STRUCTURAL PHASE TRANSITIONS IN AgCu$_{0.5}$Te$_{0.5}$ CRYSTALS

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ABSTRACT

AgCu$_{0.5}$Te$_{0.5}$ single crystals were synthesized and grown. Structural transformations were studied by high temperature X-ray diffraction analysis. Lattice parameters of both orthorhombic and both primitive cubic phases were calculated. Using temperature dependence of the lattice parameters, thermal expansion coefficients along main crystallographic directions were calculated. At 444 K, the orthorhombic-to-cubic transitions occur.

Keywords: crystal, homogeneous, phase transition, x-ray diffraction, lattice parameters,

I. INDRODUCTION

The crystal of low temperature AgCuSe phase has been determined [1] as tetragonal one with lattice parameters a=4,083⬚, c=6,30⬚, space group (D$^7_{4h}$), P4/mmm and Z=2. Frueh and others in their later work [2] showed that AgCuSe at room temperature crystallize as orthorhombic structure with lattice parameters a=4,105⬚, b =20,35⬚, c=6,30⬚, Z=10. As it is seen, the parameter b of orthorhombic structure is multiple of five parameters a of tetragonal lattice, i.e. b$_{ort}$=5a$_t$. AgCuSe orthorhombic phase parameters are similar to those of low temperature Cu$_2$Se phase, for which Stevels and Jellinek [3] show that it crystallize as orthorhombic crystal system with lattice parameters a=4,118⬚, b =20,36⬚, c=7,208⬚.

Ag atoms in AgCuSe structure are located in planes perpendicular to axis C. Around each of them there are four Ag atoms at 2,96⬚ and six Se atoms at 2,67⬚ (4 Se), 3,59⬚ (1 Se) and 3,64⬚ (1 Se). Se atoms form tetrahedrons with Cu atoms in center. The distances Se-Se=3,03⬚, Cu-Se=2,06-2,50⬚ and the lefts distance Cu-Ag=2,98⬚.

Regarding structural transformations Frueh and others [2] mention that only AgCuSe low-temperature modification is stable up to 463-438 K.

X-ray diffraction studies (XDS) [4] indicate that low-temperature orthorhombic phase in artificial AgCuSe single crystal at 504±1 K transforms to high-temperature FCC modification with lattice parameters a=4,105⬚. Structural transformations in AgCuSe are reversible and take place according to monocrystal-polycrystal model. Reason is the big difference in density, i.e. ρ=0,48 gr/cm³.

In current work the influence of partial isomorphic replacement of Se atoms by Te atoms on the structure and phase transitions in AgCuSe$_{0,5}$Te$_{0,5}$ has been considered.

II. SPECIMEN PREPARATION

Homogeneous AgCuSe$_{0,5}$Te$_{0,5}$ specimens were prepared by reacting appropriate elemental mixtures in double-wall ampoules 1,2mm in inner diameter and 10 cm in length, made of high-quality, thermally stable quartz which ensured quality containment and prevented oxidation of materials being synthesized. To avoid explosion as for the full homogenization of Se (T$_{melt}$=1357 K), Te (T$_{melt}$=725 K) with Ag (T$_{melt}$=1233,5 K) and Cu (T$_{melt}$=1375 K), temperature in the furnace was slowly set to the melting temperature of Se and to that of Te and was kept at each of then for two hours, then temperature was brought up to higher than Cu melting temperature at a rate of 50 K/hour. After two-hour exposure at that temperature with cycle vibration, ampoules were slowly cooled to 423 K and homogenized for 200 hours.

XRD studies have been carried out on DRON-3M (CuK$_α$ radiation, Ni- filtered) diffractometer. The powder XRD patterns taken form different parts of the sample showed identical sets of reflections, which could be indexed in orthorhombic unit cell of Cu$_2$Te with a=7,319⬚, b =22,236⬚, c=36,458⬚ [5], except for d=2,6823 and d=2,0590. Most of reflections could also be indexed on the basis of AgCuTe orthorhombic unit cell with a=4,1065⬚, b=20,4124⬚, c=6,2994⬚. Besides, some of interplanar distances could be indexed as (220), (222), (321), (400) and (440) which belong to primitive cubic phase with a=7,319⬚ (Table 1, Fig. 1).

This implies that replacement of some Se atoms by Te atoms in AgCuSe leads to three-phase state. AgCuSe$_{0,5}$Te$_{0,5}$ single crystals were obtained using experimentally found combination of vertical Bridgman process and slow cooling. Synthesized compounds were loaded into ampoules (specially made for Bridgman process) made of high quality quartz tubes 10 cm in length and 1 cm in inner diameter, which were then pumped down to 10^{-3} Pa.
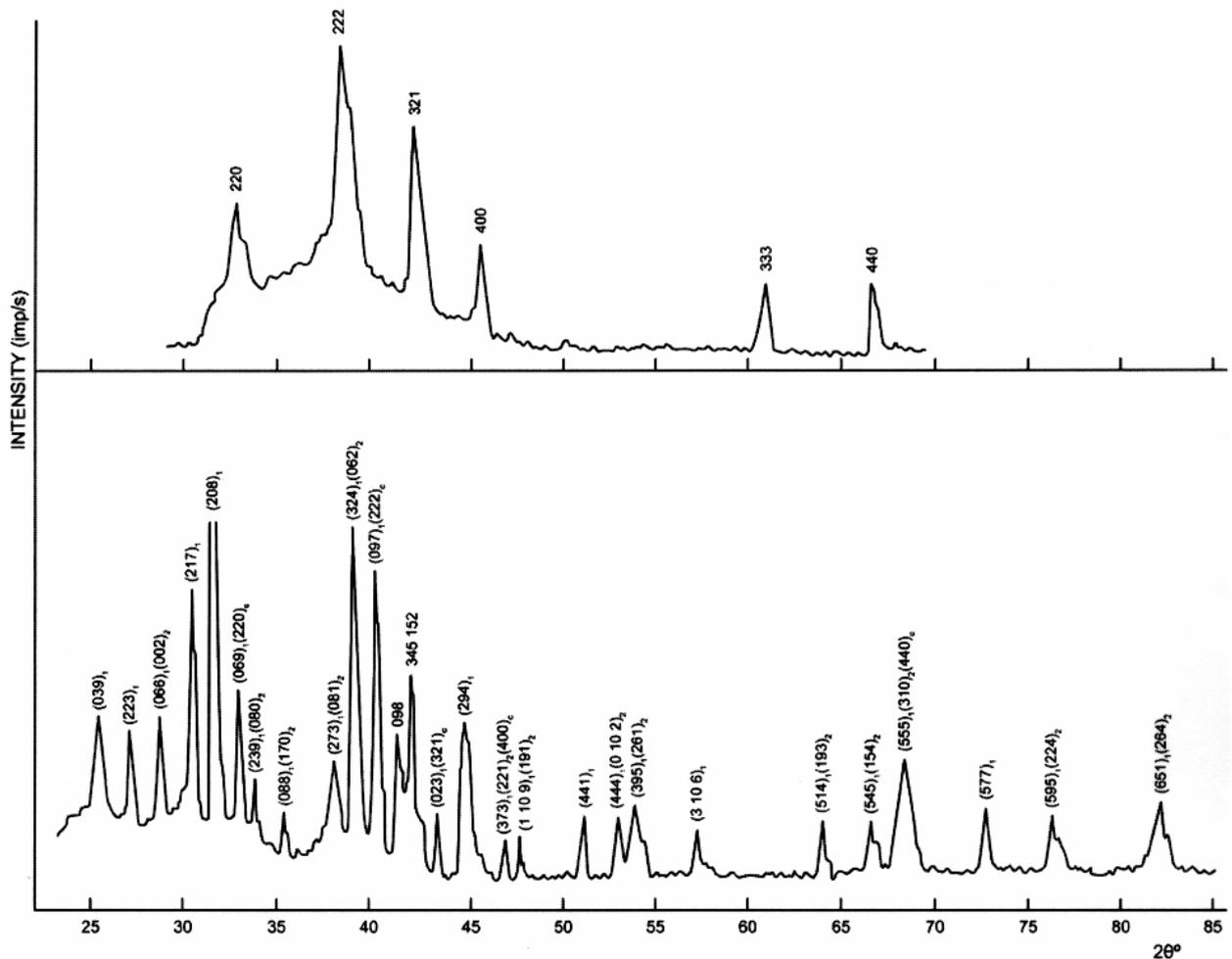
Fig.1. Fragments of diffraction patterns of $AgCuSe_{0,5}Te_{0,5}$ crystas. $(hkl)_1$ – orthorhombic phase of Cu_2Te; $(hkl)_2$ – orthorhombic phase of AgCuSe and $(hkl)_c$- cubic phase

Ampoules were placed to upper zone of three-zone furnace equipped with a temperature controller. Temperature of upper zone was set 50 degree higher and temperature of the second zone to 50 degree lower than melting temperature of Cu_2Te (T_{melt}=1400 K). In the furnace upper zone the compound was in molten state. Nucleus of high temperature phase is formed when sharp end of ampoule enters second zone. Moving ampoule at the rate of 2mm/hour was found suitable for nucleus growth. During further ampoule lowering it passes through all temperature points of structural transitions. When the ampoule passed second zone to the third one, both upper zones of the furnace have been turned off, ampoule motion stopped and the third one, both upper zones of the furnace have been turned off, ampoule motion stopped and the grown crystals were annealed in third zone at constant temperature (400K) for four weeks. Obtained samples of $AgCuSe_{0,50}Te_{0,50}$ were single-crystals, but quality mainly depends on the type of phase transitions.

III. RESULTS

High-temperature XRD studies were carried out in vacuum (10^{-1} Pa) in a continuous scan mode on the same diffractometer equipped with a URVT-2000 high-temperature attachment. Angular resolution was≈0,1′. Diffraction angles were measured with an accuracy $\Delta\theta=\pm0,02°$.

At room temperature, the XRD patterns form 5×5×1 mm arbitrary oriented $AgCuSe_{0,5}Te_{0,5}$ single-crystal showed 22 diffraction peaks. They matched peaks form synthesized sample (in Table 1 they marked[*]). As we see on Table 1 and Fig. 1, $AgCuSe_{0,5}Te_{0,5}$ consist of three phases: the first phase is identical to low-temperature Cu_2Te as regards size of unit cell, the second phase has unit cell that corresponds to low-temperature phase of AgCuSe and metastably existing primitive cubic phases. Most diffraction peaks form three phases being observed overlap each other. The reason of being multi-phase of $AgCuSe_{0,5}Te_{0,5}$ compound is mainly distribution of anions (Se and Te) and cations (Ag and Cu) respectively.

Table 1. Powder XRD data for AgCuSe$_{0,50}$Te$_{0,50}$

T	θ	$\dfrac{I}{I_0}$	$d_{exp.}$(Å)	Cu$_2$Te		CuAgSe		Cubic		Lattice parameters, Å
				$d_{exp.}$(Å)	hkl	$d_{exp.}$(Å)	hkl	$d_{exp.}$(Å)	hkl	
290 K	12⁰32′	30	3,5525	3,5546	039	-	-	-	-	
	13⁰20′	20	3,3430	3,3430	223	-	-	-	-	
	14⁰06′	25	3,1646*	3,1646	071,066	3,1550	002	-	-	
	15⁰03′	50	2,9696*	2,9675	217	-	-	-	-	
	15⁰41′	100	2,8520*	2,8534	208	-	-	-	-	Cu$_2$Te
	16⁰23′	35	2,7336*	2,7344	069	-	-	2,7276	220	a=7,319
	16⁰42′	14	2,6823*	-	-	2,6813	042	-	-	b=22,236
	17⁰36′	10	2,5493*	2,5498	239	2,5437	080	-	-	c= 36,458
	18⁰56′	15	2,3756*	2,3736	088	2,3725	170	-	-	
	19⁰07′	15	2,3539*	2,3536	273	2,3593	081	-	-	
	19⁰33′	65	2,3039*	2,3055	324	2,3101	062	-	-	
	20⁰12′	55	2,2336*	2,2322	097	-	-	2,2271	222	
	20⁰48′	25	2,1709*	2,1720	098	-	-	-	-	
	21⁰09′	40	2,1366*	2,1360	345	2,1312	152	-	-	CuAgSe
	21⁰59′	8	2,0590	-	-	2,0598	023	2,0619	321	
	22⁰42′	30	1,9977*	1,9979	294	-	-	-	-	a=4,1065
	23⁰ 41′	4	1,9196*	1,9108	273	1,9169	221	1,9287	400	b=20,4124
	24⁰11′	4	1,8821	1,8838	1 10 9	1,8896	191	-	-	c= 6,2994
	26⁰22′	10	1,7359*	1,7358	441	-	-	-	-	
	26⁰50′	10	1,7078*	1,7073	444	1,7101	0 10 2	-	-	
	27⁰09′	10	1,6895*	1,6889	395	1,6917	231	-	-	
	29⁰03′	5	1,5875*	1,5865	3 10 6	-	-	-	-	
	32⁰18′	7	1,4426*	1,4423	514	1,4419	193	-	-	Cubic
	33⁰42′	8	1,3895	1,3896	545	1,3847	154	-	-	
	34⁰22′	20	1,3356*	1,3658	555	1,3653	310	1,3638	440	a=7,7149
	36⁰45′	5	1,2884	1,2881	577	-	-	-	-	
	38⁰22′	8	1,2419*	1,2410	595	1,2414	224	-	-	
	41⁰00′	10	1,1750*	1,1758	651	1,1735	264	-	-	
373 K	15⁰40′	30	2,8551	2,8537	208	-	-	-	-	
	16⁰21′	4	2,7385	2,7385	069	-	-	2,7325	220	
	16⁰38′	20	2,6926	2,.6958	219	2,6880	042	-	-	Cu$_2$Te
	17⁰34′	15	2,5543	2,5528	177	2,5549	080	-	-	a=7,3127
	18⁰15′	20	2,4622	2,4641	178	-	-	-	-	b=22,3607
	18⁰36′	20	2,4165	2,4161	302	-	-	-	-	c= 36,5148
	19⁰30′	59	2,3095	2,3051	324	2,3168	062	-	-	
	20⁰10′	100	2,2358	2,2308	341	2,2277	171	2,2310	222	CuAgSe
	21⁰28′	32	2,1062	2,1077	353	-	-	-	-	
	21⁰54′	36	2,0668	2,0695	279	-	-	2,0656	321	a=4,1100
	23⁰39′	14	1,9220	-	-	1,9195	221	1,9322	400	b=20,4419
	25⁰58′	12	1,7604	1,7568	433	1,7604	260	-	-	c= 6,3224
	27⁰07′	10	1,6913	1,6925	395	1,6829	192	-	-	
	29⁰00′	10	1,5901	1,5905	3 10 6	1,5805	004	-	-	
	31⁰26′	9	1,4782	1,4838	486	1,4782	144	-	-	
	31⁰48′	4	1,4628	1,4594	510	1,4671	0 10 3	-	-	Cubic
	32⁰16′	2	1,4439	1,4411	514	1,4493	2 10 0	-	-	
	33⁰36′	20	1,3930	1,3901	545	1,3877	154	-	-	a=7,7287
	34⁰20′	5	1,3668	1,3662	555	1,3669	310	1,3662	440	
	37⁰12′	8	1,2751	1,2831	584	1,2751	283	-	-	
	39⁰03′	10	1,2237	1,2213	5 8 10	1,2275	045	-	-	
473 K	16⁰19′	38	2,7431	2,7431	220					
	20⁰08′	100	2,2397	2,2397	222					
	21⁰49′	75	2,0739	2,0716	321					a=7,7587
	23⁰25′	30	1,9398	1,9396	400					
	31⁰05′	30	1,4931	1,4931	333					
	34⁰12′	35	1,3714	1,3715	440					

Note: Diffraction peaks form crystal marked by*
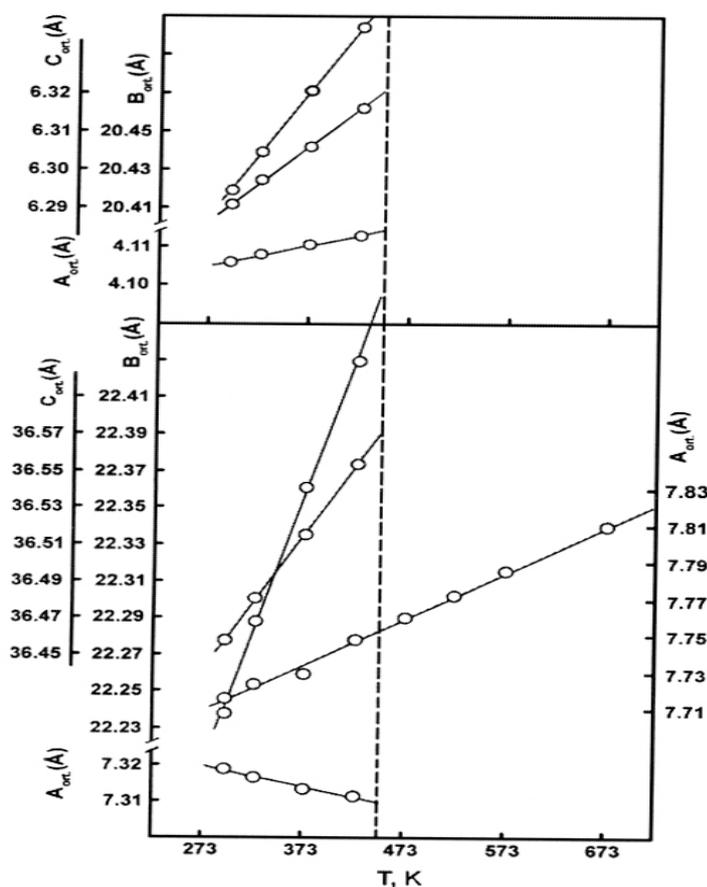
Fig.2. Temperature dependence of lattice parameters

After XRD patterns at room temperature have been recorded the furnace was turned on and reference recordings were taken every 50 K. The sample temperature prior to every record was kept constant for 40 minutes.

At these conditions $AgCuSe_{0,5}Te_{0,5}$ sample remains three-phase and at 444 ± 1 K both orthorhombic phases transform to primitive cubic one. These transitions are reversible, i.e. when cooled samples transform back to initial state.

Fig.2 shows temperature dependence of unit cell lattice parameters for all $AgCuSe_{0,5}Te_{0,5}$ phases existing in the temperature range 293-673 K. It is seen that parameters of bouth orthorhombic and cubic phases increase linearly with temperature. As it is seen form Fig.2 while both orthorhombic phases transform to cubic, parameter $a_c = f(t)$ does not deviate form linearity. It follows that cubic phase acts as nucleated in transitions process of both orthorhombic phases.

Form temperature dependence of lattice parameters thermal expansion coefficient has been calculated for the first orthorhombic phase crystallizing as Cu_2Te structure 10^{-6} K^{-1}: $\alpha_{[100]}= -10,76$, $\alpha_{[010]}=70,10$, $\alpha_{[001]}=19,47$; for the second orthorhombic phase crystallizing as AgCuSe structure $\alpha_{[100]}= 10,65$, $\alpha_{[010]}= 18,06$, $\alpha_{[001]}= 45,63$ and cubic phase $\alpha= 22,36$.

IV. CONCLUSION

Thermal expansion coefficients of both orthorhombic phases along different crystallographic directions are very big and strong anisotropy takes place. Coefficient of thermal expansion for orthorhombic phase crystallized as Cu_2Te structure along [100] is negative.

Strong anisotropy of thermal expansion coefficient is one of the main reasons of lattice instability of both orthorhombic phases.

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