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Effect of elementary Se and Te on the sign of the temperature coefficient of electroconductivity of metallic Sb and Bi

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The effect of Se and Te additions on the electroconductivity of molten Sb and Bi was investigated. The compositions of the systems metal (Sb, Bi) – chalcogen (Se, Te), where sign inversion of the temperature coefficient of electroconductivity takes place, were determined. Changes of the values and character of the conductivity in the investigated systems are explained by chemical interaction of the components and by modification of the chemical bonds from metallic (for Sb and Bi) to covalent, characteristic of chalcogenides.

Electroconductivity / Temperature coefficient / Melts

Introduction

It is well known that the temperature dependence of the electroconductivity of metals is characterized by a negative temperature coefficient. From scientific and practical viewpoints it is interesting to determine the concentration correlation metal–chalcogen where the electroconductivity of a chemical system changes its temperature dependence.

Melts of the systems Sb–Se, Sb–Te, Bi–Se, and Bi–Te were investigated in a wide temperature interval to determine the concentration limits of the effect of the chalcogens (Se, Te) on the properties of natural metals (Sb, Bi), namely the temperature dependence of electroconductivity.

Experimental

The samples were prepared by direct fusion with periodic mixing of appropriate quantities of metal and chalcogen, in quartz test tubes with an inert atmosphere of Ar, at temperatures 50°C higher than the melting point of the metal. After synthesis the samples were analyzed by methods described in [1-3].

The electroconductivity of metallic Sb and Bi was investigated by the contact method in a quartz cell with a constant not lower than 10^3 cm^{-1}, using an alternating current.

Results and discussion

The effect of Se and Te on the sign of the temperature coefficient of electroconductivity ($\Delta\sigma/\Delta T$) of metallic Sb and Bi was investigated.

System Sb–Se. The electroconductivity (σ) of Sb melts with 0, 4.0 or 14.0 at.% Se was measured at different temperatures. The results are given in Fig. 1.

As Fig. 1 shows, the electroconductivity of pure Sb melts and Sb melts with small Se additives is high (several thousands of S/cm) and has a negative temperature coefficient.

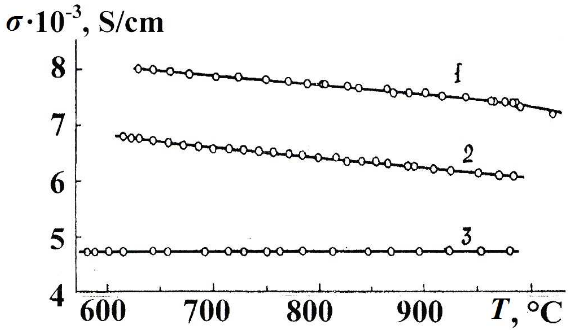


Fig. 1 Electroconductivity polytherms for Sb–Se melts: 1 – 0, 2 – 4.0, 3 – 14.0 at.% Se.

Fig. 1 shows that the electroconductivity of composition 3 is independent of temperature ($\Delta\sigma/\Delta T = 0$). An increase of the Se content to more than 14 at.% leads to inversion of the temperature coefficient.

System Sb–Te. The electroconductivity was investigated for melts with 9.6, 19.3, and 29.0 at.% Te at different temperatures. The results are given in Table 1.

As shown in Table 1, σ for pure antimony, and for the sample with 9.6 at.% Te, decreases with increasing temperature. For the composition with 19.3 at.% Te, a slow increase of the electroconductivity is observed at the beginning, and then, starting from 650°C, σ slowly decreases. Further increase of the Te content is accompanied by a change of the temperature coefficient from negative to positive, and the electroconductivity increases with increasing temperature.

System Bi–Se. The electroconductivity of Bi–Se melts in the composition interval from 0 to 53.3 at.% Se was investigated at different temperatures. The experimental results are given in Table 2.

The data in Table 2 show that increasing Se contents in molten Bi decrease the electroconductivity and change its character. The electroconductivity of the melts 1–4 is characterized by a negative temperature coefficient. The absolute value of the coefficient becomes smaller with increasing Se content, and approaches zero for composition 4. For composition 5, the sign of the temperature coefficient $\Delta\sigma/\Delta T$ becomes positive.

System Bi–Te. The electroconductivity of six melts containing from 0 to 60.03 at.% Te was studied at different temperatures.

The experimental results are given in Fig. 2. The electroconductivity of melts of all the investigated compositions is high, reaching values of thousands of S/cm.

The electroconductivity of compositions 1, 2, and 3 decreases slightly with increasing temperature, and $\Delta\sigma/\Delta T$ is practically independent of temperature. The electroconductivity of compositions 4 and 5 has similar character: the polytherms show a concavity to the temperature axis. For composition 6 (60.03 at.% Te) the electroconductivity has a positive temperature coefficient in the whole temperature interval.

Reciprocal peculiarities of the influence of the components on the electroconductivity are shown in Fig. 3, where σ isotherms are drawn for the investigated systems.

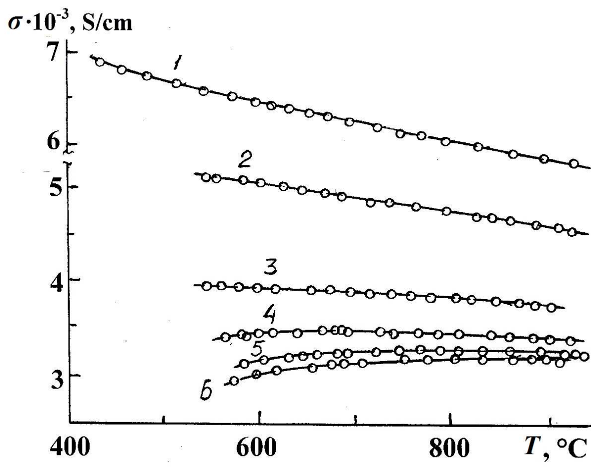


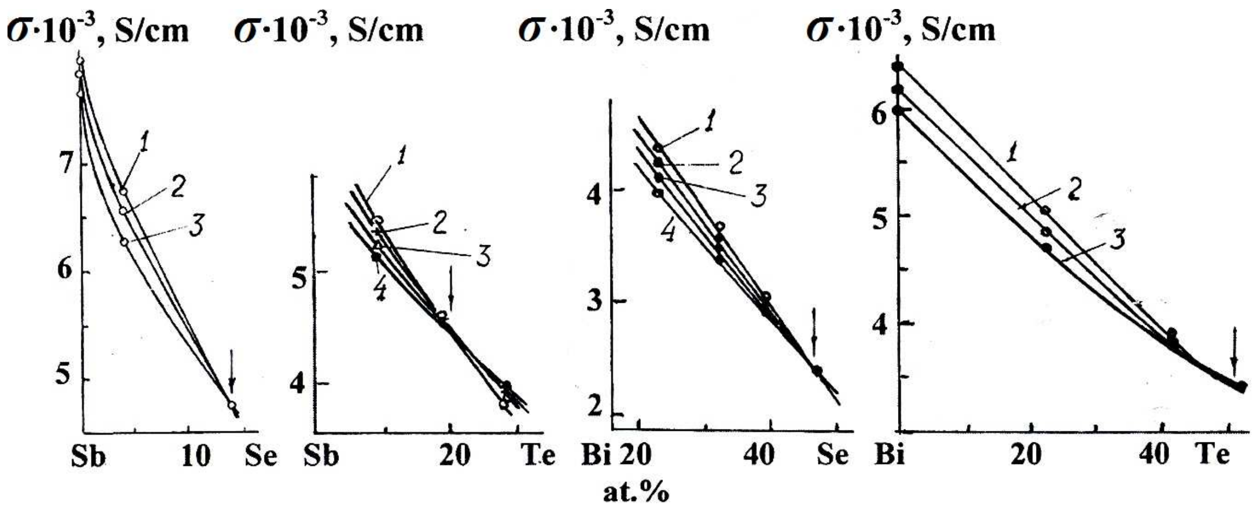
Fig. 2 Electroconductivity polytherms for Bi–Te melts: 1 – 0, 2 – 22.41, 3 – 41.71, 4 – 52.24, 5 – 57.84, 6 – 60.03 at.% Te.

Table 1 Electroconductivity of molten samples in the system Sb–Te.

Sb		9.6 at.% Te		19.3 at.% Te		29.0 at.% Te	
T, °C	*σ*, S/cm	*T*, °C	*σ*, S/cm	*T*, °C	*σ*, S/cm	*T*, °C	*σ*, S/cm
1020	7204	983	5117	1022	4470	964	3932
990	7313	952	5117	980	4470	924	3932
983	7351	910	5154	952	4470	896	3932
976	7427	868	5179	924	4518	868	3946
963	7427	840	5243	896	4518	828	3969
940	7504	798	5282	868	4566	805	3969
902	7583	770	5309	816	4566	787	3969
865	7664	728	5349	784	4616	757	3969
827	7705	700	5376	757	4616	728	3969
804	7746	675	5417	722	4616	700	3932
771	7788	644	5445	700	4636	667	3896
752	7830	613	5445	672	4636	644	3860
703	7873	600	5473	644	4636	612	3791
660	7960	594	5588	616	4616	560	3629
630	8004	588	5588	567	4470	541	3539

Table 2 Electroconductivity of molten samples in the system Bi–Se.

Bi (1)		22.8 at.% Se (2)		38.9 at.% Se (3)		46.8 at.% Se (4)		53.3 at.% Se (5)	
T, °C	*σ*, S/cm	*T*, °C	*σ*, S/cm	*T*, °C	*σ*, S/cm	*T*, °C	*σ*, S/cm	*T*, °C	*σ*, S/cm
932	5768	1014	3937	1019	2893	1012	2370	1016	1942
900	5820	1004	3832	1018	2888	1007	2370	983	1946
871	5864	980	4025	1009	2892	992	2370	961	1963
834	5935	961	4047	987	2905	980	2370	938	1958
800	6020	937	4070	983	2905	948	2378	916	1947
776	6076	902	4117	955	2928	921	2385	889	1936
754	6089	885	4095	925	2940	888	2393	864	1921
729	6159	850	4164	890	2965	858	2401	830	1901
700	6220	819	4213	858	2989	832	2401	811	1896
678	6280	784	4263	834	3001	809	2409	793	1886
657	6318	752	4314	792	3014	780	2409	778	1876
635	6366	729	4340	765	3040	753	2409	756	1857
600	6440	698	4393	738	3053	731	2417	724	1842
576	6500	670	4447	703	3079	710	2417	708	1828
546	6573	644	4475	674	3092	683	2417	673	1810
519	6640	616	4531	647	3119	664	2417	658	1801
488	6735	576	4618	627	3119	631	2417	630	1671
462	6789	545	4678	599	3146	614	2417	628	1623
438	6889	529	4709			599	2417	624	1566



(a) (b) (c) (d)

Fig. 3 Electroconductivity isotherms for molten samples in chalcogenide systems of antimony and bismuth; the arrows indicate the compositions at which sign inversion of the temperature coefficient takes place: (a) 1 – 650, 2 – 750, 3 – 850°C; (b) 1 – 620, 2 – 700, 3 – 800, 4 – 900°C; (c) 1 – 710, 2 – 800, 3 – 900, 4 – 1000°C; (d) 1 – 580, 2 – 700, 3 – 800°C.

As Fig. 3 shows, the electroconductivity falls with increasing chalcogen content in the antimony and bismuth melts. The temperature coefficient in the composition interval from the pure metal to the composition marked by a vertical arrow, has a negative sign.

Subsequent chalcogen adding (in the Sb–Se system more than 14 at.% Se; in Sb–Te > 19 at.% Te; in Bi–Se > 47 at.% Se; in Bi–Te > 51 at.% Te) is accompanied by a sign inversion of $\Delta\sigma/\Delta T$ from negative to positive.

The changes of the values and the character of the conductivity in the investigated systems can be explained by chemical interaction of the components and the modification of the chemical bonds from metallic (for Sb and Bi) to covalent, characteristic of the chalcogenides that form accordingly to the phase diagrams [4,5].

Conclusions

The composition dependence of the electroconductivity of melts was studied in the metal-rich region of the systems Sb–Se, Sb–Te, Bi–Se, and Bi–Te. The compositions where the temperature coefficient of electroconductivity changes signs from negative to positive, were determined.

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