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Article *in* Japanese Journal of Applied Physics · February 1992

DOI: 10.1143/JJAP.31.L145

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Jpn. J. Appl. Phys. Vol. 31 (1992) pp. L 145–L 147
Part 2, No. 2B, 15 February 1992

Optical Absorption Spectra in $CuAlS_2$ Doped with Vanadium

Igor AKSENOV*, Yuki KUDO and Katsuaki SATO**

Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184

(Received November 13, 1991; accepted for publication December 21, 1991)

Optical absorption spectra were measured at room temperature in undoped and V-doped single crystals of $CuAlS_2$ grown by the chemical vapour transport technique. Intense absorption bands characteristic of vanadium have been observed. These bands were attributed to the d-d type transitions between 3d-originated orbitals of V^{3+} ion as well as to the charge-transfer type transitions from the valence band of the host crystal to the 3d-shell orbitals of V^{3+} ion.

KEYWORDS: single crystals of $CuAlS_2$, vanadium transition atom impurity, optical absorption spectrum, d-d type transition, photoionization transition

In recent years ternary compounds with a chalcopyrite-type crystal structure have been receiving much interest as perspective materials for optoelectronics. $CuAlS_2$ ternary semiconductor is the widest band gap member of ternaries which is expected to be a possible candidate for blue-to-ultraviolet LED application.[1] It is necessary for technical application to have information about defect energy levels in $CuAlS_2$ compound, including data on transition atom impurities which are found to be present in ternaries and have great influence on optical properties of these compounds. With detailed optical studies of Fe, Mn and Cr transition atom ions in $CuAlS_2$ host crystals having been conducted,[2-4] and ESR data on Ti, Fe, Co, and Ni ions in $CuAlS_2$ compound having also been reported,[5-8] it is turned out that for all transition atoms only vanadium has been put aside uninvestigated since there is no data for vanadium ions not only in $CuAlS_2$ host but for any chalcopyrite host compounds. Therefore the study of the behaviour of V ions in $CuAlS_2$ lattice is considered by us to be challenging from both scientific and practical points of view.

In this study we present the results of optical absorption investigations of $CuAlS_2$ single crystals doped with vanadium.

Single crystals of $CuAlS_2$ compound doped with 0.1 and 1 mol% of V were grown by the temperature variation chemical vapour transport (CVT) technique in a closed system using iodine as a transporting agent. The starting materials used were the powders of polycrystalline $CuAlS_2$:V prepared by the direct melting of constituent elements (Cu, Al, V, S–99.9999%, the total charge being 10 g) in a BN crucible held in a sealed silica ampoule, the maximal temperature used was 1300°C. The source material thus obtained (about 3 g) was sealed in a quartz ampoule (18 mm ID and 20 cm in length) in a vacuum (10^{-6} Torr) with iodine in the concentration of 10 mg/cm^3 of inner volume of the ampoule. The ampoule was placed in a two-zone furnace to grow single crystals by CVT, the growth-zone temperature being 700°C and the source-zone temperature having been raised from 600°C to 850°C during 10 days. The resulting single crystals were typically bulk-shaped with dimensions of about $2 \times 2 \times 2$ mm^3, the coloration of the crystals varying from transparent orange to opaque brown with the increase of vanadium concentration from 0.1 mol% to 1 mol%. Although the concentrations of vanadium denoted below are only nominal, it is known that the nominal values can be used in order to estimate the approximate concentration of transition atom impurities in chalcopyrite- type crystals obtained by CVT.[9] Absorption spectra were measured at room temperature in the spectral range 300–2400 nm by using Hitachi type U-3410 spectrophotometer. The crystals used for absorption measurements had been mirror-polished to the thickness of 0.2–0.3 mm using the lapping films.

The typical absorption spectra of undoped and vanadium-doped samples are shown in Fig. 1. The absorption spectrum of undoped $CuAlS_2$ consists of two broad bands at 620 and 920 nm, causing the green colouration of the crystals. These bands are originating from charge-transfer transitions related to residual Fe^{3+} ions on Al sites.[10] Doping of the crystals with 0.1 mol% of vanadium leads to an elimination of Fe^{3+}-related ab-

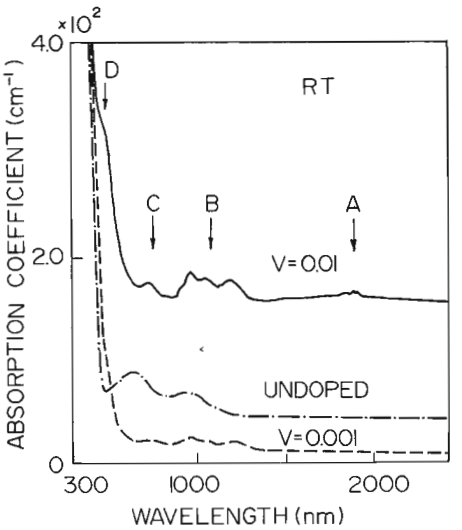

Fig. 1. The optical absorption spectra of undoped and V-doped $CuAlS_2$ crystals at room temperature.

*On leave from Institute of Physics of Solids and Semiconductors, Academy of Sciences of Buelorussian Republic, Minsk, USSR.
**To whom reprint requests should be addressed.

sorption bands and to a decrease of absorption coefficient in the 500–2400 nm spectral range by one order of magnitude. The observed elimination of the Fe^{3+}-related absorption bands in V-doped samples can be explained assuming that V ions substitute Cu^{+}-site, because in this case the substitution of Cu^{+}-sites by either V^{2+} or V^{3+} ions leads to the reduction of iron ions valency from Fe^{3+} to Fe^{2+} in order to satisfy the charge neutrality conditions, and it is well known that the divalent iron ions do not introduce any absorption bands in the spectral range under consideration.[3]

It can also be seen from Figs. 1–3 that the absorption spectrum of $CuAlS_2:V_{0.001}$ samples consists of a very weak unresolved broad A- band at about 1860 nm, triply peaked B- band of medium intensity centered at 1100 nm, broad C- band at 725 nm, and D- band superposed on a steeply rising edge absorption of the $CuAlS_2$ host matrix. The increase of vanadium concentration up to 1 mol% serves to increase the intensities and to sharpen the structures of all bands observed. In this case the A- band becomes resolved as a triply peaked structure (Fig. 2), and fourth subband seems to appear in the B- band structure (Fig. 3).

A comparison of the spectra obtained in this work with that reported for V-doped ZnS[11] and CdS[12] host crystals (Table I) shows that the spectral positions of the A-, B-, and C- absorpion bands in $CuAlS_2$:V are essentially the same as the positions of excitation and emission bands for ZnS:V crystals, although in the latter case the structures of the A- and B- bands were not resolved. On the other hand for CdS:V crystals the spectral positions of the subbands belonging to the B- absorption band are the same as in $CuAlS_2$:V crystals, although in the former case the A- band was not discovered.

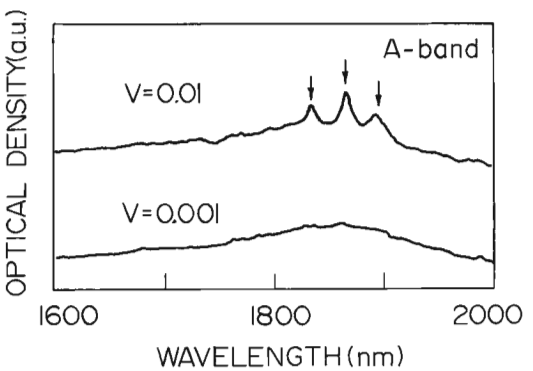

Fig. 2. The structure of A- absorption band in $CuAlS_2$:V at room temperature.

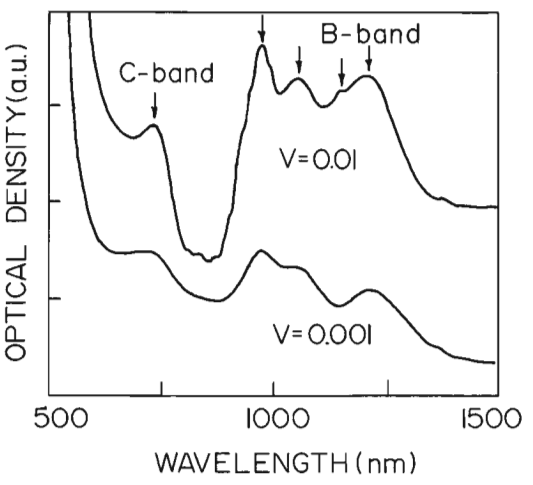

Fig. 3. The structure of B- and C- absorption bands in $CuAlS_2$:V at room temperature.

Results on V-doped ZnS and CdS compounds were tentatively interpreted as the transitions between 3d-originated multiplets of trivalent V ions. This interpretation seems to be valid also for V-doped $CuAlS_2$ crystals. If we assume that vanadium ions in $CuAlS_2$ host are trivalent (d^2-system) then the positions of the intrasystem (same spin multiplicity) bands are fixed by only two parameters Dq and B, if non-cubic crystal field component and spin-orbit coupling effects are ignored. Therefore the values of Dq and B parameters can be determined from the observed positions of the A- and B- bands baricenters. Since the ground state of ions with d^2-configuration in tetrahedral crystal field has A_2 symmetry and nearest excited intrasystem levels have T_2 and T_1 symmetry, we can assign the A- and B- absorption bands to the intrasystem transitions from the ground state to the excited T_2 and T_1 states, correspondingly. Having made this assignment we obtain the values $Dq=538\ cm^{-1}$ and $B=453\ cm^{-1}$.

A more accurate evaluation of the energy levels positions should take into account the splitting of the terms due to non-cubic component of the crystal field in chalcopyrite lattice as well as spin-orbit coupling effects. Energy level diagram for d^2-electronic system immersed in a field of tetrahedral symmetry taking into account the spin-orbit interaction have been plotted by Liehr,[13] the part of this diagram is shown in Fig. 4 together with the spectral positions of the absorption bands observed. Taking into account the energy level diagram we can assign the C- band to the intrasystem transition from the ground state of V^{3+} ion to the excited $^3T_1$ state, originated from p-orbital of the free ion, since the

Table I. Peak positions of the absorption bands observed in V-doped $CuAlS_2$ single crystals. The positions of excitation and emission bands observed in ZnS:V[11] and that of absorption bands observed in CdS:V[12] are also shown.

band	$CuAlS_2$:V wavelength (nm)	$CuAlS_2$:V energy (cm^{-1})	ZnS:V energy (cm^{-1})	CdS:V energy (cm^{-1})	assignment
	1895	5280			
A	1865	5360	5320	—	$^3A_2(F)\rightarrow{}^3T_2(F)$
	1830	5460			
	1215	8230		8280	
	1150	8700		8700	
B			9100	8920	$^3A_2(F)\rightarrow{}^3T_1(F)$
	1050	9520		9520	
	975	10250		10250	
				12300	
C	725	13800	14100	13820	$^3A_1(F)\rightarrow{}^3T_1(F)$
				14700	
D	470	21300	—	—	charge transfer

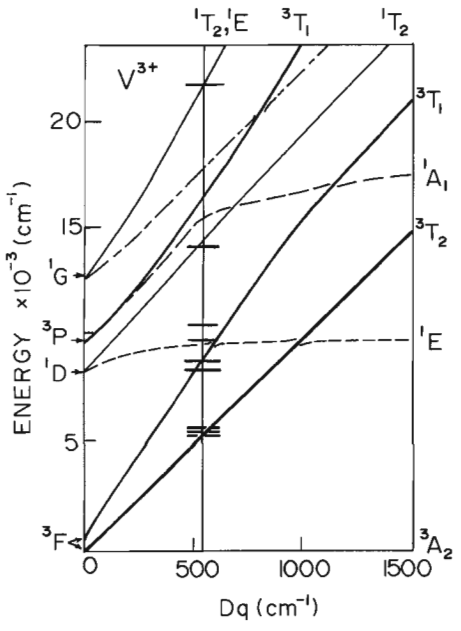

Fig. 4. Energy level diagram for V^{3+}-ion (d^2-system) in a field of tetrahedral symmetry for $\lambda = 65\ cm^{-1}$. The spectral positions of the absorption bands observed are shown.

oscillator strength of intrasystem transition is expected to be of several orders of magnitude higher as compared with the oscillator strength for intersystem transitions to the nearby $^1A_1$ and $^1T_2$ levels. The energy positions of baricenters of the A- and B- bands are in a rather good agreement with theoretical calculations, whereas the C-band is shifted towards lower energies probably due to configurational mixing of the excited states at the energies of about 15000 cm^{-1}.

The spin-orbit coupling coefficient λ for V^{3+} ions in $CuAlS_2$ host can be estimated from ESR data on ZnS:V[14] and is rather small ($\approx 40\ cm^{-1}$). Therefore the large observed splitting of the B band ($\approx 650\ cm^{-1}$) can not be attributed to the spin-orbit interaction and is supposed to be caused by a strong mixing of $^3T_2(F)$ level with ^1E level originating from ^1D free ion term as well as by the non-cubic component of the crystal field, that causes the 2-fold splitting of T_1 orbital triplet ($T_1 \rightarrow A_2 + T_2$).

The absorption band D has been attributed to the $V^{3+} \rightarrow V^{2+}$ photoionization transition, in other words it can be interpreted as a charge-transfer type transition from the valence band of the host crystal to the donor-like 3d-shell originated orbitals of vanadium ion. The reason for such an interpretation is that molecular orbitals corresponding to uppermost valence band states of $CuAlS_2$ compound are composed of sulfur 3p and copper 3d orbitals, that makes possible the charge transfer from ligand 3p orbitals of the valence band to the 3d-shell orbitals of vanadium ion. On the other hand the molecular orbitals of conduction band of the host crystal are composed of 3s orbitals of copper and aluminium, therefore acceptor state (3d-shell)-conduction band (3s-orbitals) transitions are parity forbidden. Detailed studies, including low-temperature absorption and ESR measurements, are planned to gain further information on the electronic structure of the vanadium introduced deep levels in $CuAlS_2$.

This work has been partially supported by Japan Society for the Promotion of Science and by Grant-in-Aid for scientific research on Priority Areas (No. 03204005) from the Ministry of Education, Science and Culture, which is deeply appreciated.

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