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Note

CONDITIONS FOR SYNTHESIS AND THERMAL DISSOCIATION OF GALLIUM TELLURITES

G.G. GOSPODINOV

Department of Inorganic Chemistry, Higher Institute of Chemical Technology, Bourgas 8010 (Bulgaria)

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ABSTRACT

Recently, metal tellurites have been the subject of increasing interest in connection with their possible application in laser techniques (tellurites of Zn, Cd, Hg, Pb) [1], medicine (tellurites of K and Na) [2], and as prospective initial substances for the synthesis of tellurides used in semi-conductors [3,4]. Tellurites of stoichiometric composition may have practical applications.

In order to determine conditions for synthesizing gallium tellurites, the solubility isotherm of the system $Ga(NO_3)_3–K_2TeO_3–H_2O$ was studied at 25 and 100°C.

EXPERIMENTAL

X-ray phase analysis was accomplished on a DRON-3 apparatus with $Cu K_\alpha$ radiation. Chemical analysis for Ga^{3+} was made by reverse complexometric titration [5]. Tellurium ions were determined iodometrically and gravimetrically (by precipitation with $N_2H_4 \cdot HCl$ and SO_2 as elementary tellurium) [6]. Derivatographic analysis was made with an OD-102-type derivatograph (MOM, Hungary).

RESULTS AND DISCUSSION

To characterize interactions in the system $Ga(NO_3)_3–K_2TeO_3–H_2O$ at equilibrium, Tananaev's method of "residual concentrations" [8] at 25°C was used. While the solutions were mixed, $Ga(NO_3)_3$ concentration was kept constant (0.5 g-mol l^{-1}) at constant volume, and only the ratio, n, between K_2TeO_3 and $Ga(NO_3)_3$ was varied. The systems thus obtained were subjected to continuous thermostatting in thermostatting bottles, circulating water being introduced from a U-10 ultrathermostat. The samples were thermostatted for 45 days, since, by studying equilibrium kinetics, we found that the concentration of Ga^{3+} and TeO_3^{2-} in the liquid and solid phases does not change after this period of time.

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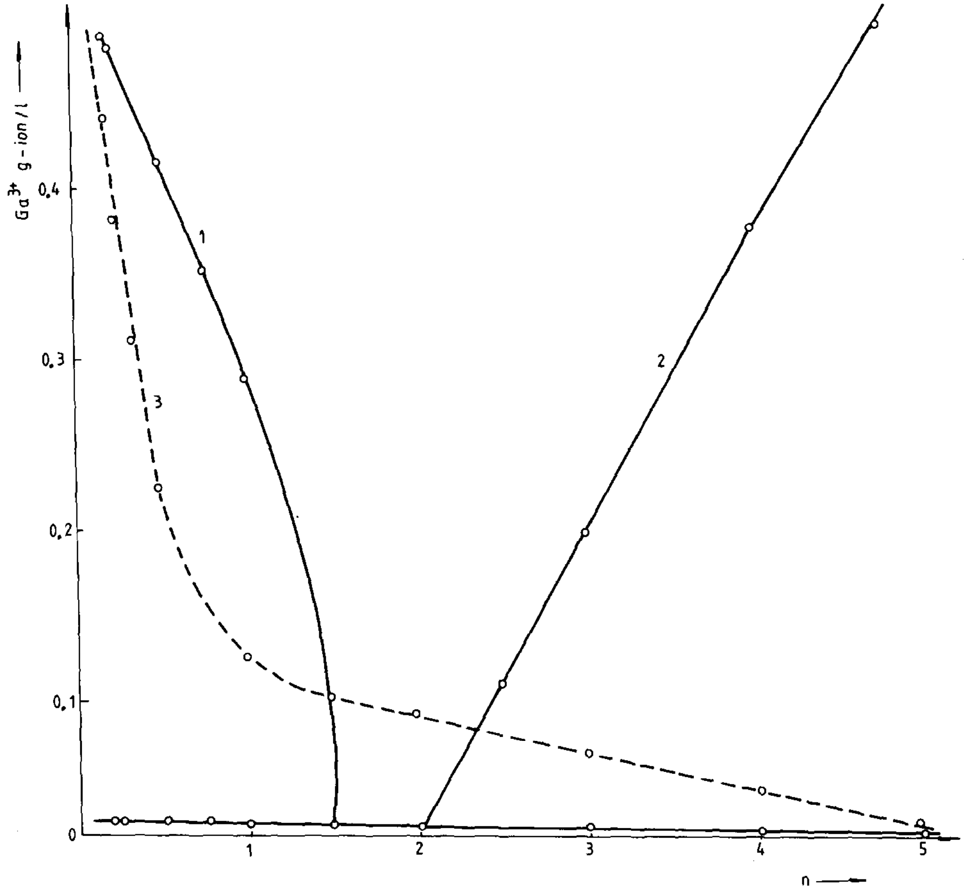

Fig. 1. Solubility isotherm of the system $Ga(NO_3)_3$–K_2TeO_3–H_2O at 25 (1) and (2) and 100°C (3).

The technique of studying the system at 100°C has been reported previously [9].

At both 25 and 100°C the liquid and solid phases were separated by filtration and subjected to chemical analysis.

Figure 1 presents the solubility isotherm of the system $Ga(NO_3)_3$–K_2TeO_3–H_2O at 25 and 100°C. The data adduced show that with increasing K_2TeO_3 content in the system to $n \leq 1.5$ a solid phase of precipitate is formed and the concentration of Ga^{3+} in the solution decreases (curve 1). Up to $n = 2$ practically all the tellurite introduced is in the solid phases (curve 2). At $n > 2$ the concentration of tellurium in the liquid phases increases abruptly. At 25°C, up to $n = 1.5$, $Ga_2(TeO_3)_3 \cdot 22H_2O$ is formed in the system $Ga(NO_3)_3$–K_2TeO_3–H_2O. At $n \geq 2$ a complex tellurite with composition $KGa(TeO_3)_2 \cdot 3H_2O$ is formed in the system. Unlike $Ga_2(TeO_3)_3 \cdot 22H_2O$ which is an X-ray amorphous phase, $KGa(TeO_3)_2 \cdot 3H_2O$ is crystalline. As X-ray phase analysis of $KGa(TeO_3)_2 \cdot 3H_2O$ shows, the values obtained for *I* and *d* are in good agreement with the literature [7].

The solubility isotherm of the system at 100°C (Fig. 1, curve 3) shows that complex processes take place with the phases obtained at 25°C. Because of the increasing hydrolysis due to raising the temperature, it is not only $Ga_2(TeO_3)_3$ (at $n > 0.5$) but also the double salt (at $n \geq 2$) that is subjected to hydrolytic changes. What is more, the concentration of Ga^{3+} in the solid phases is reduced, reaching 2–3%.

$Ga_2(TeO_3)_3 \cdot 22H_2O$ obtained at 100°C at $n = 0.2$, 0.25, 0.33 and 0.5 is also in the X-ray amorphous state but, unlike $Ga(NO_3)_3$, it does not contain

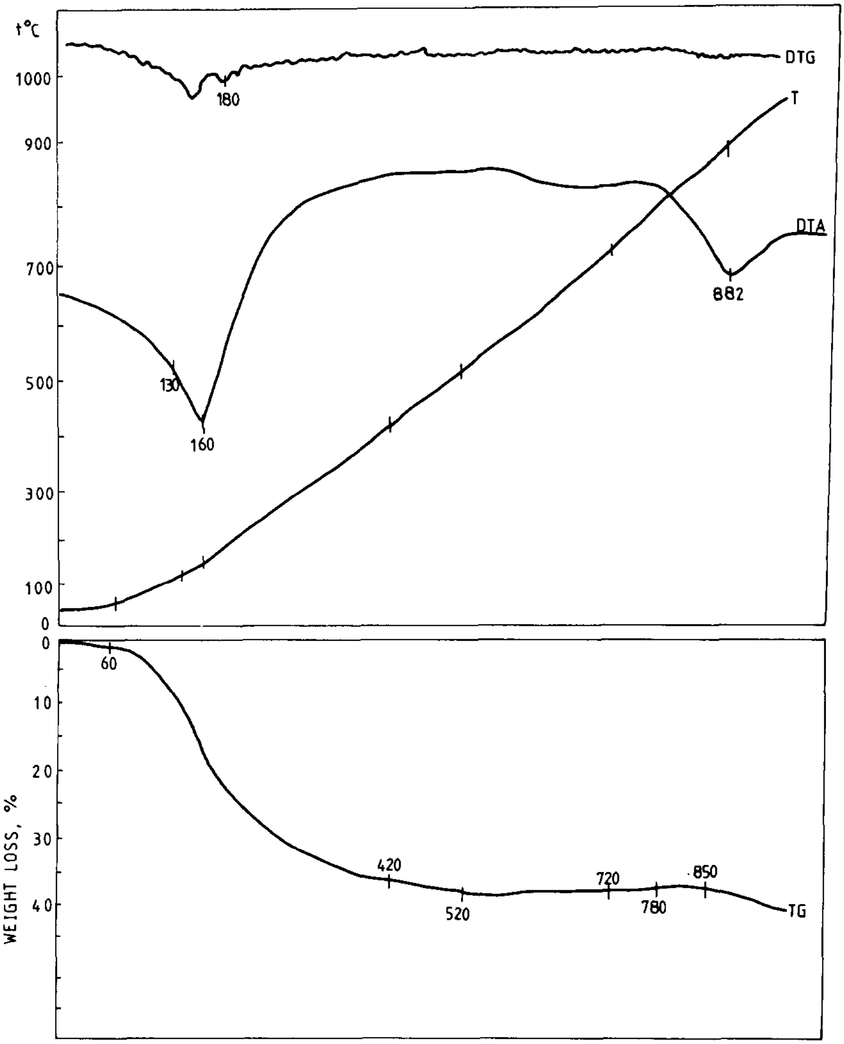

Fig. 2. Derivatogram of $Ga_2(TeO_3)_3 \cdot 22H_2O$.

$Ga(NO_3)_3$ (reaction with diphenyl amine). It is obvious that, although both substances are X-ray amorphous, their dispersion is different.

The derivatogram of $Ga_2(TeO_3)_3 \cdot 22H_2O$ is presented in Fig. 2. Dehydration begins at 60°C and proceeds in two stages. The endothermic peak exhibited on the thermogram is complex and consists of a superposition of two endothermic peaks at 130 and 160°C. The first endothermic peak corresponds to the liberation of 6 moles of water and the formation of $Ga_2(TeO_3)_3 \cdot 16H_2O$. Further water is liberated at 160°C. More complete dehydration of the sample is observed as early in the derivatogram as at 420°C. Both $Ga_2(TeO_3)_3 \cdot 22H_2O$ and $Ga_2(TeO_3)_3$ are X-ray amorphous. The minor exothermic peak on the derivatogram at 520°C corresponds to the crystallization of this X-ray amorphous phase and its becoming crystalline. This is shown by X-ray phase analysis of a dehydrated sample and a sample heated at and above this temperature in an inert medium. At 520°C and above, the thermogravimetric curve shows an increase in sample weight owing to oxidation of $Ga_2(TeO_3)_3$ to gallium tellurate. Oxidation takes place at this particular temperature since, according to Hedval [10], the reactivity of a given solid substance reaches a maximum value at the temperature at which a fundamental change in the arrangement of the building elements of the crystal lattice takes place. During the "loosening" of the crystal lattice and regrouping of the building particles into a new arrangement, the system becomes rich in energy resulting in a corresponding increase in reactivity. At 850°C tellurate liberates oxygen and becomes tellurite. At this temperature tellurite melts and its thermal decomposition takes place in the melted state. This assertion was verified by heating gallium tellurite in a Stepanov vacuum vessel. Tellurite melts without decomposing. This melting temperature agrees well with the temperature published in the literature. Thus, the endothermic peak exhibited on the derivatogram is a complex one and consists of two endothermic peaks, at 850 and 882°C, corresponding to the melting and decomposition of the compound. The weight loss observed on the thermogravimetric curve in the interval from 850 to 950°C is negligible; it is only 5–7%.

Based on the results of the derivatograph and chemical (of samples heated to the corresponding temperature) and X-ray analyses the following scheme of thermal dissociation may be suggested

$$Ga_2(TeO_3)_3 \cdot 22H_2O \overset{130°C}{\rightleftarrows} Ga_2(TeO_3)_3 \cdot 16H_2O \overset{\geq 160°C}{\rightleftarrows}$$

$$Ga_2(TeO_3)_{3(\text{amorph})} \overset{\geq 520°C}{\rightleftarrows} \text{gallium tellurate} \overset{850°C}{\rightleftarrows}$$

$$Ga_2(TeO_3)_{3(\text{melt})} \overset{\geq 882°C}{\rightleftarrows} Ga_2O_3$$

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