Structural Characterization and Magnetic Properties of CuCr$_2$Te$_4$ Spinel Obtained by Mechanical Alloying and Heat Treatment

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CuCr$_2$Te$_4$ can be obtain by mechanical alloying followed by heat treatment. The obtained phase crystallizes in the spinel-type structure of the space group *Fd3m*. The calculated crystallite size equals to 100 nm. Magnetic susceptibility measurements showed ferrimagnetic order below 21 K.

1. Introduction

CuCr$_2$Te$_4$ crystallizes in the cubic spinel type structure (space group *Fd-3m* [1]), with lattice parameter $a_0 = 11.125$ nm. It has a normal cation distribution with copper ions located at the tetrahedral sites and chromium ions in octahedral coordination. CuCr$_2$Te$_4$ belongs to the group of spinel chalcogenides with general formula CuCr$_2$X$_4$ where X = S, Se and Te. This group of compounds reveals interesting magnetic and electrical properties: ferromagnetics with high Curie temperature (for CuCr$_2$Te$_4$, $T_C = 362$ K) and metallic conductivity. This group of compounds are promising materials for commercial application as magnetic [2] or thermoelectric devices [3]. Although extensive studies have been made on spinel chalcogenides, only a few related to telluride-spinel compounds have been reported.

This paper presents the synthesis, structural characterization, and magnetic properties of CuCr$_2$Te$_4$ spinel.

2. Experimental details

Mechanical alloying (MA) was carried out from pure elements: Cu, Cr, and Te (99.99% purity). The milling process [4] was performed in the Fritsch Pulverisette 6 planetary ball mill equipped with a hardened steel vial (80 ml) and balls (15 mm in diameter) in a protective atmosphere of argon. The balls to powder weight ratio and rotational speed were 10:1 and 500 rpm, respectively. To avoid excessive temperature increase milling times of 20 min were alternated with 15 min periods of rest. Process of MA was performed by two methods: "wet milling" — with an addition of isopropanol as process control agent (PCA) in aim to improve synthesis results and "dry milling" — without PCA addition. Small amounts of the milled powder were withdrawn after selected time intervals in order to examine the progress of MA by the X-ray diffraction (XRD) method. The milled powders were compacted by cold pressing and next annealed under vacuum at 1173 K for 60 min in order to reach an equilibrium structure.

The XRD measurements were performed on the Philips X'Pert PW 3040/60 diffractometer with Cu K_α radiation ($\lambda = 1.5405$ Å). X'Pert Highscore Plus software and ICDD (PDF-4+, 2014) files were used for phase identification. Surface morphology of compacted CuCr$_2$Te$_4$ powder was studied by scanning electron microscope (JEOL JSM-6480). Magnetization and magnetic susceptibility were measured with the use of Quantum Design Physical Properties Measurement System (QD-PPMS) in the temperature range 1.8–360 K and at magnetic field up to 70 kOe.

3. Results and discussion

Figures 1–3 show the XRD patterns of the following products: (1) after 80 h of dry milling, (2) after 60 h of wet milling, (3) after 80 h of dry milling and further heat treatment at 1173 K. The product of milling is a mixture of copper telluride, chromium telluride, tellurium and CuCr$_2$Te$_4$ phase (Figs. 1, 2). It could be noticed that wet milling is more efficient method of CuCr$_2$Te$_4$ synthesis compared to dry one, as the amount of created spinel phase during wet milling is much greater ($\approx$28 wt%) than for dry milling ($\approx$1 wt%). An application of subsequent
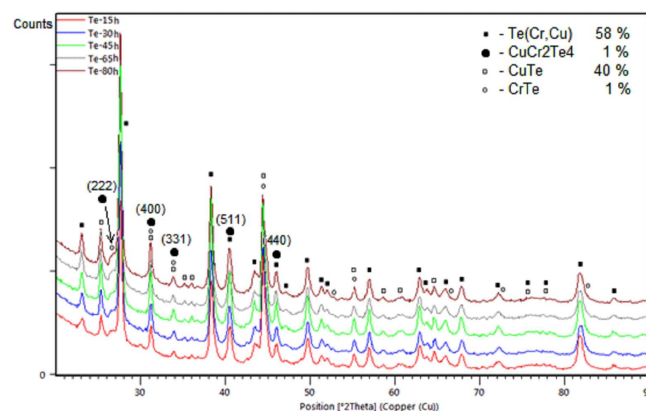

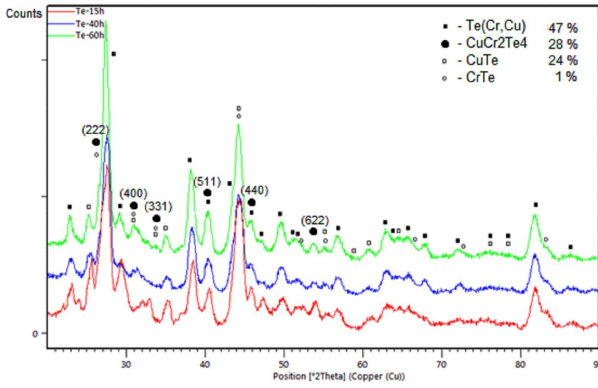Fig. 1. XRD pattern of the dry milling products.

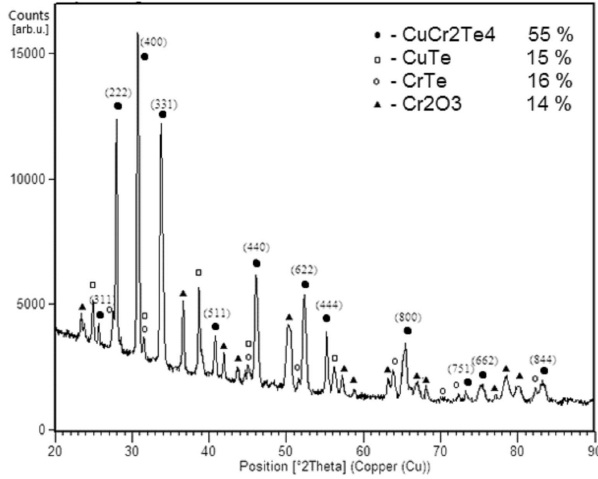Fig. 2. XRD pattern of the wet milling products.

Fig. 3. XRD pattern of the CuCr$_2$Te$_4$ spinel obtained by the dry milling and subsequent heating at 1173 K.

heat treatment of the milled powder leads the increase in the amount of spinel phase to about 55 wt% (Fig. 3). It could be assumed that the wet milling and subsequent annealing favor faster homogenization of milled powder, which facilitates the interdiffusion of its components.

CuCr$_2$Te$_4$ crystallizes in the spinel type structure — *Fd3m*. The lattice parameter *a* was calculated with the use of the Rietveld refinement by the High Score Plus PANalytical software. Results of the refined unit cell parameters, the values of crystallite sizes and lattice strains are presented in Table I (at the end of the paper).

Surface morphology of investigated powders was examined by scanning electron microscope (SEM). The SEM images of milled powders, as shown in Fig. 4a–c, are typical for the materials subjected to mechanical alloying. They demonstrate the effects of different, repeated processes occurring in the course of MA, such as the formation of small particles as a result of crushing, subsequent agglomeration by cold welding, fracturing and re-welding. These processes often lead to formation of smaller or larger agglomerates consisting of nanosized particles.

The results of magnetic measurements showed typical behaviour for ferrimagnetics which can be seen from the
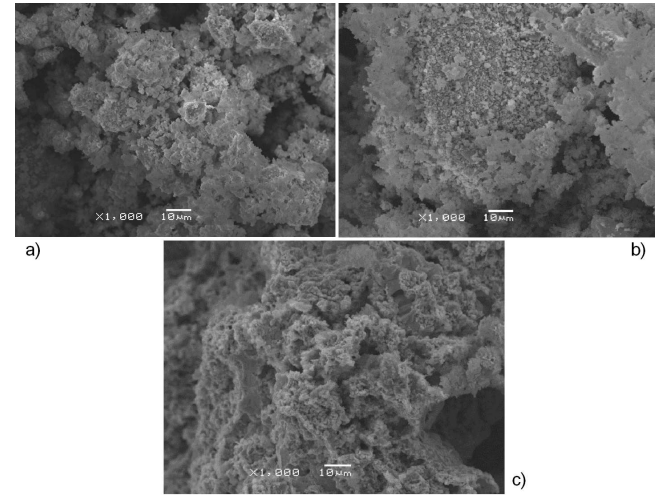

Fig. 4. The SEM images of the sample surfaces: (a) after 80 h of dry milling, (b) after 60 h of wet milling and (c) after 80 h of dry milling and heating at 1173 K.
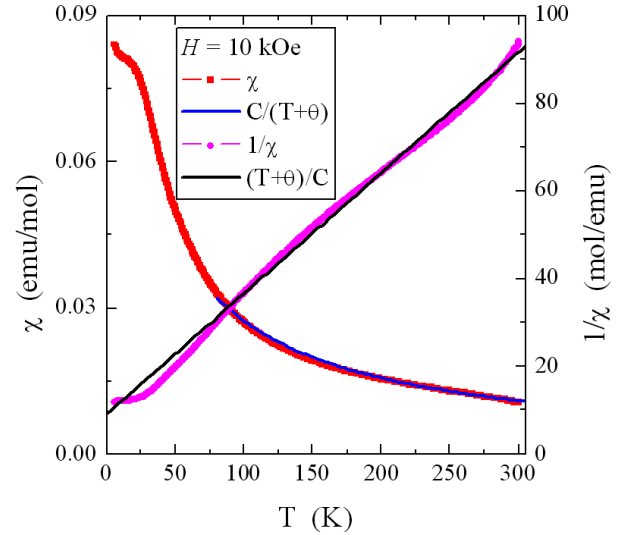

Fig. 5. Magnetic susceptibility χ vs. temperature T at 10 kOe for CuCr$_2$Te$_4$. The solid (blue) line, $C/(T+\theta)$, is for an estimation of the Landé factor from the Curie constant. The solid (black) line, $(T+\theta)/C$, indicates a Curie–Weiss behaviour.

deviation of the reciprocal magnetic susceptibility curve downward from its linear part (Fig. 5). The temperature dependence of magnetic susceptibility, $\chi(T)$, and its reverse, $1/\chi(T)$, indicate the Curie–Weiss behaviour and antiferromagnetic (AFM) short-range interaction visible in the negative paramagnetic Curie–Weiss temperature ($\theta = -33$ K) as well as in an effective magnetic moment $\mu_{eff} = 5.395\ \mu_B$/f.u. characteristic for the half-filled t_{2g} ground state of the Cr^{3+} ions orbitally nondegenerated. Similar ferrimagnetic behavior for nanoparticles CuCr$_{1.65}$Se$_4$ was found. However, due to strong spin-orbit coupling CuCr$_{1.65}$Se$_4$ nanoparticles crystallized in the monoclinic Cr$_2$Se$_3$-type structure of the space group *I2/m* [5].

4. Conclusions

CuCr$_2$Te$_4$ phase with the spinel structure ($Fd3m$) can be obtain by mechanical alloying followed by heat treatment.

The SEM images of milled powders, as shown in Fig. 4a–c, are typical for the materials subjected to mechanical alloying. They demonstrate the effects of different, repeated processes occurring in the course of MA, such as the formation of small particles as a result of crushing, subsequent agglomeration by cold welding, fracturing, and re-welding.

Magnetic studies of CuCr$_2$Te$_4$ spinel showed ferrimagnetic order below 21 K and AFM short-range interactions.

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TABLE I

Phase composition, lattice parameters, crystallite sizes and lattice strains.

ICDD card number	Chemical composition	Space group, crystallographic system	Literature lattice parameters [Å]	Refined lattice parameters [Å]	Phase constitution [wt.%]	D_{hkl} [Å]	ε [%]
sample after dry milling							
00-036-1452	Te(Cu,Cr)	$P3_12_1$ hexagonal	$a = 4.4590$ $c = 5.9280$	$a = 4.4611(1)$ $c = 5.9255(7)$	58	250	0.25
01-089-2395	CuCr2Te4	Fd-$3m$ cubic	$a = 11.2600$	$a = 11.2037(1)$	1	> 1000	0.10
01-070-8050	CuTe	$Pmmn$ orthorombic	$a = 3.1550$ $b = 4.0920$ $c = 6.9560$	$a = 3.1564(2)$ $b = 4.0903(1)$ $c = 7.0066(4)$	40	195	0.16
98-016-9767	CrTe	Fm-$3m$ cubic	$a = 5.7270$	$a = 5.2825(2)$	1	> 1000	0.10
sample after wet milling							
00-036-1452	Te(Cu,Cr)	$P3_12_1$ hexagonal	$a = 4.4590$ $c = 5.9280$	$a = 4.4542(4)$ $c = 5.9164(8)$	47	107	0.30
01-089-2395	CuCr2Te4	Fd-$3m$ cubic	$a = 11.2600$	$a = 11.5196(4)$	28	95	0.35
01-070-8050	CuTe	$Pmmn$ orthorombic	$a = 3.1550$ $b = 4.0920$ $c = 6.9560$	$a = 3.4110(6)$ $b = 4.1049(5)$ $c = 6.5087(1)$	24	80	0.32
98-016-9767	CrTe	Fm-$3m$ cubic	$a = 5.7270$	$a = 5.3270(1)$	1	106	0.30
sample after dry milling and subsequent annealing at 1173 K							
01-089-2395	CuCr2Te4	Fd-$3m$ cubic	$a = 11.2600$	$a = 11.2214(6)$	55	> 1000	0.32
01-070-8050	CuTe	$Pmmn$ orthorombic	$a = 3.1550$ $b = 4.0920$ $c = 6.9560$	$a = 3.4110(6)$ $b = 4.1049(5)$ $c = 6.5087(1)$	15	> 1000	0.49
98-016-9767	CrTe	Fm-$3m$ cubic	$a = 5.7270$	$a = 5.9271(1)$	16	> 1000	0.45
04-008-3294	Cr$_2$O$_3$	R-$3c$ rhombohedral	$a = 4.9300$ $c = 13.5200$	$a = 4.9654(8)$ $c = 13.6194(1)$	14	350	0.79