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Abstract

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PREPARATION OF TITANYL OXALATES OF DIVALENT METALS AND PHYSICOCHEMICAL STUDY OF THEIR THERMAL DECOMPOSITION

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It is known that titanium in the form of the titanyl ion is capable of forming complex compounds with the oxalate ion. Thus, in the solid state titanyl oxalic acid of composition $H_2(TiO(C_2O_4)_2) \cdot 2H_2O$ and some salts of this acid have been obtained; among salts with divalent cations, however, only the barium salt has been isolated ([1,2]).

The present work is devoted to the synthesis of salts of titanyl oxalic acid with divalent cations and to a physicochemical study of the decomposition of these salts on heating. We developed a procedure that makes it possible to obtain both barium titanyl oxalate and the titanyl oxalates of strontium, lead, and calcium. The procedure was as follows. To an aqueous solution of titanium tetrachloride (concentration 0.2–0.3 g/ml), prepared by the method of ([3]), a concentrated solution of oxalic acid was added with stirring. To the titanyl oxalate solution obtained, at room temperature and with constant stirring, an aqueous solution of the corresponding salt of the divalent cation (barium chloride, strontium chloride, or lead nitrate) was added. The complex salts formed precipitated as white precipitates. In this way the titanyl oxalates of barium, strontium, and lead were obtained. Since we were unable to obtain calcium titanyl oxalate in aqueous solution under these conditions, the synthesis of this complex salt was carried out in an acetone medium. Preparation of the acetone solution of titanium tetrachloride was carried out analogously to obtaining its aqueous solution. The precipitate formed is thoroughly washed with acetone. As a result, a white powder of calcium titanyl oxalate is obtained. We give the chemical analysis of the compounds obtained for the oxides of the divalent metals, titanium dioxide, the oxalate ion, and water:

$BaTiO(C_2O_4)_2 \cdot 4H_2O$. Found, %: MeO 33.72; 33.83; TiO_2 17.57; 17.62; C_2O_4'' 38.72; 38.84; H_2O 17.03; 16.67
Calculated, %: MeO 34.13; TiO_2 17.78; C_2O_4'' 39.19; H_2O 16.03

$SrTiO(C_2O_4)_2 \cdot 5.5H_2O$. Found, %: MeO 24.28; 24.36; TiO_2 18.72; 18.78; C_2O_4'' 41.25; 41.38; H_2O 23.25; 23.24
Calculated, %: MeO 24.29; TiO_2 19.73; C_2O_4'' 41.26; H_2O 23.22

$PbTiO(C_2O_4)_3 \cdot 4H_2O$. Found, %: MeO 36.67; 36.82; TiO_2 13.13; 13.18; C_2O_4'' 43.38; 43.56; H_2O 12.07; 11.72

Calculated, %: MeO 36.76; TiO_2 13.16; C_2O_4'' 43.89; H_2O 11.87

$CaTiO(C_2O_4)_2 \cdot 5H_2O$. Found, %: MeO 15.12; 15.20; TiO_2 21.54; 21.65; C_2O_4'' 47.46; 47.70; H_2O 24.50; 24.11
Calculated, %: MeO 15.15; TiO_2 21.59; C_2O_4'' 47.56; H_2O 24.34

Analysis showed that the compounds obtained have the compositions $BaTiO(C_2O_4)_2 \cdot 4H_2O$; $SrTiO(C_2O_4)_2 \cdot 5.5H_2O$; $PbTiO(C_2O_4)_3 \cdot 4H_2O$ and $CdTiO(C_2O_4)_2 \cdot 5H_2O$.

X-ray phase-analysis data and the results of a crystallo-optical study indicate that the complex salts obtained are fine isotropic crystals. The refractive indices, determined by the immersion method, were found to be: for barium titanyloxalate $N = 1.66$, for strontium titanyloxalate $N = 1.621$, for calcium titanyloxalate $N = 1.593$, and for lead titanyloxalate $N > 1.78$.

A combined thermographic and thermogravimetric study showed that the thermal decomposition of the titanyloxalates of barium, strontium, lead, and calcium is stepwise in character and is accompanied by a number of endothermic and exothermic processes (Fig. 1). As shown by the data of X-ray, thermogravimetric, and chemical analyses, upon heating the first process is the release of water of crystallization and the salts pass into the amorphous state.

Fig. 1. Combined thermographic and thermogravimetric study of the thermal decomposition of titanyloxalates:
A—barium, —strontium, —lead, —calcium; **1**—simple thermocouple, **2**—thermogravimetric curve, **3**—differential thermocouple.

At the same time, for the barium and lead titanyloxalates this process is accompanied by one endothermic effect at temperatures of 175 and 140°, respectively; for strontium titanyloxalate by two (170 and 230°); and for calcium titanyloxalate by three endothermic effects (160, 220, 260°). (The process of release of water of crystallization is reversible, and the dehydrated salts are capable of ob

to add back the water lost on heating). Then, at almost the same temperature (320-360°), in all the salts under consideration an endothermic process occurs, associated with destruction of the oxalate groups and evolution of carbon dioxide. This indicates that the oxalate groups are, apparently, mainly bound to the titanyl ion and that the cation has no appreciable effect on the strength of this bond. The exothermic process occurring after destruction of the oxalate groups is not accompanied, except in the case of calcium titanyloxalate, by a sharp loss of weight. This process, as shown by X-ray phase-analysis data, is associated with the formation of the metatitanates of barium, strontium, lead, and calcium. Further heating leads to complete removal of the carbon oxides still present in the salts, which is accompanied by a sharp loss of weight of the salts and by endothermic effects. Thus, the process of thermal decomposition of the titanyloxalates of barium, strontium, lead, and calcium is completed for all salts at approximately 800°. Reheating of the final products of decomposition of the salts proceeds practically without thermal effects, which indicates the irreversibility of the process of complete thermal decomposition of the obtained titanyloxalates of divalent metals.

Table 1

Calcination temp., °C	Specific gravity, g/cm^3			
	$BaTiO(C_2O_4)_2 \cdot 4H_2O$	$SrTiO(C_2O_4)_2 \cdot 5{,}5H_2O$	$PbTiO(C_2O_4)_3 \cdot 4H_2O$	$CaTiO(C_2O_4)_2 \cdot 5H_2O$
Room	$2{,}27_9$	$2{,}11_8$	$2{,}84_1$	$1{,}45_9$
230	$3{,}10_7$	$2{,}58_5$	$3{,}83_4$	$2{,}44_2$
300	—	—	—	—
370	$3{,}67_2$	$3{,}18_2$	5,74	$2{,}77_5$
600	$5{,}05_8$	$4{,}46_3$	$6{,}57_3$	$3{,}45_4$
850	5,98	$4{,}76_7$	7,52	$4{,}09_9$

From the data of chemical and X-ray phase analyses it follows that the final products of decomposition of the titanyloxalates of barium, strontium, lead, and calcium are the metatitanates of these metals, having a perovskite-type structure. In parallel, we determined the specific gravities both of the starting salts and of the products of their thermal decomposition (Table 1). As was to be expected, the specific gravity of the salts increases as the calcination temperature rises and the volatile decomposition products are removed, up to the maximum value corresponding to the specific gravities of the titanates of barium, strontium, calcium, and lead.

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named after M. V. Lomonosov

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