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Abstract

Full Text

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ON THE POLYMORPHISM OF THALLIUM BISULFATE

(Presented by Academician G. G. Urazov on 6 XII 1956)

Thallium bisulfate crystallizes from aqueous solutions of sulfuric acid in the form of square plates and prismatic needles ([1–5]). In connection with this it was assumed that this compound is dimorphous ([1,2,6]). The existence of two modifications of $TlHSO_4$ has been confirmed by us by crystallographic investigation ([5]).

It was necessary to clarify the nature of this polymorphic transformation, to find its temperature and the conditions for the stable existence of one or the other modification of thallium bisulfate. For this purpose, and also in order to find as yet unknown phase transformations in the solid state, we investigated $TlHSO_4$ by the method of thermographic analysis.

Fig. 1. Heating curve of α-$TlHSO_4$ (a) and β-$TlHSO_4$ (b)

Thermographic analysis was carried out on a recording pyrometer of N. S. Kurnakov with a differential chromel-alumel thermocouple. In order to obtain well reproducible data, necessary for comparison of the thermograms of the two ([5]) modifications of thallium bisulfate, single crystals ([5]) of each modification were subjected separately to thermographic investigation. For thermographic recording of the heating and cooling curves, single crystals of $TlHSO_4$ were placed in small Stepanov vessels ([7]).

The heating curves of the needle-shaped crystals—α-$TlHSO_4$—and of the crystals in the form of plates—β-$TlHSO_4$—are presented in Fig. 1. From a comparison of the differential heating curves it is seen that they differ by an additional endothermic effect of the α-modification of thallium bisulfate. This effect occurs in the temperature interval 40—49°.

The remaining effects of the thermograms are identical. The minimum of the differential heating curve corresponding to the first of them, a slight but well

Fig. 2. Heating curve of molten $TlHSO_4$ after slow cooling

Figure 2: Fig. 2. Heating curve of molten $TlHSO_4$ after slow cooling

reproducible endothermic effect, fluctuates on different thermograms within the limits 96—108°. The second endothermic

the effect occurs in the temperature interval 113-120° and the third in the interval 124-128°.

From the cooling curves and subsequent heating of the molten salt, as well as from visual observations of these processes, one may conclude that the first two effects of β-$TlHSO_4$ correspond to enantiotropic polymorphic transformations of thallium bisulfate. The last effect corresponds to melting of the salt. The low-temperature endothermic effect of the α modification of thallium bisulfate corresponds to the transition of the α form of thallium bisulfate into its β form. This is confirmed by the fact that, upon heating to 60°, the needle-like crystals of α-$TlHSO_4$, without changing their external crystalline form, change their refractive indices, which after heating become equal to the refractive indices of β-$TlHSO_4$ ([5]). The reverse transition of the β modification of thallium bisulfate into the α modification was not recorded either by ordinary cooling curves or by curves of subsequent heating of the molten salt.

Fig. 2. Heating curve of molten $TlHSO_4$ after slow cooling

By investigating phase transformations under different cooling conditions for molten crystals of thallium bisulfate, we were able to establish that the reverse transition of β-$TlHSO_4$ to the low-temperature α modification takes place only under conditions of very slow cooling. If crystals of thallium bisulfate are melted and then left to cool in a closed electric furnace with good thermal insulation, the subsequent heating curves of such molten samples record the low-temperature endothermic effect characteristic of α-$TlHSO_4$ (Fig. 2). This indicates that, in the process of slow cooling, the β modification passes into the α modification.

It is characteristic that the temperature of the endothermic effect corresponding to the transformation of the α form into the β form of $TlHSO_4$ for the slowly cooled melt of thallium bisulfate (Fig. 2) is higher than that at which this transformation is recorded in the process of heating crystals of α-$TlHSO_4$ directly (Fig. 1a).

As a result of the investigation it was established that thallium bisulfate has three enantiotropic polymorphic transformations and melts without decomposition. The melting temperature of thallium bisulfate found is higher than that known from the literature ([8], [9]).

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