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High-field hopping magnetotransport in kesterites

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ABSTRACT

Transport properties of the kesterite-like single crystals of Cu_2ZnSnS_4, $Cu_2ZnSn_xGe_{1-x}Se_4$ and Cu_2ZnGeS_4 are investigated in pulsed magnetic fields up to $B = 20$ T. The Mott variable-range hopping (VRH) conduction is established by investigations of the resistivity, $\rho(T)$, in all the materials mentioned above within broad temperature intervals of $\Delta T_{v4} \sim 50$–150 K, 50–250 K and 100–200 K, respectively. In addition, the Shklovskii-Efros VRH conductivity below $T_{v2} \sim 3$–4 K, the nearest-neighbour hopping (NNH) charge transfer between $T \sim 250$–320 K and the conductivity by activation of holes on the mobility threshold at temperatures outside ΔT_{v4}, respectively, are observed in these materials. In Cu_2ZnSnS_4, magnetoresistance (MR) contains only a positive contribution, connected mainly to a shrinkage of impurity wave functions by the magnetic field. At the same time, a negative contribution to MR, attributable to interference effects in VRH, is observed in $Cu_2ZnSn_xGe_{1-x}Se_4$ and, especially, in Cu_2ZnGeS_4. The joint analysis of the MR and $\rho(T)$ data has yielded important electronic parameters of the materials. This includes widths of the acceptor band W and of the Coulomb gap Δ, the NNH activation energy E_n, the localization radius a, the acceptor concentration N_A and the density of the localized states at the Fermi level, $g(\mu)$. A dramatic increase of a in Cu_2ZnSnS_4 with decreasing T is observed, whereas in $Cu_2ZnSn_xGe_{1-x}Se_4$ all the parameter W, E_n, $g(\mu)$, a and N_A are non-monotonic functions of x. Finally, in Cu_2ZnGeS_4 the Hall coefficient $R_H(T)$ is negative (despite of the p-type conduction), exhibiting the dependence close to that of $\rho(T)$ in the Mott VRH interval.

1. Introduction

Interest to Cu-based group I_2-II-IV-VI_4 chalcogenide semiconductors with a kesterite or other similar (disordered kesterite, stannite or wurtzstannite) structure [1–4], referred below simply as *kesterites* for briefness, is connected mainly to their high potential for utilization in photovoltaic conversion. Indeed, the efficiency exceeding 11% for Cu_2ZnSnS_4 (CZTS) based solar cells [5], and up to 12.6% for devices based on $Cu_2ZnSn(S,Se)_4$ solid solutions [6], have been achieved recently. In addition, such compounds contain usually low-cost, low-toxic and abundant elements in the crust.

Important trends in investigations of kesterites are focused on their solid solutions with a partial anion substitution, as presented in the $Cu_2ZnSn(S,Se)_4$ alloys above. However, although the band gap of these alloys can be tuned to optimum values of $E_g \sim 1.4$–1.5 meV, the efficiency improvement is limited. This suggests a search for alternative solutions, where $Cu_2ZnSn_xGe_{1-x}Se_4$ (CZTGeSe) alloys with partial cation substitution are promising candidates for such a purpose. Indeed, their band gap can be readily tuned to the optimum values above, and the Ge inclusion showed an increase of a minority lifetime [7]. On the other hand, recent investigations yielding the power-conversion efficiency up to 10.1% have demonstrated a high potential of the CZTGeSe based solar cells [8].

Another way for a further development of the kesterite-based solar cells deals with tandem devices, where a kesterite compound is used in a top device with a higher band gap [9]. In this context, Cu_2ZnGeS_4 (CZGeS) with $E_g \sim 2.1$–2.3 eV [4,10,11] is a good candidate for utilization, having the absorption coefficient above 10^4 cm^{-1} as an additional advantage [11].

Although structural, optical and photovoltaic properties of kesterites are already well studied [1–11] (see also Refs. [12–19,9] and references therein), investigations of their electronic transport are

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still insufficient. At this point, the Mott variable-range hopping (VRH) conduction [20] is well established within a wide temperature range in single crystals [21–23], polycrystalline thin films [24,25] and powder samples [26,27]. However, these investigations have been done only in absence of the magnetic field, which limits a possibility to obtain a valuable microscopic information, whereas the data on other conductivity mechanisms are less confident [22,25] or even lacking.

Here, are presented investigations of the magnetotransport in CZTS, CZTGeSe and CZGeS in pulsed magnetic fields up to $B = 20$ T. The purpose is identification of the charge transfer mechanisms in various temperature ranges and determination of important electronic parameters of charge carriers. The general aim of this paper is to summarize mainly our experimental efforts undertaken within the last years. Therefore, some results published earlier in Refs. [28] and [29] have been included, too.

2. Materials and methods

Single crystals of all investigated compounds were grown by chemical vapor transport method. The CZTS was prepared by the direct synthesis from stoichiometric quantities of elements [28], whereas those of CZGeS and CZTGeSe were preliminary synthesized under certain conditions (for details see Refs. [4] and [29], respectively). The composition of the three CZTS samples (#1, #2 and #3) and of the five CZTGeSe samples between $x = 0$–1 was determined with the energy dispersive X-ray microanalysis (EDX), while the X-ray fluorescence method was used for the three CZGeS samples (S1, S2 and S3). The composition of all the materials above was found to lie close to stoichiometry. Investigations of Raman spectra did not show presence of any secondary phases. In addition, they indicated predominance of the kesterite structure, excluding CZGeS, which exhibited a wurtzstannite structure [4] observed from the X-ray diffraction analysis. The hot probe method, addressing to the thermopower measurements, showed *p*-type conductivity in all samples of the investigated materials. The resistivity, $\rho\ (T)$, was measured with a standard dc method, and magnetoresistance (MR) was investigated in the pulsed magnetic field B up to 20 T (for further details see Refs. [28] and [29]).

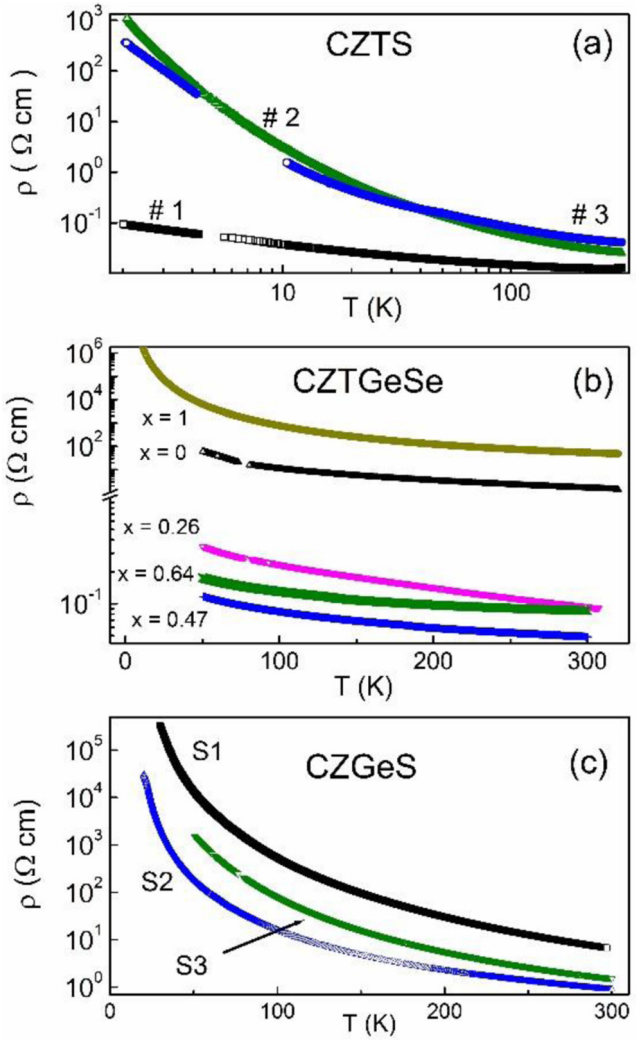

Fig. 1. Temperature dependence of the resistivity in CZTS [28] (a), CZTGeSe [29] (b) and CZGeS (c) samples.

3. Results and discussion

3.1. Temperature dependence of resistivity at $B = 0$

As can be seen in Fig. 1, all the samples of each investigated material exhibit only an activated conduction. The samples #1–#3 (CZTS) [28] and S1–S3 (CZGeS) do not contain any controlled parameters, and their different behavior in Fig. 1 is connected only to some inevitable fluctuations of the preparation process. However, the different strength of the activated $\rho\ (T)$ dependence is attributable to various proximity of the samples to the metal-insulator transition (see below). On the other hand, one can find a more regular dependence of $\rho\ (x)$ for the CZTGeSe samples, including a clear minimum at $x_m = 0.47$ [29].

A good linearization of the resistivity, given in the Mott VRH region by the law $\rho\ (T) = C_4\ T^{1/4} \exp\ [(T_{04}/T)^{1/4}]$, takes place for all the investigated samples of any material within broad intervals of temperature, ΔT_{v4}. An example of such behavior for CZGeS is given in Fig. 2(a). Here, C_4 is a Mott VRH prefactor constant, $T_{04} = \beta_4\ [k_B\ a^3\ g\ (\mu)]^{-1}$ is the Mott VRH characteristic temperature, $\beta_4 = 21$ is a numerical constant, a is the localization radius of holes and $g\ (\mu)$ is the density of states (DOS) at the Fermi level μ, lying among the localized states of the acceptor band (AB) [30]. The values of $\Delta T_{v4} \sim 50$–150 K, 50–250 K and 100–200 K and those of $T_{04} = (0.18–8.8) \times 10^4$ K, 6.2×10^3–2.3×10^6 K and $(0.3–1.4) \times 10^7$ are obtained in CZTS [28], CZTGeSe [29] and CZGeS, respectively. The data of $T_0\ (x)$ in CZTGeSe [29] are displayed in detail in Fig. 3(a).

This common resistivity feature of the Mott conduction is accompanied in CZGeS by another conduction mechanism, connected to activation of holes on the mobility threshold, E_c. The parameters E_c and E_c' (defined below) are addressed to the acceptor band (AB) of the Anderson type [20]. AB is characterized by a finite width of $2W$ and by a coexistence of the localized and extended impurity states, the latter lying within an interval (E_c, E_c') around the band center, E_A [20]. The corresponding resistivity law, $\rho\ (T) = \rho_0 \exp\ [E_a/(k_B T)]$, where ρ_0 is a prefactor and $E_a = |\mu – E_c|$ [20], is observed in all CZGeS samples. Examples for S2 and S3 are shown in Fig. 2(b). Generally, this conduction mechanism dominates within intervals $\Delta T_a = 215$–255 K, 20–40 K and 60–75 K lying above and below those of ΔT_{v4} for samples S1, S2 and S3, respectively. The values of E_a are collected in Table 1.

In turn, as follows from Fig. 2(c), the CZTGeSe samples exhibit the nearest-neighbor hopping (NNH) conduction according to the law $\rho\ (T) = DT \exp\ [E_n/(k_B T)]$, where D is the NNH prefactor constant and E_n is the NNH activation energy [30]. This type of the charge transfer takes place within the temperature intervals ΔT_n, lying all above those of ΔT_{v4}, whereas the dependence of $E_n\ (x)$ is exhibited in Fig. 3(a) [29].

An additional mechanism of the charge transfer, or the Shklovskii-Efros (SE) VRH conduction, connected to opening of

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