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Luminescent and Transport Properties of Metastable Quaternary Compounds in the Cd, M^{III} || S, Te (M^{III} = In, Ga) Systems

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Abstract—Metastable quaternary compounds in the reciprocal systems Cd, M || S, Te (M = In, Ga) are prepared by liquid quenching, and their luminescent and transport properties are studied for the first time. $Cd_3In_2S_2Te_4$, $Cd_3Ga_2S_2Te_4$, $Cd_2Ga_2S_2Te_3$, and $CdGa_2S_2Te_2$ are photosensitive and exhibit efficient near-IR or red ($CdGa_2S_2Te_2$) luminescence. The properties of the compounds $Cd_2M_6S_2Te_9$ (M = In, Ga) are also described. All of the synthesized compounds are semiconductors. Their band gaps are evaluated from luminescence data. The peak positions in their luminescence spectra are found to be composition-independent within the homogeneity ranges of $Cd_3M_2S_2Te_4$–$Cd_5M_2S_2Te_6$ (M = In, Ga).

INTRODUCTION

The Cd, Ga || S, Te system was studied in [1]. At 755 K, the stable equilibria in this system involve solid solutions based on constituent components and ternary compounds. The quaternary compounds $Cd_3Ga_2S_2Te_4$, $Cd_2Ga_2S_2Te_3$, $CdGa_2S_2Te_2$, and $Cd_2Ga_6S_2Te_9$ were obtained in a metastable state. The exchange reaction $Cd_3S_3 + In_2Te_3 \rightleftharpoons Cd_3Te_3 + In_2S_3$ has not yet been studied. Our results indicated the existence of the quaternary compounds $Cd_3In_2S_2Te_4$ and $Cd_2In_6S_2Te_9$. Multicomponent cadmium chalcogenide compounds are of practical interest as potential photosensitive materials.

In this work, we report the cathodoluminescence (CL) spectra and transport properties of quaternary compounds in the systems in question.

EXPERIMENTAL

Starting materials. In our preparations, we used high-purity CdS single crystals grown by the Markov–Davydov method. The impurity composition of the crystals was specified in a previous study [2]. High-purity CdTe single crystals were prepared by vapor phase growth. Mixed chalcogenides were synthesized from CdS, Ga_2S_3, Ga_2Te_3, In_2Te_3, In_2S_3, and CdTe. The indium and gallium chalcogenides were prepared from Ekstra V-4 tellurium, 3N indium, 3N gallium, and OSCh 16-5 sulfur (sulfur was additionally purified by vacuum distillation).

Synthesis of mixed chalcogenides. Synthesis was carried out in graphitized silica tubes. Metastable quaternary compounds were prepared by liquid quenching from 1320–1330 K. To this end, the tubes were dropped into a saturated aqueous NaCl solution maintained at 273 K. The cooling rate was about 190–200 K/s.

Characterization techniques. Phase composition of the samples was determined by x-ray diffraction (XRD) using an FR-552 Guinier focusing camera. Density was determined by the Archimedes method using extrapure-grade bromoform additionally purified by double distillation as the buoyancy fluid. Microstructures were examined under an MII-4 optical microscope. Electron probe x-ray microanalysis (EPXMA) was performed with a Cameca instrument.

The carrier concentration and mobility were inferred from four-probe electrical conductivity and Hall effect measurements. CL and photoconductivity (PC) spectra were recorded as described elsewhere [2].

RESULTS AND DISCUSSION

Synthesis and XRD characterization of quaternary metastable compounds. New metastable chalcogenides were prepared by quenching superheated melts from 1320–1330 K. At high temperatures, the intermixing of particles in the melt leads to the formation of both M–S and M–Te bonds. In light of this, quenching (cooling at a rate of about 200 K/s) was expected to ensure the formation of metastable quaternary compounds.

In this way, we obtained a number of metastable compounds in the Cd, M || S, Te (M = In, Ga) systems. It seems likely that their formation proceeded through diffusionless crystallization. This assumption is supported by the fact that the samples were single-phase, with no second-phase inclusions, as determined by EPXMA and microstructural analysis. The process was

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reproducible: in some cases, identical results were obtained in up to ten experiments. The exchange reaction $Cd_3S_3 + In_2Te_3 \rightleftharpoons Cd_3Te_3 + In_2S_3$ yields no stable quaternary compounds (the 755-K section of the phase diagram in question will be reported in a forthcoming paper).

The homogeneity ranges of the compounds $Cd_3M_2S_2Te_4$ include the compositions $Cd_5M_2S_2Te_6$ (phase I for M = Ga and phase V for M = In). We assume that the formula of these compounds is $Cd_3M_2S_2Te_4$ rather than $Cd_5M_2S_2Te_6$ because the XRD peaks from $Cd_5M_2S_2Te_6$ are broader than those from $Cd_3M_2S_2Te_4$. At CdTe contents above that of $Cd_5M_2S_2Te_6$, the samples consist of phase I or V and a CdTe-based solid solution. Compound I has an fcc (sphalerite) structure, and compound V has a hexagonal (wurtzite) structure. No superlattice reflections were detected in the XRD patterns of $Cd_3M_2S_2Te_4$ and $Cd_5M_2S_2Te_6$ (M = In, Ga), which attests to random distributions of Cd, M, cation vacancies, S, and Te. Mössbauer studies of these compounds also revealed no ordering (the results will be presented in a forthcoming paper).

The lattice parameters of $Cd_3In_2S_2Te_4$ are a = 0.4344(4) nm and c = 0.7103(6) nm. The unit-cell volume of the wurtzite phase is $V_w = 0.1161$ nm$_3$. The total hexagonal cell contains one $Cd_3In_2S_2Te_4$ formula unit: $V_{total} = 3V_w = 0.3483$ nm^3. All of the anion sites are occupied by S and Te, whereas some of the cation sites are vacant: $(Cd_3In_2\square)(S_2Te_4)$. The measured density (5.42 ± 0.01 g/cm^3) is close to the x-ray density (5.44 g/cm^3).

$Cd_5Ga_2S_2Te_6$ (phase I) has the sphalerite structure with a = 0.6415(5) nm and a unit-cell volume V_s = 0.2640 nm^3 (half of a $Cd_5Ga_2S_2Te_6$ formula unit per cell). All of the anion sites are occupied by S and Te atoms, whereas some of the cation sites are vacant: $(Cd_{2.5}Ga\square_{0.5})STe_3$. The measured density (4.79 ± 0.01 g/cm^3) is close to the x-ray density (4.81 g/cm^3).

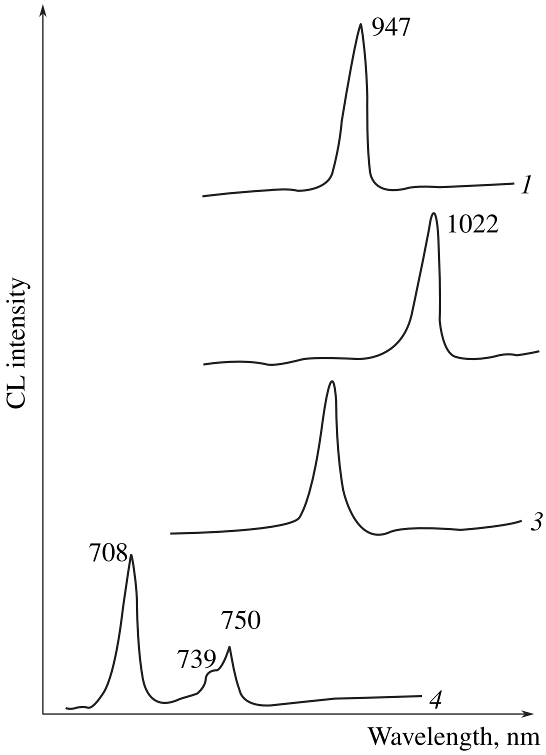
$Cd_2In_6S_2Te_9$ (phase VI) has an fcc (sphalerite) structure with a = 0.6415(5) nm.

$Cd_2Ga_2S_2Te_3$ (phase II) has a rhombohedrally distorted sphalerite structure with a = 0.6395(5) nm and α = 98.35(7)°. The XRD patterns of phases II and VI showed no superlattice reflections.

Compound IV ($Cd_2Ga_6S_2Te_9$) has an fcc subcell with a = 0.5969(5) nm. The presence of weak superlattice reflections in its XRD pattern attests to a more complex crystal structure.

$CdGa_2S_2Te_2$ (phase III) crystallizes in the tetragonal system with a = 0.7058(5) nm and c = 1.0164(7) nm.

All these compounds are metastable and, during annealing at 755 K, decompose into mixtures of equilibrium phases. $Cd_3Ga_2S_2Te_4$, $Cd_2Ga_2S_2Te_3$, and $CdGa_2S_2Te_2$ decompose to form CdTe-based solid solutions and Ga_2S_2Te. $Cd_3In_2S_2Te_4$ decomposes into a mixture of $CdIn_2S_4$, $CdIn_2Te_4$, and CdTe. $Cd_2Ga_6S_2Te_9$ decomposes into a mixture of Ga_2S_2Te, CdTe, and $CdGa_2Te_4$; and $Cd_2In_6S_2Te_9$, into a mixture of $CdIn_2S_4$, $CdIn_8Te_{13}$, and $CdIn_2Te_4$.



78-K CL spectra of (*1*) $Cd_3Ga_2S_2Te_4$, (*2*) $Cd_3In_2S_2Te_4$, (*3*) $Cd_2Ga_2S_2Te_3$, and (*4*) $CdGa_2S_2Te_2$.

At room temperature, these quaternary compounds may persist for a long time (at least a year).

78-K CL spectra. The CL spectrum of $Cd_3Ga_2S_2Te_4$ shows only one line, at 947 nm (figure, spectrum *1*), due to edge emission. The band gap E_g evaluated from its position is 1.31 eV. The spectrum of $Cd_3In_2S_2Te_4$ also shows a single line, at 1022 nm (spectrum *2*), which corresponds to E_g = 1.21 eV. A noteworthy feature of single-phase samples of phase V is that, even though $Cd_3In_2S_2Te_4$ and $Cd_5In_2S_2Te_6$ differ drastically in composition (Te : S = 2 : 1 and 3 : 1, respectively), the peak positions in their CL spectra differ very little (Table 1), as do those in the spectra of $Cd_3Ga_2S_2Te_4$ and $Cd_5Ga_2S_2Te_6$ (phase I). This is probably due to the random distributions of Cd, M, cation vacancies, S, and Te in the structures of phases I and V.

The CL spectrum of $Cd_2Ga_2S_2Te_3$ shows a single line, at 928 nm, corresponding to edge emission (figure, spectrum *3*). $CdGa_2S_2Te_2$ exhibits edge emission in the red spectral region (spectrum *4*). An important point is that the quaternary compounds with a cubic structure ($Cd_3Ga_2S_2Te_4$) or a slightly distorted cubic structure

Table 1. Peak position of edge emission in the CL spectrum and band gap of metastable quaternary compounds

Phase	Composition	Wavelength, nm		E_g, eV	
		78 K	298 K	78 K	298 K
I	$Cd_3Ga_2S_2Te_4$	947	962	1.31	1.29
I	$Cd_5Ga_2S_2Te_6$	947	963	1.31	1.29
II	$Cd_2Ga_2S_2Te_3$	928	954	1.33	1.30
III	$CdGa_2S_2Te_2$	708	715	1.75	1.73
IV	$Cd_2Ga_6S_2Te_9$	961	972	1.29	1.27
V	$Cd_3In_2S_2Te_4$	1022	1006	1.21	1.23
V	$Cd_5In_2S_2Te_6$	1022	1007	1.21	1.23
VI	$Cd_2In_6S_2Te_9$	1036	1042	1.19	1.18

Table 2. Transport properties of *p*-type metastable quaternary compounds

Phase	Composition	$N \times 10^{-16}$, cm^{-3}	μ, cm^2/s	σ, S/cm
I	$Cd_3Ga_2S_2Te_4$	7.2	90	0.013
I	$Cd_5Ga_2S_2Te_6$	7.2	88	0.019
II	$Cd_2Ga_2S_2Te_3$	6.5	99	0.021
III	$CdGa_2S_2Te_2$	1.1	81	0.001
IV	$Cd_2Ga_6S_2Te_9$	8.4	105	0.045
V	$Cd_3In_2S_2Te_4$	9.6	109	0.032
V	$Cd_5In_2S_2Te_6$	9.6	105	0.038
VI	$Cd_2In_6S_2Te_9$	11.3	112	0.059

($Cd_2Ga_2S_2Te_3$), as well as the compound with the wurtzite structure ($Cd_3In_2S_2Te_4$), exhibit efficient IR luminescence at 78 K.

298-K CL spectra. The room-temperature CL spectra of $Cd_3Ga_2S_2Te_4$, $Cd_2Ga_2S_2Te_3$, and $Cd_3In_2S_2Te_4$ (and those for compositions lying in their homogeneity ranges) also show a single line (Table 1), which is slightly shifted as compared to the 78-K spectra. The luminescence intensity at 298 K is lower than that at 78 K.

Transport properties and PC spectra. All of the synthesized quaternary compounds are *p*-type semiconductors. Their transport properties (electrical conductivity, hole concentration, and hole mobility) are summarized in Table 2. It is of interest to note that, in different samples within the homogeneity ranges of $Cd_3M_2S_2Te_4$–$Cd_5M_2S_2Te_6$ (M = In, Ga), the hole concentration and mobility are constant to within the present measurement accuracy (Table 2).

$Cd_3In_2S_2Te_4$, $Cd_3Ga_2S_2Te_4$, $Cd_2Ga_2S_2Te_3$, and $CdGa_2S_2Te_2$ are photosensitive, with a ratio of dark to light (10^3 lx) resistance of 430, 720, 850, and 980, respectively. The compounds $Cd_2In_6S_2Te_9$ (M = In, Ga) have an insignificant photoresponse. The 298-K PC spectra of $Cd_3Ga_2S_2Te_4$, $Cd_3In_2S_2Te_4$, and $Cd_2Ga_2S_2Te_3$ show each a single peak, at 960, 1010, and 955 nm, respectively. The spectrum of $CdGa_2S_2Te_2$ shows a peak at 715 nm with a shoulder at 750 nm.

CONCLUSIONS

Metastable quaternary compounds in the reciprocal systems Cd, M || S, Te (M = In, Ga) were prepared by liquid quenching.

XRD data for $Cd_3In_2S_2Te_4$, $Cd_3Ga_2S_2Te_4$, and $Cd_2Ga_2S_2Te_3$ attests to random distributions of Cd, M, cation vacancies, S, and Te in their structures. These compounds are photosensitive and exhibit efficient near-IR luminescence. $CdGa_2S_2Te_2$ exhibits red luminescence.

The luminescent properties of the compounds studied are composition-independent within the homogeneity ranges of $Cd_3M_2S_2Te_4$–$Cd_5M_2S_2Te_6$ (M = In, Ga). These compounds, disordered in both the cation and anion sublattices, have interesting structural and physical properties.

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