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A. O. Onishenko

M.N. Mikheev Institute of Metal Physics of Ural Branch of Russian Academy of Sciences, Yekaterinburg, Russia

E. A. Suslov

M.N. Mikheev Institute of Metal Physics of Ural Branch of Russian Academy of Sciences, Yekaterinburg, Russia

M. S. Postnikov

M.N. Mikheev Institute of Metal Physics of Ural Branch of Russian Academy of Sciences, Yekaterinburg, Russia

A. S. Shkvarin

M.N. Mikheev Institute of Metal Physics of Ural Branch of Russian Academy of Sciences, Yekaterinburg, Russia

A. N. Titov

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M.N. Mikheev Institute of Metal Physics of Ural Branch of Russian Academy of Sciences, Yekaterinburg, Russia
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A.O. Onishenko, E.A. Suslov, M.S. Postnikov,
A.S. Shkvarin, A.N. Titov, A.I. Merentsov*

M.N. Mikheev Institute of Metal Physics of Ural Branch of Russian Academy of Sciences, Yekaterinburg, Russia

E-mail: alexander.merentsov@urfu.ru

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Cu_xCrSe_2 materials can exist in the form of delafossite with a layered structure and exhibit multiferroic properties, or in the form of spinel and exhibit ferromagnetic properties, depending on the copper concentration. The stability of both forms of Cu_xCrSe_2 has been studied with regards to defectivity in the copper sublattice. The boundaries of the Cu_xCrSe_2 homogeneity regions for the delafossite-like structure and for the cubic spinel CuCr_2Se_4 were determined by coulometric titration at room temperature. Analysis of the time dependence of cell polarization allowed us to estimate the diffusion coefficients in these materials.

Keywords: delafossite; layered structure; multiferroic properties; cubic spinel; ferromagnetic properties

Introduction

Multiferroic magnetoelectric materials exhibit ferroelectric and ferromagnetic properties, providing technological prospects in new multifunctional devices

[1–3]. For example, multiferroics are used in memory devices [4]. It is known [5, 6], that various alloys with magnetic properties are widely used in various microdevices, however layered dichalcogenides like CuCrSe_2 also exhibit interesting magnetic properties and memory elements can be developed based on such materials [1–3]. In layered materials like CuCrSe_2 with $R\bar{3}m$ structure, Cu atoms are distributed only in one tetrahedral plane [7]. As a result, the crystal lattice is non-centrosymmetric, allowing for electric polarization of the crystal along the c axis [1]. The temperature of spontaneous polarization coincides with the temperature of magnetic ordering in the Cr sublattice. It is known [8] that the main interaction in the Cr sublattice is ferromagnetic. However, the regular triangular sublattice prohibits ferromagnetic ordering and leads to frustrations. It seems that frustrations are highly dependent on the level of defectivity in the Cu sublattice. This is because the asymmetric environment in the chromium sublattice causes the material to be multiferroic. Therefore, it is crucial to investigate the level of defectiveness in this material. Studying defectiveness in spinel is significant as it helps to understand the impact of the lattice structure on the permissible level of defectiveness.

CuCrSe_2 has a crystal structure [9] similar to that of delafossite (CuCrO_2) [10], which is shown in Figure 1a. The compound CuCr_2Se_4 (or $\text{Cu}_{0.5}\text{CrSe}_2$) is known for its spinel structure [11] (Figure 1b). The delafossite lattice of CuCrSe_2 can be described as a lattice of CrSe_2 layers intercalated with copper. While there is literature available on spinel CuCr_2Se_4 , there is a need for data on phase diagrams in the Cu_xCrSe_2 system needs to be present [12]. The similarity with intercalation compounds suggests a possible region of homogeneity for both CuCrSe_2 and $\text{Cu}_{0.5}\text{CrSe}_2$.

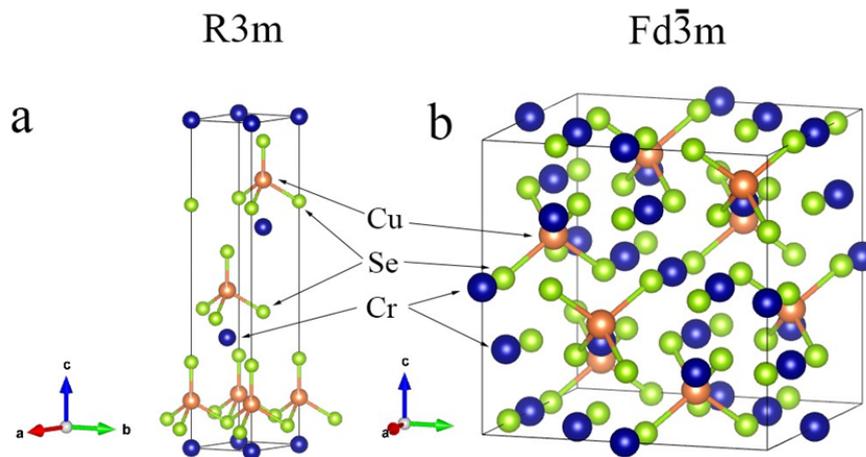


Figure 1. Unit cells of CuCrSe_2 (a) and CuCr_2Se_4 (b).

The density of Cr 3d states in CrSe_2 was theoretically predicted to be half-metallic with 100% spin polarization [13]. The possibility of obtaining CrSe_2 from K_xCrSe_2 was demonstrated in [14, 15] according to the following reaction:



CrSe_2 layered and spinel structures can be obtained using this approach.

CrSe₂ material should be obtained without heating since it is unstable and decomposes at a temperature of 600 K according to reaction (2) [15]:

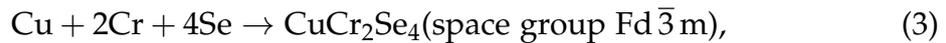


The aim of this study was to investigate phase equilibria in the CrSe₂–Cu_xCrSe₂ (delafossite) and CrSe₂–Cu_xCr₂Se₄ (spinel) systems at room temperature.

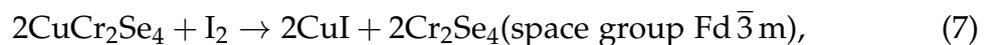
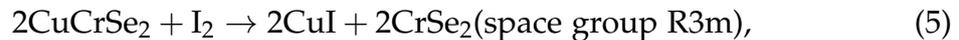
Methods

Samples of Cu_xCrSe₂ and Cu_xCr₂Se₄ were synthesized using precise weighed amounts (0.0001 g) of elements in evacuated quartz ampoules via the solid-phase method. This approach ensures purer products free of chloride impurities during syntheses from solutions [16]. The synthesis was carried out in several stages with repeated homogenization. Based on the experience of the authors [14, 15], CrSe₂ from CuCrSe₂ was obtained using a similar method through the following reactions:

1st stage



2nd stage



Single-phase finely dispersed CuCrSe₂ and CuCr₂Se₄ powders, crystalline iodine I₂, and acetonitrile CH₃CN were used for synthesis. Prior to synthesis, residual water was removed from acetonitrile using molecular sieves (4A NaA). A stoichiometric amount of compounds and iodine was taken and 10 wt. % excess of iodine was added. Being the synthesis medium, acetonitrile was taken in excess. The synthesis was carried out for one week with periodic stirring of the samples in an ultrasonic bath once a day for 30 minutes. After 7 days, the resulting products were filtered and washed with acetonitrile to remove CuI, then dried to remove acetonitrile vapor.

The homogeneity of the synthesized samples was checked using X-ray powder diffraction (XRD) on a Shimadzu XRD 7000 Maxima diffractometer (monochromatic CuK α radiation, $\lambda = 1.5406 \text{ \AA}$, scanning 2θ angle range of $10^\circ - 90^\circ$, Bragg-Brentano geometry) in the Collective Use Center "Ural-M" of the Institute of Metallurgy, Russian Academy of Sciences, Ural Division.

Copper was removed from CuCrSe_2 and CuCr_2Se_4 electrochemically using the galvanostatic intermittent titration method (GITT) for coulometric titration. The electrochemical cells used were $\text{Cu}|\text{Cu}^+|\text{Cu}_x\text{CrSe}_2$ and $\text{Cu}|\text{Cu}^+|\text{Cu}_x\text{Cr}_2\text{Se}_4$ for the Cu_xCrSe_2 and $\text{Cu}_x\text{Cr}_2\text{Se}_4$ systems, respectively. Metallic copper was used as the counter and negative electrode. The cathode material consisted of $\text{Cu}_x\text{Cr}_y\text{Se}_z$:C45 Carbon Black:Polyvinylidene fluoride at 80:10:10 wt.%, respectively. A 0.1M solution of CuI in acetonitrile was used as an electrolyte. The search for phase boundaries was conducted through coulometric titration with a titration step of $dx=0.025$ mol (2.5 mol%). Electrochemical measurements were conducted at room temperature using a BTS-4000 (5V, 10mA) potentiostat. The principles of determining phase boundaries through the electromotive force (EMF) method and the GITT method are described in [17–20].

Results and discussion

The results of coulometric titration are presented in Figure 2.

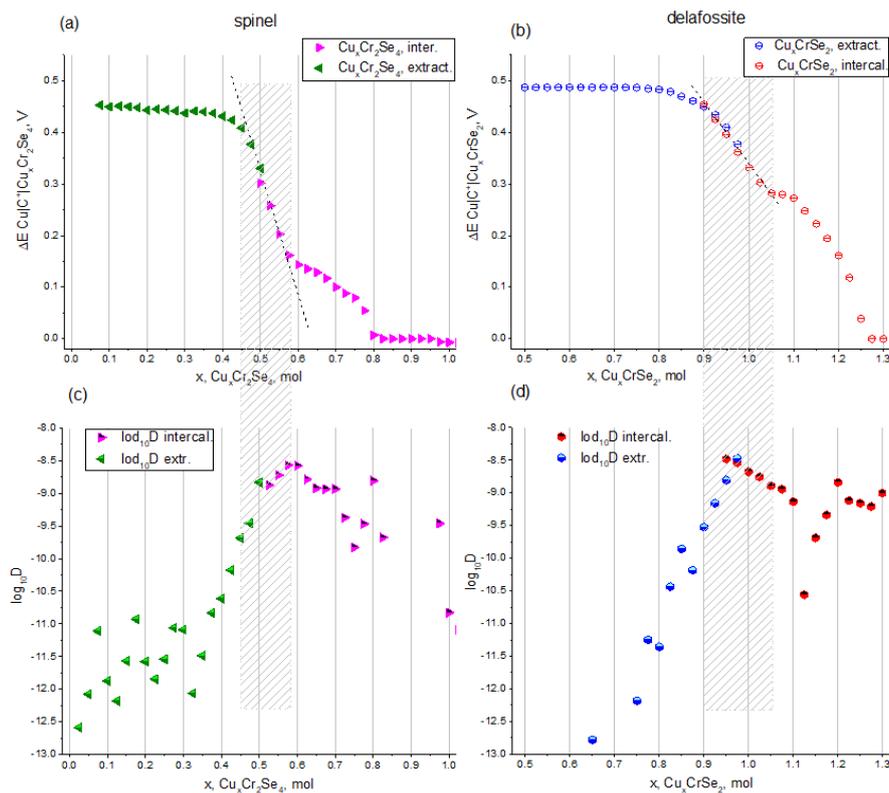


Figure 2. Dependencies of coulometric titration $\Delta E \sim f(x)$ in electrochemical cells $\text{Cu}|\text{Cu}^+|\text{Cu}_x\text{CrSe}_2$ (a) and $\text{Cu}|\text{Cu}^+|\text{Cu}_x\text{Cr}_2\text{Se}_4$ (b); dependence of the logarithm of the diffusion coefficient ($\log_{10}D$) on the Cu content in spinel $\text{Cu}_x\text{Cr}_2\text{Se}_4$ (c) and delafossite CuCrSe_2 (d).

Figure 2 shows a large homogeneity region of approximately 15 mol.% and wide two-phase regions for both Cu_xCrSe_2 (spinel and delafossite) systems. Homogeneity regions were found to be in the Cu concentration range of $0.9 < x < 1.2$ ($0.45 < x < 0.6$ in terms of $\text{Cu}_{0.5}\text{CrSe}_2$) for spinel $\text{Cu}_x\text{Cr}_2\text{Se}_4$ and of $0.9 < x < 1.05$ for delafossite Cu_xCrSe_2 . The Cu concentration range of $x > 0.8$ for $\text{Cu}_x\text{Cr}_2\text{Se}_4$ corresponds to the precipitation of Cu or to the formation of Cu dendrites in the

electrochemical cell. A similar region exists at $x > 1.27$ for the Cu_xCrSe_2 system. The ranges of $x < 0.45$ and of $0.6 < x < 0.8$ correspond to two-phase regions for $\text{Cu}_x\text{Cr}_2\text{Se}_4$. Similarly, the ranges of $x < 0.9$ and of $1.05 < x < 1.1$ correspond to two-phase regions for Cu_xCrSe_2 . The range of $1.1 < x < 1.27$ is presumed to correspond to a two or three-phase region, possibly including $\text{Cu}_{1+\sigma}\text{CrSe}_2$, $\text{Cu}_{1.75-1.82}\text{Se}$, and Cu.

The experimental data analysis enabled us to determine the diffusion coefficient order. In this case, we used the technique described in [21–23], which involves analyzing the dependence of $\Delta E \sim f(t)$ after turning the titration current on and off and solving equation (8):

$$D = \frac{4}{\pi t} L^2 \left(\frac{\Delta E_s}{\Delta E_t} \right)^2 t \ll L^2 / D, \quad (8)$$

where t is the duration of the current pulse; L – diffusion length (electrode thickness); ΔE_s – potential difference when the current is turned off; ΔE_t is the potential difference when passing current excluding iR .

Figure 2c and Figure 2d show the Cu concentration dependences of the diffusion coefficients for CuCr_2Se_4 and CuCrSe_2 , respectively. The maximum diffusion mobility for CuCr_2Se_4 ($D = 10^{-8.5} \text{ cm}^2/\text{s}$) and CuCrSe_2 ($D = 10^{-8.5} \text{ cm}^2/\text{s}$) corresponds to the stoichiometric compositions. Deviation from stoichiometry may result in a deficiency of mobile Cu ions or vacancies available for filling.

The diffusion coefficients decrease when defects occur with increasing and decreasing Cu content, as in the case of CuCr_2Se_4 spinel. The diffusion coefficient reaches a minimum value at $x = 0.3$ and remains almost constant with a further decrease in Cu content (Figure 2c). This Cu concentration is in good agreement with the percolation threshold for a cubic lattice (0.31 for the problem of cubic lattice nodes with interaction between nearest neighbors [24]). Forming of $\text{Cu}_{1.75-1.82}\text{Se}$ is possible when moving towards compositions with high Cu content. The decrease of D at $x > 0.7$ may be associated with the work to destroy the structure.

Figure 2d shows the dependence of the diffusion coefficient on the Cu content for the CuCrSe_2 system. The maximum value of D corresponds to the composition $\text{Cu}_{0.95}\text{CrSe}_2$. Increasing or decreasing the Cu content results in a decrease in D values, which may be attributed to the hindered movement of Cu ions due to defects along its sublattice.

It is worth noting that the boundary of the region with a sharp increase in the scatter of the Cu diffusion coefficient in CuCr_2Se_4 ($0 < x < 0.3$ in Figure 2c) coincides with the boundary of the single-phase region according to electrochemical data. This may be due to the material's inhomogeneity (CrSe_2), which complicates the diffusion process. However, in the case of CuCrSe_2 , such an increase in scatter when crossing the boundary of the single-phase region is not observed (Figure 2d). The difference between copper's role in the lattice of layered CrSe_2 and spinel CuCr_2Se_4 is evident. In the former, copper acts as an intercalated impurity, while in the latter, it is an essential part of the crystal structure. In the regions corresponding to cubic CrSe_2 , copper's mobility is negligible.

To determine the chemical composition of the samples obtained by chemical extraction of Cu, an energy-dispersive X-ray (EDX) analysis was used. The averaging of the chemical composition was conducted over at least 10 points. Scanning electronic microscope (SEM) images were obtained on a Quanta-200 microscope. Figure 3 shows SEM images of CrSe_2 , $\text{Cu}_{0.5}\text{CrSe}_2$ and CuCr_2Se_4 at the same magnification.

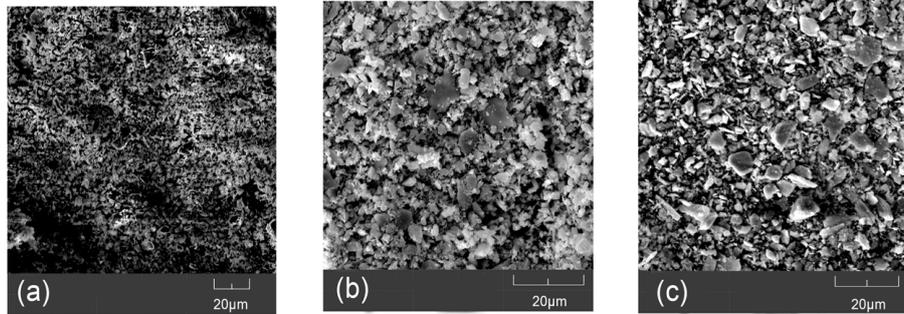


Figure 3. SEM images of CrSe_2 (a), $\text{Cu}_{0.5}\text{CrSe}_2$ (b) and CuCr_2Se_4 (c) after chemical extraction of copper.

SEM images of CrSe_2 , $\text{Cu}_{0.5}\text{CrSe}_2$, and CuCr_2Se_4 were processed using the ImageJ software package [25]. The resulting distribution of the number of grains by their area is shown in Figure 4.

The chemical compositions of the obtained samples are listed in Table 1.

Table 1.

Chemical composition of Cu_xCrSe_2 compounds before and after copper extraction.

Initial compound	Expected compound	Chemical composition of the obtained samples
CuCrSe_2	CrSe_2	$\text{Cu}_{0.24}\text{CrSe}_2$
CuCrSe_2	$\text{Cu}_{0.5}\text{CrSe}_2$	$\text{Cu}_{0.568}\text{CrSe}_2$
CuCrSe_2	CrSe_2	$\text{Cu}_{0.76}\text{Cr}_2\text{Se}_{3.74}$

The initial CuCr_2Se_4 crystal structure is described by cubic ordering $\text{Fd}\bar{3}\text{m}$ with a lattice parameter of $a = 10.326 \text{ \AA}$, which agrees with the literature data [12].

The diffraction pattern's general profile remained unchanged after copper was chemically extracted from CuCr_2Se_4 . An additional low-intensity peak at 46 degrees, corresponding to elemental copper, appeared. This peak was most likely formed during the decomposition of the CuI reaction product. The lattice parameter of $a = 10.323 \text{ \AA}$ remains unchanged within the calculation error. Table 2 presents the results of a full-profile analysis of the diffraction patterns performed using the GSAS II software package [26]. A copper defectivity of 6% in the CuCr_2Se_4 phase is observed.

A full-profile analysis of an XRD pattern of CrSe_2 obtained from CuCrSe_2 (Figure 5) shows that even after chemical extraction of Cu, it remains within the lattice to some extent. This may be due to the presence of both large and small particles in the starting substance powder, as shown in Figure 3, which causes non-uniform reaction. A lattice copper concentration according to full-profile analysis is of $x = 0.24$, which is consistent with the EDX findings presented in Table 1.

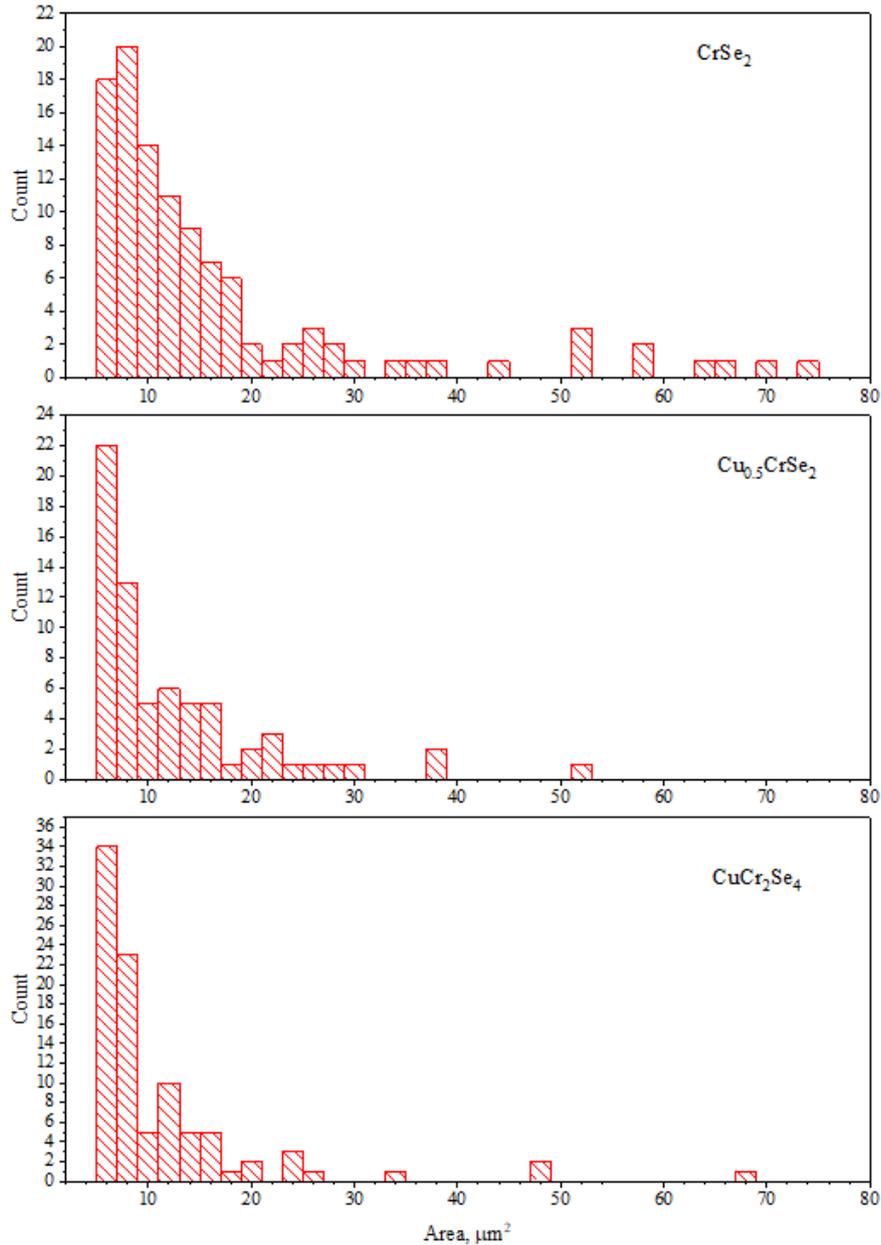


Figure 4. Distribution of the number of grains by their area for CrSe_2 , $\text{Cu}_{0.5}\text{CrSe}_2$ and CuCr_2Se_4 .

Table 2.

Full-profile refinement results for CuCr_2Se_4 .

Compound	Unit cell	Atom	Coordinates	Filling	Convergence Options
CuCr_2Se_4	$\text{Fd}\bar{3}\text{m}$ $a=10.326\text{\AA}$	Cu	0.125 0.125 0.125	1	$R^2=9.17\%$
		Cr	0.5 0.5 0.5	1	wRp=13.65%
		Se	0.257 0.257 0.257	1.0494	$\chi^2=4.356$
CuCr_2Se_4 after Cu extraction	$\text{Fd}\bar{3}\text{m}$ $a=10.323\text{\AA}$	Cu	0.125 0.125 0.125	0.9405	$R^2=11.14\%$
		Cr	0.5 0.5 0.5	1	wRp = 11.79%
		Se	0.257 0.257 0.257	1	$\chi^2=4.337$

It is worth noting that for isostructural CuCrS_2 , a single-phase material with a composition of approximately $\text{Cu}_{0.66}\text{CrS}_2$ was obtained through the chemical

extraction of copper [14]. This composition coincides with the composition of spinel – CuCr_2S_4 ; however, it retains a layered structure with trigonal symmetry. The EMF of the electrochemical cell's "plateau" region indicates that it is composed solely of a mixture of CrSe_2 and CuCrSe_2 . This suggests that there is no layered compound with the composition of $\text{Cu}_{0.5}\text{CrSe}_2$ present in this system.

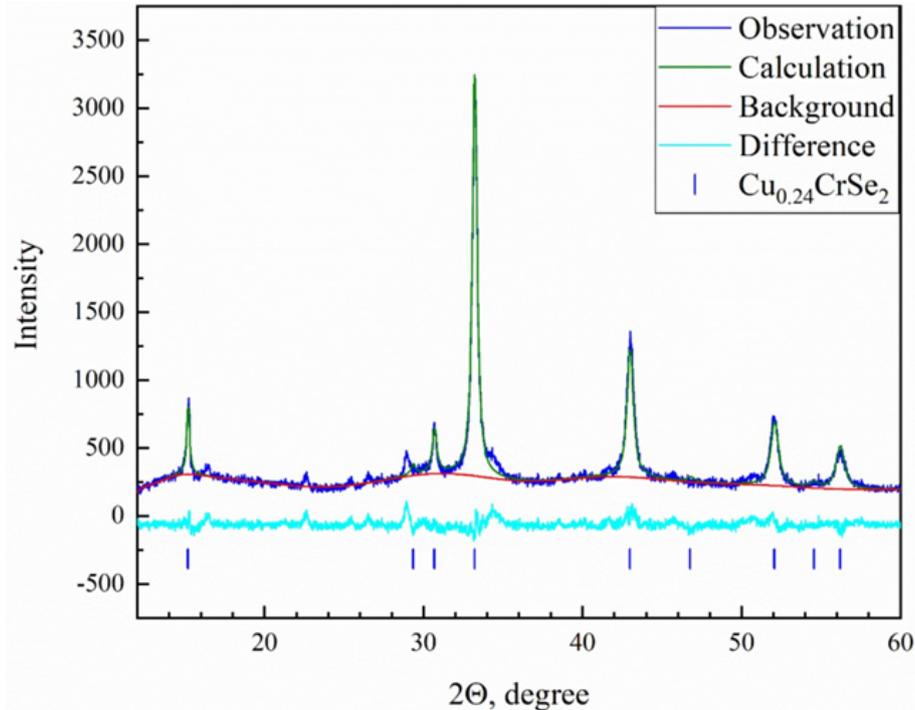


Figure 5. XRD pattern of $\text{Cu}_{0.24}\text{CrSe}_2$ after chemical copper extraction.

It can be assumed that the defectiveness of the resulting sample is associated with a blocking effect. This means that copper is extracted from the surface of crystals [27].

Conclusions

The current study has established for the first time the copper homogeneity regions for CuCrSe_2 with a delafossite structure and CuCr_2Se_4 with a spinel structure and assessed their width. In thermodynamic analysis of phase relationships, it is important to consider the presence of noticeable regions of homogeneity in these materials.

Chemical and electrochemical methods were used to partially extract copper from the CuCrSe_2 and CuCr_2Se_4 compounds. It was found that chemical extraction is gentler and does not damage the matrix. The maximum value of diffusion coefficients $D=10^{-8.5} \text{ cm}^2/\text{s}$ was achieved at compositions close to stoichiometric for both CuCrSe_2 and CuCr_2Se_4 systems. An increase in the number of defects results in a decrease in the values of diffusion coefficients.

Acknowledgements

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