Crystalline and band energy structure of Ag_2CdI_4

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Abstract

Ag_2CdI_4 compound belongs to the so called superionic materials of A_2BX_4 type (A=Ag, Cu; B=Hg, Cd, Zn, Pb and other). These materials are considered in modern physics as the model objects to study phase transitions into state with high ionic conductivity. Among different compounds of A_2BX_4 type. Superionic material Ag_2HgI_4 has been investigated better than all other. Solid electrolyte Ag_2CdI_4 is not investigated so completely. Electrical conductivity and optical properties of bulk and thin films of Ag_2CdI_4 compound have been studied previously. This article deals with the investigation of crystalline and band energy structure of bulk Ag_2CdI_4 material.

Synthesis and crystalline structure of Ag_2CdI_4

Previous studies show, that Ag_2CdI_4 is the only compound in AgI-CdI_2 system possessesing the peritectical type of crystallisation [1]. Therefore, synthesis methods of such a compound are based on the solid state chemical reactions (SSCR) at temperatures, lower than peritectical temperature ($T_{pr} = 384$ K). For synthesis of fine quality crystals AgI and CdI_2 powders in stoichiometric amount were mixed and consolidated at pressure $\sim 10^6$-10^8 Pa. Obtained in such a munner samples with diameter ~ 15 mm and thickness ~ 2-3 mm were annealed at $T \le T_{pr}$ during ~ 240 hours. Precise investigation of structural data on more than 20 samples, obtained at different conditions (value of pressure, time and temperature of annealing) have shown, that obtained in such a munner Ag_2CdI_4 compound possesses tetragonal unit cell with parameters $a = 6.3421(5)$ Å,

$c = 12.668(2)$ Å, and space group $I\bar{4} = S_4^2$. Atomic coordinates are shown in Table 1.

Band energy structure and optical spectra of Ag_2CdI_4

Band energy structure calculation of Ag_2CdI_4 has been done using strong band approximation according to semi-empirical Harrison's method. As the basis, $4s$ and $4d$ atomic orbitals of Ag, $5s$ and $5p$ atomic orbitals of Cd and I were used.

This calculation scheme is simpler compared to the first-principle methods, but it demands some empirical parameters (for example E_g), which can be obtained from experiment. Accordingly, the optical spectra of bulk and thin film samples of Ag_2CdI_4 were investigated. Optical absorption spectra of thin-films of Ag_2CdI_4 ($d \sim 1$ μm) at $T = 290$ K possesse an complicated structure in region $2.76\ldots3.26$ eV (Figure 1.a, curve 1). Using program for spectrum approximation, four bands

with maximums of 2.76, 2.91, 2.97 and 3.26 eV were distinguished. The values of absorption coefficients of these bands are equal to 8.1×10^3, 6.9×10^3, 19.1×10^3 and 110.5×10^3 cm^{-1} respectively. Absorption band at 2.91 eV, whose existence was also indicated in [2], is connected with the transition between levels of basic $4d^{10}$ and excited $4d^3 5s^1$ electronic configurations of Ag$^+$ ions, which possesse tetrahedral coordination of I$^-$ ions.

Diffusion reflection spectra of Ag$_2$CdI$_4$ (Figure 1.a, curve 2) were also used for the evaluation of band energy gap of bulk samples. Using this spectrum, the Gurevich-Kubelka-Munk (GKM) function for Ag$_2$CdI$_4$ has been calculated. The band gap of Ag$_2$CdI$_4$ has been evaluated by extrapolation of the GKM-function

to the cross section with the abscissa axis: $E_g = 3.05$ eV at $T = 290$ K (Figure 1.a, curve 3).

Band energy structure of Ag$_2$CdI$_4$ is shown in Figure 1.b. Calculation results show some grouping of energy levels into subbands. Thus, it is possible to distinguish three regions in the spectrum of density of states, corresponding to the valence band of Ag$_2$CdI$_4$: lower region corresponds to 5s–state of iodine, middle (with high intensity) region corresponds to 5p–states of iodine and the upper forms the ceiling of valence band and corresponds to 4d–states of silver.

Spectrum part, corresponding to the conductivity band also has three regions: bottom of conductivity band which is connected with 5s–states of silver and two regions with higher

Table 1. Atomic fractional coordinates for Ag$_2$CdI$_4$

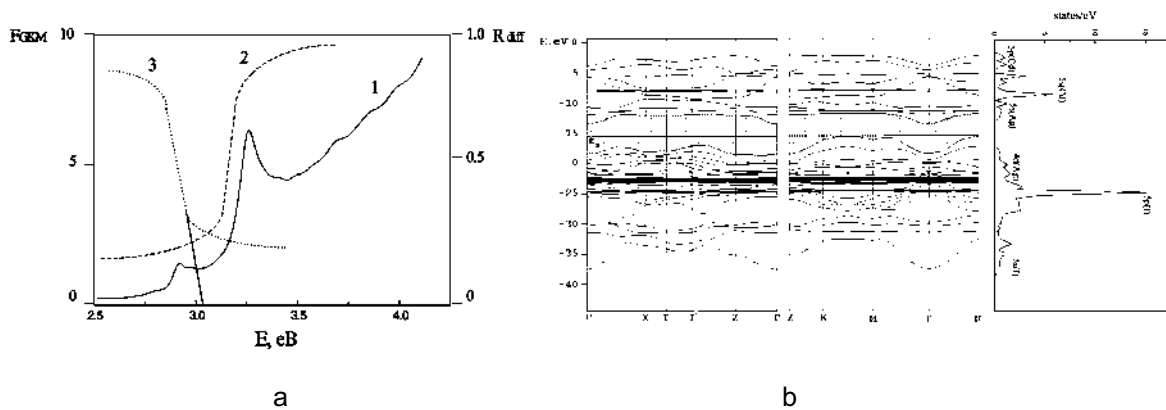| Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Ag (1)	0.0000	0.5000	0.7500	Ag (1)	0.0000	0.0000	0.5000
Ag (2)	0.5000	0.0000	0.2500	Ag (2)	0.5000	0.5000	0.0000
Cd	0.0000	0.0000	0.0000	Cd	0.5000	0.5000	0.5000
I (1)	0.2419	0.2736	0.1367	I (1)	0.7419	0.7736	0.6367
I (2)	0.7581	0.7264	0.1367	I (2)	0.2581	0.2264	0.6367
I (3)	0.2736	0.7581	0.8633	I (3)	0.7736	0.2581	0.3633
I (4)	0.7264	0.2419	0.8633	I (4)	0.2264	0.7419	0.3633

Fig. 1. a) Absorption spectra of Ag$_2$CdI$_4$ thin film (1), diffusion reflection spectra (2) and Gurevich-Kubelka-Munk function (3) of Ag$_2$CdI$_4$. b) Band energy structure and electronic density of state of Ag$_2$CdI$_4$

energy, corresponding to $5s–$ and $5p–$states of cadmium. As it was established, valence band's maximum is in N–point of Brillouin's zone, and the conductivity band's minimum is localized in Γ–point (Figure 1.b). Therefore, fundamental absorption edge of Ag_2CdI_4 may be connected with indirect optical transitions. At variation of ionization potentials of $s–$states of cadmium and $p–$states of iodine it was established that energy value 2.75 eV corresponds to the indirect optical transition. Values of E_g in $\Gamma–$ and N–points are equal 5.52 and 4.23 eV respectively.

In the framework of calculated zone scheme, optical absorption spectrum of Ag_2CdI_4 thin films can be interpreted in the following way. Absorption bands at 2.76, 2.91 and 2.97 eV correspond to indirect transitions between the ceilling of valence band formed mostly by $d–$states of Ag and bottom of conductivity band formed by s-states of Ag. Such interpretation does not contradict conclusions [2] on the connection of absorption bands of Ag_2CdI_4 in the region 2.75…3.0 eV with electronic transitions in Ag^+, however they should be interpreted as interband transitions. Such a conclusion is confirmed by calculations of partial states densities and by existing of photoconductivity phenomena of Ag_2CdI_4 in this spectrum region [3].

As $d–s$ transitions are indirect and forbidden according to the selection rule $\Delta l = \pm 1$, their intensities are small. Maybe, they are not manifested in the spectra of diffusion reflection of bulk samples Ag_2CdI_4, and therefore only band 3.25 eV was registered in these spectra. That is why value $E_g = 3.05$ eV, obtained from diffusion reflection spectrum, should be considered as too high.

High intensity band of optical absorption of Ag_2CdI_4 films at 3.26 eV (Figure 1.a, curve 1) is connected with the interband transitions between $p–$states of iodine and $s–$states of cadmium band.

Conclusions

Synthesis method was elaborated and optimal synthesis conditions for superionics Ag_2CdI_4 by solid state chemical reaction were established.

X-ray analysis of Ag_2CdI_4 compound has been done, space group symmetry has been refined. Unit cell parameters and atomic coordinates have been established.

Band structure of Ag_2CdI_4 was calculated by semi-empirical method using strong band approximation. Origin of existing bands and possibility of indirect optical transitions were established. Interpretation of optical spectra of Ag_2CdI_4 thin films absorption has been done using of semi-empirical calculations results.

References

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