

THERMAL DECOMPOSITION OF TITANYL OXALATES

IV. STRONTIUM AND CALCIUM TITANYL OXALATES

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ABSTRACT

Thermal decomposition of strontium titanyl oxalate tetrahydrate and calcium titanyl oxalate hexahydrate have been studied employing TG, DTA, gas and chemical analysis. The decompositions proceed through three major steps: dehydration, decomposition of the oxalate to a carbonate and the decomposition of the carbonate to yield the final products, the metatitanates. The intermediates of the oxalate decomposition are found to be $\text{Sr}_2\text{Ti}_2\text{O}_{4+x}(\text{CO}_3)_{2-x}(\text{CO}_2)_x$ and $\text{Ca}_2\text{Ti}_2\text{O}_4(\text{CO}_3)_2$, respectively. The entrapment of carbon dioxide in the former and the presence of non-equivalent carbonate groups in the latter are substantiated by their i.r. spectra. The penultimate solid residues are poorly crystalline $\text{Sr}_2\text{Ti}_2\text{O}_5\text{CO}_3$ and amorphous $\text{Ca}_2\text{Ti}_2\text{O}_5\text{CO}_3$. Decompositions of these carbonates are accompanied by growth in particle size of the products, SrTiO_3 and CaTiO_3 , respectively.

INTRODUCTION

The need for pure, fine-grained metatitanates of bivalent metals, led to the development of chemical methods for their preparation. Pure and stoichiometric metatitanates can be prepared by the thermal decomposition of the corresponding titanyl oxalates. Chemically prepared materials have better sinterability than those prepared by ceramic methods. Chemical reactivity, particle size and sinterability are influenced by the calcination temperature of the precursors, viz., the corresponding titanyl oxalates. This has necessitated the investigation of the decomposition characteristics of titanyl oxalates.

Strizhakov et al.¹ have reported the thermal decomposition of the titanyl oxalates of alkaline earths and lead. Gallagher et al.^{2,3} have investigated the mode of decomposition of barium and strontium titanyl oxalates. Our previous communications^{4,5} on barium and lead titanyl oxalates have shown clearly that the schemes proposed by the earlier investigators for the decomposition of these titanyl oxalates are incorrect. Therefore we considered it desirable to investigate the thermal decomposition of the titanyl oxalates of strontium and calcium. The results of our recent study are presented here.

EXPERIMENTAL

Materials

All reagents were either BDH AnalaR or E. Merck "pro-analyse" grade. Strontium titanate tetrahydrate (STO) was prepared by the method of Clabaugh et al.⁶ by substituting strontium chloride for barium chloride. The yield of STO was only around 50%, owing to the solubility of STO in acid medium.

Calcium titanate hexahydrate (CTO) could not be prepared under similar conditions, owing to its complete solubility in the highly acidic medium. The method was modified as follows: calcium carbonate was added to an aqueous solution of titanate chloride to get a Ca:Ti mole ratio of 1:1. This mixture was added to the stoichiometric quantity of aqueous oxalic acid. No precipitate was obtained. The solution was kept over sodium hydroxide pellets in a desiccator. After 4 to 5 days, by

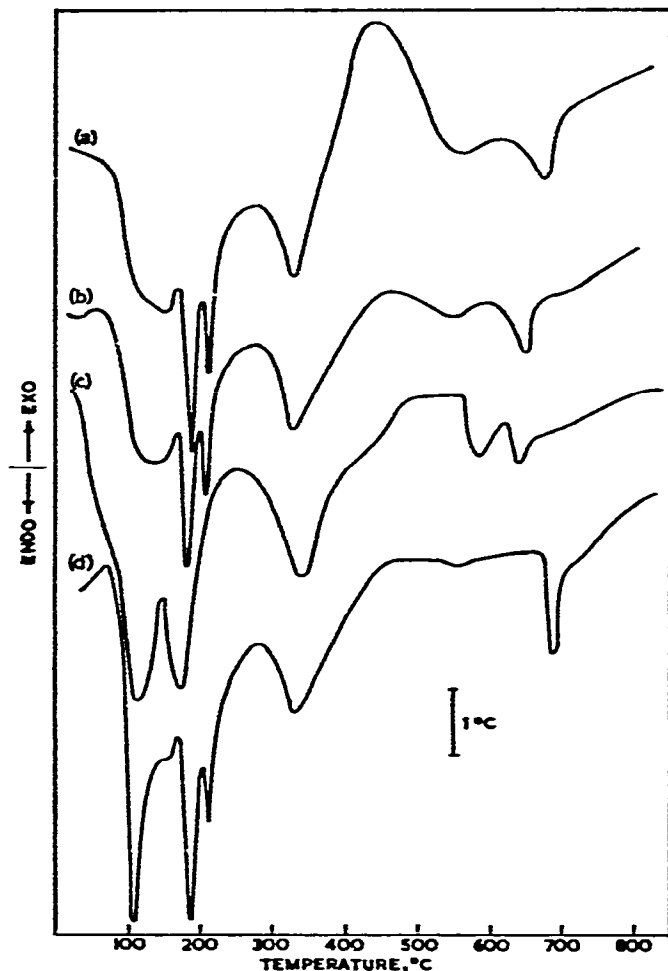


Fig. 1. DTA of STO in (a) oxygen, (b) nitrogen, (c) vacuum; and (d) carbon dioxide.

vigorous agitation of the concentrated solution, a white solid was thrown out, which was insoluble in water but easily soluble in acids. The precipitated solid was filtered, washed thoroughly with distilled water, finally with acetone and air-dried.

The wet chemical analyses of the preparations are as follows: STO gave, Sr: 22.01, TiO: 15.98, C_2O_4 : 43.58 and H_2O : 18.00%; calculated for $SrTiO(C_2O_4)_2 \cdot 4H_2O$: Sr: 21.93, TiO: 15.99, C_2O_4 : 44.05, H_2O : 18.02%. For CTO: Ca: 10.22, TiO: 16.51, C_2O_4 : 45.18, H_2O : 28.50%; calculated values for $CaTiO(C_2O_4)_6 \cdot 6H_2O$ are Ca: 10.33, TiO: 16.47, C_2O_4 : 45.36 and H_2O : 27.84%.

Methods

The procedures for physical studies like DTG, DTA, i.r. spectroscopy, X-ray powder diffraction and surface area measurements are described elsewhere⁴. Methods for the analysis of the residues and the gaseous products at different stages of decomposition were also similar to those already reported by us⁴.

RESULTS

Figures 1-4 give the DTA and DTG curves in flowing oxygen, nitrogen, a vacuum and carbon dioxide for STO and CTO. Figure 2 also shows the TG curve for STO in oxygen while the corresponding curve for CTO is shown in Fig. 4. All the thermal effects are accompanied by weight losses. As in the case of barium and lead

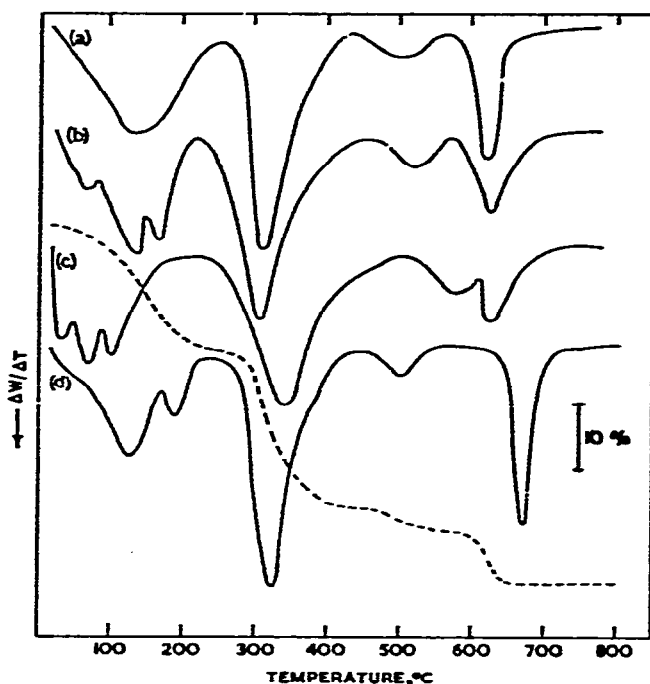


Fig. 2. DTG of STO in (a) oxygen; (b) nitrogen; (c) vacuum; and (d) carbon dioxide.

TABLE 1
TEMPERATURE RANGES AND OBSERVED WEIGHT LOSSES FOR THE DECOMPOSITION OF STO

Decomposition step	Calc. % weight loss	Gas atmosphere			Nitrogen			Carbon dioxide		
		Oxygen		Vacuum	Nitrogen		Carbon dioxide			
		Temp. range	% Weight loss	Temp. range	% Weight loss	Temp. range	% Weight loss	Temp. range	% Weight loss	
Dehydration	18.02	20-250	18.95	20-210	18.67	20-225	19.51	20-250	18.76	
Oxalate decomposition	25.03	250-430	24.11	210-500	27.11	225-460	24.85	250-440	23.32	
1st stage carbonate decomposition	5.50	430-570	3.67	500-610	4.33	460-570	4.07	440-580	2.83	
2nd stage carbonate decomposition	5.50	570-730	8.10	610-750	5.83	570-750	7.07	580-800	9.40	
Total weight loss	54.05		54.83		55.94		55.50		54.31	

TABLE 2
TEMPERATURE RANGES AND OBSERVED WEIGHT LOSSES FOR THE DECOMPOSITION OF CTO

Decomposition step	Calc. % weight loss	Gas atmosphere			Nitrogen			Carbon dioxide		
		Oxygen		Vacuum	Nitrogen		Carbon dioxide			
		Temp. range	% Weight loss	Temp. range	% Weight loss	Temp. range	% Weight loss	Temp. range	% Weight loss	
Dehydration	27.87	20-250	29.05	20-210	27.40	20-250	29.29	20-260	28.57	
Oxalate decomposition	26.00	250-450	27.00	210-560	29.34	250-500	28.36	260-510	27.35	
1st stage carbonate decomposition	5.67	450-540	1.13	560-640	3.69	500-570	1.75	510-610	0.71	
2nd stage carbonate decomposition	5.67	540-660	8.19	640-750	4.62	570-680	7.22	610-750	8.90	
Total weight loss	65.21		65.37		65.09		66.62		65.53	

titanyl oxalates^{4,5}, there are three major steps in the decomposition: dehydration of the hydrate, decomposition of the oxalate to a carbonate and the decomposition of the carbonate to give the corresponding metatitanates, SrTiO_3 or CaTiO_3 . These major reactions are not influenced much by the surrounding atmosphere. The temperature ranges and the observed weight losses for the decomposition of STO and CTO are given in Tables 1 and 2, respectively.

Dehydration of the hydrate

Dehydration of STO takes place in the temperature range 25–200°C in three steps, which however overlap in the thermograms. Weight losses and the composition of the residues obtained in static experiments correspond to the formation of dihydrate, monohydrate and anhydrous oxalate. The dehydration is completely reversible and the intermediate hydrates as well as the anhydrous salt are amorphous to X-rays. From the vapor pressure measurements of the different hydrates in suitable temperature ranges, enthalpies of dehydration for the different steps have been evaluated as 5.34, 9.8 and 22.8 kcal mol⁻¹ of H₂O. From the closeness of the first two values to each other, the dehydration steps could be expected to overlap and may

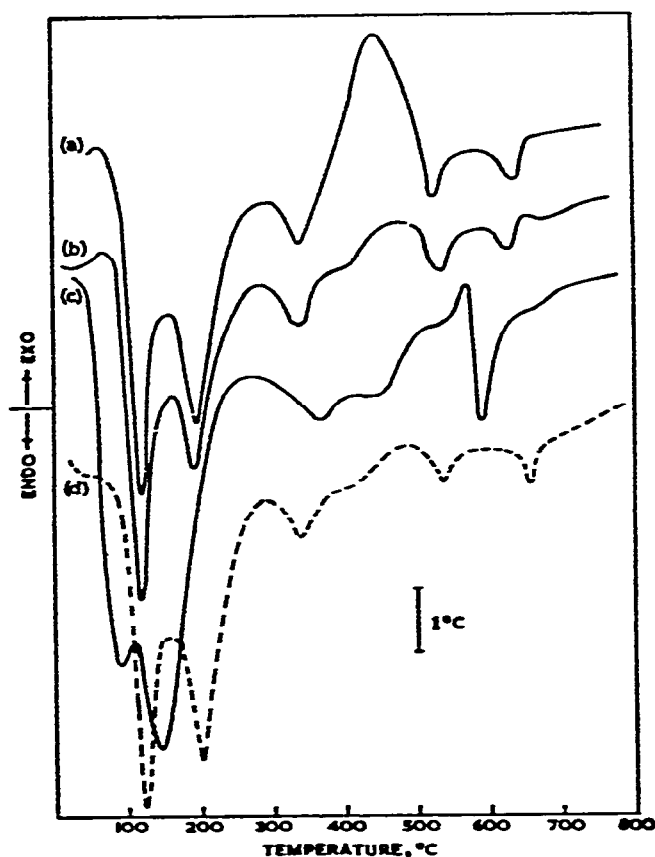


Fig. 3. DTA of CTO in (a) oxygen; (b) nitrogen; (c) vacuum; and (d) carbon dioxide.

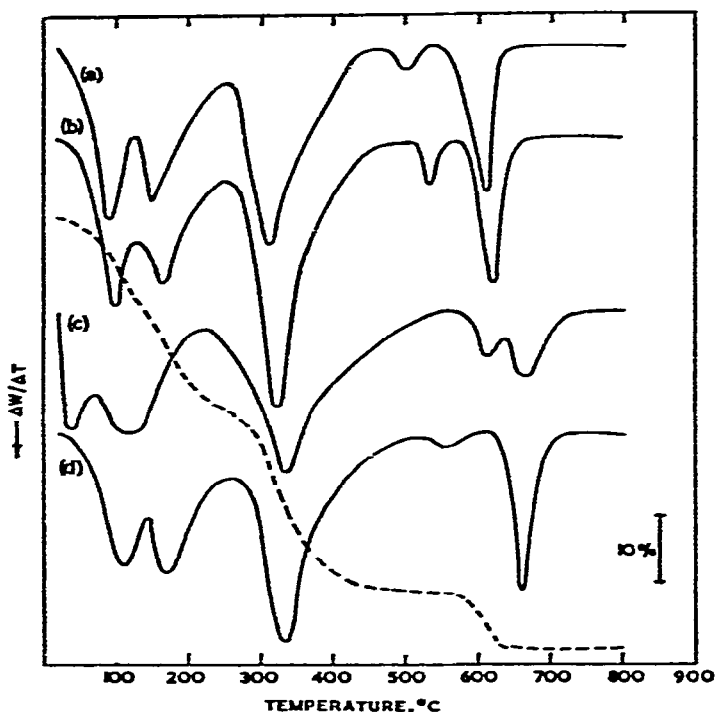


Fig. 4. DTG of CTO in (a) oxygen; (b) nitrogen; (c) vacuum; and (d) carbon dioxide.

be incompletely resolved in the thermal curves. The relative variations in the magnitudes of the dehydration peaks are due to minor changes in the gas flow-rates and the consequent variation of the partial pressure of water vapour over the system.

CTO dehydrates into the tetrahydrate and then to anhydrous oxalate. The dehydration is not completely reversible as the anhydrous oxalate takes up only four water molecules on rehydration. The tetrahydrate as well as the anhydrous oxalate are amorphous to X-rays. The weight loss varies from 27.4 to 29.20%, the excess weight loss being due to adsorbed water. The two dehydration steps are well resolved on all the thermal curves.

Decomposition of the oxalate

The decomposition of the oxalate groups in the case of STO, appears to be a single-step process, in the temperature range 210–450°C. The reaction starts as an endotherm in oxygen but soon becomes exothermic due to the secondary reaction of carbon monoxide. In a vacuum or non-oxidising atmosphere, it is endothermic and peak maxima are at nearly the same temperature. Carbon monoxide and carbon dioxide are the only gaseous products and their ratio varies with the temperature of decomposition. The residue corresponds to the general composition, $\text{SrTiO}_2\text{CO}_3$. The i.r. spectrum of this residue (Fig. 5a) shows the presence of a small amount of retained carbon dioxide in the solid as indicated by the absorption band at 2350 cm^{-1} . The residue can therefore be better formulated as $\text{Sr}_2\text{Ti}_2\text{O}_{4+x}(\text{CO}_3)_{2-x}(\text{CO}_2)_x$ where

$x < 1$. The amount of retained carbon dioxide is highest in carbon dioxide atmosphere and lowest in vacuum. The residue though amorphous to X-rays is non-porous as shown by its low surface area (around $2 \text{ m}^2 \text{ g}^{-1}$).

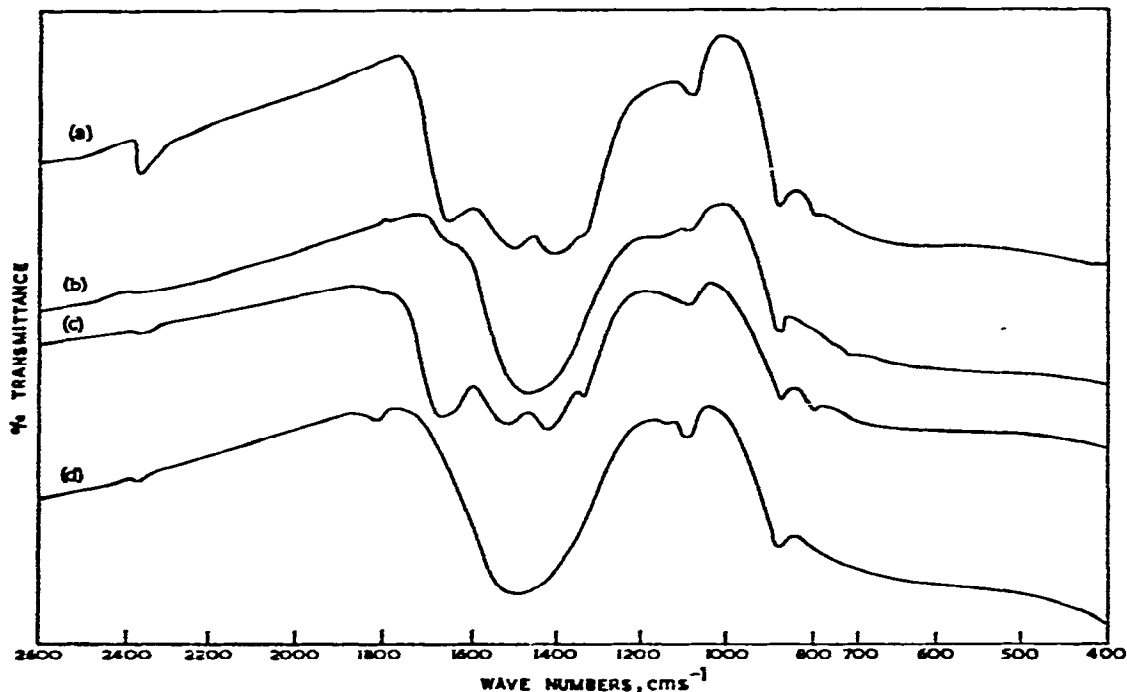


Fig. 5. I.R. spectra of (a) $\text{Sr}_2\text{Ti}_2\text{O}_{4+x}(\text{CO}_3)_{2-x}(\text{CO}_2)_x$; (b) $\text{Sr}_2\text{Ti}_2\text{O}_5\text{CO}_3$; (c) $\text{Ca}_2\text{Ti}_2\text{O}_4(\text{CO}_3)_2$; and (d) $\text{Ca}_2\text{Ti}_2\text{O}_5\text{CO}_3$.

The oxalate in CTO decomposes in an analogous fashion to that of STO, except that the residues do not contain any retained carbon dioxide. The net composition of the residue corresponds to $\text{CaTiO}_2\text{CO}_3$. The i.r. spectrum (Fig. 5c) shows the absence of free carbon dioxide while the carbonate bands are split up. There are four bands in the region 1300 to 1700 cm^{-1} , indicating a monodentate and a bidentate carbonate group (for which the ν_3 band splits to different extent)⁷ are present. The weight losses are identical in oxygen, carbon dioxide and nitrogen atmospheres, supporting the non-retention of carbon dioxide in the residue. In a vacuum the loss in weight is slightly higher, possibly due to further surface decomposition of the residue. The residue is appropriately formulated as $\text{Ca}_2\text{Ti}_2\text{O}_4(\text{CO}_3)_2$.

In non-oxidising atmospheres or a vacuum, the residues are black because of the presence of elemental carbon formed by the disproportionation of carbon monoxide. This has secondary influence on the temperature range of subsequent decomposition.

Decomposition of the carbonate

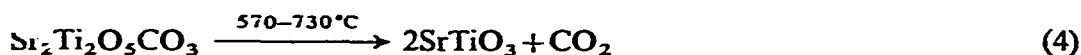
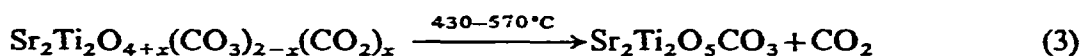
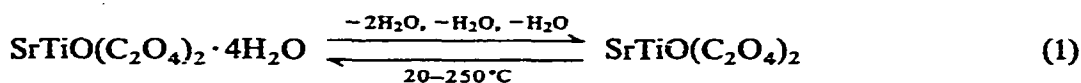
The intermediate strontium titanium carbonate $\text{Sr}_2\text{Ti}_2\text{O}_{4+x}(\text{CO}_3)_{2-x}(\text{CO}_2)_x$ decomposes in two steps. In the first step retained carbon dioxide and one of the

carbonate groups decomposes. In vacuum, this step is pronounced and well resolved as most of the carbon dioxide from the carbonate decomposition is also lost. In other atmospheres the loss of carbon dioxide is only partial while the rest is retained. Isothermal heating of STO at 480 °C for 24 h gives a crystalline residue of composition $\text{Sr}_2\text{Ti}_2\text{O}_5\text{CO}_3$. The X-ray powder diffraction pattern of this residue (though not of good quality) does not correspond to that of SrCO_3 , any polymorph of TiO_2 or SrTiO_3 . The carbonate $\text{Sr}_2\text{Ti}_2\text{O}_5\text{CO}_3$ further decomposes in the temperature range of 570–750 °C to produce the final product SrTiO_3 . The weight loss corresponding to this step is higher in dynamic experiments because of the release of occluded carbon dioxide from the previous decomposition step. The release of retained carbon dioxide is facilitated because of the loosening of the lattice during the final decomposition. The final residue gives a well-defined X-ray diffraction pattern of SrTiO_3 . ($a = 3.9045 \text{ \AA}$)

The carbonate $\text{Ca}_2\text{Ti}_2\text{O}_4(\text{CO}_3)_2$ decomposes first in the temperature range of 450–600 °C to give $\text{Ca}_2\text{Ti}_2\text{O}_5\text{CO}_3$ and carbon dioxide. The intermediate $\text{Ca}_2\text{Ti}_2\text{O}_5\text{CO}_3$, unlike its strontium analogue is amorphous and retains most of the carbon dioxide from the previous decomposition step. The extent of retention depends on the surrounding atmosphere and is a maximum in carbon dioxide and a minimum in vacuum. In the final stage retained carbon dioxide as well as the carbon dioxide from the decomposition of $\text{Ca}_2\text{Ti}_2\text{O}_5\text{CO}_3$ is released in the temperature range of 570–750 °C. The final crystalline residue is CaTiO_3 (pseudo cubic, $a = 15.18 \text{ \AA}$).

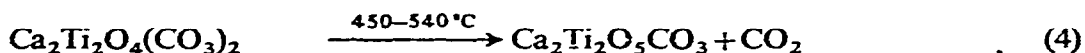
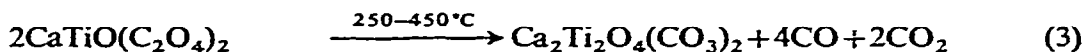
DISCUSSION

From the above results the scheme of decomposition for STO can be formulated as follows: (temp. ranges in oxygen)



The maximum ratio of $\text{CO}:\text{CO}_2$ is 1.6:1.0 in vacuum, against the expected 2:1 as per reaction (2). This is due to the disproportionation of carbon monoxide, as evidenced by the black residue containing elemental carbon. In step (3) expulsion of retained carbon dioxide is accompanied by partial decomposition of a carbonate also. The intermediate $\text{Sr}_2\text{Ti}_2\text{O}_5\text{CO}_3$ has a better crystallinity than the barium analogue and shows little or no tendency to retain free carbon dioxide in the matrix.

The corresponding scheme for the decomposition of CTO may be formulated as follows: (temperature ranges for oxygen)



Of the two non-equivalent carbonate groups in $\text{Ca}_2\text{Ti}_2\text{O}_4(\text{CO}_3)_2$, one may be considered equivalent to free carbon dioxide retained in the matrix of the intermediate $\text{Ba}_2\text{Ti}_2\text{O}_5(\text{CO}_3)(\text{CO}_2)^4$ from barium titanyl oxalate.

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