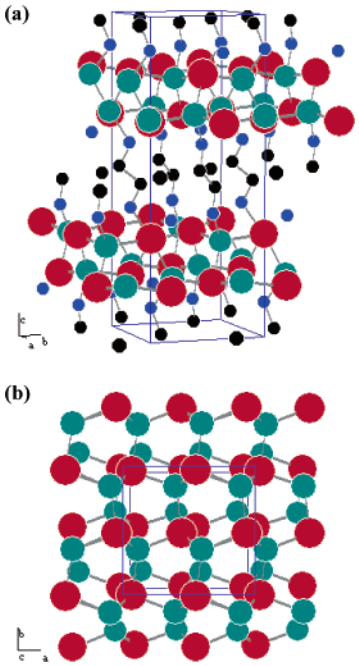

Figure 1. View of the structure of ZnSe·0.5en along the *a* axis (a, top) and along the *c* axis (b, bottom). Green (middle) circles are Zn, red (large) circles are Se, black and blue (small) circles are C and N, respectively; the unit cell was outlined as well. The atomic coordinates in ref 15 were cited in this figure.

3.2. Mn Content Dependence of PL Intensities of $Zn_{1-x}Mn_x$-Se·0.5hda. Figure 3d shows the PL spectra of the as-prepared $Zn_{1-x}Mn_xSe$·0.5hda ($x = 0.195$), where a strong emission peak at 595∼600 nm can be seen. The Mn content dependence of this PL emission intensity is shown in Figure 2. The monotonically decreasing curve indicates that, in the range of low Mn content ($x < 0.2$), high intensities are obtained. In our experiments, the maximal intensity appears at $x = 0.046$. When $x > 0.4$, the intensity decreases to about 10% of the maximum, and when $x = 0.8$, only 5% exists. In the excitation spectra of $Zn_{1-x}Mn_xSe$·0.5hda (not shown), sharp peaks with a slight blue shift (from 300 nm ($x = 0.046$) to 291 nm ($x = 0.779$)) are found, which may result from the structural distortion of $Zn_{1-x}Mn_xSe$·0.5hda due to Mn^{2+} substitution.

3.3. Luminescence-Enhancement Effect of $Zn_{1-x}Mn_xSe$·0.5L ($x \approx 0.2$). Figure 3 shows the PL excitation (left) and emission (right) spectra of the isomorphous $Zn_{1-x}Mn_xSe$·0.5L ($x \approx 0.2$). All have emission peaks at 2.07 eV (595−600 nm) with a half-width of 0.24 eV. In the excitation spectra, the sharp peaks at 4.09 eV (303 nm) for L = en and 4.16 eV (298 nm) for L = pda (also bda and hda) reflect their band gaps and are both

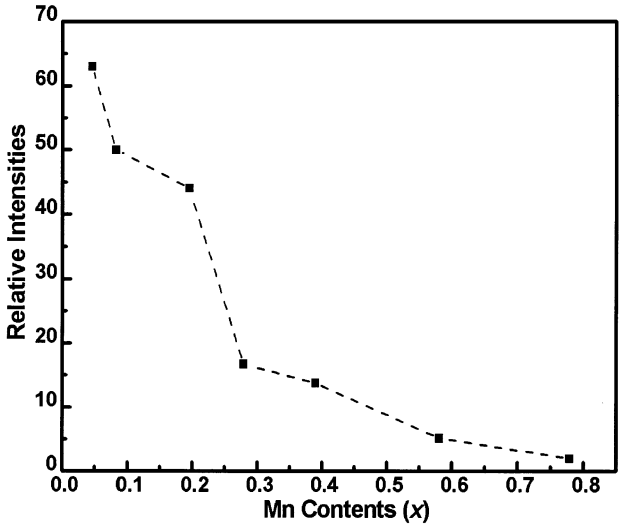

Figure 2. Mn content dependence of PL intensities of $Zn_{1-x}Mn_x$-Se·0.5hda.

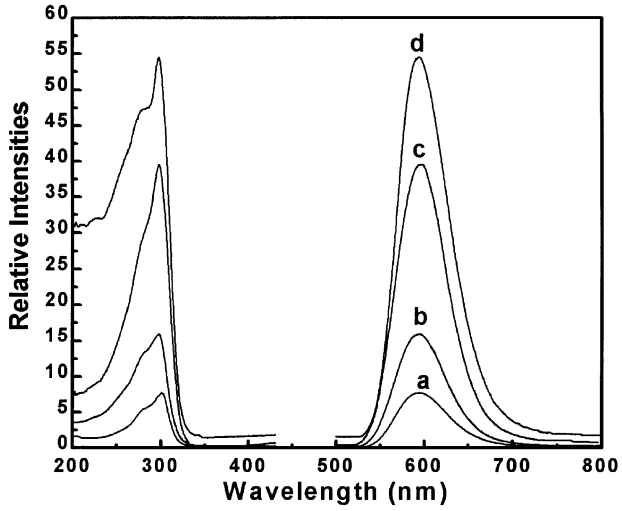

Figure 3. PL excitation and emission spectra of $Zn_{1-x}Mn_xSe$·0.5L ($x \approx 0.2$): (a) L = en; (b) L = pda; (c) L = bda; (d) L = hda.

greater than the estimated values of 4.0 eV (~310 nm) and 3.9 eV (318 nm) from optical absorption spectra,[15] respectively. Therefore, the excitation for 2.07 eV emission originates from a band−band transition of a ZnSe host like traditional $Zn_{1-x}Mn_xSe$ DMS. Compared with the emission at 2.12 eV (585 nm) of bulk $Zn_{1-x}Mn_xSe$,[26,27] the emission peaks of $Zn_{1-x}Mn_xSe$·0.5L ($x \approx 0.2$) can be assigned to the Mn^{2+} internal transition ($^4T_1 \rightarrow {}^6A_1$) with a red shift of 10−15 nm. At the present Mn content level (~ 0.2), the red shift can be ascribed to the formation of Mn^{2+} pairs.[28] The half-widths of the emission peaks (0.24 eV) indicate that the inhomogeneous broadening is not obvious; that is, Mn^{2+} ions have homogeneous coordinate environments. The emission intensities increase monotonically from 7.0 (L = en) to 54 (L = hda), which can be attributed to the lengthening of diamine molecules because the Mn contents are approximately identical. It appears that the longer the diamine molecules (the more distant from each other the $[Zn_{1-x}Mn_xSe]$ monolayers), the stronger the intensities become.

The luminescence-enhancement effect has been studied in the $CdS-N(C_2H_5)_3$ and $Cd_3As_2-N(C_2H_5)_3$[29] colloids and ZnS-en-MCM-41 mesoporous nanosized composites.[30] Triethylamine ($N(C_2H_5)_3$) acts as a donor to enhance the PL intensities by dramatically lowering the nonradiative decay in CdS and Cd_3As_2 colloids.[29] Diamines are Lewis bases for Zn^{2+} and Mn^{2+} ions, which can also act as electron donors to reduce the nonradioactive decay. In the lattices of $Zn_{1-x}Mn_xSe$·0.5L, all the Zn/Mn ions are linked by the orderly intercalated diamine molecules and form distorted tetrahedra $Zn/MnNSe_3$ with Zn/Mn−N bonds (2.16/2.18 Å[15]). Compared with the interaction between CdS or Cd_3As_2 nanoparticles and $N(C_2H_5)_3$ molecules capped at their surface, the formation of Zn/Mn−N bonds is more effective on the enhancement of PL intensities.

Furthermore, diamines are also spacers for $[Zn_{1-x}Mn_xSe]$ DMS layers. The luminescence process, including the energy transfer of excited electron/hole pairs into Mn^{2+} ions and a subsequent efficient radiative recombination of the 3d electron, are confined in the 2D DMS layers, which are similar to those in quantum wells or superlattices. When the diamine molecules become longer, the interlayer distances of $[Zn_{1-x}Mn_xSe]$ layers increase and the interaction between DMS layers is weakened, and the 2D-confined character of the PL process becomes more prominent, which undoubtedly contributes to the luminescence-enhancement effect (as shown in Figure 3). Certainly, more detailed research is needed to verify this deduction.

4. Conclusion

In summary, 2D-DMS $Zn_{1-x}Mn_xSe$·0.5L (L = diamines) and their host compounds ZnSe·0.5L were prepared by solvothermal reaction in solvent L at 190 °C. They are isomorphous orthorhombic crystals with almost identical intralayer structures ($Zn/MnNSe_3$ coordination tetrahedra) and different interlayer distances of $[Zn_{1-x}Mn_xSe]$ layers. The orthorhombic lattice in the *ab* plane of ZnSe·0.5en is a shrunken $\sqrt{3}a \times c$ 2D superlattice of the (110) plane of hexagonal ZnSe. A strong Mn^{2+}-related emission peak at 600 nm is found in the PL spectra of $Zn_{1-x}Mn_xSe$·0.5L at room temperature. The Mn content (x) dependence of the PL intensities of $Zn_{1-x}Mn_xSe$·0.5hda are especially researched, and the maximum of PL intensities can be obtained when $x < 0.2$. For $x \approx 0.2$, the PL intensities of $Zn_{1-x}Mn_xSe$·0.5L increase monotonically with the lengthening of the diamine molecules. This luminescence-enhancement effect can be ascribed to the formation of Zn/Mn−N bonds and the 2D character of the PL process in the $[Zn_{1-x}Mn_xSe]$ layers. Our results indicate that $Zn_{1-x}Mn_xSe$·0.5L are 2D DMS with strong Mn^{2+}-related luminescence whose structural, optical, and other properties are worth investigating further due to their unique 2D structural characteristics.

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