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Thermal Decomposition of Ba(II) & Sr(II) Bis(oxalato)-oxovanadates(IV)

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Preparation, characterization and thermal decomposition of barium and strontium bis-oxalato-oxovanadates, $MVO(C_2O_4)_2.4H_2O$ are reported. Dehydration of the tetrahydrates takes place in two steps of three and one water molecule. In an oxygen atmosphere, the anhydrous oxalates decompose exothermically, vanadium(IV) is oxidized to vanadium(V) and the decomposition proceeds through an intermediate carbonate to the pyrovanadate, $M_2V_2O_7$. In non-oxidizing atmospheres, the endothermic decomposition of the oxalates results in the formation of the metavanadates, MVO_3 through the intermediate carbonates MVO_2CO_3 and $M_2V_2O_5CO_3$. Free carbon dioxide is found to be trapped in the solid residue during the decomposition of the oxalates.

INTEREST in the vanadates of alkaline earth metals of the type MVO_3 and their solid solutions with lanthanide vanadates $LnVO_3$, stems from their electrical properties[1-6]. Lack of literature of the preparation, characterization and the thermal decomposition of alkaline earth bis-oxalato-oxovanadates(IV), prompted us to undertake the title investigation. The titanates of alkaline earth metals have been prepared by the thermal decomposition of the corresponding titanyl oxalates; the details of these decompositions have been reported by us earlier[7-10]. It is of interest to extend a similar work to bis-oxalato-oxovanadates(IV) wherein it is possible that vanadium may exhibit more than one oxidation state during thermal decomposition. This may bring in considerable variation in the mode of decomposition of the oxalato complex.

Materials and Methods

All the reagents used were of either BDH (AR) or E. Merck (pro-analysi) grade. Vanadium(V) oxide was prepared by decomposing ammonium metavanadate (Reanal-Budapest) at 450° to constant weight.

Barium and strontium bis-oxalato-oxovanadates-(IV) were prepared by adapting the procedure of Satyanarayana[11] for the preparation of ammonium bis-oxalato-oxovanadate(IV). Vanadium(V) oxide (3·638 g, 0·02 mole) was added to aqueous oxalic acid (12·6 g, 0·1 mole). A vigorous reaction took place on warming; vanadium was reduced and went into solution. To the resulting deep blue solution, barium chloride dihydrate (9·77 g) or strontium acetate (8·23 g, 0·04 mole) was added and the solution concentrated. Excess acetone was added when a deep blue viscous layer separated. This on vigorous stirring threw out the bis-oxalato-oxovanadate(IV) in the form of an easily settling powder. This was filtered, washed with acetone and air-dried.

Barium and strontium in these complexes were determined as sulphates after destroying the oxalate. Total oxalate and vanadium(IV) was determined by permanganimetry. In order to determine vanadium, a known weight of the material was heated at 600° in air, whereby oxalate was decomposed and vanadium(IV) was oxidized. The resulting vanadium(V) was determined by titration with standard ferrous solution using N-phenylanthranilic acid as indicator. Water was determined by heating a known weight of the material and absorbing the evolved water in anhydrous magnesium perchlorate.

The chemical analysis of the barium compound is as follows: Ba, 31·02; V, 11·2; C_2O_4, 38·52; H_2O, 16·31% [Calculated for $BaVO(C_2O_4)_2.4H_2O$ (BVO): Ba, 30·36; V, 11·27; C_2O_4, 38·91; H_2O, 15·92%]. For the strontium compound, the results of chemical analysis are: Sr, 21·82; V, 12·53; C_2O_4, 43·97; H_2O, 18·29% [Calculated for $SrVO(C_2O_4)_2.4H_2O$ (SVO): Sr, 21·77; V, 12·66; C_2O_4, 43·72; H_2O, 17·88%].

Apparatus for thermal analyses and other physical techniques have been described in an earlier paper[7].

Gas analysis — Gases evolved during the thermal decomposition were detected by means of a MS 10 mass spectrometer and were found to be only carbon monoxide and carbon dioxide. Amounts of carbon monoxide and carbon dioxide evolved in a flowing atmosphere of oxygen were determined as follows: A known weight of the material was completely decomposed and the evolved carbon dioxide was absorbed in ascarite. In a second experiment, carbon monoxide was oxidized to carbon dioxide by means of heated copper(II) oxide and all the carbon dioxide was absorbed in ascarite.

Effluent gas analysis (EGA) was carried out using a vacuum system wherein 2 or 3 mg of the anhydrous sample was heated in a quartz reaction tube attached to a vacuum line, at a constant rate of 5° min^{-1}. In one experiment, the total pressure due to both carbon monoxide and carbon dioxide was measured at 10° intervals, using a Pirani gauge. In a second experiment, carbon dioxide was condensed using a liquid nitrogen trap and only carbon monoxide pressure was recorded. Carbon dioxide pressure was found by difference. In each case,

the rate of increase in pressure was plotted against temperature at 10° interval to obtain the EGA plot.

For obtaining residues at different temperatures, known weight of the material was heated under a dynamic vacuum of 10^{-3} mm in a conventional vacuum line.

Results

The DTA of BVO in flowing atmospheres of oxygen and carbon dioxide and in a dynamic vacuum are presented in Fig. 1. The corresponding DTG are plotted in Fig. 2, while the EGA results are shown in Fig. 3. Similar results for SVO are presented in Figs. 4-6. The thermal analyses carried out in flowing atmospheres of nitrogen and argon are similar to those in a vacuum. Hence, only the TG traces in argon for BVO and SVO are presented in Figs 2 and 5 respectively for the sake of comparison. From the thermoanalytical curves it is clear that the mode of decomposition of both BVO and SVO in oxygen atmosphere is different from that in non-oxidizing atmospheres except for the initial dehydration step.

The decomposition takes place in three stages: dehydration of the tetrahydrate, decomposition of the oxalate to form a carbonate; and decomposi-

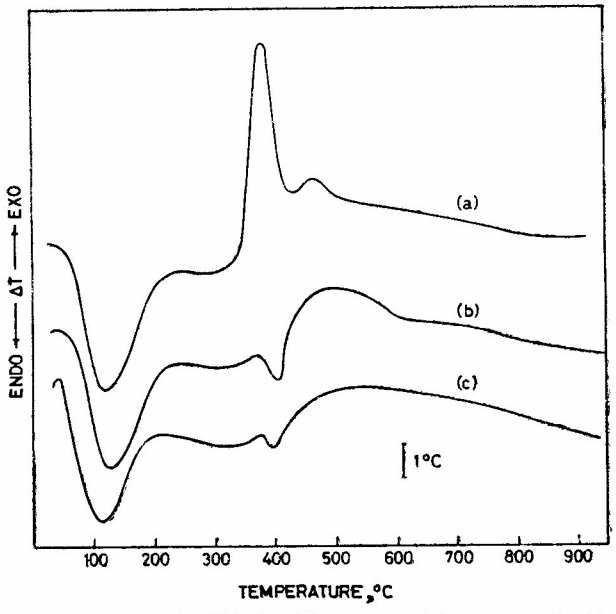

Fig. 1 — DTA of BVO in (a) oxygen, (b) carbon dioxide and (c) a vacuum

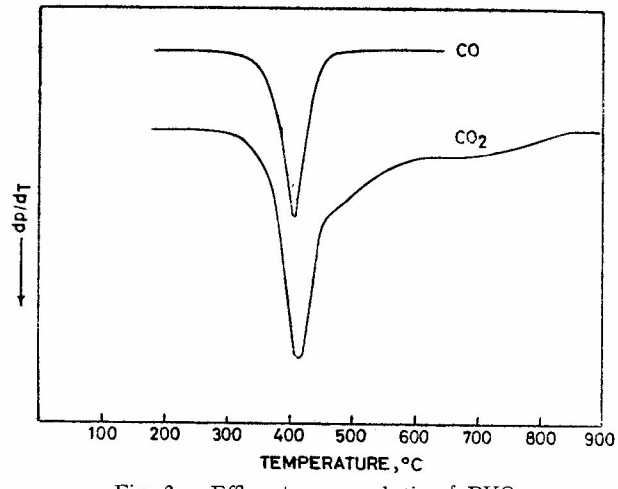

Fig. 3 — Effluent gas analysis of BVO

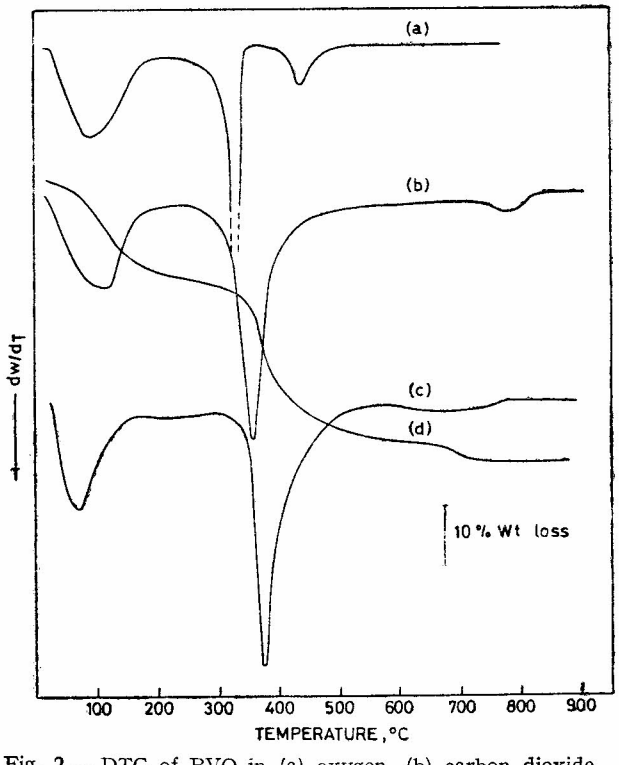

Fig. 2 — DTG of BVO in (a) oxygen, (b) carbon dioxide and (c) a vacuum, (d) TG of BVO in argon

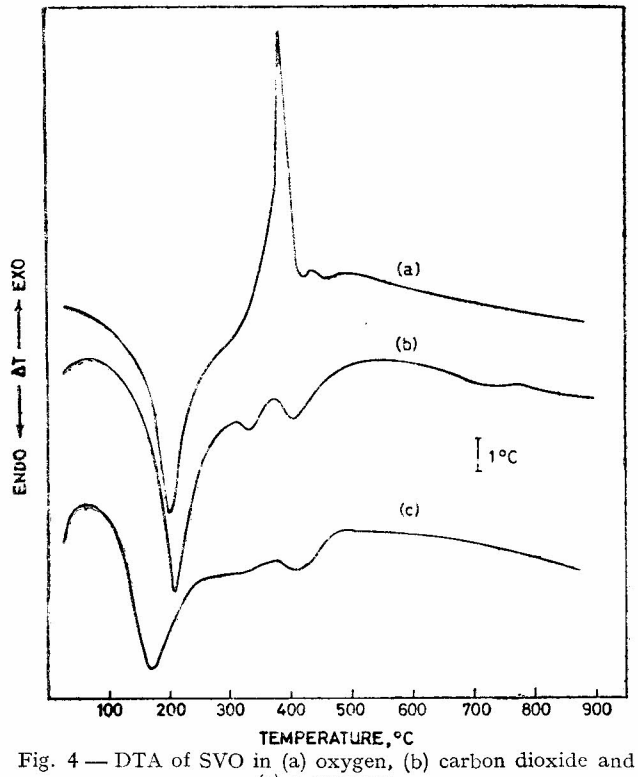

Fig. 4 — DTA of SVO in (a) oxygen, (b) carbon dioxide and (c) a vacuum

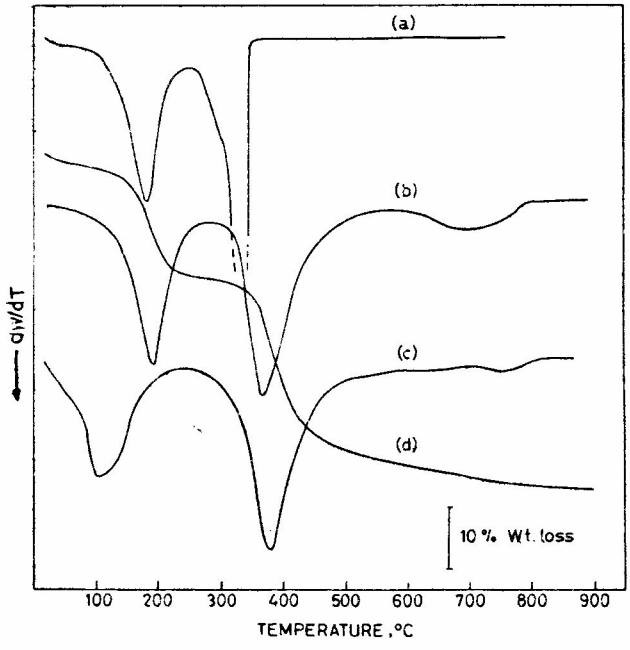

Fig. 5 — DTG of SVO in (a) oxygen, (b) carbon dioxide and (c) a vacuum, (d) TG of SVO in argon

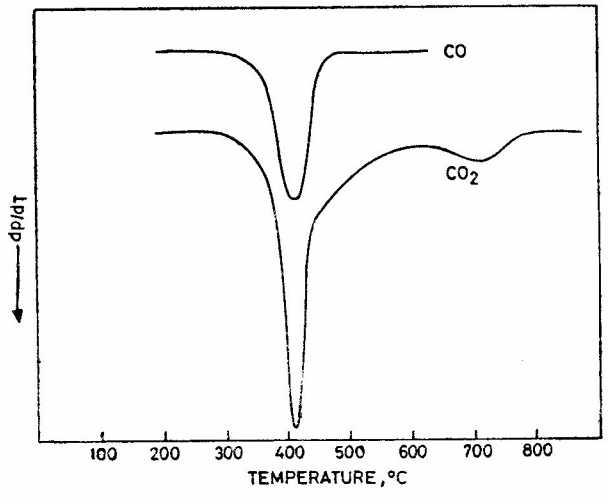

Fig. 6 — Effluent gas analysis of SVO

tion of the carbonate to form the vanadate. There is one to one correspondence between the DTA and DTG curves indicating that every thermal change is accompanied by a corresponding weight loss.

Dehydration — BVO is a dark bluish grey powder and is amorphous to X-rays. It turns dark grey on dehydration. The powder X-ray diffraction pattern of sky-blue SVO indicates its crystalline nature with a low symmetry class. It is slightly soluble in water. Dehydration of SVO results in a grey powder, amorphous to X-rays. Magnetic moments of both BVO and SVO correspond to the presence of one unpaired electron and hence there is no spin-spin interaction in these as observed in many vanadium(IV) compounds[12]. The IR spectra of BVO and SVO are almost identical with the IR spectrum of ammonium bis-oxalato-oxovanadate (IV)[11]. Thermograms indicate that they dehydrate in two steps losing three and one water molecule respectively. The first stage of dehydration takes place around 130° for BVO and 205° for SVO at ambient pressure. In a vacuum, the temperatures are lowered to 115° and 180° respectively. The second dehydration step is not well resolved in the thermograms and occurs around 300° for both BVO and SVO. Isothermal experiments also indicate that the last water molecule is strongly bound and can be removed only above 200° at ambient pressure or at 150° in a vacuum. Both the dehydration steps are irreversible for BVO while SVO can be rehydrated. However, it reabsorbs more water than required for the tetrahydrate. This rehydrated stuff still retains the grey colour and is amorphous to X-rays. The surface area of the isothermally dehydrated products is around 10 m^2g^{-1}.

Decomposition of the oxalate — Anhydrous BVO decomposes exothermically in oxygen. The exothermic nature is due to (i) oxidation of carbon monoxide evolved during the decomposition and (ii) oxidation of vanadium(IV) to vanadium(V). The residue indicated by the thermograms around 400° is pale yellow and is amorphous to X-rays. Its chemical analysis and IR spectrum indicate it to contain unidentate carbonate and to possess the composition $Ba_2V_2O_{7-x}(CO_3)_x (x \sim 0{\cdot}5)$. The same-residue can be obtained by isothermal heating of BVO in air at 280°. Both carbon monoxide and carbon dioxide are evolved and over 70% of the former is oxidized to carbon dioxide.

For anhydrous SVO decomposition in oxygen, there is no step on the thermogram corresponding to the formation of an intermediate carbonate. However, isothermal heating of SVO at 300° in air for 12 hr results in a yellow residue which contains carbonate as indicated by chemical analysis as well as IR spectrum. It is, however, thermally unstable and continues to lose weight with further heating. This indicates that a transient carbonate is formed during the decomposition of SVO. The final product of decomposition is $Sr_2V_2O_7$.

In non-oxidizing atmospheres anhydrous BVO and SVO start decomposing around 300°. The TG curves show a change in slope after about half the decomposition. EGA indicates that both carbon monoxide and carbon dioxide are simultaneously evolved though carbon dioxide is present in larger quantities indicating extensive disproportionation of carbon monoxide. The EGA curve for carbon monoxide is symmetrical and returns to the base line after 480°. On the other hand, the EGA curve for carbon dioxide is highly asymmetric, broad above 450° and returns to base line only above 750°. This indicates that carbon dioxide continues to evolve after the completion of oxalate decomposition (which is marked by the cessation of carbon monoxide evolution). This can be explained on the basis of the formation of unstable intermediate carbonates. Such intermediate carbonates could, in fact, be obtained by careful isothermal heating experiments.

The results of the isothermal heating experiments in a vacuum are summarized in Table 1. The

TABLE 1 — RESULTS OF ISOTHERMAL HEATING OF BVO AND SVO IN A VACUUM AT VARIOUS TEMPERATURES

Compound	Heating temp. °C	Heating period (hr)	Obs. total wt loss (%)	Comp. of residue	Calc. wt loss (%)	Surface area ($m^2\ g^{-1}$)	IR spectral results
BVO	150-200	12	16·31	$BaVO(C_2O_4)_2$	15·92	10	Oxalate
SVO	150-200	12	18·29	$SrVO(C_2O_4)_2$	17·88	11	do
BVO	350	24	21·52	—	—	33	Oxalate, carbonate, carbon dioxide
SVO	350	24	38·5	—	—	36	
BVO	400	24	41·0	$Ba_2V_2O_5CO_3$	42·89	4	Unidentate carbonate
SVO	400	24	43·32	$SrVO_2CO_3$	42·55	56	
BVO	500	24	42·11	$Ba_2V_2O_5CO_3$	42·89	2	Unidentate carbonate
SVO	500	24	48·09	$Sr_2V_2O_5CO_3$	48·01	2	Ionic carbonate
BVO	600	24	47·7	$BaVO_3$	47·75	Small	—
SVO	600	24	54·4	$SrVO_3$	53·47	do	—

residue at 350° contains both oxalate and carbonate. It is not stable and the oxalate group decomposes on further heating. The major features of the IR spectra of the intermediates are given in Table 1. The residue at 350° shows, in addition to the bands due to oxalate and carbonate, the 2350 cm^{-1} band due to gaseous carbon dioxide. The IR spectra of the carbonate residues have been interpreted on the basis of whether the ν_3 band is split or not, and, if split, on the magnitude of separation[13].

All the intermediate residues are dark grey and are amorphous to X-rays.

Decomposition of carbonate — In oxygen, the carbonate $Ba_2V_2O_{7-x}(CO_3)_x$ decomposes in the temperature range 360°-600° to form $Ba_2V_2O_7$ which is almost colourless. SVO forms directly $Sr_2V_2O_7$.

In non-oxidizing atmospheres, the final step in the thermograms in the temperature range 550°-800° corresponds to the decomposition of the carbonates $M_2V_2O_5CO_3$ to form MVO_3. DTA does not clearly show this peak probably due to low enthalpy change involved and also due to the large temperature range. EGA shows the evolution of only carbon dioxide as expected.

The final products of decomposition, MVO_3, are distinctly crystalline. The X-ray powder diffraction pattern of $BaVO_3$ is in good agreement with those reported by Feltz and Schmalfuss[2] as well as by Palanisamy *et al.*[3]. The powder diffraction pattern of $SrVO_3$ is in agreement with those reported by Chamberland and Danielson[1]. Further, the preliminary electrical conductivity measurements on pelletized samples indicate that $BaVO_3$ is a semiconductor and $SrVO_3$ is metallic, in agreement with available reports[1,3]. The vanadates $M_2V_2O_7$ obtained by decomposing the oxalates in oxygen can be reduced to MVO_3 by means of hydrogen around 800° as reported by Feltz and Schmalfuss as also by Palanisamy *et al.*

Discussion

The position of peaks on thermograms depend on experimental conditions. Yet in related compounds, they indicate the strength of the bond that is rupturing. Hence, structural details of the materials under investigation assume importance.

The structure of both BVO and SVO are not known. However, the structure of ammonium bis-oxalato-oxovanadate(IV) has been recently solved[14,15] and the close resemblance between this and BVO and SVO in spectral and magnetic properties indicates that at least, the coordination sphere around vanadium atom in these compounds is the same. Accordingly, vanadium in both BVO and SVO can be six-coordinated; the two oxalate groups, *cis* to each other, occupy four coordination positions; the vanadyl (V=O) oxygen is in the fifth position and the sixth position is occupied by a water molecule. The remaining three water molecules are structural waters. On dehydration, these three water molecules of crystallization are removed first bringing about a collapse in the crystal structure. The higher temperature required for this process in SVO compared to BVO is because of its crystallinity. The fourth water molecule, coordinated to vanadium, is removed around 300° as indicated on the thermograms.

The scheme of dehydration may, therefore, be written as shown in Eqs. (1) and (2):

$$MVO(C_2O_4)_2.4H_2O \xrightarrow{<200^\circ} MVO(C_2O_4)_2.H_2O + 3H_2O \quad \ldots(1)$$

$$MVO(C_2O_4)_2H_2O \xrightarrow{200-300^\circ} MVO(C_2O_4)_2 + H_2O \quad \ldots(2)$$

Decomposition of the oxalate takes place in a single step, though, to start with, the two oxalates are not equivalent. When the coordinated water molecule is removed, the coordination sphere around vanadium is rearranged [most probably to a square pyramidal configuration which is preferred by oxovanadium(IV) in many of its complexes[16]] to bring about equivalence of the two oxalate groups.

In oxygen atmosphere, the steps (3 and 4) are involved in the decomposition of the anhydrous oxalates.

$$2MVO(C_2O_4)_2 + 1/2O_2 \longrightarrow M_2V_2O_{7-x}(CO_3)_x + 4CO + (4-x)CO_2 \quad \ldots(3)$$

$$M_2V_2O_{7-x}(CO_3)_x \longrightarrow M_2V_2O_7 + xCO_2 \quad \ldots(4)$$

In non-oxidizing atmospheres, the decomposition follows steps (5-7) (temperatures are for isothermal heating).

$$MVO(C_2O_4)_2 \xrightarrow{400^\circ} MVO_2CO_3 + 2CO + CO_2 \quad \ldots(5)$$

$$2MVO_2CO_3 \xrightarrow{500^\circ} M_2V_2O_5CO_3 + CO_2 \quad ...(6)$$

$$M_2V_2O_5CO_3 \xrightarrow{600^\circ} 2MVO_3 + CO_3 \quad ...(7)$$

Though for BVO the intermediate $BaVO_2CO_3$ cannot be isolated, EGA clearly indicates its transient formation.

The scheme of decomposition given above for BVO and SVO in non-oxidizing atmospheres is closely similar to those proposed by us for the thermal decomposition of titanyloxalates[7-10]. The temperature range of decomposition for BVO and SVO are higher than those for the titanyloxalates, indicating that the oxalato complexes of oxovanadium(IV) are stabler than those of oxotitanium(IV). Further, the surface area increases considerably during the decomposition of BVO and SVO whereas it is almost constant in the decomposition of the titanyloxalates. Here again, we observe that free carbon dioxide is trapped in the solid residue during the initial stages of the decomposition of the oxalate. The trapped gas is given out as the oxalate decomposition is completed. Since the surface area and hence the porosity also increases with oxalate decomposition, the trapped carbon dioxide may find easy channels for diffusing out with increasing extent of decomposition of oxalate. Such a situation is not present in the case of the residues obtained by decomposing titanyloxalates which remain non-porous throughout the decomposition and hence escape of trapped carbon dioxide is hindered in them. This is in accordance with Gafner's[17] treatment of the problem of occlusion of gases in a solid as a result of slow diffusion from homogeneously decomposing particles.

Though it is claimed[18] that the IR band at 2350 cm^{-1} often occurs in the spectra of carbonates and carbonatocomplexes, the reported IR spectra[13,19] do not bear this out. Indeed, it is significant to observe that this band appears in only those materials that are obtained by thermal decomposition as was noted by van de Velde *et al.* in the thermal decomposition of ammonium[20] and lead titanyloxalates[18] and in our own studies on titanyloxalates.

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