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THERMODYNAMIC STABILITY OF PHASES IN THE Bi–Sr–Cu–(O) SYSTEM

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Abstract

An effort for a better understanding of the phase formation and their stability in the ternary system Bi_2O_3–SrO–CuO led to investigations of the phase equilibria, particularly in the sub-solidus region. To extend this phase region about the respective solid-liquid equilibria the isothermal and pseudobinary cuts of the $BiO_{1.5}$–SrO–CuO ternary system in the temperature range from 810 to 850°C were determined. A particular attention was also devoted to the thermodynamic stability of the $Bi_{2+x}Sr_{2-y}CuO_{6+\delta}$ phase.

Keywords: bismuth phase superconductors, DTA, phase diagram, solid-liquid equilibria, superconducting phase, X-ray analysis

Introduction

In spite of a relatively long time since the first report on the superconductivity in ternary bismuth cuprates an interest about them still outlasts. The superconducting bismuth cuprates form a family of phases with a layered structure. Their composition can be formally expressed by the general formula $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ with $n=1,2,3$ depending on a number of $(CuO_2)_n$ layers. In fact all these phases exhibit a certain variation of the cation ratio and the real composition can be different from the stoichiometric one.

A typical example is the first member of the series, ($n=1$), which forms a relatively large homogeneity region of the pseudotetragonal solid solution ($a\cong b\cong 5.38$ Å, $c=4.59$ Å) lying outside the ideal composition $Bi_2Sr_2Cu_1O_{6+\delta}$ [1–9]. This solid solution (R) is formed by partial substitution of bismuth for strontium. In addition, if the excess of Bi (x) exceeds the deficit of Sr (y) in the general formula $Bi_{2+x}Sr_{2-y}CuO_{6+\delta}$, a part of Bi sites in –BiO– planes is probably occupied by copper [8, 9]. There is, however, a rather large discrepancy in the results of the individual authors as regards the stability of the solid solution. Very close to the nominal stoichiometry $Bi_2Sr_2CuO_6$ another phase (I) exists with the monoclinic C-centered symmetry and lattice parameters $a=24.451$ Å, $b=5.425$ Å, $c=21.95$ Å, and $\beta=105.41°$ [1].

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In this context it is evident that the investigation of the respective phase equilibria has the fundamental importance. Many authors devoted an attention to the sub-solidus region [2–10]. However, there is apparently little known about respective solid–liquid equilibria, although such knowledge has the essential importance for the growth of the single crystals. Therefore the present work was also devoted to the determination of the equilibria of the above mentioned phases with liquid. To estimate the evolution of these phase boundaries with increasing temperature the CuO–Bi_2SrO_4 pseudobinary phase diagram was also determined. Due to the wide spread of the experimental data concerning the determination of the thermodynamic stability region of the $Bi_{2+x}Sr_{2-y}CuO_{6+\delta}$ solid solutions a particular attention was devoted to the solution of this problem.

Experimental techniques

Preparation of samples

The samples of various composition were prepared by the usual mixing of the respective high purity powdered Bi_2O_3, $SrCO_3$, and CuO reagents at given ratios. The content of cation impurities being less than 0.01 weight% as well as the corrections for volatile impurities were determined by chemical analysis.

The samples used for the investigation of the equilibria in subsolidus region (single phase samples of $Bi_{2+x}Sr_{2-y}CuO_{6+\delta}$ and multi-phase samples of compositions in the vicinity of the homogeneity region) were calcined three times at the temperatures 760, 800, and 830°C for 24 h in each step. After the last calcination the mixtures were pressed into pellets of about 10 mm in diameter and 3 mm thick which were further heated for ~170 h at the temperature of the equilibrium studied, i.e. 850°C.

The precursors for the study of solid–liquid equilibria were calcined one time for 24 h at 725°C before pelletization. The final heat treatment was carried out repeatedly with an intermediate grinding at 750°C for the total time of 100 h. All procedures were performed in purified air.

Differential thermal analysis

Apparatus NETZSCH on line connected to computer and equipped by DDK measuring head with Pt-PtRh10 thermocouples and Pt crucibles was employed to determine the respective invariant points and liquidus curves. The temperature data were calibrated on the melting points of the well known metallic standards like Al, Ag, Au, Ni as well as on transition temperatures of ICTA standards.

Soaking experiments

The experimental procedure already successfully applied in Y–Ba–Cu–O and Bi–Sr–Cu–O system [11, 12] is based on a separation of the liquid phase from solid residue in the studied samples. The samples are placed on a highly porous alumina pellet into a horizontal tube furnace and there are heated for 24 h. The liquid phase arising due to a partial melting of the sample is soaked into the Al_2O_3 substrate until the solid residue becomes almost free of the liquid. The chemical composition of the solid residue is then checked by chemical analysis and the chemical composition of the liquid phase (expressed in molar fractions) can be calculated according to the equations derived from the lever rule:

$$X_B^L = (X_B^O M_R - X_B^R M_O \omega)/(M_R - M_O \omega) \tag{1}$$

$$X_C^L = (X_C^O M_R - X_C^R M_O \omega)/(M_R - M_O \omega) \tag{2}$$

where B = $BiO_{1.5}$, C = CuO; *O, L, R,* designate original sample, liquid and solid residue, respectively; M_O and M_R are 'molecular weights' and $\omega = w_R/w_O$ the weight ratios of the solid residue and the original sample.

Table 1

	$Bi_{2+x}Sr_{2-y}O_{6+\delta}$				$Bi_{2+x}Sr_{2-y}O_{6+\delta}$		
	x	y	phase comp.		x	y	phase comp.
1	0.0	0.0	*I, R*	14	0.6	0.6	*R*, β, *L*
2	0.0	0.1	*I, R*	15	0.07	0.2	*R*
3	0.0	0.2	*I, R*	16	0.08	0.25	*R*
4	0.0	0.3	*R*	17	0.1	0.3	*R*
5	0.0	0.4	*R*	18	0.13	0.4	*R*
6	0.0	0.5	*R*	19	0.17	0.5	*R*
7	0.0	0.6	*R,C*	20	0.0	–0.1	*I*, B_2S_3
8	0.1	0.1	*I, R*	21	0.3	0.0	*R, I*, γ
9	0.15	0.15	*R*	22	0.6	0.0	*R*, γ
10	0.2	0.2	*R*	23	0.75	–0.5	*I, R*
11	0.3	0.3	*R*	24	0.19	–0.13	*I, R*
12	0.4	0.4	*R*	25	0.43	–0.28	*I, R*
13	0.5	0.5	*R*, β,*L*	26			

I– ~ $Bi_2Sr_2CuO_{6+\delta}$, *R*– $Bi_{2+x}Sr_{2-y}CuO_{6+\delta}$, *L*– liquid phase, B_2S_3– $Bi_2Sr_3O_6$, β– rhombohedral solid solution $(Bi,Cu)_{1+x}SrO_\gamma$, γ– tetragonal solid solution near $Bi_{1.22}SrO_\gamma$, C–CuO

X-ray analysis

The X-ray analysis was carried out using X-ray diffractometer DRON-III; CuK_{α} radiation filtered by Ni-filter was employed. The phases present in the investigated samples were identified by a comparison with reported diffraction data [1, 7, 13, 14] and data obtained from the X-ray analysis of the additionally prepared phases, namely Bi_2SrO_4, Bi_2CuO_4, $(BiO_{1.5})_{1-x}(SrO)_x$ and $Bi_{2+x}Sr_{2-y}CuO_{6+\delta}$ solid solutions.

Chemical analysis

The contents of Bi, Sr and Cu were determined by various methods of chemical analysis. Two methods were used for the determination of Bi contents, complexometry for samples of high Bi concentrations and atomic absorption spectrometry at 306.8 nm in the air-acetylene flame for Bi contents lower than 20 wt%. The latter method was also used for the determination of Sr and Cu. Relative standard deviations estimated from two parallel sets of Bi, Sr and Cu determinations were 2.1, 1.5 and 1.3 rel%, respectively.

The composition homogeneity of the single phase $Bi_{2+x}Sr_{2-y}CuO_{6+\delta}$ samples was checked using the electron microprobe analysis (JEOL SUPER-

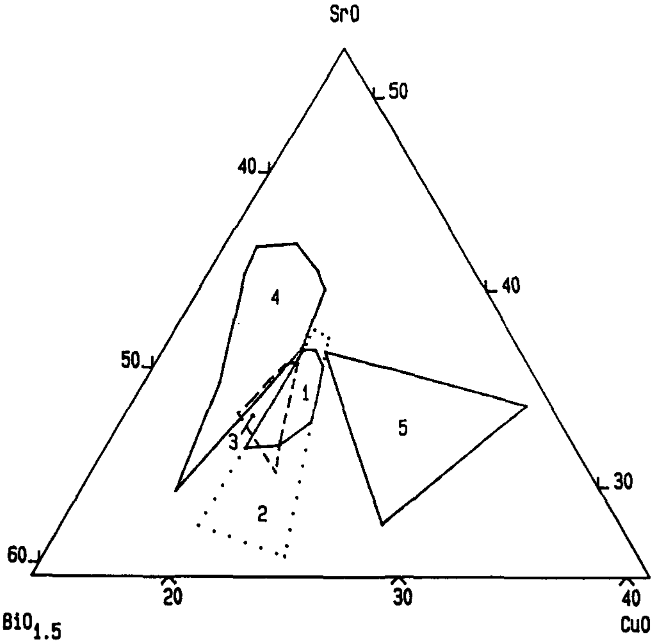

Fig. 1a The region of thermodynamic stability of the solid solutions *R* (1- our results [9], 2- Ikeda [4], 3- Roth [1, 7], 4- Schulze [6], and 5- Horyñ [3])

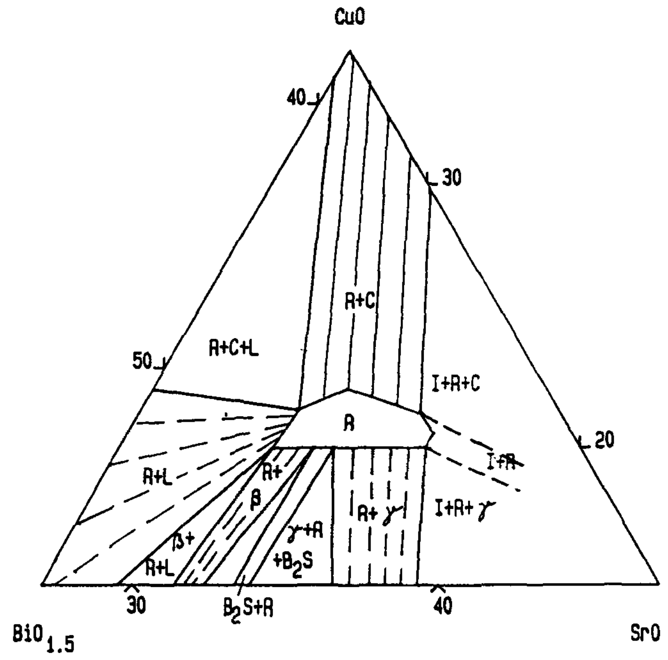

Fig. 1b Proposed phase equilibria of the *R*-phase with the monoclinic $Bi_2Sr_2Cu_1O_{6+\delta}$ phase (I), CuO (C), melt (L), β and γ (solid solutions in $BiO_{1.5}$–SrO binary system) at 850°C in air

PROBE 733) in line scan profile regime. The found fluctuations of composition did not exceed 4 rel%.

The values of the mean valence state (total oxygen stoichiometry) were not determined in the present study and it is therefore supposed that in the studied samples bismuth is present in trivalent state and copper in bivalent state.

Results and discussion

Isothermal cuts of the $BiO_{1.5}$–SrO–CuO phase diagram

The differential thermal analysis of the $Bi_{2+x}Sr_{2-y}CuO_{6+delta}$ samples showed two endothermic peaks with the onset temperatures of about 880 and 890°C, respectively. The first one can be attributed to the peritectic decomposition of the *R*-phase into a liquid and the monoclinic '*I*' phase. The peritectic effect was proved by separating the melt by use of soaking method, while in the solid residue only '*I*' phase was detected. The second peak is ascribed to the subsequent melting of the separated '*I*' phase. Thus it was possible to restrict the study on the solid-liquid equilibria within 800–850°C temperature range.

Table 2 List of soaking experiments

No.	Starting composition			Heating	Solid residue					Liquid phase	
					Phase analysis	Weight fraction	Chemical analysis			Calculated composition	
	$X_{BiO_{1.5}}$/	X_{SrO}/	X_{CuO}/	T/			$X_{BiO_{1.5}}$/	X_{SrO}/	X_{CuO}/	$X_{BiO_{1.5}}$	X_{CuO}
		mol%		°C				mol%		mol%	
1	90	5.0	5.0	800	$B+\beta$	0.1069	92.75	6.14	1.11	89.68	5.45
2	70	15.0	15.0	800	β	0.6927	77.84	7.60	14.55	54.96	15.86
3	62	23.8	14.2	800	β	0.4235	70.99	14.65	14.37	55.81	14.09
4	62	23.8	14.2	800	β	0.2372	69.90	15.94	14.16	59.59	14.20
5	60	10.0	30.0	800	C	0.0818	9.96	1.07	88.97	68.81	19.62
6	56	24.5	19.5	800	R	0.8778	61.10	19.83	19.07	21.84	28.25
7	50	17.5	32.5	800	$R+C$	0.2135	24.56	13.05	62.39	60.12	20.60
8	65	5.0	30.0	800	B_2C+C	0.5073	63.24	0.34	36.42	66.89	23.09

Table 2 Contiuned

No.	Starting composition			Heating	Solid residue					Liquid phase	
					Phase analysis	Weight fraction	Chemical analysis			Calculated composition	
	$X_{BiO_{1.5}}$/	X_{SrO}/	X_{CuO}/	T/			$X_{BiO_{1.5}}$/	X_{SrO}/	X_{CuO}/	$X_{BiO_{1.5}}$/	X_{CuO}/
		mol%		°C				mol%		mol%	
9	65	5.0	30.0	850	C	0.0505	5.12	<0.10	94.72	71.96	22.47
10	65	5.0	30.0	850	C	0.0326	6.86	<0.10	93.03	69.05	25.61
11	65	5.0	30.0	850	C	0.0535	6.86	<0.10	93.03	71.97	22.44
13	60	30.0	10.0	850	$\beta+R$	0.2849	62.15	30.92	6.93	59.16	11.19
14	60	10.0	30.0	850	C	0.0623	0.55	<0.10	99.35	69.26	19.19
15	56	24.5	19.5	850	R	0.6377	59.69	22.34	17.96	50.00	22.00
16	55	27.5	17.5	850	R	0.8138	60.94	22.48	16.57	34.21	20.75
17	55	27.5	17.5	850	R	0.6802	57.06	21.14	21.80	50.75	8.62
18	52.5	26.25	21.25	850	R	0.6319	56.22	20.58	23.20	46.87	18.30
19	50	17.5	32.5	850	$R+C$	0.0916	15.47	5.94	78.58	55.64	24.97
20	50	17.5	32.5	850	$R+C$	0.0852	7.48	3.33	89.19	57.44	22.58
21	49	32.5	18.5	850	R	0.5579	56.82	24.98	18.20	40.36	18.83

The results of the phase analysis of the samples the composition of which is expressed by the general formula $Bi_{2+x}Sr_{2-y}CuO_{6+\delta}$ and is situated both inside and in the close surrounding of the supposed homogeneity region of the *R*-phase are summarized in Table 1.

The determined existence region of this solid solution is depicted in the phase diagram (Fig. 1) for the temperature of 850°C. Figure 1a shows our stability region of the *R*-phase compared to the results of several studies published before [1, 3, 4, 6]. In contrast to a strong discrepancy with the most of previous works [2, 3, 6] a relatively good agreement was achieved with the study of Roth [1, 7] and Fleming [8]. Nevertheless let us note that according to our findings the stability region of the *R*-phase shifts towards lower concentrations of Bi ions, which resembles the results of Ikeda *et al.* [4]. However, in comparison with this study we found the border series $x=0$ and $x=y$ to be limited only in the range of $0.3 \le y \le 0.5$ and $0.15 \le y \le 0.4$, respectively. In the series in which the coefficients are related by $x=y/3$ the phase is stable for $0.2 \le y \le 0.5$. On (Fig. 1b) there is an enlarged area of the phase diagram (850°C, air) showing the equilibria of the tetragonal solid solutions *R* with other phases in the Bi- and Cu-rich part of pseudoternary system of interest.

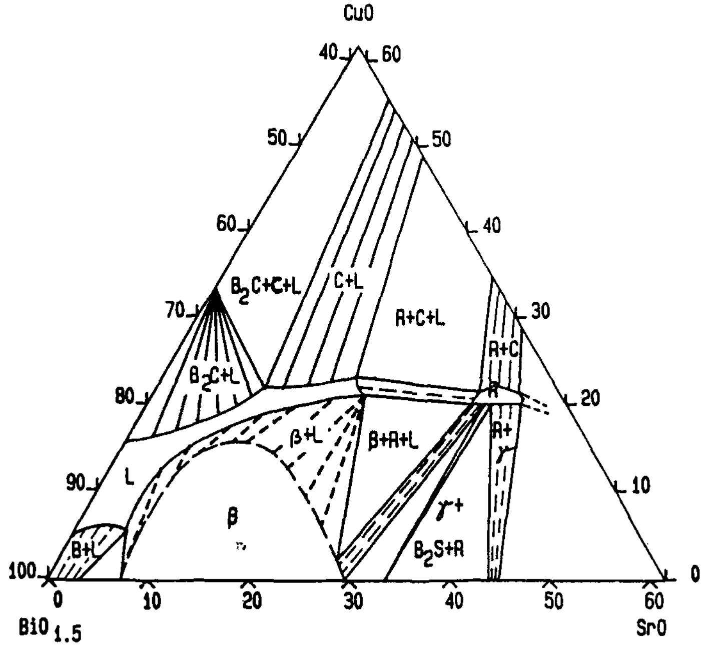

Fig. 2 Isothermal cut of Bi–Sr–Cu–(O) ternary phase diagram in air at 800°C (capitals denote the coexisting phases: C–CuO, B-Bi_2O_3, β–$(BiO_{1.5})_{1-x}(SrO)_x$, B_2C –Bi_2CuO_4, I-$Bi_2Sr_2CuO_6$, *R*–$Bi_{2+x}Sr_{2-y}CuO_{6+\delta}$ and L-melt; full lines – boundaries proposed according to the determined data; dashed lines – estimated boundaries and conodes)

The results obtained during the soaking experiments at 800 and 850°C, i.e. the determined phases and chemical compositions of the solid residues together with compositions of the coexisting liquid phase calculated according to the Eqs (1) and (2) are listed in Table 2. The reproducibility of the calculated data is given by an uncertainty of the compositions which was less than 2.46 mol% for $BiO_{1.5}$ and 0.99 mol% for CuO components.

Besides that an attention was paid to rhombohedral solid solutions $(BiO_{1.5})_{1-x}(SrO)_x$ (β). In contrast to the data reported in [7, 14, 15] the width of their existence region deduced from the determined composition dependence of the c lattice parameter was found to be $0.72 \leq x \leq 0.92$. In addition, let us note that according to our finding the existence region of the solid solutions extends into the ternary system $BiO_{1.5}$–SrO–CuO up to ~15 mol% CuO.

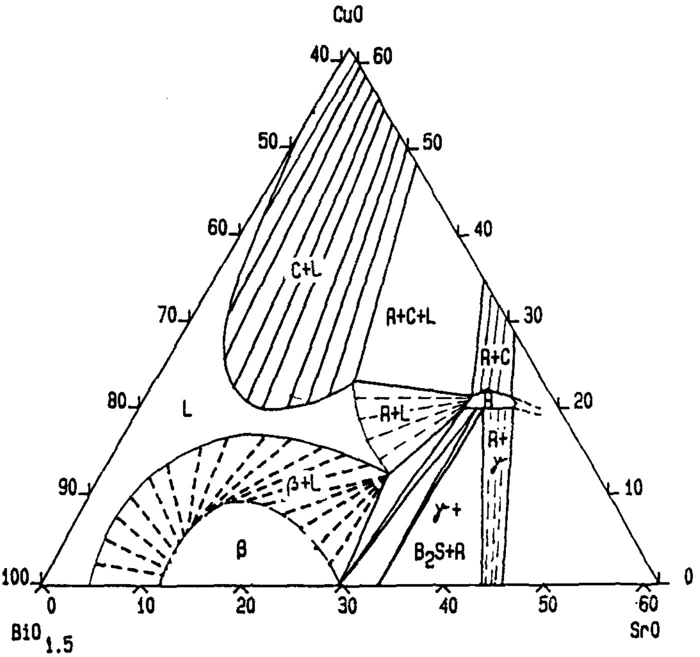

Fig. 3 Isothermal cut of Bi–Sr–Cu–(O) ternary phase diagram in air at 850°C (capitals denote the coexisting phases: C–CuO, B–Bi_2O_3, β–$(BiO_{1.5})_{1-x}(SrO)_x$, B_2C–Bi_2CuO_4, I–$Bi_2Sr_2CuO_6$, R-$Bi_{2+x}Sr_{2-y}CuO_{6+\gamma}$ and L-melt; full lines – boundaries proposed according to the determined data; dashed lines – estimated boundaries an conodes)

Our experimental data were further completed by the extends of the $BiO_{1.5}$+L, L and Bi_2CuO_4+L regions lying on $BiO_{1.5}$–CuO line, extracted from the phase diagram reported in [16]. Thus it was possible to propose the particular phase boundaries at 810 and 850°C in a limited part of the studied system, see Figs 2 and 3.

Pseudobinary Bi_2SrO_4–CuO phase diagram

To estimate the evolution of the above proposed phase boundaries with increasing temperature the Bi_2SrO_4–CuO pseudobinary phase diagram was investigated. The study was carried out on the series of prepared samples $(x)Bi_2SrO_4.(1-x)CuO$. The composition was changed within the range from $x=0$ to $x=0.5$ by the step varying from 0.0125 to 0.1. DTA showed several sets of endothermic peaks which are denoted in Fig. 4 by the open circles and can be ascribed successively to the effects summarized in Table 3. The other ones can be attributed to the liquidus temperatures of the individual Bi_2SrO_4, *R* and CuO phases.

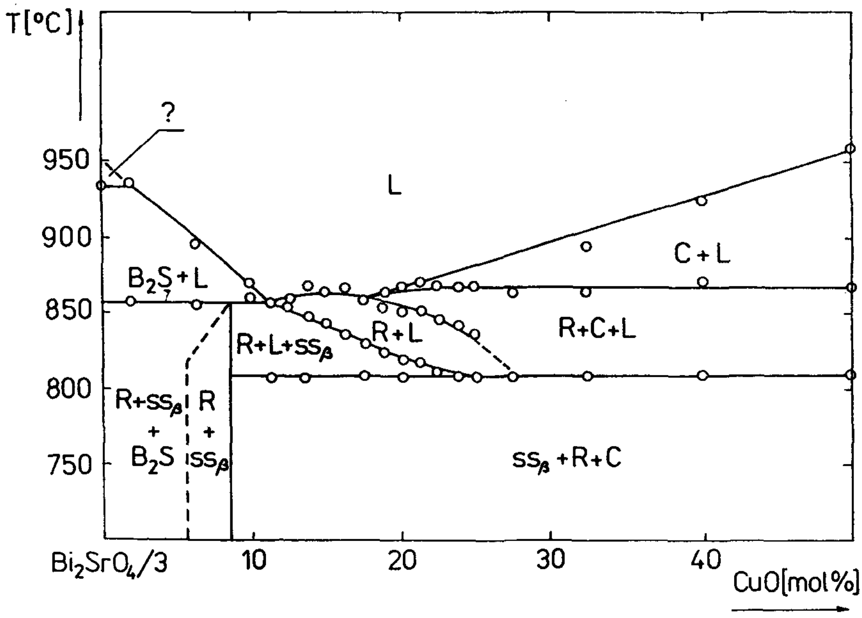

Fig. 4 Phase diagram of the Bi_2SrO_4–CuO pseudobinary system in air (capitals denote coexisting phases *R*-$Bi_{2+x}Sr_{2-y}CuO_{6+\gamma}$, ss$_\beta$ – $(BiO_{1.5})_{1-x}(SrO)_x$, and L-melt; open circles – DTA experiments)

Table 3

Observed and identified endothermic effects		
Temperature/ °C	Compositional range/ mol% CuO	Effect
810	8.5–50	ternary eutectic melting
810–855	0.0–23	melting of β
855–865	20.0–50	peritectic reaction R + C + L = C + L

Table 4 Phase analysis of the annealed samples and solid residues from the soaking experiments

Starting composition			Temperature/Phases						
$X_{BiO_{1.5}}$/	X_{SrO}/	X_{CuO}/	750/	800/	825/	850/	875/	900/	925/
	mol%					°C			
66.66	33.33	00.00	B_2S	B_2S	B_2S	B_2S	B_2S	B_2S	B_2S
65.55	32.78	01.67	$B_2S+ss_\beta+R$	$B_2S+ss_\beta+R$	$B_2S+ss_\beta+R$	$B_2S+ss_\beta+R$	B_2S+L	B_2S+L	B_2S+L
62.50	31.25	06.25	$ss_\beta+R$	$ss_\beta+R$	$ss_\beta+R$	$B_2S+ss_\beta+R$	B_2S+L	B_2S+L	L
60.00	30.00	10.00	$ss_\beta+R+C$	$ss_\beta+R+C$	$ss_\beta+R$+L	$ss_\beta+R$+L	L	L	L
57.50	28.75	13.75	$ss_\beta+R+C$	$ss_\beta+R+C$	$ss_\beta+R$+L	R+L+(?ss_β)	L	L	L
55.00	27.50	17.50	$ss_\beta+R+C$	$ss_\beta+R+C$	$ss_\beta+R$+L	R+L+(?ss_β)	L	L	L
52.50	26.25	21.25	$ss_\beta+R+C$	$ss_\beta+R+C$	R+L+(?ss_β)	R+L+(?ss_β)	L	L	L
50.00	25.00	25.00	$ss_\beta+R+C$	$ss_\beta+R+C$	$R+C$+L+(?ss_β)	$R+C$+L+(?ss_β)	C+L	L	L
45.00	22.50	32.50	$ss_\beta+R+C$	$ss_\beta+R+C$	$R+C$+L+(?ss_β)	$R+C$+L+(?ss_β)	C+L	C+L	L
40.00	20.00	40.00	$ss_\beta+R+C$	$ss_\beta+R+C$	$R+C$+L+(?ss_β)	$R+C$+L+(?ss_β)	C+L	C+L	C+L
33.33	16.67	50.00	$ss_\beta+R+C$	$ss_\beta+R+C$	$R+C$+L+(?ss_β)	$R+C$+L+(?ss_β)	C+L	C+L	C+L

B_2S – Bi_2SrO_4, ss_β – $(BiO_{1.5})_{1-x}(SrO)_x$, R – $Bi_{2+x}Sr_{2-y}CuO_6+\gamma$, C – CuO

The regions established using the thermoanalytical data were further precised by the X-ray phase analysis of the annealed and soaked samples, see Table 4. Unfortunately, the separation of the liquid phase from the solid residue up to 850°C was incomplete. Thus the recrystallized β-phase was also detected in the region where its presence is thermodynamically excluded and it made extremely difficult to clarify the phase equilibria in the concentration range of 18–50 mol% CuO.

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Zusammenfassung — Ein Versuch zum besseren Verständnis der Phasenbildung und Phasenstabilität im ternären System Bi_2O_3–SrO–CuO führte zu Untersuchungen des Phasengleichgewichtes, insbesondere in der sub-solidus Region. Zur Erweiterung dieser Phasenregion über das jeweilige Fest-Flüssig-Gleichgewicht hinaus wurden isotherme und pseudobinäre Schnitte des ternären Systemes $BiO_{1.5}$–SrO–CuO im Temperaturbereich von 810 bis 850°C ermittelt. Besonderes Augenmerk wurde der thermodynamischen Stabilität der Phase $Bi_{2+x}Sr_{2-y}CuO_{6+\delta}$ geschenkt.