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Hüsnü ÖZKAN

Nizami GASANLY

İbrahim YILMAZ

Ali ÇULFAZ

Vyaceslav NAGIEV

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# Crystal Data for $A_3B_5C_9$-Type Ternary Compounds

**Hüsnü ÖZKAN, Nizami GASANLY, İbrahim YILMAZ**
*Physics Department,*
*Middle East Technical University,*
*06531 Ankara - TURKEY*
**Ali ÇULFAZ**
*Department of Chemical Engineering,*
*Middle East Technical University,*
*06531 Ankara - TURKEY*
**Vyaçeslav NAGIEV**
*Department of Physics,*
*Baku State University,*
*370073 Baku - AZERBAIJAN*

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**Abstract**

X-ray powder diffraction data were obtained for $Cu_3Ga_5Se_9$, $Cu_3In_5Se_9$, $Cu_3In_5Te_9$, $Ag_3In_5S_9$, $Ag_3Ga_5S_9$, $Ag_3In_5Se_9$, and $Ag_3Ga_5Te_9$ ternary compounds. The data indicate that these compounds crystallize in orthorhombic, monoclinic, orthorhombic, monoclinic, tetragonal, tetragonal, and orthorhombic systems, respectively.

## 1. Introduction

The possibility of formation of $A_3B_5C_9$-type ternary compounds (where A = Cu or Ag; B = Ga or In and C = S, Se or Te) has been revealed based on the physico-chemical analysis and the state diagram of $ABC_2$-$B_2C_3$ quasi-binary systems [1]. The analysis of the X-ray powder diffraction data of $Cu_3Ga_5Se_9$, $Cu_3In_5Se_9$ and $Cu_3In_5Te_9$ crystals, obtained by Debye-Scherrer film method, shows that all three compounds crystallize in the hexagonal system with the lattice parameters given in the same order as: $a = 8.01, 8.47$ and $8.78A^\circ$, and $c = 16.46, 17.41$ and $18.66A^\circ$ [1]. In a previous paper [2] we have presented the crystal data for $Cu_3In_5Se_9$ and $Cu_3In_5Te_9$ compounds. Preliminary indexing of the data indicated them to crystallize in orthorhombic and tetragonal systems, respectively. No other crystal data are available in the literature for these and other members of the ternary compounds stated above.

In this paper we present for the first time the crystal data for $Ag_3In_5S_9$, $Ag_3Ga_5S_9$, $Ag_3In_5Se_9$, and $Ag_3Ga_5Te_9$ ternary compounds and the new crystal data for $Cu_3Ga_5Se_9$ compound. Moreover, previously obtained X-ray powder diffraction data for $Cu_3In_5Se_9$ and $Cu_3In_5Te_9$ compounds were reanalysed, testing all the symmetries by using the latest version of the Treor programs "Treor-90", and revised crystal data are presented for them.

## 2. Experimental

$A_3B_5C_9$-type polycrystals were synthesized from particular high purity elements (at least 99.999%) taken in stoichiometric proportions. Single crystals studied were grown from the polycrystals by a zone crystallization method. The resulting ingots appear grey-black in color, except $Ag_3Ga_5S_9$ which had yellow color. Prepared samples were ground and characterized by X-ray powder diffraction using a Philips diffractometer "PW 1740" with a monochromatized CuK$\alpha$ radiation at scan speed of $0.02°2\theta$/sec.

**Table 1.** X-ray powder diffraction data for $Cu_3Ga_5Se_9$ compound.

| $h\ k\ l$ | $d_{obs}(A°)$ | $d_{calc}(A°)$ | $I/I_0$ |
|---|---|---|---|
| 1 1 1 | 3.204 | 3.204 | 100 |
| 1 0 2 | 1.980 | 1.980 | 11 |
| 2 0 2 | 1.957 | 1.957 | 54 |
| 8 2 0 | | 1.956 | |
| 1 3 1 | 1.679 | 1.680 | 19 |
| 7 0 2 | | 1.679 | |
| 12 0 1 | 1.662 | 1.662 | 20 |
| 8 2 2 | 1.394 | 1.395 | 5 |
| 15 0 1 | 1.373 | 1.373 | 4 |
| 3 4 0 | 1.370 | 1.371 | 3 |
| 4 4 1 | 1.280 | 1.280 | 5 |
| 3 1 3 | 1.270 | 1.270 | 8 |
| 5 4 1 | 1.262 | 1.261 | 4 |

## 2. Results

X-ray powder diffractograms of $A_3B_5C_9$-type compounds, which are different from each other, were indexed by using the computer program "Treor-90". The Miller indices ($hkl$), the observed and calculated interplanar spacings ($d$) and the relative intensities ($I/I_0$) of the diffraction lines for $Cu_3Ga_5Se_9$; $Cu_3In_5Se_9$ and $Cu_3In_5Te_9$; $Ag_3In_5S_9$ and $Ag_3Ga_5S_9$; $Ag_3In_5Se_9$ and $Ag_3Ga_5Te_9$ are listed in Tables 1, 2, 3 and 4, respectively. The calculated interplanar spacings are in good agreement with the observed ones.

**Table 2.** X-ray powder diffraction data for $Cu_3In_5Se_9$ and $Cu_3In_5Te_9$ compounds.

| $Cu_3In_5Se_9$ | | | | | | $Cu_3In_5Te_9$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| h | k | l | $d_{obs}(A^\circ)$ | $d_{calc}(A^\circ)$ | $I/I_0$ | h | k | l | $d_{obs}(A^\circ)$ | $d_{calc}(A^\circ)$ | $I/I_0$ |
| 1 | 3 | 0 | 3.469 | 3.470 | 100 | 2 | 0 | 1 | 3.573 | 3.571 | 100 |
| | | | | | | 0 | 2 | 1 | 2.439 | 3.438 | 3 |
| 1 | 0 | 1 | | 3.467 | | 4 | 0 | 0 | 3.088 | 3.091 | 5 |
| 0 | 3 | 1 | 3.356 | 3.358 | 77 | 4 | 2 | 0 | 2.700 | 2.702 | 8 |
| 1 | 1 | 1 | | 3.353 | | 4 | 2 | 1 | 2.300 | 2.299 | 4 |
| 0 | 0 | 2 | 2.600 | 2.600 | 9 | 1 | 5 | 0 | 2.187 | 2.189 | 88 |
| 2 | 2 | 0 | | 2.595 | | 0 | 0 | 2 | | 2.187 | |
| -1 | 1 | 2 | 3.536 | 2.537 | 11 | 0 | 2 | 2 | 2.034 | 2.035 | 5 |
| | | | | | | 2 | 5 | 1 | 1.888 | 1.888 | 3 |
| -2 | 2 | 1 | | 2.534 | | 6 | 0 | 1 | 1.865 | 1.864 | 60 |
| 1 | 1 | 2 | 2.155 | 2.158 | 41 | 1 | 5 | 2 | 1.547 | 1.547 | 13 |
| 2 | 2 | 1 | | 2.156 | | 5 | 5 | 1 | | 1.547 | |
| | | | | | | 1 | 1 | 3 | 1.436 | 1.436 | 4 |
| -2 | 4 | 1 | 2.111 | 2.110 | 67 | 0 | 2 | 3 | 1.410 | 1.410 | 8 |
| -2 | 2 | 2 | 2.056 | 2.054 | 72 | | | | | | |
| -2 | 3 | 2 | 1940 | 1.940 | 11 | 8 | 2 | 1 | | 1.410 | |
| -3 | 2 | 1 | 1.832 | 1.832 | 40 | 8 | 5 | 0 | 1.269 | 1.269 | 4 |
| -1 | 1 | 3 | 1.753 | 1.753 | 47 | | | | | | |
| -1 | 7 | 2 | 1.523 | 1.523 | 14 | | | | | | |
| 1 | 2 | 3 | | 1.522 | | | | | | | |
| 2 | 7 | 1 | 1.453 | 1.453 | 13 | | | | | | |
| -2 | 5 | 3 | 1.396 | 1.396 | 13 | | | | | | |
| -3 | 3 | 3 | 1.396 | 1.369 | 17 | | | | | | |
| -1 | 4 | 4 | 1.396 | 1.235 | 23 | | | | | | |

The determined values of the unit cell parameters are given in Table 5 (where $Z$ is the number of molecules in the unit cell) together with the calculated densities ($D_x$) of the samples. The uncertainities in the evaluated lattice parameters are quite low. The diffraction and crystal data presented in Tables 1, 2 and 5 indicate that $Cu_3Ga_5Se_9$, $Cu_3In_5Se_9$ and $Cu_3In_5Te_9$ compounds crystallize in orthorhombic, monoclinic and orthorhombic systems, respectively. These findings about the crystal systems differ from the previously published ones reporting all three compounds to be hexagonal [1] and last two compounds to be orthorhombic and tetragonal, respectively [2]. Our revised results for $Cu_3In_5Se_9$ and $Cu_3In_5Te_9$ compounds can be explained as follows. It appears that in order to obtain the correct crystal data all the possible symmetries including the lower ones should be tested. Such analysis is automatically done using the "Treor-90" program by giving an initial negative unit cell volume.

The diffraction and crystal data for $Ag_3In_5S_9$, $Ag_3Ga_5S_9$, $Ag_3In_5Se_9$, and $Ag_3Ga_5Te_9$ presented in Tables 3, 4 and 5 indicate that these compounds crystallize in monoclinic, tetragonal, tetragonal and orthorhombic systems, respectively.

**Table 3.** X-ray powder diffraction data for $Ag_3In_5S_9$ and $Ag_3Ga_5S_9$ compounds.

| $Ag_3In_5S_9$ | | | | | | $Ag_3Ga_5S_9$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| h | k | l | $d_{obs}(A^\circ)$ | $d_{calc}(A^\circ)$ | $I/I_0$ | h | k | l | $d_{obs}(A^\circ)$ | $d_{calc}(A^\circ)$ | $I/I_0$ |
| 0 | 2 | 0 | 3.827 | 3.830 | 29 | 1 | 1 | 2 | 3.200 | 3.196 | 100 |
| 1 | 1 | 1 | 3.551 | 3.547 | 27 | 2 | 0 | 0 | 2.882 | 2.880 | 16 |
| 2 | 0 | 1 | 3.340 | 3.344 | 38 | 0 | 0 | 4 | 2.578 | 2.578 | 6 |
| 3 | 1 | 0 | 3.261 | 3.260 | 100 | | | | | | |
| -2 | 1 | 1 | 3.141 | 3.142 | 44 | 2 | 1 | 0 | | 2.576 | |
| 4 | 0 | 0 | 2.703 | 2.703 | 46 | 2 | 1 | 1 | 2.500 | 2.499 | 7 |
| 3 | 3 | 0 | 2.083 | 2.083 | 67 | 2 | 2 | 0 | 2.036 | 2.036 | 31 |
| 5 | 1 | 0 | | 2.080 | | | | | | | |
| | | | | | | 2 | 0 | 4 | 1.921 | 1.921 | 48 |
| 2 | 3 | 1 | 2.030 | 2.029 | 25 | 3 | 0 | 0 | | 1.920 | |
| 0 | 4 | 0 | 1.914 | 1.915 | 91 | 0 | 0 | 6 | 1.717 | 1.719 | 52 |
| 5 | 0 | 1 | | 1.914 | | 3 | 1 | 2 | | 1.717 | |
| -3 | 3 | 1 | 1.891 | 1.893 | 31 | 2 | 2 | 4 | 1.598 | 1.598 | 9 |
| -3 | 0 | 2 | | 1.891 | | 3 | 2 | 0 | | 1.597 | |
| 1 | 1 | 3 | | 1.410 | | 1 | 1 | 0 | 1.584 | 1.584 | 16 |
| 3 | 5 | 0 | 1.410 | 1.410 | 22 | 4 | 0 | 0 | 1.439 | 1.440 | 10 |
| -6 | 0 | 2 | | 1.410 | | 2 | 2 | 6 | 1.313 | 1.314 | 11 |
| 1 | 1 | 3 | 1.251 | 1.251 | 26 | 3 | 3 | 2 | | 1.313 | |
| | | | | | | 4 | 2 | 0 | 1.288 | 1.288 | 6 |
| | | | | | | 3 | 1 | 6 | 1.250 | 1.250 | 14 |
| | | | | | | 4 | 2 | 2 | | 1.249 | |

As we have stated above, there is no structural information in the literature for the ternary $A_3B_5C_9$-type compounds. In our previous studies [3-4] we have reported that the members of the $TIBC_2$-type compounds have different crystal systems depending on the sizes of the atoms substituted. The variety of the crystal systems found in this study for the different members of $A_3B_5C_9$-type compounds may also be due to the different sizes of the substituted cations and anions in the compounds.

**Table 4.** X-ray powder diffraction data for $Ag_3In_5Se_9$ and $Ag_3Ga_5Te_9$ compounds.

| $Ag_3In_5S_9$ | | | | | | $Ag_3Ga_5S_9$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| h | k | l | $d_{obs}(A^\circ)$ | $d_{calc}(A^\circ)$ | $I/I_0$ | h | k | l | $d_{obs}(A^\circ)$ | $d_{calc}(A^\circ)$ | $I/I_0$ |
| 0 | 0 | 3 | 3.476 | 3.477 | 81 | 0 | 2 | 0 | 3.577 | 3.582 | 100 |
| 2 | 0 | 0 | 3.357 | 3.357 | 100 | 2 | 1 | 1 | 3.444 | 3.443 | 78 |
| 2 | 2 | 2 | 3.158 | 2.160 | 24 | 3 | 0 | 1 | | 3.439 | |
| 3 | 0 | 2 | 2.057 | 2.059 | 69 | 4 | 0 | 1 | 2.984 | 2.987 | 12 |
| 2 | 0 | 4 | | 2.057 | | 1 | 0 | 2 | 2.232 | 2.234 | 43 |
| 3 | 2 | 1 | 1.834 | 1.833 | 28 | 2 | 0 | 2 | 1.172 | 2.171 | 67 |
| 3 | 2 | 2 | 1.753 | 1.753 | 45 | | | | | | |
| 2 | 1 | 7 | 1.335 | 1.335 | 18 | 7 | 1 | 0 | | 2.170 | |
| | | | | | | 0 | 1 | 1 | 2.110 | 2.111 | 66 |
| | | | | | | 4 | 1 | 2 | 1.894 | 1.895 | 42 |
| | | | | | | 1 | 2 | 2 | | 1.893 | |
| | | | | | | 3 | 2 | 2 | 1.798 | 1.797 | 36 |

**Table 5.** Crystal data for $A_3B_5C_9$-type compounds.

| | $Cu_3Ga_5Se_9$ | $Cu_3In_5Se_9$ | $Cu_3In_5Te_9$ | $Ag_3In_5S_9$ | $Ag_3In_5Se_9$ | $Ag_3Ga_5S_9$ | $Ag_3Ga_5Te_9$ |
|---|---|---|---|---|---|---|---|
| $a, A^\circ$ | 21.947(5) | 5.784(4) | 12.364(3) | 10.813(5) | 6.714(2) | 5.759(1) | 15.94(6) |
| $b, A^\circ$ | 5.581(1) | 13.195(9) | 11.118(5) | 7.661(4) | 6.714(2) | 5.759(1) | 7.164(8) |
| $c, A^\circ$ | 3.977(1) | 5.327(2) | 4.374(1) | 4.362(1) | 10.430(4) | 10.314(3) | 4.512(4) |
| $\beta$, deg. | 90 | 102.58(5) | 90 | 91.73(3) | 90 | 90 | 90 |
| $V, A^{\circ 3}$ | 487.21 | 396.84 | 601.33 | 361.17 | 470.14 | 342.10 | 515.27 |
| $D_x$, g/cm$^3$ | 4.26 | 6.17 | 5.28 | 5.49 | 5.71 | 4.69 | 5.90 |
| Space group | $C^1_{2v}$ | $C^1_2$ or $C^1_s$ | $C^1_{2v}$ | $C^1_2$ or $C^1_s$ | $C^1_4$ or $C^1_{4v}$ | $C^1_4$ or $C^1_{4v}$ | $C^1_{2v}$ |
| Z | 1 | 1 | 1 | 1 | 1 | 1 | 1 |

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