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CRYSTALLIN STRUCTURE AND DIFFERENTIAL THERMAL ANALYSIS OF CuTlS COMPOUND

R.S. Madatov[1], G.B. Baylarov[2], R.M. Mamishova[1], M.N. Mirzayev[1]

[1]Institute of Radiation Problems of ANAS
[2]Ganja State University

Abstract: Herein, the X-ray phase analysis (XPA) and differential-thermal analysis (DTA) of the CuTlS compound obtained by the Bridgman-Stockbarger method have been investigated. As a result of the study, it has been estimated the values of energy absorption and mass losses of CuTlS compounds depending on the temperature and given their change mechanisms.

Keywords: X-ray phase analysis, differential-thermal analysis, heat flux, activation energy

1. Introduction

One of the promising areas of modern material science and physical chemistry is the acquisition and comprehensive study of synthetic materials in accordance with the requirements of emerging new scientific and technical fields. It is known that successful solutions of research work in this direction can only be achieved on the basis of the latest achievements in physics, chemistry, structure analysis, crystallochemistry and materials science and their intended use. One of the most important issues in this regard is conducting research in order to define the detailed X-ray and physical and chemical characteristics of the obtained samples and determining their application fields based on the obtained results.

Modern research focuses on nanomaterials, superconductors and multi-phase systems [1,2]. It should be noted that all these still need extensive search and research. Copper chalcogenides have long been studied by the researcher because of their significant physical and chemical properties [3,4]. It is clear from the literature that copper chalcogenides have superconductivity at very low temperatures, semiconductivity, metal conductivity at intermediate temperatures, and ion conductivity at high temperatures (T>350K).

Stoichiometric and non-stheiometric compounds formed in Cu-S(Se) systems have long been one of the major investigated objects for their application-oriented properties. This interest is due to the physical and chemical properties that are manifested in them. It should be noted that these class compounds are also interesting objects in terms of crystalline structure and phase transition [5].

Another interesting feature of these system compounds is the presence of several structural phase transitions that occur depending on temperature. Therefore, taking into account what has been said, the main purpose of the present work is to conduct the X-ray analysis of CuTlS compound crystals and to determine the structural changes in the sample depending on the temperature.

2. Methods of experiment and results

The crystalline structures of the obtained samples were studied by X-ray diffraction method. The studied CuTlS compound was grown at high temperature using the Bridgman-

Stockbarger method and had an average size of 12×4×2 mm. The research was carried out on a D2-type powder diffractometer developed with the most modern German technology. For this purpose, disperse powder with the smallest size grain was prepared from the synthesized samples. The prepared powder was placed on the diffractometer's goniometer and the X-ray diffraction spectrum of the sample was drawn at a diffraction angle of $10<2\theta<80$ (Figure 1). Then, the distance between the atomic planes (d), the intensities of the obtained spectra, the crystal system of the sample, the volume, the density of the lattice, lattice constants, and the spatial group were determined based on the obtained X-ray diffraction spectra.

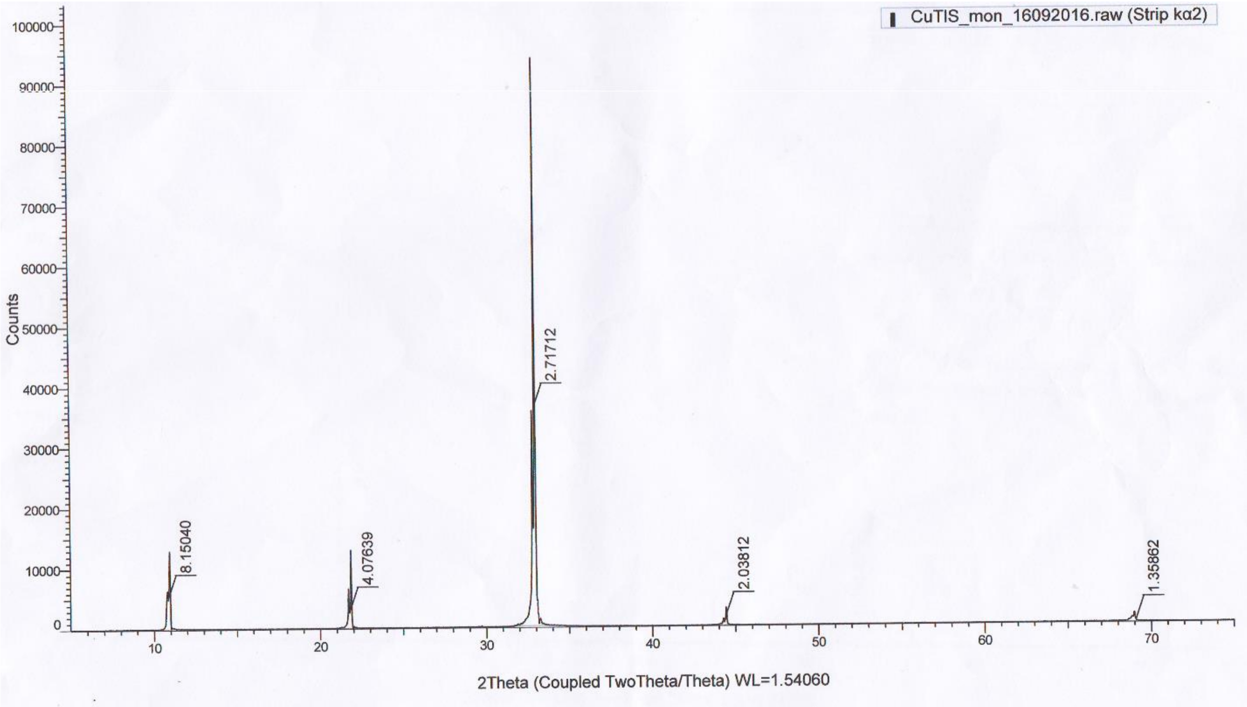

Fig. 1. X-ray diffraction images of CuTlS compound.

Table 1

Lattice parameters of the CuTlS sample defined based on the X-ray diffraction spectrum.

№	2θ	D	hkl	I/I₀	α, Å	V
1	11°36'	3.912	001	1.4	3.90	59.31
2	22°42'	1.956	002	1.5	3.91	59.77
3	33°12'	1.304	003	9.5	3.911	59.82
4	44°54'	0.978	004	0.5	3.912	59.86
5	69°36'	0.652	006	0.4	3.912	59.87

The calculations were performed based on the most important $n\lambda=2d\sin\theta$ formula of X-ray analysis. According to the study, the CuTlS compound becomes crystallized in the tetragonal crystal system and its lattice constants are a = 3.907Å, c = 8,152Å, d = 7.94g/cm^3, and the space group is P4/nmm.

Differential Thermal Analysis (DTA) was conducted using Perkin Elmer, Simultaneous Thermal Analyzer, STA 6000. In thermal processes, the influence of temperature on kinetic processes in the sample is investigated by experimental thermal analysis. In the thermal analysis, the sample was heated from 300 K to 670 K at a heating rate of 5 K/min and Ar gas flow of 20 ml/min. After heating the sample for 13 minutes, it was cooled in the PolyScience analyzer cooling system [6,7].

Figure 2 shows the linear increase rate of the temperature for the CuTlS compound (blue line), the changing kinetics of mass (TG - green line), Delta T temperature gradient between the material and the sample (purple color), and the temperature dependencies of DSC heat flux (yellow line).

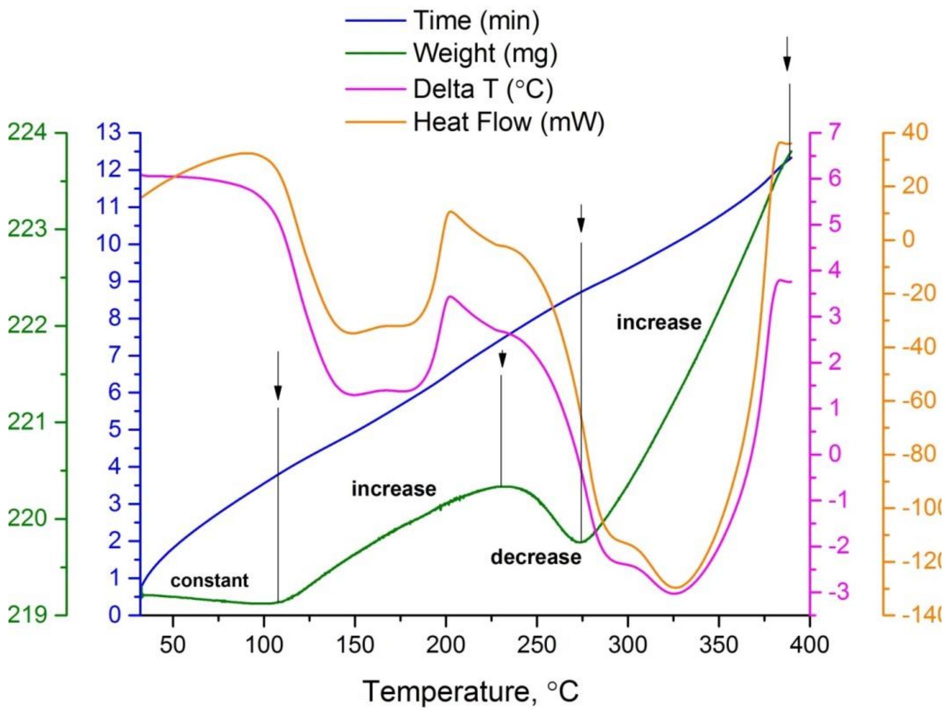

Fig. 2. Linear increase rate of CuTlS compound, change the kinetics of mass, temperature gradient and temperature dependence of differential scanning calorimetry (DSC) heat flux.

The change kinetics of heat flux with temperature gradients occurs in parallel with the changing kinetics of mass. The change dynamics of mass kinetics consists of four parts.

- $30 \le T \le 107$ °C constant region
- $107 \le T \le 230$ °C linearly increasing part (weak oxidation reaction)
- $230 \le T \le 275$ °C decomposition region
- $275 \le T \le 390$ °C rapid oxidation phase

In the first temperature region 30≤107°C, the mass kinetics and temperature gradient were stable, but the absorbance of the heat flux increased from 15 mW to 33 mW.

In the second temperature region, $107 \le T \le 230$°C, the increasing part in the mass kinetics is the oxidation reaction occurrence of the active centers on the surface by contacting the oxygen atoms in the CuTlS compound. The oxidation reaction is observed with a deep effect in the temperature gradient and the DSC spectrum, where the activation energy of this process is 0.132 kJ/mol and the energy of that area is 2820 mJ.

In the third temperature region, 230≤T≤275°C, the center of the decomposition nature endoeffect is 250°C and mass loss - 0.98 mg. In that part, the linear decrease is assumed to be a low-rate weak phase of reaction occurring with the $CuTlS+O_2 \rightarrow CuO_2+Tl_2O_3+SO_2$ mechanism. In this phase, oxides are formed only on the surface. The mass loss is just the decomposition like SO_2.

In the fourth 275≤T≤390°C region, an oxidation reaction occurs in a completed, rapid phase. As a result of oxidation in the TG spectrum, the mass is increased by 4.02 mg and has a deep effect, including the second, third and fourth effects, which are common in the temperature gradient and in the DSC spectrum. The activation energy of this process is 0.056 kJ/mol and the energy of that area is equivalent to 9988 mJ.

Thus, differential thermal analyzes of the CuTlS compound were performed at a temperature range of 30-400°C. It has been established that these compounds maintain their structure within the given temperature range. It has been calculated the values of energy absorption and mass losses and given their change mechanisms.

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КРИСТАЛЛИЧЕСКАЯ СТРУКТУРА И ДИФФЕРЕНЦИАЛЬНО-ТЕРМИЧЕСКИЙ АНАЛИЗ СОЕДИНЕНИЯ CuTlS

Р.М. Мадатов, Г.Б. Байларов, Р.М.Мамишова, М.Н. Мирзоев

Резюме: В представленной работе были исследованы рентгенофазовый анализ (РФА) и дифференциальный термический анализ (ДТА) комбинации CuTlS, полученной методом Бриджмена-Стокбаргера. В результате исследования были вычислены оценки поглощения энергии и потери массы соединений CuTlS в зависимости от температуры и приведены механизмы изменения.

Ключевые слова: рентгенофазовый анализ, дифференциально термический анализ, тепловой поток, энергия активации.

CuTlS BİRLƏŞMƏSİNİN KRİSTAL QURULUŞU VƏ DİFERENSİAL TERMİK ANALİZİ

R.S. Mədətov, Q.B. Bəylərov, R.M. Məmişova, M.N. Mirzəyev

Xülasə: Təqdim olunan işdə Bricmen-Stokbarqer üsulu ilə alınmış CuTlS birləşməsinin rentgen-faza analizi (RFA) və differensial-termik analizləri (DTA) tədqiq edilmişdir. Tədqiqat nəticəində CuTlS birləşməsinin temperaturdan asılı olaraq enerji udulmalarının və kütlə itkilərinin qiymətləri hesablanmış və onların dəyişmə mexanizmləri verilmişdir.

Açar sözlər: rentgen-faza analizi, diferensial termik analizi, istilik seli, aktivləşmə enerjisi