DOI 10.31489/2023PH3/34-39

UDC: 538.93

V.G. Kytin[1,2], E.E. Kupriyanov[1], A. Apreleva[1], V.A. Kulbachinskii[1*], I.E. Korsakov[1], T.Yu. Kiseleva[1], Zh.T. Ismailov[3]

[1]Lomonosov Moscow State University, Russia;
[2]VNIIFTRI, Mendeleevo, Moscow region, Russia;
[3]Karaganda University of the name of academician E.A. Buketov, Kazakhstan
([*]E-mail: kulb@mig.phys.msu.ru)

Features of hole transport and density of localized states in $CuCr_{1-x}Mg_xO_2$ and $CuCr_{1-y}Mg_yO_2/(MgCr_2O_4)_{x-y}$ polycrystalline ceramics

Magnesium doped polycrystalline ceramic samples of cooper chromite (I) with 0.6-4.0 at % Mg content have been synthesized. Phase composition of ceramics has been investigated by X-ray diffraction. Temperature dependencies of electrical resistivity and Seebeck coefficient have been measured by four probe method and analyzed in frame of variable range hopping conductivity. The density of localized electronic states and characteristic energy of its variation near Fermi energy have been estimated. It was obtained that the density of localized states at Fermi energy increases with an increase of Mg content, while characteristic energy of variation of localized state density near Fermi energy decreases. Obtained results show that relatively large values of Seebeck coefficient in Mg doped copper chromite (I) can be understood within variable range hopping transport of holes with rapidly increasing density toward valence band maximum.

Keywords: p-type semiconductors, thermal conductivity, electrical conductivity, density of localized states.

Introduction

Copper chromite is a *p*-type semiconductor partially transparent for the visible light [1]. It makes it promising material for transparent electrodes in optoelectronic devices [2-3]. One of the key issues is its relatively large resistivity compared to the best known *n*-type transparent semiconductors as zinc oxide or indium-tin oxide [3-4]. The resistivity of copper chromite (I) can be reduced by several orders of magnitude by doping with group II elements particularly with Mg [5-8]. The mechanism of the hole transport in pure and Mg doped copper chromite remains the subject of research now. Most often copper chromite (I) is synthesized in the form of polyctrystalline ceramic or thin films. Polycrystalline ceramic of magnesium doped copper chromite (I) is usually obtained by heating of the mixture of copper, chromium and magnesium oxides in oxygen poor atmosphere during few tens of hours [6-8]. Such material exhibits up to several hundred microvolts per kelvin Seebeck coefficient together with relatively large electrical conductivity at room temperature [6-7]. Therefore temperature dependencies of resistivity and Seebeck coefficient and their analysis in frame of different models have been reported in several publications [6-8]. Hole transport in polycrystalline ceramic of magnesium doped copper chromite (I) is affected by point defects such as oxygen vacancies, dopant atoms, microstructure and morphology of the material, as well as the presence of additional phases in doped material. The question whether the band or hopping transport of holes dominates in copper chromite (I) remains the subject discussions until now.

In the present work we report the results of the measurements and analysis of the temperature dependencies of electrical resistivity and Seebeck coefficient of polycrystalline copper chromite doped with magnesium using the procedure of chemical homogenization. Magnesium content was taken below and above solubility limit. Measured temperature dependencies have been analyzed in frame variable range hopping transport approach.

Experimental

Polycrystalline Mg doped copper cromite samples were synthesized by solid phase method from a mixture of CuO, Cr_2O_3 and MgO. This mixture was obtained by thermolysis of nitrates in liquid phase solution in NH_4NO_3. Reaction and details of nitrate thermolysis were presented in [9]. According to X-ray diffraction data obtained mixtures were amorphous. The mixtures were annealed at 500-600 ºC to dissolve the rest of nitrates. Small traces of CuO were detected by X-ray diffraction after this annealing. Then mixtures were pressed in tablets and annealed 24 hours at 1080 ºC in argon flow for final formation of Mg

doped copper chromite (I) ceramic material and cooled to room temperature. Composition and density of obtained samples are shown in Table.

Table

Mg content, density ρ, an estimated density of hole states at Fermi energy g_0, and characteristic energy of its variation δE.

Sample number	Mg content, at. %	ρ, g/cm^3	g_0, 10^{26} eV^{-1}m^{-3}	δE, eV
1	0.6	2,85	1.2	0,27
2	1,3	3,60	11	0,13
3	4	3,84	212	0,04

Typical XRD pattern of synthesized ceramics are shown in Figure 1. Only delafossite phase was detected in the samples with Mg content up to 1,3 at. %. For 4 at. % Mg content small fraction of spinel phase of $MgCr_2O_4$ was detected. This is consistent with the data of Mg solubility in copper chromite (I) reported earlier [7-10].

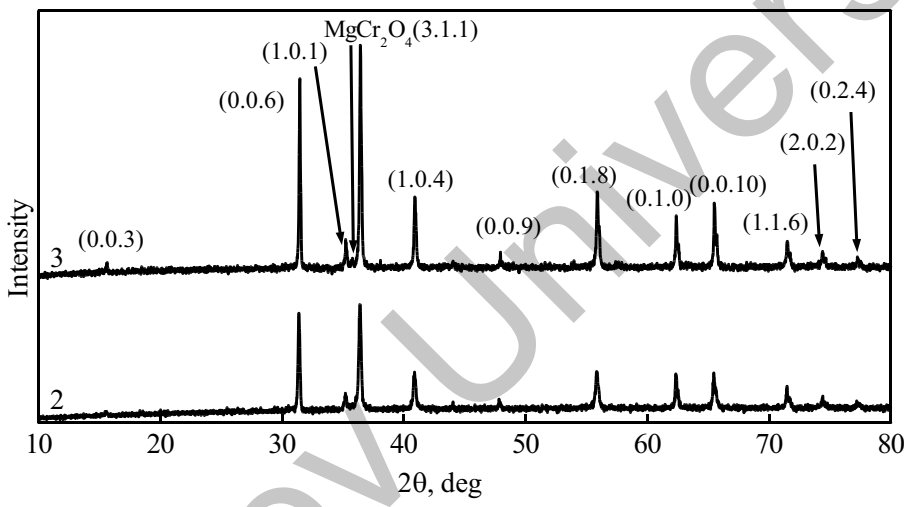

Figure 1 XRD pattern of the ceramics with different Mg content: 1 — 1,3 at %; 2 — 4 at. %

The dependence of lattice parameters on Mg content confirms incorporation of Mg in the delafossite crystalline lattice. No significant dependence of lattice parameters on the duration of synthesis was observed. Density of all samples increases with an increase of Mg content and duration of annealing.

Microstructure of synthesized samples was studied by electron microscopy and reported in previous publication [11]. The larger is the Mg content the better connected look crystallites. Fraction of empty space decreases with an increase of Mg content in accordance with observed increase of density. For the samples with 4 at % Mg formation of micrometer size $MgCr_2O_4$ crystallites is seen in SEM images.

For the measurement of electrical resistivity and Seebeck coefficient samples with rectangular shape and typical dimensions 2x2x5 mm were prepared. Electrical resistivity was measured by 4-probe method at constant current. For the measurement of Seebeck coefficient one end sample was connected to heat drain. Another end of the sample was connected to the heater. The temperature difference between potential contacts at the sample was measured by thermocouple. The voltage between these potential contacts was measured by digital multimeter for several values of temperature difference controlled by the power of the heater. Then the dependence of the voltage on the temperature difference was approximated by linear function and the value of Seebeck coefficient was obtained from the slope of the dependence.

Results and discussion

Temperature dependencies of Seebeck coefficient are shown in Figure 2. For all investigated materials Seebeck coefficient increases when temperature rises. Seebeck coefficient decreases with an increase of Mg content.

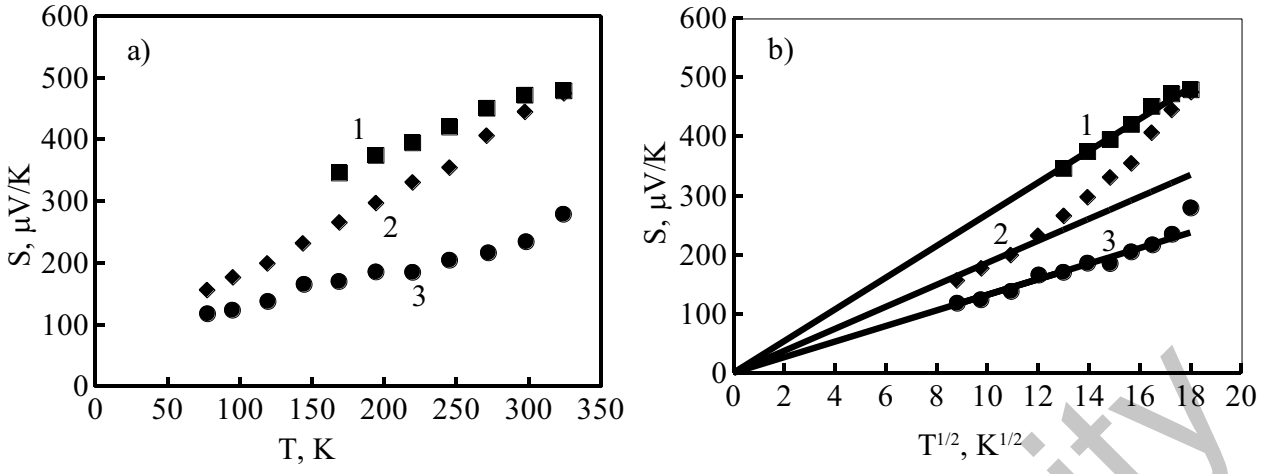

Figure 2 Temperature dependencies of Seebeck coefficient: a) S(T), b) S($T^{1/2}$) for samples with different Mg content: 1 — 0.6 at. %; 2 — 1.3 at. %; 3 — 4 at. %. Points are experimental data. Solid lines are approximation by proportional dependence for 4 lowest temperature points.

Temperature dependencies of resistivity are plotted in Figure 3. For all samples resistivity increases with lowering of temperature. Resistivity decreases by several orders of magnitude with increase of the magnesium content from 0,6 at % to 4 at %.

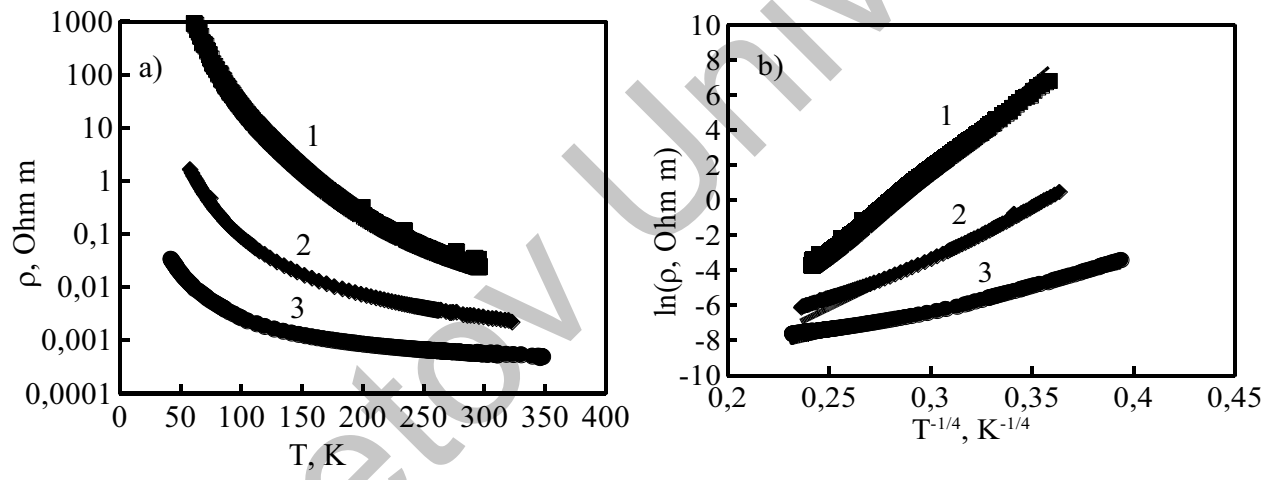

Figure 3. Temperature dependencies of resistivity: a) ρ(T) and b) ln(ρ($T^{-1/4}$)) for samples with different Mg content: 1 — 0.6 at. %; 2 — 1.3 at. %; 3 — 4 at. %. Points are experimental data. Solid lines are approximation by linear dependence in the temperature range of 4 lowest temperature points in the temperature dependence of Seebeck coefficient.

At temperatures below 180-300 K temperature dependencies of resistivity can be approximated by Motts law for variable range hopping conductivity [12]:

$$\rho = \rho_0 \exp\left[\left(\frac{T_0}{T}\right)^{1/4}\right], \tag{1}$$

where T_0 is determined by the density of localized states at Fermi energy g_0 and localization length a:

$$T_0 = \frac{21}{k_B g_0 a^3}, \tag{2}$$

where k_B is the Boltzmann constant.

We use the following expression derived for variable range hopping transport to fit temperature dependence of Seebeck coefficient [13]:

$$S = 0{,}1\frac{k_B^2}{e}\frac{(T_0 T)^{1/2}}{\delta E}, \quad (3)$$

where

$\delta E = \left(\frac{d\ln g}{dE}\right)^{-1}_{E=F}$ is the characteristic energy of the variation of the density of states, g is the density of localized states, F is the Fermi energy, e is the elementary charge. Temperature dependencies of Seebeck coefficient were fitted by expression (3) in the temperature range within 4 lowest temperature points. Temperature dependencies of resistivity were fitted by expression (1) in the same temperature range for each sample. The characteristic energy of the variation of the density of states near Fermi energy was estimated from the slopes of fitting lines. Obtained estimates are listed in Table.

To get an estimate of the density of localized states at Fermi energy we estimated localization length using expression for localization length and ionization energy E_a of shallow acceptors:

$$E_a = \frac{me^4}{2(4\pi\varepsilon_0\varepsilon)^2\hbar^2},\ a = \frac{(4\pi\varepsilon_0\varepsilon)\hbar^2}{me^2}, \quad (4)$$

where m is an effective mass of holes, ε_0 is the electric constant, ε is the dielectric constant, ħ is the Planck constant. We assumed that earlier observed activation energy of conductivity of undoped copper chromite (I) equal to 0,28 eV is the energy of ionization localized acceptor state [9]. An estimate of localization length was calculated using expression:

$$a = \frac{e^2}{(4\pi\varepsilon_0\varepsilon)E_a} \quad (5)$$

as an estimation for the dielectric constant we took $\varepsilon = \left(\varepsilon_p^2\varepsilon_l\right)^{1/3}$, where ε_p and ε_l are dielectric constants for in-plane and along c-axis polarization [14]. Obtained estimation value for *a* was equal to 0,29 nm. Obtained results point to a strong localization of holes. Estimated value of localization length is rather small and in general expressions (4) cannot be used for accurate calculation. The estimated density of states at Fermi energy calculated for this value of localization length is listed in Table.

As can be seen from table one density of states at Fermi energy increases by more than 2 orders of magnitude with an increase of Mg content from 0,6 at.% to 4 at. % and by more than 1 order of magnitude with an increase of Mg content from 1,3 at.% to 4 at. %. This fact points to an effective doping of copper chromite by Mg in the range of Mg content close to the solubility limit. The characteristic energy of the variation of the density of states decreases from 0,27 eV to 0,04 eV with an increase of Mg content from 0,6 at. % to 4 at. %. This variation of the density of states at Fermi energy and its derivative can take place because of the creation of localized acceptor states in the bandgap due to substitution of Cr by Mg and shift of the Fermi energy towards the valence band. The reduction of the characteristic energy of the variation of the density of states near Fermi energy with an enhancement of Mg content could point to the significant contribution of magnetic frustration to the energy fluctuations of localized electronic states. Substitution of Cr by Mg suppresses these frustrations [8, 10]. This suppression could make energy distribution of localized states narrower.

Conclusions

Temperature dependencies of electrical resistivity and Seebeck coefficient were measured in Mg doped polycrystalline copper chromite (I) and analyzed in frame of variable range hopping of holes. The estimated density of localized states and the characteristic energy of variation of the density of states near Fermi energy were calculated. Calculated density of states at Fermi energy increases more than 2 orders of magnitude while the characteristic energy of variation of the density of states near Fermi energy decreases several times with and enhancement of Mg content from 0,6 at % to 4 at. %. The obtained results can be explained by creation of localized acceptor states in the band gap and suppression of magnetic frustration due to substitution of Cr by Mg in the crystalline lattice.

Acknowledgments

The authors are grateful to Ministry of science and high education of Russian Federation (project № 075-15-2021-1353). Authors aknowledge Moscow University Program of development for the instrumental support.

References

1 Xiong, D., Xu, Z., Zeng, X., Zhang, W., Chen, W., Xu, X., Wang, M. & Cheng, Y.-B. (2012). Hydrothermal synthesis of ultrasmall CuCrO2 nanocrystal alternatives to NiO nanoparticles in efficient p-type dye-sensitized solar cells. *Journal of Material Chemistry, Vol. 22,* P. 24760. DOI: https://doi.org/10.1039/C2JM35101C.

2 Xiong, D., Zhang, W., Zeng, X., Xu, Z., Chen, W., Cui, J., Wang, M., Sun, L. & Cheng, Y.B. (2013). Enhanced performance of p-type dye-sensitized solar cells based on ultrasmall Mg-doped $CuCrO_2$ nanocrystals. *ChemSusChem, Vol. 6,* P. 1432-1437. DOI: https://doi.org/10.1002/cssc.201300265.

3 Batzill, M. & Diebold, U. (2005). The surface and materials science of tin oxide. *Progress in Surface Science, Vol. 79,* P 47–154. DOI: 10.1016/J.PROGSURF.2005.09.002.

4 Özgür, Ü., Alivov, Ya.I., Liu, C., Teke, A., Reshchikov, M.A., Doğan, S., Avrutin, V., Cho, S.-J. & H. Morkoç J. (2005). A Comprehensive Review of ZnO Materials and Devices. *Journal of Applied Physics, Vol. 98*(4), P. 041301-041301-103. DOI: 10.1063/1.1992666.

5 Sinnarasa, I., Thimont, Y., Presmanes, L., Barnabé, A. & Tailhades, Ph. (2017). Thermoelectric and Transport Properties of Delafossite $CuCrO_2$: Mg Thin Films Prepared by RF Magnetron Sputtering. *Nanomaterials, Vol. 7,* P. 157. DOI: 10.3390/nano7070157.

6 Moreira, M., Afonso, J., Crepelliere, J., Lenoble, D. & Lunca-Popa, P. (2022). A review on the p-type transparent Cu–Cr–O delafossite materials. *Vol. 57,* P. 3114–3142. DOI: https://doi.org/10.1007/s10853-021-06815-z.

7 Guilmeau, E., Poienar, M., Kremer, S., Marinel, S., Hébert, S., Frésard, R. & Maignan, A. (2011). Mg substitution in $CuCrO_2$ delafossite compounds. *Solid State Communications. Vol. 151,* P. 1798–1801. DOI: https://doi.org/10.1016/j.ssc.2011.08.023.

8 Okuda, T., Jufuku, N., Hidaka, S. & Terada, N. (2005). Magnetic, transport, and thermoelectric properties of the delafossite oxides $CuCr_{1-x}Mg_xO_2$ (0<x<0.04)>. *Physical Review B., Vol. 72,* P. 144403. DOI: https://doi.org/10.1103/PhysRevB.72.144403.

9 Kulbachinskii, V.A., Kondratieva, D.Yu., Konstantinova, E.A., Pavlikov, A.V., Grigoriev, A.N., Mankevich, A.S. & Korsakov, I.E. (2019). Electrical conductivity, thermoelectrical properties, and EPR spectroscopy of copper chromite ceramic samples doped with magnesium. *Low Temperature Physics, Vol. 45,* P. 194-200. DOI: https://doi.org/10.1063/1.5086413.

10 Maignan, A., Martin, C., Frésard, R., Eyert, V., Guilmeau, E., Hébert, S. & M. Poienar, D. (2009). On the strong impact of doping in the triangular antiferromagnet $CuCrO_2$. *Pelloquin Solid State Communications, Vol. 149,* P. 962-967. DOI: 10.1016/j.ssc.2009.02.026.

11 Kulbachinskii1, V.A., Kytin, V.G., Korsakov, I.E., Kupriyanov, E.E. & Ismailov, Zh.T. (2022). Effect of synthesis duration on heat and charge transport in polycrystalline CuCr1-xMgxO2. *Bulletin of the University of Karaganda –Physics, Vol. 107,* P. 6-11. DOI: 10.31489/2022PH3/6-11.

12 Shklovskii, B.I. & Efros, A.L. (2013). Electronic Properties of Doped Semiconductors. *Springer Verlag Berlin Heidelberg.* 388 P. ISBN 978-3-662-03405-8 DOI: 10.1007/979-3-662-02473-4.

13 Zvyagin, I.P. (1973). On the Theory of Hopping Transport in Disordered Semiconductors. *Physica status solidi (b), Vol. 58,* P. 443-449. DOI: 10.1002/pssb.2220580203.

14 Poienar, M. (2012). Revisiting thepropertiesofdelafossite$CuCrO_2$: A single crystal study. *Journal of Solid State Chemistry, Vol. 185,* P. 56–61 DOI: 10.1016/j.jssc.2011.10.047.

В.Г. Кутин, Е.Е. Куприянов, А. Апрелева, В.А. Кульбачинский, И.Е. Корсаков, Т.Ю. Киселева, Ж.Т. Исмаилов

$CuCr_{1-x}Mg_xO_2$ және $CuCr_{1-y}Mg_yO_2/(MgCr_2O_4)_{x-y}$ поликристалды керамикадағы кемтіктердің тасымалдануларының және локализацияланған күйлердің тығыздықтарының ерекшеліктері

Поликристалдық керамикалық Mg мөлшері 0,6-4,0 ат. % тең қоспаланған мыс (I) хромитінің үлгілері синтезделді. Керамиканың фазалық құрамы рентгендік фазалық талдау арқылы зерттелді. Электр кедергісінің және Зеебек коэффициентінің температураға тәуелділіктері төрт зондты әдіспен өлшенді және ауыспалы секіру өткізгіштігі тұрғысынан талданды. Локализацияланған электрондық күйлердің тығыздығы және оның Ферми энергиясының жанындағы өзгеруінің сипаттамалық энергиясы бағаланған. Ферми энергиясының жанында орналасқан локализацияланған күйлердің тығыздығы Mg мөлшерінің жоғарылауымен жоғарылайтыны, ал Ферми энергиясының жанындағы локализацияланған

күйлердің тығыздығының өзгеруінің сипаттамалық энергиясы төмендейтіні анықталды. Алынған нәтижелер Mg қоспаланған мыс (I) хромитіндегі Зеебек коэффициентінің салыстырмалы түрде үлкен мәндерін валенттік диапазонның максимумына қарай тығыздығы тез өсетін кемтіктердің ауыспалы диапазонда секіріп тасымалдануымен түсіндіруге болатынын көрсетеді.

Кілт сөздер: р-типті жартылай өткізгіштер, жылуөткізгіштік, электрөткізгіштік, локализацияланған күйлердің тығыздығы.

В.Г. Кутин, Е.Е. Куприянов, А. Апрелева, В.А. Кульбачинский, И.Е. Корсаков, Т.Ю. Киселева, Ж.Т. Исмаилов

Особенности транспорта дырок и плотность локализованных состояний в $CuCr_{1-x}Mg_xO_2$ и в поликристаллической керамике $CuCr_{1-y}Mg_yO_2/(MgCr_2O_4)_{x-y}$

Синтезированы легированные магнием поликристаллические керамические образцы хромита меди (I) с содержанием Mg 0,6–4,0 ат. %. Методом рентгенофазового анализа исследован фазовый состав керамики. Температурные зависимости удельного электрического сопротивления и коэффициента Зеебека измерены четырехзондовым методом и проанализированы в рамках переменной прыжковой проводимости. Оценены плотность локализованных электронных состояний и характерная энергия ее изменения вблизи энергии Ферми. Получено, что плотность локализованных состояний вблизи энергии Ферми увеличивается с повышением содержания Mg, а характерная энергия изменения плотности локализованных состояний вблизи энергии Ферми уменьшается. Полученные результаты показывают, что относительно большие значения коэффициента Зеебека в хромите меди (I), легированном Mg, можно объяснить прыжковым переносом дырок с переменным диапазоном с быстро увеличивающейся плотностью к максимуму валентной зоны.

Ключевые слова: полупроводники р-типа, теплопроводность, электропроводность, плотность локализованных состояний.