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Effect of synthesis duration on heat and charge transport in polycrystalline $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$

Magnesium-doped polycrystalline ceramic samples of copper chromite (I) have been prepared by solid phase synthesis. Phase composition and crystal structure of synthesis have been investigated by X-ray diffraction. Microstructure of samples has been investigated by scanning electron microscopy. Thermal conductivity and electrical conductivity have been measured in the temperature range $78 < T < 320$ K. Significant reduction of thermal conductivity with an increase of synthesis duration have been observed. This effect was explained by formation of small amount of MgCr_2O_4 and Cr_2O_3 and CuO crystallites operating as effective phonon scatters. Formation of the MgCr_2O_4 phase is observed in X-ray diffraction patterns and SEM images of the samples with Mg content higher than 3 at. %. Formation of a small amount of Cr_2O_3 or CuO phase could be due to deviation of precursor's content from stoichiometry. Obtained results open a perspective of thermoelectric figure of merit enhancement for copper chromite-based material.

Keywords: p-type semiconductors, thermal conductivity, electrical conductivity, copper chromite (I).

Introduction

Copper chromite (I) is an attractive material due to the unusual composition of its properties. It is known as quasi two dimensional frustrated magnetic and multiferroic [1, 2]. Simultaneously it is a p-type semiconductor partially transparent for visible light [3]. It makes it perspective material for optoelectronic devices [4, 5]. One of the key issues is its low conductivity compared to the best-known n-type transparent semiconductors such as zinc oxide or indium tin oxide [6, 7]. It has been shown however that conductivity of copper chromite (I) can be increased several orders of magnitude by doping with group II elements [8–11]. The mechanism of electron transport and conductivity enhancement by doping is still a subject of research. The variety of different factors that could affect electron transport makes its investigation relatively difficult. In particular observations of features in the temperature dependence of conductivity near magnetic (ferroelectric) transition points to the influence of the ordering of magnetic ions on hole transport [8–11]. Most often copper chromite (I) is synthesized in the form of polycrystalline ceramic or thin films. Polycrystalline ceramic of magnesium doped copper chromite (I) is usually obtained by heating the mixture of copper, chromium and magnesium oxides in an oxygen-poor atmosphere for a few tens of hours [9–11]. Such material exhibits up to several hundred microvolts per kelvin Seebeck coefficient together with relatively large conductivity at room temperature [9, 10]. Therefore its conductivity and Seebeck coefficient are investigated for understanding electron transport and for possible application as thermoelectric material at elevated temperatures [9, 10]. Ceramic material consists of connected crystallites. Electron transport in polycrystalline ceramic of magnesium-doped copper chromite (I) is affected by point defects such as oxygen vacancies, do-

part atoms, contacts between crystallites, fraction of empty space, incorporation of crystallites of other phases. Thermal conductivity of such material is more determined by contacts between crystallites, presence of other phases and fraction of other phases and is less affected by point defects. Therefore measurement and analysis of both heat and electric conductivity could help to separate factors determining electron and heat transport. There is a lack of thermal conductivity measurements in the available literature dedicated to polycrystalline copper chromite (I) doped with magnesium.

In the present work, we report the results of the investigation of temperature dependencies of thermal and electrical conductivity of polycrystalline copper chromite doped with magnesium synthesized during a different time. Longer synthesis led to an increase in the density of the material. The main objective is to study the effect of synthesis duration on a microstructure, the phase composition, thermal and electron transport.

Experimental

Polycrystalline Mg doped copper chromite samples have been synthesized by solid phase method from a mixture of CuO, Cr₂O₃, and MgO. This mixture has been obtained by thermolysis of nitrates in a liquid phase solution in NH₄NO₃. Reaction and details of nitrate thermolysis are presented in [12]. According to X-ray diffraction data, obtained mixtures were amorphous. The mixtures were annealed at 500–600 °C to dissolve the rest of the nitrates. Small traces of CuO have been detected by X-ray diffraction after this annealing. Then mixtures have been pressed in tablets and annealed for 24 hours or 48 hours at 1080 °C in argon flow for the final formation of Mg-doped copper chromite (I) and cooled to room temperature. Table 1 presents the composition and density of obtained samples.

Table 1

Mg content, duration of annealing and density ρ of some samples, ρ_0 is the density of CuCrO₂ single crystal

Mg content, at. %	Duration of annealing, hours	ρ , g/cm ³	ρ/ρ_0
0,3	24	2,73(3)	49
	48	2,97(2)	53
0,6	24	2,85(5)	51
	48	3,12(3)	56
1,3	24	3,60(3)	64
	48	4,05(3)	72
4,0	24	3,84(5)	69
	48	4,11(4)	73

Crystal structure and phase composition of obtained tablets have been characterized by X-ray diffraction. Only the delafossite phase has been detected in the samples with Mg content below 3 at. %. For larger Mg content small fraction of the spinel phase of MgCr₂O₄ has been detected. Lattice parameters of delafossite phase vary monotonously with Mg content as shown in Figure 1.

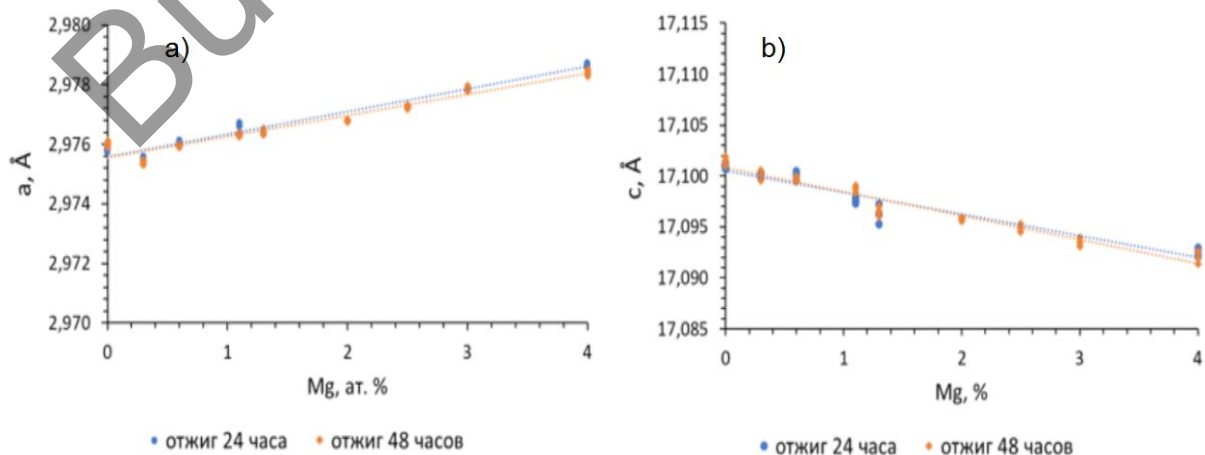


Figure 1. Dependence of lattice parameters on Mg content: a) parameter a ; b) parameter c

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

Microstructure of synthesized samples was studied by electron microscopy. Figures 2 and 3 illustrate some characteristic SEM images.

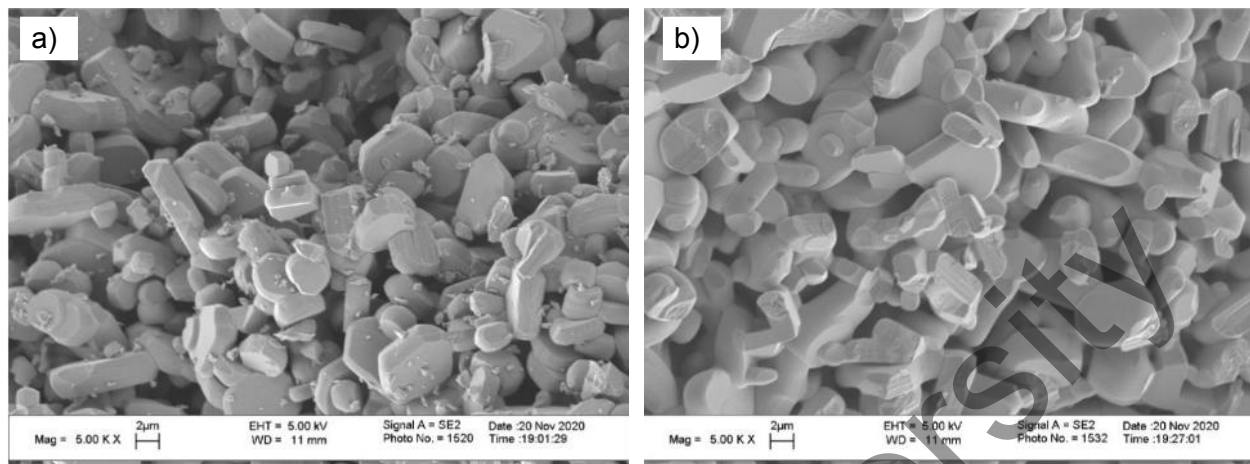


Figure 2. SEM images of the samples annealed 24 hours with different magnesium content: a) 0.6 at. %; b) 1.3 at. %.

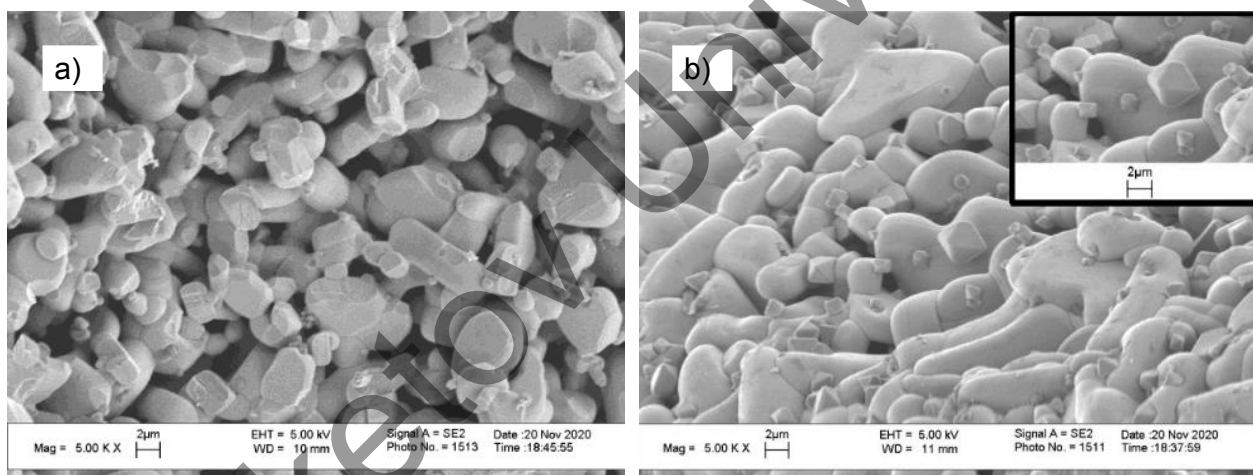


Figure 3. SEM images of the samples with 4 at. % Mg content and different duration of synthesis a) 24 hours; b) 48 hours.

Crystallites in the samples with larger Mg content look better connected. Fraction of empty space decreases with an increase in Mg content under an observed increase in density. A similar tendency was observed with an increase of annealing duration. Fraction of empty space in the samples annealed at 48 hours is smaller than in the samples annealed at 24 hours. Connection of crystallites looks better in the samples annealed at 48 hours. For the samples with 4 at. % Mg formation of micrometer size MgCr_2O_4 crystallites is seen in the SEM image (insert in Figure 3b).

For the measurement of thermal conductivity and Seebeck coefficient samples with a rectangular shape and typical dimensions of 2x2x5 mm have been prepared. Conductivity was measured by the 4-probe method at constant current. For the measurement of thermal conductivity, one end sample was connected in series with the copper wire with known thermal conductivity and dimensions. Another end of the sample was brought into thermal contact with the heater while the other end of the copper wire was brought into thermal contact with the heat drain. Temperature differences have been measured by thermocouples between 2 points at the sample and 2 points at the copper wire separated by known distance in steady-state conditions. Then thermal conductivity was calculated from the ratio of temperature differences.

Results and Discussion

Figure 4 demonstrates examples of temperature dependencies of thermal conductivity. For the samples with Mg content below 1.3 at % an enhancement of thermal conductivity was observed with an increase in Mg content. However, thermal conductivity of the sample with 4 at. % Mg is smaller than heat conductivity of the sample with 1.3 at. %. An increase of annealing duration from 24 to 48 hours leads to thermal conductivity reduction for the samples with Mg content from 0.6 to 1.3 at. %.

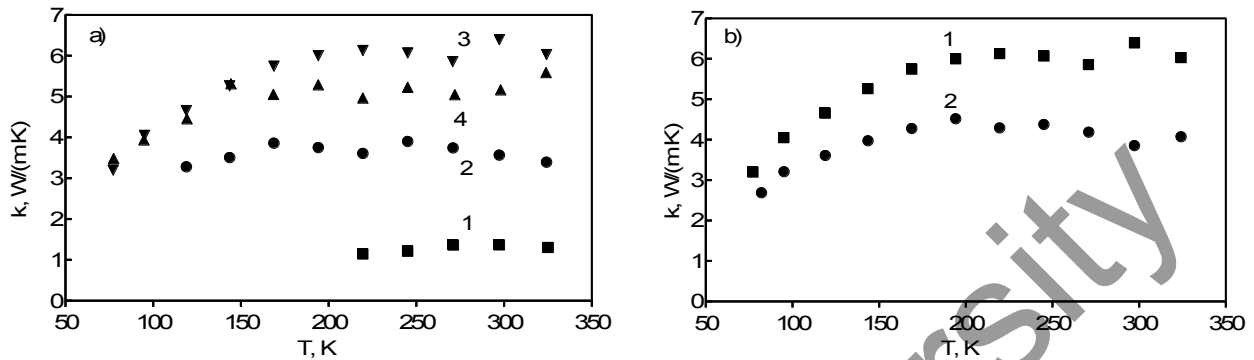


Figure 4. Temperature dependencies of thermal conductivity: a) for samples annealed 24 hours with different Mg content: 1 – 0.3 at. %; 2 – 0.6 at. %; 3 – 1.3 at. %; 4 – 4 at. %; b) for samples with 1.3 at. % Mg content with different duration of annealing: 1- 24 hours; 2 – 48 hours

Temperature dependencies of conductivity of investigated samples are shown in Figure 5.

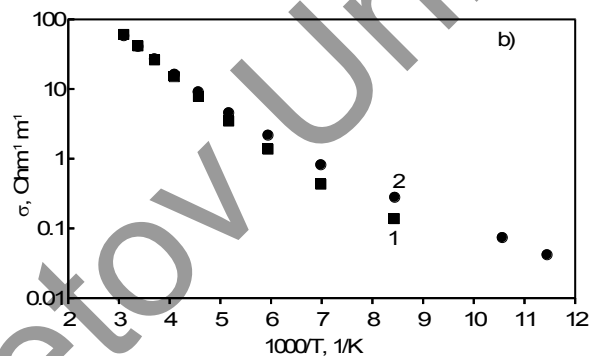


Figure 5. Temperature dependencies of conductivity: a) for samples annealed 24 hours with different Mg content: 1 – 0.3 at. %; 2 – 0.6 at. %; 3 – 1.3 at. %; b) for samples with 0.6 at. % Mg content with different duration of annealing: 1- 24 hours; 2 – 48 hours

Several orders of magnitude conductivity enhancement have been observed for an increase of Mg content from 0.3 at. % to 4 at. %. Activation energy of conductivity decreases several times with the same increase of magnesium content. Enhancement of annealing duration from 24 hours to 48 hours leads to a small decrease of conductivity at room temperature and higher temperatures. At lower temperatures conductivity of the samples annealed at 48 hours is larger than the conductivity of the samples annealed at 24 hours.

Enhancement of conductivity on Mg content could be one origin of observed variation of the density and microstructure of the polycrystalline ceramic copper chromite (I). Enhancement of conductivity with Mg content could lead to an enhancement of the mobility of ions. This, in turn, could lead to a reduction of the fraction of empty space and improvement of the connection between crystallites.

Enhancement of thermal conductivity with an increase of Mg content from 0.3 to 1.3 at. % can be explained by improvement of connection between crystallites. Smaller thermal conductivity of the sample with 4 at. % Mg content compared to thermal conductivity of the sample with 1.3 at. % Mg can be explained by formation of MgCr_2O_4 crystallites operating as effective scatterers of phonons. This suggests the stronger effect of phonon scattering by these crystallites compared to the improvement of connection between crystallites. Reduction of thermal conductivity with an increase in synthesis duration is in contradiction with an ob-

served improvement of connection between crystallites. This points to the formation of effective phonon scatterers, These scatterers could be small crystallites of copper and chromium oxides formed due to deviation of stoichiometry in the mixture of precursors. Other possible phonon scatters are oxygen vacancies formed during annealing in oxygen deficit atmosphere.

The most probable mechanism of electron transport in polycrystalline copper chromite (I) is the thermally activated hopping of holes [13]. The value of hopping conductivity is essentially determined by energy dependence of the density of localized states and the value of the density of states near Fermi energy. Density of localized states depends in particular on the energy disorder originating from randomly distributed charged defects and their complexes. Variation of conductivity during annealing from 24 hours to 48 hours can be explained by formation of oxygen vacancies. Obtained results also show relatively small contribution of contacts between crystallites to resistivity of material. Relatively small variation of conductivity with an increase of annealing time together with noticeable reduction of thermal conductivity can be useful for improvement of thermoelectric properties of polycrystalline copper chromite (I) and other materials synthesized in similar way.

Conclusions

The effect of synthesis duration thermal conductivity and conductivity have been studied for Mg-doped polycrystalline copper chromite (I). Electron microscopy shows that longer synthesis leads to the improvement of connection between crystallites and increase of the density of material. Effect of synthesis duration from 24 to 48 hours on conductivity is relatively small. This shows that conductivity is not essentially limited by contacts between crystallites. Significant reduction of thermal conductivity has been observed for enhancement of synthesis duration from 24 to 48 hours for material with Mg content from 0.6 to 4 at. %. This points to the formation of effective phonon scatter and can be used for improvement of thermoelectric properties of Mg-doped copper chromite (I) and polycrystalline materials synthesized in similar way.

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References

- 1 Hemmida, M., Krug von Nidda, H.-A., & Loidl, A. (2011). Traces of Z_2 -Vortices in CuCrO_2 , AgCrO_2 , and PdCrO_2 . *Journal of Physical Society of Japan*, 80, 053707. <https://doi.org/10.1143/JPSJ.80.053707>
- 2 Hemmida, M., Krug von Nidda, H.-A., Büttgen, M., Loidl, A., Alexander, L.K., Nath, R., Mahajan, A.V., Berger, R.F., Cava, R.J., Singh Yogesh, & Johnston, D.C. (2009). Vortex dynamics and frustration in two-dimensional triangular chromium lattices. *Physical Review*, 80, 054406. <https://doi.org/10.1103/PhysRevB.80.054406>
- 3 Zhang, K.H.L., Xi, K., Blamire, M.G., & Edgell, R.G. (2016). P-type transparent conducting oxides. *Journal of Physics Condensed Matter*, 28, 383002. <https://doi.org/10.1088/0953-8984/28/38/383002>
- 4 Xiong, D., Xu, Z., Zeng, X., Zhang, W., Chen, W., Xu, X., Wang, M., & Cheng, Y.-B. (2012). Hydrothermal synthesis of ultrasmall CuCrO_2 nanocrystal alternatives to NiO nanoparticles in efficient p-type dye-sensitized solar cells. *Journal of Material Chemistry*, 22, 24760. <https://doi.org/10.1039/C2JM35101C>
- 5 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*, 6, 1432–1437. <https://doi.org/10.1002/cssc.201300265>
- 6 Batzill, M., & Diebold, U. (2005). The surface and materials science of tin oxide. *Progress in Surface Science*, 79, 47–154. <https://doi.org/10.1016/J.PROGSURF.2005.09.002>
- 7 Özgür, Ü., Alivov, Ya.I., Liu, C., Teke, A., Reshchikov, M.A., Doğan, S., Avrutin, V., Cho, S.-J., & Morkoç, H. (2005). A Comprehensive Review of ZnO Materials and Devices. *Journal of Applied Physics*, 98(4), 041301. <https://doi.org/10.1063/1.1992666>
- 8 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*, 7, 157. <https://doi.org/10.3390/nano7070157>
- 9 Moreira M., Afonso, J., Crepellere, J., Lenoble, D., & Lunca-Popa, P. (2022). A review on the p-type transparent Cu–Cr–O delafossite materials. *Journal of Materials Science*, 57, 3114–3142. <https://doi.org/10.1007/s10853-021-06815-z>
- 10 Guilmeau, E., Poinar, M., Kremer, S., Marinel, S., Hébert, S., Frésard, R., & Maignan, A. (2011). Mg substitution in CuCrO_2 delafossite compounds. *Solid State Communications*, 151, 1798–1801. <https://doi.org/10.1016/j.ssc.2011.08.023>

11 Okuda, T., Jufuku, N., Hidaka, S., & Terada, N. (2005). Magnetic, transport, and thermoelectric properties of the delafossite oxides $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$ ($0 < x < 0.04$). *Physical Review B*, 72, 144403. <https://doi.org/10.1103/PhysRevB.72.144403>

12 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*, 45, 194–200. <https://doi.org/10.1063/1.5086413>

13 Kulbachinskii, V.A., Kytin, V.G., Duvakina, A.V., Zinoviev, D.A., Kupriyanov, E.E., Korsakov, I.E., Ovchenkov, E.A., & Kondratieva, D.Yu. (2021). Effect of magnesium doping on thermoelectric and magnetic properties of copper chromite ceramic samples. *Materials Today: Proceedings*, 44(14), 3511–3515. <https://doi.org/10.1016/j.matpr.2020.09.163>

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Синтез ұзақтығының $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$ поликристаллындағы жылу және заряд алмасу үдерісіне әсері

Магний қосылған мыс (I) хромитінің поликристалды керамикалық үлгілері қатты фазалық синтез арқылы алынды. Синтездің фазалық құрамы мен кристалдық құрылымы рентгендік дифракциялық талдау арқылы зерттелді. Сканерлеуші электронды микроскоп арқылы үлгілердің микроқұрылымы анықталды. Жылуөткізгіштік пен электрөткізгіштік $78 < T < 320$ К температура диапазонында өлшенді. Синтез ұзақтығының ұлғаюымен жылу өткізгіштіктің айтарлықтай төмендеуі байқалған. Бұл әсер MgCr_2O_4 , Cr_2O_3 және CuO кристаллиттерінің аз мөлшерде түзілуімен түсіндіріледі және олар тиімді фондық шашыратқыш ретінде әрекет жасаушы болып табылады. MgCr_2O_4 фазасының түзілуі Mg мөлшері 3 ат-% жоғары үлгілердің рентгенограммалары мен СЭМ кескіндерінде байқалады. Cr_2O_3 немесе CuO фазасының аз мөлшерінің түзілуі прекурсорлар құрамының стехиометриядан ауытқуымен байланысты болуы мүмкін. Алынған нәтижелер мыс хромит негізіндегі материалдың термоэлектрлік қасиетін арттыру перспективасын ашады.

Кілт сөздер: термоэлектрлік тиімділік, мыс хромиті, синтез ұзақтығы, жылуөткізгіштің төмендеуі.

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Влияние продолжительности синтеза на перенос тепла и заряда в поликристаллических $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$

Методом твердофазного синтеза получены поликристаллические керамические образцы хромита меди (I), легированные магнием. Методом рентгеноструктурного анализа исследованы фазовый состав и кристаллическая структура синтеза. Микроструктура образцов исследована методом сканирующей электронной микроскопии. Теплопроводность и электропроводность измерялись в интервале температур $78 < T < 320$ К. Наблюдалось значительное снижение теплопроводности с увеличением продолжительности синтеза. Этот эффект был объяснен образованием небольшого количества кристаллитов MgCr_2O_4 и Cr_2O_3 и CuO , действующих как эффективные рассеиватели фононов. Образование фазы MgCr_2O_4 наблюдается на рентгенограммах и СЭМ-изображениях образцов с содержанием Mg более 3 ат. %. Образование небольшого количества фазы Cr_2O_3 или CuO может быть связано с отклонением содержания прекурсора от стехиометрии. Полученные результаты открывают перспективу повышения термоэлектрической эффективности материала на основе хромита меди.

Ключевые слова: термоэлектрическая эффективность, хромит меди, продолжительность синтеза, снижение теплопроводности.