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Note

POSSIBLE TELLURITES OF ANTIMONY OBTAINED BY THE PRECIPITATION REACTIONS

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The only work concerning the synthesis of $Sb_2(TeO_3)_3 \cdot 5H_2O$ by mixing aqueous solutions of equimolar quantities of $SbCl_3$ and Na_2TeO_3 is that of Boncheva-Mladenova and Schopova [1]. In order to prevent $SbCl_3$ from being hydrolyzed, the latter was dissolved in 4 N HCl.

In that work, however, there are no data concerning the possibilities of the precipitation reactions to form tellurites of different composition.

EXPERIMENTAL

To characterize the interaction in the system $SbCl_3$–Na_2TeO_3–H_2O at equilibrium, the method of residual concentrations at 25 and 100°C was used. The concentration of Na_2TeO_3 in the initial solutions was kept constant (0.0125 mol per 50 ml of solution), and the ratio, n, of the reagents ($Na_2TeO_3 : SbCl_3$) was varied from 0.2 to 5. The equilibrium of the system at 25°C was achieved by thermostatic regulation of the heterogeneous system precipitate–mother solution for 24 h.

For the study at 100°C, the samples were put into glass ampules and sealed. They were left for five months in an air thermostat at 100°C, the maximum deviation from this temperature being ± 1°C, and were periodically shaken. These conditions were assumed to be equilibrium since, after the aforementioned period of five months, the concentration of Sb^{3+} and TeO_3^{2-} in the liquid and the solid phases no longer changed. The liquid phase was then separated from the solid phase by filtration, and pH values of the equilibrium liquid solutions were measured. The solid phases were washed with a 70% solution of ethanol and then dried over $CaCl_2$ with the air at room temperature to a constant weight. Chemical analysis for Sb^{3+} was made bromatometrically [2]. Tellurium was determined gravimetrically as elementary tellurium by precipitation with hydrazine hydrochloride [3].

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RESULTS AND DISCUSSION

The study of the system $SbCl_3$–Na_2TeO_3–H_2O at 25°C showed that, at $n = 1$, 2 and 3, antimony tellurite with a formula composition $Sb_2(TeO_3)_3$ is formed. The content of Sb_2O_3 in the samples was 37.80–38.04% and the content of TeO_2 was 61.95–62.20% in comparison with 37.84 and 62.16% calculated for Sb_2O_3 and TeO_2, respectively. The composition of a sample with $n = 0.5$ was found to be 47.54% of Sb_2O_3 and 52.46% of TeO_2 against 47.73 and 52.26% calculated for Sb_2O_3 and TeO_2, which corresponds to a compound with formula composition $Sb_2O_3 \cdot 2TeO_2$. The results reported in ref. 1 were not confirmed here. No compound $Sb_2(TeO_3)_3 \cdot 5H_2O$ was obtained at 25°C over the whole concentration interval. At 100°C (Fig. 1) over the concentration interval $n = 0.33$–5, the basic tellurite, $Sb_2O_3 \cdot 2TeO_2$, was synthesized. At $n = 0.2$ and 0.25 the compositions of the solid phases obtained were similar to the phase $Sb_2O_3 \cdot TeO_2$ or $(SbO)_2TeO_3$. The same conclusions may be made considering the results of pH studies (Fig. 2) and X-ray patterns (Fig. 3).

The phases obtained here are similar in composition to bismuth tellurites [6,7].

The X-ray pattern of the basic salt obtained is shown in Table 1.

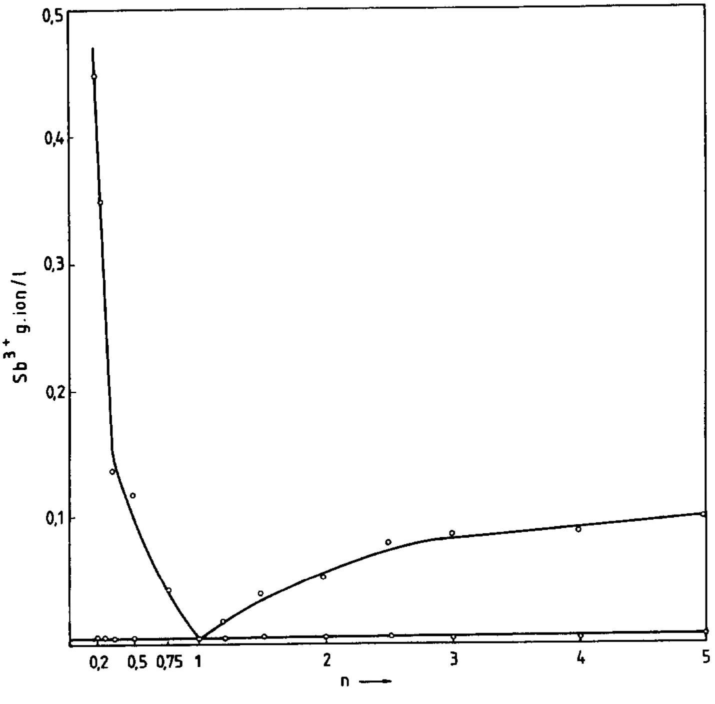

Fig. 1. Solubility isotherm of the system $SbCl_3$–Na_2TeO_3–H_2O at 100°C.

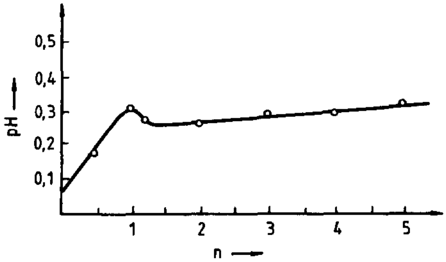

Fig. 2. Changes in pH of the equilibrium liquid solutions depending on the mol ratio $n = Na_2TeO_3/SbCl_3$.

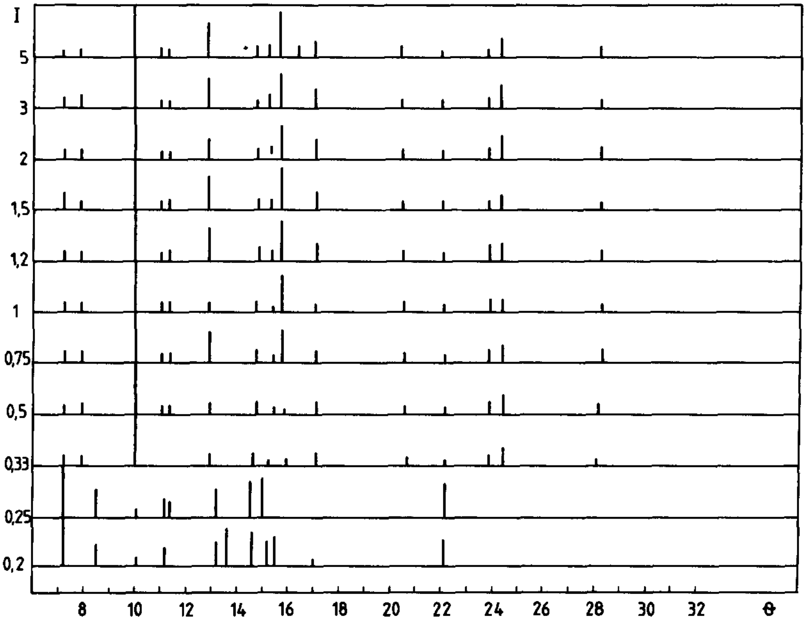

Fig. 3. X-ray pattern of the solid phases of the system $SbCl_3$–Na_2TeO_3–H_2O at 100°C.

TABLE 1

X-ray pattern of $Sb_2O_3 \cdot 2TeO_2$

I	*d* (Å)	*I*	*d* (Å)
10	6.023	4	2.813
15	5.571	15	2.598
100	4.394	10	2.190
15	4.415	10	2.039
15	3.882	20	1.891
20	3.412	10	1.858
20	3.016	10	1.620
20	2.892		

Studying the *T–X* projection of the state diagram of the system Sb_2O_3–TeO_2, Novoselova and co-workers [4] discovered that no tellurites can be obtained by direct interaction between Sb_2O_3 and TeO_2. Our results, in total, confirm the conclusion that, as a rule, the compounds obtained by crystallization from solution have a composition different from that of compounds formed in the melt or in solid phases at high temperature [5].

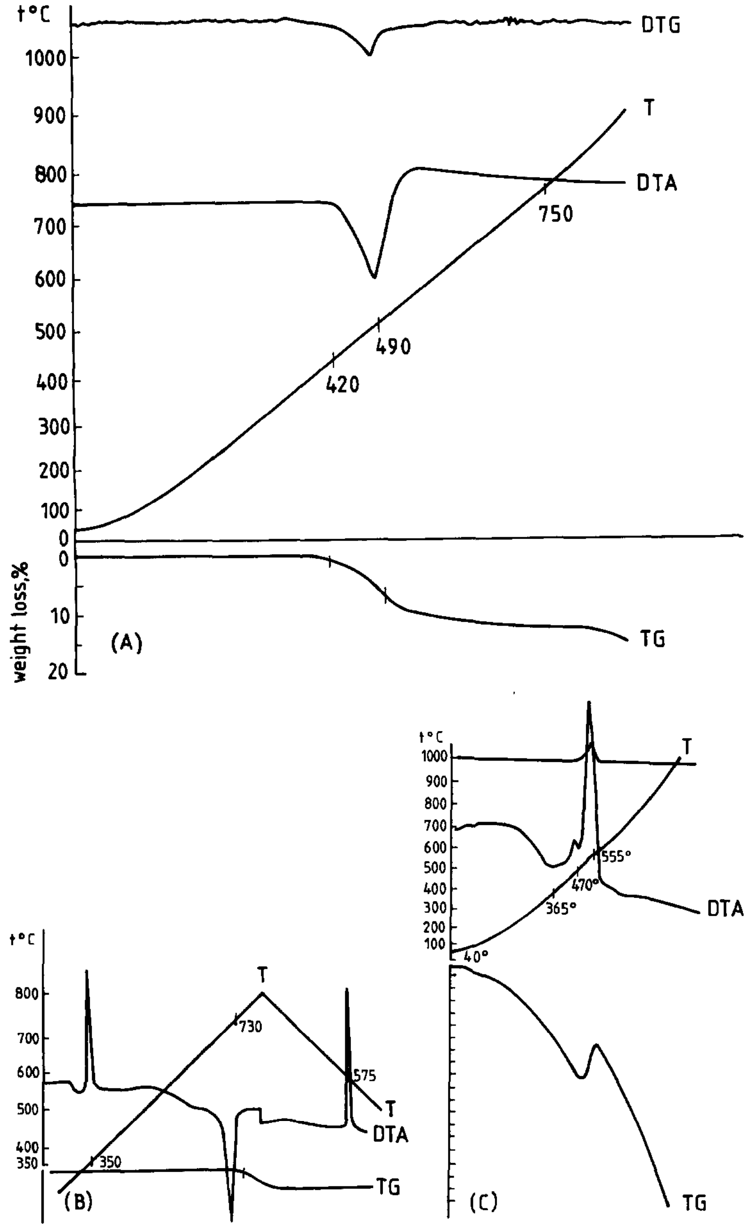

Fig. 4. Derivatograms of $Sb_2O_3 \cdot 2TeO_2$ (A), TeO_2 (B) and Sb_2O_3 (C).

The thermal dissociation of antimony tellurites was studied on a derivatograph (Paulik–Paulik–Erdey, MOM) with a sample weight of 200 mg. The sensitivity of the balance was 200, the sensitivity of DTA, 1/5 and that of DTG, 1/15. Figure 4A shows the derivatogram of $Sb_2O_3 \cdot 2TeO_2$. This compound is stable to 420°C. At 490°C it dissociates to form Sb_2O_3 and TeO_2, Sb_2O_3 mainly becoming a gaseous phase. This supposition is based on the comparison of the derivatograms of TeO_2 (Fig. 4B) and Sb_2O_3 (Fig. 4C). At 750°C the volatility of TeO_2 increases considerably leading to a greater total weight loss of the sample. At 850°C the weight loss is about 15%.

On the derivatogram of $Sb_2(TeO_3)_3$ two endothermic peaks are observed at 480 and 500°C. The derivatogram of $Sb_2O_3 \cdot TeO_2$ shows one endothermic peak at 505°C. The closeness of the thermal peaks of these compounds makes it difficult to determine the three stages of dissociation

$$Sb_2(TeO_3)_3 \rightarrow Sb_2O_3 \cdot 2TeO_2 \rightarrow Sb_2O_3 \cdot TeO_2$$

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