Optical properties of monocrystalline $CuIn_5Se_8$

S. Levcenko
Institute of Applied Physics, Academy of Sciences of Moldova, Chisinau, MD 2028, Moldova

N. N. Syrbu
Technical University of Moldova, Chisinau, MD 2004, Moldova

E. Arushanov[a)]
Institute of Applied Physics, Academy of Sciences of Moldova, Chisinau, MD 2028, Moldova and Universidad Autónoma de Madrid, Departamento Física Aplicada, C-XII, 28049 Madrid, Spain

V. Tezlevan
Institute of Applied Physics, Academy of Sciences of Moldova, Chisinau, MD 2028, Moldova

R. Fernández-Ruiz
Universidad Autónoma de Madrid, S.I.D.I., C-IX, 28049 Madrid, Spain

J. M. Merino and M. León[b)]
Universidad Autónoma de Madrid, Departamento Física Aplicada, C-XII, 28049 Madrid, Spain

(Received 29 July 2005; accepted 20 February 2006; published online 7 April 2006)

Single crystals of $CuIn_5Se_8$ have been grown by chemical vapor transport. The crystals show a deviation from stoichiometry. The temperature dependence of their optical absorption spectra was investigated in the temperature range of 10–300 K. The variation of the energy gap with temperature was studied by means of a three-parameter thermodynamic model, the Einstein model, and the Pässler model. The values of the band gap at $T=0$ K, a dimensionless constant related to the electron-phonon coupling, an effective and a cutoff phonon energy have been estimated. It was also found that the major contribution of phonons to the shift of E_g vs T in $CuIn_5Se_8$ is mainly from optical phonons. The presence of Urbach's tail just below the band edge in the absorption spectra of $CuIn_3Se_5$ has been observed. It was shown that the static structural disorders contribute mainly to the absorption below the direct band gap. © *2006 American Institute of Physics*.
[DOI: 10.1063/1.2186379]

I. INTRODUCTION

$CuInSe_2$ and related chalcopyrite-type semiconductors are leading candidates for absorbers in high efficiency heterojunction solar cells. Devices based on this material have demonstrated efficiencies up to 19.3%.[1] Recent studies showed the existence of an In-rich n-type material surface layer on the absorber in some high efficiency thin film cells. This layer has been identified as an ordered vacancy compound (OVC) with a dominant $CuIn_3Se_5$ phase following Shmid *et al.*[2] and is expected to play an important role in the performance of the high efficiency $CuInSe_2$-based solar cells. On the other side, Zhang *et al.* figured that $CuIn_5Se_8$ has the lowest formation energy in the order defect compounds[3] and that means $CuIn_5Se_8$ is easily formed.

In spite of the importance of $CuIn_3Se_5$ and $CuIn_5Se_8$ in technological applications and the understanding of basic physics, so far the characteristics of $CuIn_3Se_5$ or $CuIn_5Se_8$ single crystals have not been yet well studied. Some optical, transport, and structural measurements were carried out on $CuIn_3Se_5$ and $CuIn_5Se_8$ thin films and bulk polycrystalline samples.[1–24] A chalcopyrite type of structure with $c \approx 2a$,[12] a defect chalcopyrite,[2,8,16] or a thiogallate structure[8] have been ascribed to $CuIn_3Se_5$ while $CuIn_5Se_8$ can be both hexagonal and tetragonal as reported Tham *et al.*[7] and Kohara *et al.*,[24] where hexagonal $CuIn_5Se_8$ is a stable phase and tetragonal is a metastable phase.[24] Recently, structural analysis of $CuIn_3Se_5$ at different temperatures using synchrotron radiation has been reported. It was found that $CuIn_3Se_5$ structure fits to the $P\bar{4}2c$ spatial group.[18] The available values of the band gap of E_g are in the range of 1.1–1.3 eV for $CuIn_3Se_5$,[1–6,8,10,13,14,19,20] and in between 1.13 and 1.3 eV for $CuIn_5Se_8$.[8,9,11,21] The variation in band gap can be attributed to the difference in defect concentration, which in turn is determined by the compositional change. When compared to other semiconductor compounds, the chalcopyrites and OVCs exhibit unusually high tolerance to deviations in stoichiometry. In fact, $CuInSe_2$ shows band gap values ranging from 0.94 to 1.04 eV. In the case of $CuIn_5Se_8$, some difference in E_g can be also caused by the difference in structure of the studied material (hexagonal or tetragonal). The band gaps of $CuIn_3Se_5$ and $CuIn_5Se_8$ were estimated on the basis of optical absorption,[1,2,4–6,9,11,14,21,23] photoluminescence,[8,10,11,13,20] photoconductivity,[19,22] cathodoluminescence,[4] reflectance,[8] photoreflectance, and electroreflectance[10] measurements. Only two works on the temperature dependence of the band gap E_g in $CuIn_5Se_8$,[9,11] in a wide range of temperatures using bulk samples prepared by the Bridgman technique, have been reported. The studied materials in both Ref. 9 and Ref. 11 show hexagonal structure.

a)Electronic mail: ernest.arushanov@phys.asm.md
b)Electronic mail: maximo.leon@uam.es

