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Review

THERMAL STUDIES ON TITANYL AND ZIRCONYL OXALATES. A REVIEW

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ABSTRACT

Past work covering the year 1983 on the thermal studies on titanyl and zirconyl oxalates is reviewed.

INTRODUCTION

Mixed metal oxides of the type ABO_3 are technologically important because of their electrical properties [1–8]. This prompted the development of chemical methods for preparing these compounds as high purity materials. Chemically pure and stoichiometric mixed metal oxides can be prepared easily by the thermal decomposition of respective mixed metal oxalates. The particle size and reactivity of the end product are significantly influenced by the calcination temperature. Consequently, the thermal decomposition of the precursor assumes special significance.

It has been known for a long time that titanium forms an extensive series of compounds called titanates, in which titanium plays the role of an acidic constituent. Of particular interest have been barium titanate, $BaTiO_3$, and various other compounds in which barium has been replaced by another bivalent metal ion and titanium by zirconium or another acidic metal [9].

Owing to the possession of desirable dielectric and piezoelectric properties these titanates and zirconates have, in recent years, come into extensive use in various electrical devices. In spite of their wide use, the relationship between their composition and electrical characteristics has not been fully worked out, in part because of the presence of minor components originating as impurities in titanium or zirconium dioxide and bivalent metal carbonate used as starting materials in the commercial production of bivalent metal titanates and zirconates. Generally, the titanates and zirconates are prepared by high-temperature methods and the products are usually non-stoichiometric. Further, the calcining temperature affects the properties of the titanates and zirconates. The preparation of ceramic materials at low temperatures

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results in the formation of mixed oxides in a pure, homogeneous and finely divided form [10]. This has necessitated the development of low-temperature chemical methods for their preparation as high purity materials, to determine systematically the effect of various substituent elements on the electrical properties and to arrive at a composition that would give the most desirable product. Oxalates are particularly useful as synthetic intermediates in the potential production of a variety of both simple and complex oxides [11–13].

The incorrect identification of the intermediates by earlier workers, due to the lack of sufficient techniques, led to some confusion regarding the mechanism of decomposition of titanyl and zirconyl oxalates. To overcome this, during the past decade, the thermal properties of titanyl and zirconyl oxalates have been extensively investigated. Since the confusion still prevails, it necessitated a review of the work done in this field to correlate the results of different authors and to arrive at a conclusion which can better explain the decomposition mechanism of these materials. The present work incorporates some interesting papers on the thermal behaviour of titanyl and zirconyl oxalates.

STRUCTURE

The structure of titanyl and zirconyl oxalates may be proposed on the basis of the available IR spectral data. In general, lattice water absorbs at 3550–3200 cm^{-1} (antisymmetric and symmetric OH stretching) and at 1635–1600 cm^{-1} (HOH bending). Though OH stretching vibrations in the oxalate compounds absorb clearly at ~ 3300 cm^{-1}, the HOH bending vibrations seems to be merged with the symmetric $\nu(C{=}O)$ vibrations appearing in the range 1650–1750 cm^{-1}. According to Nakamoto [14], the band at ~ 1440 cm^{-1} can be assigned to the coupled vibrations $\nu(C{-}O) + \nu(C{-}C)$. Further, a series of coupled vibrations have been observed at around 1350, 900, 800, 525, 500 and 400 cm^{-1}, which can be assigned to $\nu(C{-}O) + \delta(O{-}C{=}O)$, $\nu_s(C{-}O) + \delta(O{-}C{=}O)$, $\delta(O{-}C{=}O) + \nu(M{-}O)$, $\nu(M{-}O) + \nu(C{-}C)$, ring deformation + $\delta(O{-}C{=}O)$ and $\nu(M{-}O)$ + ring deformation vibrations [14], respectively.

According to Dehnicke and Weidlein [15], the $\nu(Zr{=}O)$ stretching frequency vibration appears at ~ 900 cm^{-1}. Though bands of moderate intensity were observed at 900 cm^{-1}, a comparison with the oxalato complexes of titanium(IV) and zirconium(IV) [16] shows that this band belongs to the fundamental vibrations of the $\nu(C{-}O) + \nu(M{-}O) + \delta(O{-}C{=}O)$ group [17] and not to the stretching vibrations of the titanyl/zirconyl group [18]. Further, such a group has not been identified by X-ray diffraction methods [19].

By analogy with the crystal structure of $ZrCl_2 \cdot 8H_2O$ [20], Kharitonov et al. [18] proposed a complex tetramer $[Zr_4(OH)_8(C_2O_4)_8]^{8-}$ as the anion present in the zirconyl oxalates. In this anion, zirconium atoms are linked to one another by hydroxyl bridges, and each zirconium is coordinated by two bidentate oxalate groups. For this structure to be valid, the spectra of the zirconyl oxalate complex should show a sharp band in the region 3500–3700 cm^{-1} assignable to ν(O–H) and another band in the region 970–1000 cm^{-1} due to δ(Zr–O–H). The ν(O–H) is neither present in the spectra reported by Kharitonov et al., nor was it observed by Gangadevi et al. [19]. Moreover, the above type of structure cannot explain the stability of anhydrous titanyl/zirconyl oxalates, the difference in the thermal decomposition characteristics of simple titanyl/zirconyl oxalates compared to complex titanyl/zirconyl oxalates, or the non-equivalence of the two oxalate groups in the complex titanyl/zirconyl oxalates.

Considering all the above points, in the case of simple titanyl/zirconyl oxalate, the oxalate group should act as a quadridentate ligand in order to conform to molecular formula. Water molecules constitute only water of hydration and are not coordinated to the metal ion [19]. Considering all these aspects, two structures can be assigned to the simple titanyl/zirconyl oxalate (Fig. 1). In structure (**a**), all the (C–O) bonds are equivalent and have neither a double-bond nor a single-bond character, but an intermediate character; the ν_{as}(C=O) frequency should occur at 1590–1650 cm^{-1}, which, however, is not present in the IR spectrum of simple titanyl/zirconyl oxalate. A strong band at 1690 cm^{-1}, which can be assigned to ν_{as}(C=O), is present in the IR spectrum. Hence, structure (**b**) is the more likely one, with titanium/zirconium having a coordination of six.

For titanyl/zirconyl oxalic acid, pyridinium, potassium or ammonium titanyl/zirconyl oxalate and bivalent metal titanyl/zirconyl oxalates, $AMO(C_2O_4)_2 \cdot nH_2O$ (A = H_2, $(NH_4)_2$ or bivalent metal ion, n = number of water molecules of crystallisation), two possible structures can be envisaged [21].

(i) A cyclic tetranuclear structure, $[Mo_{1/2}O_{1/2}(C_2O_4)_2]_4^{8-}$, which $\bar{1}$ sym-

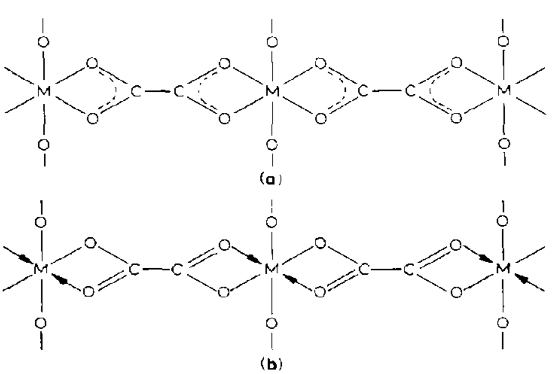
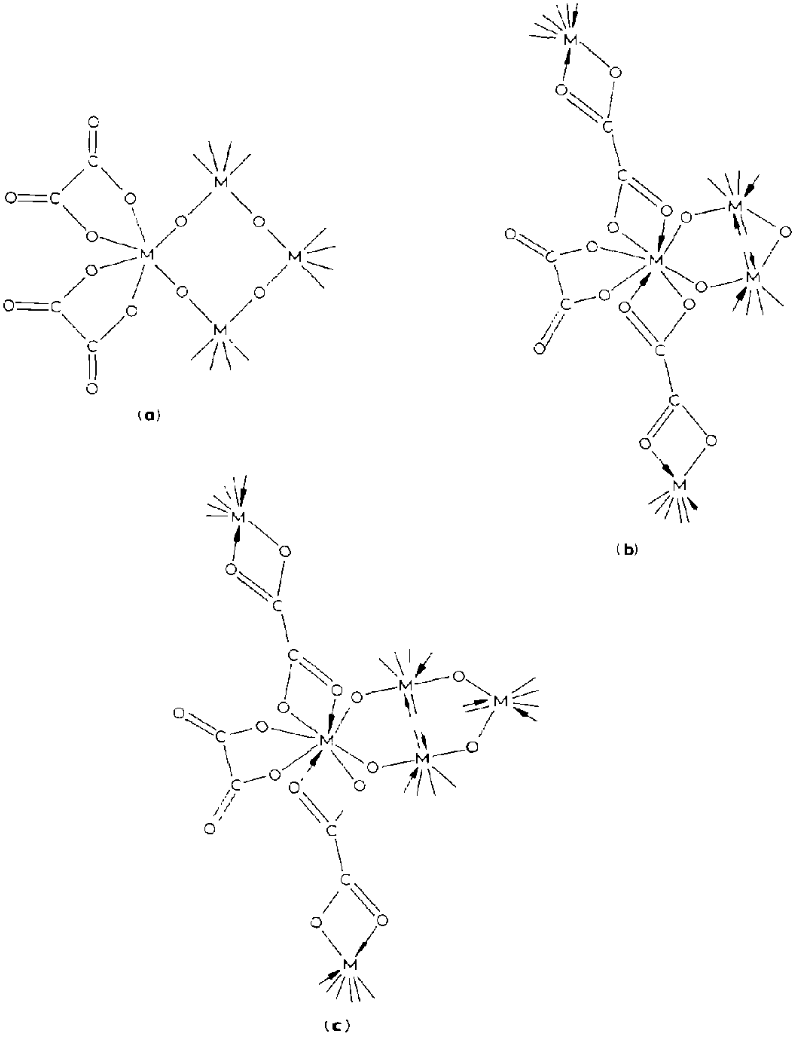


Fig. 1. Possible structures for simple titanyl/zirconyl oxalate (M = Ti, Zr).

metry (Fig. 2, structure **a**), where the titanium/zirconium is hexacoordinated with two bridging oxygen atoms and four oxygen atoms of the two bidentate oxalate groups [22], together forming a distorted octahedron. Though this structure could explain the stability of the anhydrous oxalates, it fails to account for the non-equivalence of the oxalate groups.

(ii) Another ring structure, in which one oxalate group is acting as a bidentate ligand and another two as tetradentate ligands with two bridging oxygen atoms coordinated to titanium or zirconium, corresponds to eight-coordinated geometry [20,23–26]. Here, the two bridging oxygen atoms which are in *cis* position to one another, the four oxygens from the tetradentate oxalates and two oxygens from the bidentate oxalates form a dodecahedron



(a)

(b)

(c)

Fig. 2. Possible structures for $AMO(C_2O_4)_2 \cdot nH_2O$ (A = H_2, $(NH_4)_2$, K_2, $(C_5H_5NH)_2$, bivalent metal ion; M = Ti, Zr; n = number of water molecules of hydration.

(Fig. 2, structures **b** and **c**). The basic ring structure, consisting of titanium/zirconium atoms linked through oxygen atoms, can be 6-, 8- or 12-membered, which can be confirmed only by X-ray studies.

Decomposition of titanyl oxalate

Broadbent et al. [27] investigated the thermal behaviour of titanyl oxalate. The thermogram of the compound indicates the formation of a stable residue between 613 and 773 K and above 773 K it decomposes to another residue which is stable up to 1273 K. X-ray analysis results show this to be rutile (TiO_2). The DTA results show peaks associated with each decomposition change. Their exothermic nature could be caused by gaseous reactions catalysed on the surface.

The scheme proposed by Broadbent et al. [27] is a little confusing. This confusion has been overcome by the detailed investigation of Murthy et al. [28]. The scheme proposed by these authors has the following features. Two moles of water are lost in the temperature range 298–433 K and the remaining between 433 and 533 K. The last dehydration step overlaps with the oxalate decomposition. The latter takes place in a single step and the total mass loss is in excellent agreement with the expected values. There is no indication of the formation of an intermediate carbonate. The oxalate decomposition is endothermic even in oxygen. This is because the water vapour evolved during the dehydration step displaces oxygen in the immediate surroundings of the solid so that further decomposition of oxalate takes place in an apparent atmosphere of water vapour. This prevents the exothermic oxidation of carbon monoxide [29,30]. The exothermic peak following the oxalate decomposition (unaccompanied by any mass loss) is due to the crystallisation of amorphous titanium dioxide to anatase. There is no exothermic peak around 773 K in the DTA curve of titanyl oxalate as reported by Broadbent et al. [27]. Since these authors prepared titanyl oxalate starting from a fused mixture of potassium hydroxide and titanium dioxide, there is every possibility of potassium oxalate/potassium titanyl oxalate being present as impurities in their preparations. Both these oxalates gave similar peaks in the same temperature range [28].

Decomposition of zirconyl oxalate

The thermal decomposition of zirconyl oxalate was studied systematically by Gangadevi et al. [19]. There are two major decomposition steps, viz. dehydration of the hydrate and the decomposition of the oxalate to zirconium oxide.

$$ZrO(C_2O_4)\cdot 5.5H_2O \xrightarrow{298-473\ K} ZrO(C_2O_4)\cdot 1.5H_2O + 4H_2O \tag{1}$$

$$ZrO(C_2O_4)\cdot 1.5H_2O \xrightarrow{473-673\ K} ZrO_2 + 1.5H_2O + CO + CO_2 \tag{2}$$

Dehydration of the hydrate takes place in two steps. The second step overlaps the oxalate decomposition and results in the formation of zirconium dioxide. The two steps are not resolved on either DTA or DTG. The oxalate decomposition is endothermic even in air because it takes place in an atmosphere of water vapour. There is a small exotherm between 698 and 748 K in DTA, unaccompanied by any mass loss. This is attributed to the crystallisation of amorphous ZrO_2 to the monoclinic phase. This crystallisation peak was missed by Agarwal and Naik [31]. Both isothermal experiments and the single-step decomposition of oxalate, fail to indicate the formation of an intermediate carbonate as reported by Shkarin et al. [32].

Decomposition of ammonium titanyl oxalate

Van De Velde and Oranje [33] studied the thermal decomposition of ammonium titanyl oxalate and proposed the following decomposition scheme

$$(NH_4)_2TiO(C_2O_4)_2\cdot H_2O \xrightarrow{303-353\text{ K}} (NH_4)_2TiO(C_2O_4)\cdot \tfrac{1}{2}H_2O + \tfrac{1}{2}H_2O \qquad (1)$$

$$(NH_4)_2TiO(C_2O_4)\cdot \tfrac{1}{2}H_2O \xrightarrow{363-433\text{ K}} (NH_4)_2TiO(C_2O_4)_2 + \tfrac{1}{2}H_2O \qquad (2)$$

$$\left\{\begin{array}{ll} (NH_4)_2TiO(C_2O_4)_2 \xrightarrow{483-603\text{ K}} & TiO_{2-x}(CO_3)_x + 2NH_3 + H_2O \\ & + (2-x)CO_2 + 2CO \\ 2yCO \rightarrow yC + yCO_2 & \end{array}\right. \qquad (3,4)$$

$$TiO_{2-x}(CO_3)_x \xrightarrow{803-873\text{ K}} TiO_2 + xCO_2 \qquad (5)$$

$$yC + yO_2 \xrightarrow{673-1173\text{ K}} yCO_2 \text{ (slow reaction)}$$

where $x = 0.15$, $y = 0.23$.

These results disagree with the findings of Papazian et al. [34], who reported the dehydration in steps of 1/3 and 2/3 moles of H_2O, respectively.

The oxalate decomposition in air involves three steps, two overlapping endothermal and one exothermal peak. The last one is absent in a nitrogen atmosphere. This peak most probably represents partial oxidation of CO, possibly catalysed by reactive TiO_2. The formation of the oxide–carbonate intermediate $TiO_{2-x}(CO_3)_x$ is identified by IR spectral studies. However, in nitrogen atmosphere no carbonate is formed, but only a mixture of TiO_2 and carbon. After the carbonate decomposition the residue contains fine-particle anatase with a slight impurity of carbon included.

Decomposition of pyridinium titanyl oxalate

The following decomposition mechanism is proposed for the decomposition of pyridinium titanyl oxalate by Van De Velde and Oranje [33].

$$(C_5H_5NH)_2TiO(C_2O_4)_2 \cdot 2H_2O \xrightarrow{293-353\ K} (C_5H_5NH)_2TiO(C_2O_4)_2 + 2H_2O \quad (1)$$

$$\left\{\begin{array}{lll} (C_5H_5NH)_2TiO(C_2O_4)_2 & \xrightarrow{373-673\ K} & TiO_2 \cdot x(C_5H_5N) + H_2O \\ & & +(2-x)C_5H_5N + 2CO_2 + 2CO \\ 2yCO \rightarrow yC + CO_2 & & \end{array}\right. \quad (2\text{–}4)$$

$$TiO_2 \cdot xC_5H_5N \xrightarrow{813-863\ K} TiO_2 + \text{decomp. product of pyridine} \quad (5)$$

$$(y+z)C + (y+z)O_2 \xrightarrow{673-1273\ K} (y+z)CO_2 \text{ (very slow reaction)}$$

where $x = 0.10$, $y = 0.25$, $z = 0.04$.

The dehydration of oxalate occurs in one step, during which the product becomes X-ray amorphous. The water-free compound is not hygroscopic.

The oxalate decomposition is a complicated process of four endotherms, also indicated by the bending points of the TG curve. In nitrogen atmosphere, the first and last processes are retarded. The IR oxalate peaks disappear slowly while peaks of free pyridine become observable. This means that part of the liberated pyridine is absorbed by TiO_2. No formation of carbonate could be detected.

Decomposition of zirconyl oxalic acid and ammonium zirconyl oxalate

Zaitsev et al. [35] concluded from a combination of TG and isothermal heating experiments on zirconyl oxalic acid trihydrate that dehydration takes place in two steps in the temperature ranges 298–373 and 473–493 K. It is reported that first a monohydrate and later the anhydrous oxalate is produced. Further, the oxalate is supposed to decompose in a single step between 593 and 623 K. The recent results of Gangadevi et al. [19] do not lend support to this decomposition scheme. From the results reported in their investigation, the following scheme is proposed for the decomposition of zirconyl oxalic acid.

$$H_2ZrO(C_2O_4)_2 \cdot 3H_2O \xrightarrow{298-398\ K} H_2ZrO(C_2O_4)_2 + 3H_2O \quad (1)$$

$$H_2ZrO(C_2O_4)_2 \xrightarrow{398-548\ K} H_2ZrO(C_2O_4)_{2-x}(CO)_x \quad (2)$$

$$H_2ZrO(C_2O_4)_{2-x}(CO_3)_x \xrightarrow{548-673\ K} ZrO_2 + H_2O + 2CO_2 + (2-x)CO \quad (3)$$

A similar decomposition is proposed for ammonium zirconyl oxalate by these authors [19].

$$(NH_4)_2ZrO(C_2O_4)_2 \cdot 3H_2O \xrightarrow{298-448\ K} (NH_4)_2ZrO(C_2O_4)_2 + 3H_2O \tag{1}$$

$$(NH_4)_2ZrO(C_2O_4)_2 \xrightarrow{448-533\ K} (NH_4)_2ZrO(C_2O_4)_{2-x}(CO_3)_x \tag{2}$$

$$(NH_4)_2ZrO(C_2O_4)_{2-x}(CO_3)_x \xrightarrow{533-723\ K} ZrO_2 + 2NH_3 + 2CO_2 + (2-x)CO \tag{3}$$

The dehydration of both compounds takes place in a single step, while the decomposition of anhydrous oxalate is reported to be in two consecutive steps through an oxalato–carbonate intermediate of apparent composition $A_2ZrO(C_2O_4)_{2-x}(CO_3)_x$ ($A = H$ or NH_4, $0.5 < x < 1$). The IR spectrum of this intermediate exhibits bands corresponding to oxalate at 1690 cm^{-1} and carbonate at 1390 cm^{-1}. The second stage of decomposition resulted in the formation of monoclinic zirconium oxide, irrespective of the atmosphere. In air, the reaction starts as an endotherm but soon changes to an exotherm because of the side reaction of the evolved carbon monoxide gas. In vacuo or non-oxidising atmosphere, it is endothermic.

Decomposition of a mixture of barium oxalate with titanyl or zirconyl oxalate

The thermal behaviour of a 1 : 1 mixture of barium oxalate, $Ba(C_2O_4) \cdot 1.5H_2O$, with titanyl oxalate, $TiO(C_2O_4) \cdot 3.5H_2O$, or zirconyl oxalate, $ZrO(C_2O_4) \cdot 5H_2O$, was investigated by Narayanana Kutty and co-workers [19,28]. The DTA of mixed oxalates show all the peaks of individual oxalates at nearly the same temperatures [15,36]. The only difference noticed is that the peak corresponding to the dehydration of barium oxalate is shifted to a higher temperature. This is due to the larger vapour pressure of the oxalate. In the DTA of the mixtures there is no indication of any solid–solid reaction between barium carbonate and titanium or zirconium oxide up to 1273 K. The X-ray diffraction pattern of the residues showed that it it is a mixture of barium carbonate and titanium or zirconium oxide. This shows that even in freshly formed barium carbonate and titanium or zirconium dioxide, there is no enhanced reactivity and thus below 1273 K solid–solid reaction between the two, as reported by Gallagher and Thomson [13] and Sheinkman et al. [37], can be ruled out.

Decomposition of potassium titanyl oxalate

The thermal behaviour of potassium titanyl oxalate dihydrate, $K_2TiO(C_2O_4)_2 \cdot 2H_2O$, was investigated by Broadbent et al. [27]. The dehydration of the oxalate takes place between 343 and 473 K. The anhydrous oxalate then breaks down rapidly in two steps as shown by an inflexion in the curve. An inclined plateau occurs between 563 and 743 K. At 1098 K, the final residue is identified as potassium metatinate, which is stable up to 1273 K. The dehydration process is endothermic in all atmospheres. All other decomposition reactions are exothermic in nitrogen and carbon dioxide.

Decomposition of beryllium titanyl and zirconyl oxalates

The thermal behaviour of beryllium titanyl and zirconyl oxalates under non-isothermal conditions has been investigated by Sharma et al. [38] using TG, DTG and DSC techniques in nitrogen and air atmospheres. The intermediates obtained at the end of various decomposition steps were identified on the basis of chemical analysis and IR spectral studies. The decomposition proceeds through three major steps, viz. dehydration of the hydrate, decomposition of the oxalate to the carbonate and decomposition of the carbonate to the oxide. However, for beryllium zirconyl oxalate two consecutive substeps are observed for the decomposition of the oxalate to the carbonate. In the first step the oxalate groups are partly decomposed to the carbonate resulting in the formation of an oxalato carbonate complex, which further decomposes in the next step to give the respective carbonate. The oxalato–carbonate complex has been assigned the composition $Be_2Zr_2O_3(C_2O_4)_2CO_3$, on the basis of mass loss and chemical analysis. The IR spectrum of this intermediate product shows peaks for both oxalate and carbonate groups. As expected, all three thermal decomposition steps are endothermic reactions. However, for beryllium titanyl oxalate an extra exothermic peak is observed unaccompanied by any weight loss. This is probably due to the transition of beryllium titanate, formed after the decomposition of carbonate, from one crystalline state to another. The following schemes have been proposed for the thermal decomposition of these oxalates.

Decomposition of beryllium titanyl oxalate

$$BeTiO(C_2O_4)_2 \cdot 4H_2O \xrightarrow{338-463\text{ K}} BeTiO(C_2O_4)_2 + 4H_2O \tag{1}$$

$$2BeTi(C_2O_4)_2 \xrightarrow{463-533\text{ K}} Be_2Ti_2O_5CO_3 + 4CO + 3CO_2 \tag{2}$$

$$Be_2Ti_2O_5CO_3 \xrightarrow{543-643\text{ K}} 2BeTiO_3 + CO_2 \tag{3}$$

$$BeTiO_3 \xrightarrow{643-670\text{ K}} BeTiO_3{}^* \tag{4}$$

Decomposition of beryllium zirconyl oxalate

$$BeZrO(C_2O_4)_2 \cdot 4H_2O \xrightarrow{303-453\ K} BeZrO(C_2O_4)_2 + 4H_2O \tag{1}$$

$$2BeZrO(C_2O_4)_2 \xrightarrow{453-533\ K} Be_2Zr_2O_3(C_2O_4)_2CO_3 + CO_2 + 2CO \tag{2}$$

$$Be_2Zr_2O_3(C_2O_4)_2CO_3 \xrightarrow{533-668\ K} Be_2Zr_2O_5CO_3 + 2CO_2 + 2CO \tag{3}$$

$$Be_2Zr_2O_5CO_3 \xrightarrow{673-993\ K} 2BeZrO_3 + CO_3 \tag{4}$$

Calculations of the apparent activation energies and order of reactions were performed in nitrogen atmosphere employing the graphical method of Coats and Redfern [39]. The plot of $-\log[-\log(1-\alpha)/T^2]$ against $1/T \times 10^3$ for $n = 1$ (where α is the fraction decomposed. T is the temperature (K) and n is the apparent order of reaction) results in a straight line with a slope of $-E/2.303R$ for the second and last decomposition steps.

Decomposition of magnesium titanyl and zirconyl oxalates

The thermal decomposition of magnesium titanyl oxalate was studied by Murthy et al. [40] in a flowing atmosphere of oxygen, nitrogen, carbon dioxide and in vacuum, by TG and DTA techniques. The thermal behaviour of magnesium zirconyl oxalate was investigated by Sharma et al. [41] in a dynamic atmosphere of oxygen and nitrogen with the aid of TG, DTG and DSC techniques. All the thermal effects in both compounds were accompanied by a weight loss which consists of four steps: dehydration, decomposition of anhydrous oxalate to oxalato-carbonate intermediate, decomposition of oxalato-carbonate intermediate to carbonate and decomposition of carbonate to yield $MgTiO_3$ or $MgZrO_3$.

The dehydration of magnesium titanyl oxalate heptahydrate takes place in three steps with the elimination of 2, 3 and 2 water molecules per mole, respectively. The last stage of dehydration overlaps the first stage of oxalate decomposition. Magnesium zirconyl oxalate heptahydrate is dehydrated in a single step. The expected endothermic behaviour for the dehydration associated with these compounds has been observed from DTA and DSC curves.

The decomposition of oxalate to carbonate occurs in two steps. The first stage of decomposition results in the formation of the oxalato-carbonate intermediate of composition $Mg_2Ti_2O_4(C_2O_4)CO_3$ or $Mg_2Zr_2O_4(C_2O_4)CO_3$, which, in the second step, produces a carbonate of composition $Mg_2TiO_5CO_3$ or $Mg_2Zr_2O_5CO_3$. The intermediates are coloured, white in oxygen atmosphere and brown to black in non-oxidising atmosphere or in vacuum. The colour in the latter cases is due to the presence of elemental carbon arising from the disproportionation of carbon monoxide. The oxalate decomposition is unique in that it is endothermic even in oxygen.

The carbonate is finally decomposed to the oxide with a shallow endothermic peak in DTA or DSC. The final product is crystalline $MgTiO_3$ or $MgZrO_3$ of ilmenite structure.

Decomposition of magnesium titanyl oxalate

$$MgTiO(C_2O_4)_2 \cdot 7H_2O \xrightarrow{293-533\ K} MgTiO(C_2O_4)_2 + 7H_2O \quad (1)$$

$$2MgTiO(C_2O_4)_2 \xrightarrow{533-653\ K} Mg_2Ti_2O_4(C_2O_4)CO_3 + 3CO + 2CO_2 \quad (2)$$

$$Mg_2Ti_2O_4(C_2O_4)CO_3 \xrightarrow{653-793\ K} Mg_2Ti_2O_5CO_3 + CO + CO_2 \quad (3)$$

$$Mg_2Ti_2O_5CO_3 \xrightarrow{793-973\ K} 2MgTiO_3 + CO_2 \quad (4)$$

Decomposition of magnesium zirconyl oxalate

$$MgZrO(C_2O_4)_2 \cdot 7H_2O \xrightarrow{298-523\ K} MgZrO(C_2O_4)_2 + 7H_2O \quad (1)$$

$$2MgZrO(C_2O_4)_2 \xrightarrow{523-593\ K} Mg_2Zr_2O_4(C_2O_4)CO_3 + 3CO + 2CO_2 \quad (2)$$

$$Mg_2Zr_2O_4(C_2O_4)CO_3 \xrightarrow{593-653\ K} Mg_2Zr_2O_5CO_3 + CO + CO_2 \quad (3)$$

$$Mg_2Zr_2O_5CO_3 \xrightarrow{673-733\ K} 2MgZrO_3 + CO_2 \quad (4)$$

The reaction kinetics for second and fourth decomposition steps of magnesium zirconyl oxalate are calculated and the reactions are found to follow first-order kinetics.

Decomposition of barium titanyl oxalate

A number of reports are available regarding the mode of thermal decomposition of barium titanyl oxalate [13,42–47], but all are contradictory or inconclusive. Subsequently, it has been reported that the Ba : Ti δ ratio of barium titanyl oxalate prepared from hydrochloric acid solution may vary [48,49]. The mode of thermal decomposition of barium titanyl oxalate and the nature of the final product can thus be altered. On the basis of the available literature data, the following five decomposition schemes may be proposed for the decomposition of barium titanyl oxalate. The dehydration step is common to all schemes, though the temperature varied from 303 to 573 K.

Scheme A

$$BaTiO(C_2O_4) \cdot 4H_2O \rightarrow BaTiO(C_2O_4)_2 + 4H_2O$$

$$BaTiO(C_2O_4)_2 \xrightarrow[-2CO_2]{623\ K} BaTiOC_2O_4 \xrightarrow{793\ K} BaTiO_3(CO)_2$$

$$\xrightarrow[-2CO]{943\ K} BaTiO_3 \xrightarrow{983\ K} BaTiO_3{}^*$$

Scheme B

$$\mathrm{BaTiO(C_2O_4)_2} \xrightarrow[-4\mathrm{CO}]{573-873\ \mathrm{K}} \mathrm{BaTiO_5} \xrightarrow[-\mathrm{O_2}]{873-1073\ \mathrm{K}} \mathrm{BaTiO_3}$$

Scheme C

$$\mathrm{BaTiO(C_2O_4)_2} \xrightarrow[-2\mathrm{CO_2}]{523-573\ \mathrm{K}} \mathrm{BaTiOC_2O_4} \xrightarrow[-\mathrm{CO}]{633-833\ \mathrm{K}} \mathrm{BaTiO_3(CO)}$$

$$\xrightarrow[-\mathrm{CO}]{848-903\ \mathrm{K}} \mathrm{BaTiO_3} \xrightarrow{1048\ \mathrm{K}} \mathrm{BaTiO_3^*}$$

Scheme D

$$\mathrm{BaTiO(C_2O_4)_2} + \tfrac{1}{2}\mathrm{O_2} \xrightarrow[-(\mathrm{CO}+2\mathrm{CO_2})]{498-738\ \mathrm{K}} \mathrm{BaCO_3} + \mathrm{TiO_2} \xrightarrow[-\mathrm{CO_2}]{738-973\ \mathrm{K}}$$

$$\mathrm{BaTiO_3}$$

Scheme E

$$\mathrm{BaTiO(C_2O_4)_2}\cdot(4+x)\mathrm{H_2O} \xrightarrow[-\text{extra water}]{373\ \mathrm{K}} \mathrm{BaTiO(C_2O_4)_2}\cdot 4\mathrm{H_2O}$$

$$\xrightarrow[-4\mathrm{H_2O}]{393-453\ \mathrm{K}} \mathrm{BaTiO(C_2O_4)_2} \xrightarrow[-\mathrm{CO}]{453-523\ \mathrm{K}} \mathrm{Ba_2Ti_2O_2(C_2O_4)_3CO_3}$$

$$\xrightarrow[-(2\mathrm{CO_2}+3\mathrm{CO})]{523-723\ \mathrm{K}} \mathrm{Ba_2Ti_2O_5CO_3(CO_2)} \xrightarrow[-\mathrm{CO_2}]{723-873\ \mathrm{K}} \mathrm{Ba_2Ti_2O_5CO_3}$$

$$\xrightarrow[-\mathrm{CO_2}]{873-1023\ \mathrm{K}} 2\mathrm{BaTiO_3}$$

The step $\mathrm{BaTiO_3} \rightarrow \mathrm{BaTiO_3^*}$ in Schemes A and C represents an ordering process.

An analysis of gaseous products shows that the gas evolved at the low temperature decomposition of barium titanyl oxalate is CO and no formation of O_2 is indicated at any temperature [45]. As Schemes A and/or B fail to explain these observations, they are therefore untenable. Further, in Schemes A and C, the formation of an intermediate with CO group(s) is indicated which is not indicated in the IR spectra of the intermediates [45]. Schemes A and C are therefore highly objectionable. Again, as the formation of $BaTiO_3$ is ruled out by the solid–solid reaction between $BaCO_3$ and TiO_2 below 1273 K, Scheme D is rejected on these grounds.

On the basis of the above discussion, out of the five decomposition schemes proposed by different authors for the decomposition of barium titanyl oxalate tetrahydrate, Scheme E, of Murthy et al. [45], is the most reasonable. According to these authors, decomposition proceeds through five steps and is not greatly affected by the surrounding gas atmosphere. The first step, which is the dehydration of the tetrahydrate, is followed by a low-temperature decomposition of the oxalate groups. In the temperature range 453–523 K half a mole of carbon monoxide is evolved with the formation of a transient intermediate containing both the oxalate and carbonate groups. The oxalate groups are completely destroyed in the range 523–723 K, resulting in the formation of a carbonate which retains free carbon dioxide in the matrix. The trapped carbon dioxide is released in the temperature range 723–873 K. The final decomposition of the carbonate takes place between 873 and 1023 K and yields barium titanate. The IR spectra, surface area measurements and X-ray powder diffraction data support the entrapment of carbon dioxide in the matrix.

Montegomery [50] studied the kinetics of the reaction between barium carbonate and titanium dioxide supposed to be formed by the partial decomposition of barium titanyl oxalate. Since confusion still prevails as to the chemical nature of this intermediate, it may be mentioned that an intermediate of composition $Ba_2Ti_2O_5CO_3(CO_2)_x (x \leqslant 1)$ is formed. When $x = 1$ this intermediate has a composition equivalent to $BaCO_3 + TiO_2$. The (α, t) curves presented by Montegomery show a rapid decomposition corresponding to about 50% of the reaction, while the remaining part of the curve has a significant character (above 873 K). In effect, the initial step corresponds to the escape of free carbon dioxide.

Murthy et al. [51] studied the kinetics of the thermal decomposition of barium titanyl oxalate. The decomposition of the anhydrous oxalate is complex and deceleratory throughout. The kinetics of the decomposition of the intermediate carbonate $Ba_2Ti_2O_5CO_3$ are greatly influenced by thermal effects during its formation. The sigmoidal (α, t) curve obeys a power law equation followed by first-order decay. The presence of carbon in the vacuum-prepared carbonate has a strong deactivating effect.

Decomposition of barium zirconyl oxalate

The thermal behaviour of barium zirconyl oxalate of doubtful stoichiometry has been investigated by various workers [41,52–55]. On the basis of the available literature, four different decomposition schemes may be proposed for the decomposition of barium zirconyl oxalate.

Scheme A

$$BaZrO(C_2O_4)_2 \cdot 5H_2O \xrightarrow{RT-413\ K} BaZrO(C_2O_4)_2 \cdot 3H_2O + 2H_2O \tag{1}$$

$$BaZrO(C_2O_4)_2 \cdot 3H_2O \xrightarrow{413-513\ K} BaZrO(C_2O_4)_2 + 3H_2O \tag{2}$$

$$BaZrO(C_2O_4)_2 \xrightarrow{513-653\ K} BaCO_3 + ZrO_2 + 2CO + CO_2 \tag{3}$$

$$BaCO_3 + ZrO_2 \xrightarrow{673-873\ K} BaZrO_3(CO) + \tfrac{1}{2}O_2 \tag{4}$$

$$BaZrO_3(CO) \xrightarrow{873-1173\ K} BaZrO_3 + CO \tag{5}$$

Scheme B

$$BaZrO(C_2O_4)\cdot 4.5H_2O \xrightarrow{373-463\ K} BaZrO(C_2O_4)_2\cdot 2.5H_2O + 2H_2O \qquad (1)$$

$$BaZrO(C_2O_4)_2\cdot 2.5H_2O \xrightarrow{463-533\ K} BaZrO(C_2O_4)_2 + 2.5H_2O \qquad (2)$$

$$2BaZrO(C_2O_4)_2 \xrightarrow{533-733\ K} Ba_2Zr_2O_5CO_3(CO) + 3CO_2 + 3CO \qquad (3)$$

$$Ba_2Zr_2O_5CO_3(CO) \xrightarrow{733-1033\ K} \tfrac{1}{2}Ba_2Zr_2O_5CO_3 + BaZrO_3 + CO + \tfrac{1}{2}CO_2 \qquad (4)$$

$$\tfrac{1}{2}Ba_2Zr_2O_5CO_3 \xrightarrow{1033-1193\ K} BaZrO_3 + \tfrac{1}{2}CO_2 \qquad (5)$$

Scheme C

$$BaZrO(C_2O_4)_2\cdot 7H_2O \xrightarrow{298-393\ K} BaZrO(C_2O_4)_2\cdot 2H_2O + 5H_2O \qquad (1)$$

$$BaZrO(C_2O_4)_2\cdot 2H_2O \xrightarrow{393-473\ K} BaZrO(C_2O_4)_2 + 2H_2O \qquad (2)$$

$$2BaZrO(C_2O_4)_2 \xrightarrow{473-633\ K} Ba_2Zr_2O_2(C_2O_4)_{2.5}(CO_3)_{1.5} + 1.5CO \qquad (3)$$

$$Ba_2Zr_2(C_2O_4)_{2.5}(CO_3)_{1.5} \xrightarrow{633-773\ K} Ba_2Zr_2O_5CO_3 + 2.5CO + 3CO_2 \qquad (4)$$

$$Ba_2Zr_2O_5CO_3 \xrightarrow{773-1073\ K} 2BaZrO_3 + CO_2 \qquad (5)$$

Scheme D

$$BaZrO(C_2O_4)_2\cdot 4H_2O \xrightarrow{333-473\ K} BaZrO(C_2O_4)_2 + 4H_2O \qquad (1)$$

$$2BaZrO(C_2O_4)_2 \xrightarrow{473-623\ K} Ba_2Zr_2O_2(C_2O_4)_3CO_3 + CO \qquad (2)$$

$$Ba_2Zr_2O_2(C_2O_4)_3CO_3 \xrightarrow{623-683\ K} Ba_2Zr_2O_5CO_3(CO_2) + 2CO_2 + 3CO \qquad (3)$$

$$Ba_2Zr_2O_5CO_3(CO_2) \xrightarrow{693-933\ K} Ba_2Zr_2O_5CO_3 + CO_2 \qquad (4)$$

$$Ba_2Zr_2O_5CO_3 \xrightarrow{948-1013\ K} 2BaZrO_3 + CO_2 \qquad (5)$$

As can be seen from the above schemes different groups of workers have given a different molarity of hydration to the barium zirconyl oxalate. In fact, this is only due to the different methods and experimental conditions (like pH and concentration of reactants) employed for the preparation of the compound in each case. Further, the resolution of the substeps of dehydration is highly dependent on the flow rate of gas, the heating rate of the sample and the sensitivity of the instrument employed. Therefore, the difference observed in the dehydration process proposed by different workers is not very surprising.

The decomposition of anhydrous oxalate to carbonate is a two-step process that takes place through the formation of the oxalato–carbonate intermediate $Ba_2Zr_2O_2(C_2O_4)_3CO_3$. This intermediate is identified with the aid of weight loss, chemical analysis and IR spectral studies. The second step of oxalate decomposition results in carbonate complex of composition $Ba_2Zr_2O_5CO_3(CO_2)$. The residue is crystalline and the reflections in the X-ray powder diffraction pattern do not correspond to the strongest reflections of barium carbonate, zirconium dioxide or barium zirconate. Thus, the residue is not a mixture of barium carbonate and zirconium dioxide, but a separate compound. The possibility of the formation of a mixture of barium carbonate and zirconium oxide as the intermediate decomposition product of barium zirconyl oxalate is further ruled out by the experiments of Gangadevi et al. [19]. They investigated the thermal decomposition of a 1 : 1 mixture of barium oxalate and zirconyl oxalate and proved that the barium carbonate and zirconium dioxide produced during the decomposition of the mixture do not show any enhanced reactivity and no barium zirconate is produced from these two solids up to 1273 K. Schemes A and B, proposed by Sheinkman et al. [52] and Reddy and Mehrotra [53], are unable to explain these observations and are therefore rejected on these grounds. Further, Gangadevi et al. [54] (Scheme C) were unable to isolate the carbonate intermediate with entrapped CO_2 as shown in Scheme D by Sharma et al. [41]. This is probably due to the high heating rate and/or chart speed employed by these authors or may be due to the highly unstable nature of this intermediate.

The carbonate $Ba_2Zr_2O_5CO_3$ finally decomposes between 948 and 1013 K with the evolution of carbon dioxide, to a crystalline barium metazirconate. All the decomposition reactions are endothermic including the decomposition of oxalate to carbonate in air.

The kinetics for the second and last stages of the decomposition of barium zirconyl oxalate were studied by Sharma et al. [41]. Both decomposition reactions are reported to follow first-order kinetics.

Decomposition of strontium titanyl oxalate

The thermal decomposition of strontium titanyl oxalate hexahydrate was studied by Murthy et al. [55] employing TG, DTG, gas and chemical analyses. The dehydration of the compounds takes place in the temperature range 293–523 K in three steps, which, however, overlap in the thermograms. Weight losses and the composition of the residue obtained in static experiments correspond to the formation of dihydrate, monohydrate and anhydrous oxalate. The dehydration is completely reversible and the intermediate hydrates and the anhydrous salts are amorphous to X-rays.

The decomposition of the oxalate appears to be a single-step process, in the temperature range 523–703 K. The reaction starts as an endotherm in oxygen but soon becomes exothermic due to the secondary reactions of carbon monoxide. In a vacuum or non-oxidising atmosphere, it is endothermic and peak maxima are at the same temperatures. The residue corresponds to the general composition $SrTiO_2CO_3$. The IR spectrum of this residue shows the presence of a small amount of retained carbon dioxide as indicated by the absorption band at 2350 cm^{-1}. The residue can therefore be better formulated as $Sr_2Ti_2O_{4-x}(CO_3)_{2-x}(CO_2)_x$ where $x = 1$. The residue, though amorphous to X-rays, is non-porous as shown by its surface area (~ 2 m^2 g^{-1}).

The intermediate strontium titanyl carbonate, $Sr_2Ti_2O_{4-x}(CO_3)_{2-x}(CO_2)_x$, decomposes in two steps. In the first step it retains carbon dioxide and one mole of the carbonate group decomposes giving a crystalline residue of composition $Sr_2Ti_2O_5CO_3$. The X-ray powder diffraction pattern of this residue does not correspond to that of $SrCO_3$, or any polymorph of TiO_2 or $SrTiO_3$. The carbonate $Sr_2Ti_2O_5CO_3$ further decomposes in the temperature range 843–1003 K to produce the final product $SrTiO_3$. The final residue gives a well-defined X-ray diffraction pattern of $SrTiO_3$ ($a = 3.9045$ Å).

From the above results the decomposition scheme for STO can be formulated as follows

$$SrTiO(C_2O_4)_2 \cdot 4H_2O \xrightarrow[293-523\ K]{-2H_2O,\ -H_2O,\ -H_2O} SrTiO(C_2O_4)_2 \tag{1}$$

$$2SrTiO(C_2O_4)_2 \xrightarrow{523-703\ K} Sr_2Ti_2O_{4-x}(CO_3)_{2-x}(CO_2)_x + 4CO + 2CO_2 \tag{2}$$

$$Sr_2Ti_2O_{4+x}(CO_3)_{2-x}(CO_2)_x \xrightarrow{703-843\ K} Sr_2Ti_2O_5CO_3 + CO_2 \tag{3}$$

$$Sr_2Ti_2O_5CO_3 \xrightarrow{843-1003\ K} 2SrTiO_3 + CO_2 \tag{4}$$

Decomposition of strontium zirconyl oxalate

The thermal decomposition of strontium zirconyl oxalate hexahydrate in air was first investigated by Reddy and Mehrotra [56]. The decomposition mechanism proposed by these authors may be summarised as follows

$$SrZrO(C_2O_4)_2 \cdot 6H_2O \xrightarrow{298-463\ K} SrZrO(C_2O_4)_2 \cdot 3H_2O + 3H_2O \tag{1}$$

$$SrZrO(C_2O_4)_2 \cdot 3H_2O \xrightarrow{463-598\ K} SrZrO(C_2O_4)_2 + 3H_2O \tag{2}$$

$$2SrZrO(C_2O_4)_2 \xrightarrow{598-748\ K} Sr_2Zr_2O_5CO_3(CO_2) + 2CO_2 + 4CO \quad (3)$$

$$Sr_2Zr_2O_5CO_3(CO_2) \xrightarrow{748-923\ K} Sr_2Zr_2O_5CO_3 + CO_2 \quad (4)$$

$$2Sr_2Zr_2O_5CO_3 \xrightarrow{923-1103\ K} Sr_2Zr_2O_5CO_3 + 2SrZrO_3 + CO_2 \quad (5)$$

$$Sr_2Zr_2O_5CO_3 \xrightarrow{1103-1273\ K} 2SrZrO_3 + CO_2 \quad (6)$$

The dehydration of the hydrated oxalate takes place between 298 and 598 K in two stages. The second stage, though visible in the DTA curve, is combined in TG with oxalate decomposition.

The decomposition of oxalate is a multistage process in the range 598–748 K. From the DTA curve it is evident that before the dehydration is complete, oxalate decomposition begins. The IR spectrum of the residue obtained from isothermal experiments at 723 K shows a band at 2310 cm^{-1} due to trapped CO_2 in addition to the carbonate bands. No oxalate bands are observed. The DTA curve for this decomposition stage shows an endothermic peak around 603 K followed by an exothermic band around 773 K. The latter peak may be due to the oxidation of evolved carbon monoxide.

The weight loss between 748 and 923 K corresponds to the evolution of trapped carbon dioxide. The next weight loss occurs between 923 and 1103 K, which corresponds to the loss of half a mole of carbon dioxide. The final decomposition of the remaining carbonate is observed between 1103 and 1273 K, resulting in the formation of strontium zirconyl oxalate.

Further studies on the thermal behaviour of strontium zirconyl oxalate were carried out by Gangadevi et al. [57]. The findings of these authors do not agree with those of Reddy and Mehrotra [56], and a separate decomposition scheme is proposed.

$$SrZrO(C_2O_4)_2 \cdot 4H_2O \xrightarrow{298-398\ K} SrZrO(C_2O_4)_2 \cdot 2H_2O + 2H_2O \quad (1)$$

$$SrZrO(C_2O_4)_2 \cdot 2H_2O \xrightarrow{398-498\ K} SrZrO(C_2O_4)_2 + 2H_2O \quad (2)$$

$$2SrZrO(C_2O_4)_2 \xrightarrow{523-648\ K} Sr_2Zr_2O_2(C_2O_4)_3CO_3 + CO \quad (3)$$

$$Sr_2Zr_2O_2(C_2O_4)_3CO_3 \xrightarrow{648-773\ K} Sr_2Zr_2O_5CO_3 + 3CO + CO_2 \quad (4)$$

$$Sr_2Zr_2O_5CO_3 \xrightarrow{773-998\ K} 2SrZrO_3 + CO_2 \quad (5)$$

Each thermal effect is accompanied by a mass loss and is not greatly influenced by the surrounding gas atmosphere. The end products of each thermal decomposition stage are identified by IR and/or X-ray methods.

However, the authors failed to isolate the oxalato–carbonate intermediate by isothermal experiments.

Decomposition of calcium titanyl oxalate

Murthy et al. [55] investigated the mode of decomposition of calcium titanyl oxalate and the following decomposition mechanism is formulated.

$$\mathrm{CaTiO(C_2O_4)_2 \cdot 6H_2O \xrightarrow{293-403\ K} CaTiO(C_2O_4)_2 \cdot 4H_2O + 2H_2O} \qquad (1)$$

$$\mathrm{CaTiO(C_2O_4) \cdot 4H_2O \xrightarrow{403-523\ K} CaTiO(C_2O_4)_2 + 4H_2O} \qquad (2)$$

$$\mathrm{2CaTiO(C_2O_4)_2 \xrightarrow{523-723\ K} Ca_2Ti_2O_4(CO_3)_2 + 4CO + 2CO_2} \qquad (3)$$

$$\mathrm{Ca_2Ti_2O_4(CO_3)_2 \xrightarrow{723-813\ K} Ca_2Ti_2O_5CO_3 + CO_2} \qquad (4)$$

$$\mathrm{Ca_2Ti_2O_5CO_3 \xrightarrow{813-933\ K} 2CaTiO_3 + CO_2} \qquad (5)$$

All the thermal effects were accompanied by a weight loss. The dehydration of the hydrate takes place in two consecutive steps. The hexahydrate is first dehydrated to tetrahydrate and then to anhydrous oxalate. This dehydration is not completely reversible, as anhydrous oxalate only takes up four water molecules on rehydration.

The decomposition of the anhydrous oxalate appears to be a single-step process, in the temperature range 523–723 K, resulting in the formation of a carbonate of composition $\mathrm{Ca_2Ti_2O_4(CO_3)_2}$. The IR spectrum of the residue at this stage indicates the presence of a monodentate and a bidentate group [14].

The carbonate, $\mathrm{Ca_2Ti_2O_4(CO_3)_2}$ decomposes first in the temperature range 723–813 K to give $\mathrm{Ca_2Ti_2O_5CO_3}$ and carbon dioxide. The intermediate $\mathrm{Ca_2Ti_2O_5CO_3}$, 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 maximum in carbon dioxide and minimum in vacuum. In the final stage, retained carbon dioxide, and carbon dioxide from the decomposition of $\mathrm{Ca_2Ti_2O_5CO_3}$, is released in the temperature range 813–933 K. The final crystalline residue is $\mathrm{CaTiO_3}$ (pseudo cubic, $a = 15.18$ Å).

Decomposition of calcium zirconyl oxalate

The thermal decomposition of calcium zirconyl oxalate heptahydrate was studied by Gangadevi et al. [57]. The decomposition proceeds through five steps

$$\mathrm{CaZrO(C_2O_4)_2 \cdot 7H_2O \xrightarrow{298-398\ K} CaZrO(C_2O_4)_2 \cdot 4H_2O + 3H_2O} \quad (1)$$

$$\mathrm{CaZrO(C_2O_4)_2 \cdot 4H_2O \xrightarrow{398-498\ K} CaZrO(C_2O_4)_2 + 4H_2O} \quad (2)$$

$$\mathrm{2CaZrO(C_2O_4)_2 \xrightarrow{523-648\ K} Ca_2Zr_2O_4(CO_3)_2 + 2CO_2 + 4CO} \quad (3)$$

$$\mathrm{Ca_2Zr_2O_4(CO_3)_2 \xrightarrow{648-773\ K} Ca_2Zr_2O_5CO_3 + CO_2} \quad (4)$$

$$\mathrm{Ca_2Zr_2O_5CO_3 \xrightarrow{823-923\ K} 2CaZrO_3} \quad (5)$$

The hydrated oxalate is completely dehydrated in the temperature range 298–498 K in two well-resolved steps. First a tetrahydrate and then the anhydrous oxalate is formed.

The decomposition of anhydrous oxalate takes place between 523 and 648 K, resulting in the formation of a monocrystalline carbonate of composition $\mathrm{CaZrO_2CO_3}$. The IR spectrum of the residue shows bands of both unidentate and bidentate carbonate groups and the absence of free carbon dioxide. The formula of the carbonate is therefore better represented by $\mathrm{Ca_2Zr_2O_4(CO_3)_2}$.

The carbonate $\mathrm{Ca_2Zr_2O_4(CO_3)_2}$ decomposes in two steps. In the temperature range 648–773 K it decomposes to give $\mathrm{Ca_2Zr_2O_5CO_3}$. This is an ionic carbonate as suggested by its IR spectrum. The second stage of carbonate decomposition results in the formation of calcium zirconate. The X-ray powder diffraction pattern confirms the final product to be the pseudo cubic phase of calcium zirconate.

Decomposition of copper zirconyl oxalate

Reddy et al. [58] investigated the decomposition of copper zirconyl oxalate tetrahydrate and the following three-step decomposition mechanism is proposed.

$$\mathrm{CuZrO(C_2O_4)_2 \cdot 4H_2O \xrightarrow[-2.5H_2O]{303-423\ K} CuZrO(C_2O_4)_2 \cdot 1.5H_2O}$$

$$\mathrm{\xrightarrow[-1.5H_2O,\ 2CO,\ (2-x)CO_2]{423-673\ K} CuZrO_{3-x}(CO_3)_x \xrightarrow[-xCO_2]{673-1013\ K} CuZrO_3}$$

TG analyses indicate that the acetone-washed sample of copper zirconyl oxalate loses about 2.5 moles of water between 303 and 423 K giving another hydrate. The remaining 1.5 moles of water are lost along with the decomposition of oxalate beteen 423 and 673 K. This is indicated by an endothermic peak at 583 K in DTA followed by an exothermic band around 693 K. The latter is probably due to the oxidation of carbon monoxide and/or oxidation of carbon produced during the disproportionation of carbon monoxide. The second decomposition stage results in the formation of a non-stoichiometric intermediate of composition $CuZrO_{3-x}(CO_3)_x$. The IR spectrum of this intermediate shows bands for the carbonate group [59] as well as for free carbon dioxide, probably adsorbed on the solid. The final mass loss due to the decomposition of the non-stoichiometric intermediate carbonate occurs between 673 and 1013 K. The IR spectrum of the end product shows all the fundamental bands of a zirconate [60]. X-ray powder diffraction of the end product indicates its orthorhombic structure [61].

Decomposition of zinc titanyl oxalate

Sharma and Kaushik [62] described the following mechanism for the thermal decomposition of zinc titanyl oxalate tetrahydrate in a dynamic nitrogen atmosphere.

$$ZnTiO(C_2O_4)_2 \cdot 4H_2O \xrightarrow{333-383\ K} ZnTiO(C_2O_4)_2 + 4H_2O \qquad (1)$$

$$2ZnTiO(C_2O_4)_2 \xrightarrow{393-475\ K} Zn_2Ti_2O_5CO_3 + 4CO + 3CO_2 \qquad (2)$$

$$Zn_2Ti_2O_5CO_3 \xrightarrow{580-683\ K} 2ZnTiO_3 + CO_2 \qquad (3)$$

The dehydration of zinc titanyl oxalate occurs in a single step in the temperature range 333–383 K. The expected endothermic behaviour for the dehydration is observed from the DSC curve in this temperature range. The decomposition of the anhydrous oxalate to the corresponding carbonate starts immediately after dehydration and continues up to 475 K. The DSC curves corresponding to this step show a doublet (endothermic) which may be due to the non-equivalence of the oxalate groups. The carbonate intermediate is decomposed to zinc titanate in the temperature range 580–683 K. The DSC curve corresponding to this step shows that the initial reaction is endothermic and is followed by an exothermic reaction. The exothermic reaction is probably due to the transition from one crystalline form of the zinc titanate to another.

The kinetic parameters for the second and third decomposition reactions of zinc zirconyl oxalate have been calculated using the Coats and Redfern method. These reactions are found to follow first-order kinetics [62].

Decomposition of zinc zirconyl oxalate

Reddy et al. [63] investigated the decomposition pattern of zinc zirconyl oxalate employing TG, DTG and DTA techniques. The first step of decomposition is the dehydration process which occurs between 303 and 473 K. In the second step the decomposition of oxalate began, which continues up to 613 K resulting in the formation of carbonate. The destruction of the carbonate intermediate is observed between 613 and 833 K to give the final product zinc zirconate. The IR spectral and X-ray diffraction data confirm the formation of $ZnZrO_3$ [60].

$$ZnZrO(C_2O_4)_2 \cdot 5H_2O \xrightarrow{303-473\text{ K}} ZnZrO(C_2O_4)_2 + 5H_2O \quad (1)$$

$$2ZnZrO(C_2O_4)_2 \xrightarrow{473-613\text{ K}} Zn_2Zr_2O_4(C_2O_4)CO_3 + 2CO_2 + 3CO \quad (2)$$

$$Zn_2Zr_2O_4(C_2O_4)CO_3 \xrightarrow{613-833\text{ K}} 2ZnZrO_3 + 2CO_2 + CO \quad (3)$$

There is a 1 : 1 correlation between the TG and DTA curves showing that all the thermal changes are accompanied by a mass loss. All the decomposition steps are endothermic reactions.

Recently, Sharma and Kaushik [64] investigated the thermal behaviour of this compound further, giving a slightly different interpretation.

$$ZnZrO(C_2O_4)_2 \cdot 6H_2O \xrightarrow{313-353\text{ K}} ZnZrO(C_2O_4)_2 \cdot 4H_2O + 2H_2O \quad (1)$$

$$ZnZrO(C_2O_4)_2 \cdot 4H_2O \xrightarrow{353-413\text{ K}} ZnZrO(C_2O_4)_2 + 4H_2O \quad (2)$$

$$2ZnZrO(C_2O_4)_2 \xrightarrow{433-548\text{ K}} Zn_2Zr_2O_5CO_3 + 4CO + 3CO_2 \quad (3)$$

$$Zn_2Zr_2O_5CO_3 \xrightarrow{573-713\text{ K}} 2ZnZrO_3 + CO_2 \quad (4)$$

The dehydration of the hydrated complex is observed in two steps. The first step results in the loss of two water molecules giving the tetrahydrate which further loses the remaining four water molecules in the next step, resulting in the formation of anhydrous oxalate. The difference in the dehydration processes between the two mechanisms is due to the presence of a different number of molecules of water in the parent compound, resulting from the different methods employed in the preparation of the zinc zirconyl oxalate.

The decomposition of anhydrous oxalate to carbonate takes place in a single step and no formation of an oxalato–carbonate complex is observed as evidenced by the IR spectral data of the intermediate. However, the DSC curve corresponding to this decomposition stage shows a doublet indicating the two-step decomposition of oxalate due to the non-equivalence of the oxalate groups. This is not resolved from TG curves due to the highly unstable nature of the intermediate.

The decomposition of carbonate takes place in a single step resulting is the formation of synthetically pure zinc zirconate.

Decomposition of cadmium titanyl oxalate

The thermal decomposition of cadmium titanyl oxalate tetrahydrate was investigated in a nitrogen atmosphere by Sharma and Kaushik [62]. The decomposition proceeds through three well-defined stages, viz. dehydration of the hydrated oxalate, decomposition of the anhydrous oxalate to carbonate and finally the decomposition of carbonate to cadmium titanate.

$$CdTiO(C_2O_4)_2 \cdot 4H_2O \xrightarrow{320-383\ K} CdTiO(C_2O_4)_2 + 4H_2O \qquad (1)$$

$$2CdTiO(C_2O_4)_2 \xrightarrow{393-483\ K} Cd_2Ti_2O_5CO_3 + 4CO + 3CO_2 \qquad (2)$$

$$Cd_2Ti_2O_5CO_3 \xrightarrow{513-735\ K} 2CdTiO_3 + CO_2 \qquad (3)$$

All these steps are endothermic reactions. A doublet is observed in DSC for the second stage decomposition reaction. This is probably due to the non-equivalence of the oxalate groups. An exothermic peak, unaccompanied by any mass loss, appeared following the endothermic band of the third decomposition stage. This is probably due to the ordering process of the cadmium titanate formed as the end product after the carbonate decomposition.

Decomposition of cadmium zirconyl oxalate

Reddy and Mehrotra [65] investigated the thermal behaviour of cadmium zirconyl oxalate in an air atmosphere. The decomposition mechanism of cadmium zirconyl oxalate proposed by these authors is very simple in comparison to the other mixed metal oxalates. The decomposition proceeds through two stages, the first being the dehydration and the second the decomposition of oxalate.

$$CdZrO(C_2O_4)_2 \cdot 5H_2O \xrightarrow{RT-463\ K} CdZrO(C_2O_4)_2 + 5H_2O \qquad (1)$$

$$CdZrO(C_2O_4)_2 \xrightarrow{463-823\ K} CdZrO_3 + 2CO_2 + 2CO \qquad (2)$$

The dehydration is a single-step process and takes place between room temperature (RT) and 463 K. The decomposition of the oxalate is rather complex and the reaction takes place soon after the dehydration. At this stage the anhydrous cadmium zirconyl oxalate decomposes directly to give a mixed oxide between 463 and 823 K. This change is very clear in DTA around 598 K and in DTG around 593 K. Two extra exothermic peaks are observed in DTA, immediately following the decomposition of the oxalate. The first may be attributed to the oxidation of CO and/or disproportionation of CO and the oxidation of the carbon produced, while the second is probably due to the crystallisation of the product formed during the oxalate decomposition. X-ray diffraction studies show that the end product, cadmium zirconate, belongs to the orthorhombic crystal system.

Recently, Sharma and Kaushik [64] also investigated the thermal behaviour of cadmium zirconyl oxalate giving the following decomposition mechanism.

$$CdZrO(C_2O_4)_2 \cdot 4H_2O \xrightarrow{323-413\ K} CdZrO(C_2O_4)_2 \cdot 2H_2O + 2H_2O \tag{1}$$

$$CdZrO(C_2O_4)_2 \cdot 2H_2O \xrightarrow{413-513K} CdZrO(C_2O_4)_2 + 2H_2O \tag{2}$$

$$2CdZrO(C_2O_4)_2 \xrightarrow{523-573\ K} Cd_2Zr_2O_4(C_2O_4)CO_3 + 3CO + 2CO_2 \tag{3}$$

$$Cd_2Zr_2O_4(C_2O_4)CO_3 \xrightarrow{573-623\ K} Cd_2Zr_2O_5CO_3 + CO + CO_2 \tag{4}$$

$$Cd_2Zr_2O_5CO_3 \xrightarrow{653-888\ K} 2CdZrO_3 + CO_2 \tag{5}$$

The acetone-washed sample contains four moles of H_2O per mole of cadmium zirconyl oxalate. The dehydration of the hydrated compound is completed in two stages between 323 and 513 K through the formation of dihydrate, while for the decomposition of anhydrous oxalate to cadmium zirconate three stages are observed. In the first decomposition stage, oxalate groups are partially distroyed to form the oxalato–carbonate intermediate of composition $Cd_2Zr_2O_4(C_2O_4)CO_3$. The IR spectrum of the residue at this stage shows bands belonging to both oxalate and carbonate groups. In the second decomposition stage, oxalate groups are completely destroyed to give the carbonate. At this stage the residue is an ionic carbonate of apparent composition of $Cd_2Zr_2O_5CO_3$, as evidenced by its IR spectrum. Finally, the decomposition of carbonate results in the formation of cadmium zirconate.

Decomposition of lead titanyl oxalate

The thermal decomposition of lead titanyl oxalate of the doubtful composition $PbTiO(C_2O_4)_3 \cdot 4H_2O$ was studied by Strizhakov et al. [66]. The scheme proposed by these authors is confusing. The latest and most detailed investigation on the thermal behaviour of lead titanyl oxalate is that of Murthy et al. [67], who proposed the following decomposition mechanism in both air and oxygen.

$$PbTiO(C_2O_4)_2 \cdot 4H_2O \xrightarrow{298-488\ K} PbTiO(C_2O_4)_2 + 4H_2O \tag{1}$$

$$2PbTiO(C_2O_4)_2 \xrightarrow{488-648\ K} Pb_2Ti_2O_5CO_3 + 4CO + 3CO_2 \tag{2}$$

$$Pb_2Ti_2O_5CO_3 \xrightarrow{648-793\ K} 2PbTiO_3 + CO_2 \tag{3}$$

However, in vacuum and non-oxidising atmosphere partial reduction of

Pb(II) to Pb(0) takes place, therefore steps (2) and (3) of above scheme may be modified as follows:

$$2PbTiO(C_2O_4)_2 \rightarrow Pb_{2(1-x)}Ti_2O_{5-2x}CO_3 + 2xPb + (4-2x)CO + (3+2x)CO_2 \qquad (2')$$

$$Pb_{2(1-x)}Ti_2O_{5-2x}CO_3 \rightarrow (2-3x)PbTiO_3 + xPbTi_3O_7 + CO_2 \qquad (3')$$

x can be estimated from the amounts of free lead formed.

There are three major reactions: dehydration; decomposition of oxalate to a carbonate; and decomposition of the carbonate to lead titanate. Side reactions occur, dependent on the nature of the surrounding gas and the ease of reduction of Pb(II) to Pb(0) during the decomposition of oxalate.

The dehydration of the hydrate takes place in the temperature range 298–488 K and is reversible. After dehydration the material becomes amorphous to X-rays. The anhydrous oxalate decomposes between 488 and 648 K by a two-step process, the steps being separated by about 30 K. They are resolved in vacuum or inert atmospheres, but in oxygen, owing to the strong exothermic oxidation of carbon monoxide, they are not. The composite thermal curve implies the non-equivalence of the two oxalate groups. Although the composite nature of oxalate decomposition, both in DTA and DTG, indicates the formation of an intermediate combining both oxalate and carbonate, no residue of apparent composition $Pb_2Ti_2O_x(C_2O_4)_y$-$(CO_3)_z$, where $x+y+z=6$, could be isolated.

The decomposition of carbonate is straightforward and takes place between 648 and 793 K. The endothermic peak in DTA at 748 K represents this decomposition. This is followed by an exotherm unaccompanied by any weight loss. The residue after this stage is crystalline lead metatitanate (tetragonal with $a = 3.89$ Å, $c = 4.11$ Å). In an inert atmosphere or in vacuum, the decomposition of the carbonate is complicated by the presence of lead. The final product cannot be expected as pure $PbZrO_3$. The X-ray powder diffraction pattern of this product shows the presence of two phases, the major phase is tetragonal $PbTiO_3$ and the second phase is identified as $PbTi_3O_7$ [68].

Decomposition of lead zirconyl oxalate

The thermal behaviour of lead zirconyl oxalate was investigated by Reddy and Mehrotra [69]. The decomposition proceeds through four steps.

$$PbZrO(C_2O_4)_2 \cdot 6H_2O \xrightarrow{300-428\ K} PbZrO(C_2O_4)_2 \cdot 2H_2O + 4H_2O \qquad (1)$$

$$PbZrO(C_2O_4)_2 \cdot 2H_2O \xrightarrow{428-533\ K} PbZrO(C_2O_4)_2 + 2H_2O \qquad (2)$$

$$2PbZrO(C_2O_4)_2 \xrightarrow{533-688\text{ K}} Pb_2Zr_2O_5CO_3 + 3CO_2 + 4CO \quad (3)$$

$$Pb_2Zr_2O_5CO_3 \xrightarrow{688-848\text{ K}} 2PbZrO_3 + CO_2 \quad (4)$$

The dehydration of the hydrate occurs in two consecutive steps. The first stage extending up to 428 K results in the loss of four water molecules, while the rest of the water molecules are lost between 428 and 533 K. This is represented by two endotherms in DTA at 303 and 523 K.

As soon as dehydration is completed, the decomposition of oxalate starts. It occurs between 533 and 688 K giving an intermediate carbonate, $Pb_2Zr_2O_5CO_3$. In DTA an exothermic peak appears at 603 K as a small doublet, which may be due to the non-equivalence of the oxalate groups.

The decomposition of carbonate occurs between 688 and 848 K resulting in the formation of lead zirconate. This reaction is represented by an endothermic peak in DTA at 823 K.

Recently, Sharma et al. [41] also studied the thermal decomposition of lead zirconyl oxalate of composition $PbZrO(C_2O_4)_2 \cdot 4H_2O$ and a three-step decomposition mechanism has been proposed.

$$PbZrO(C_2O_4)_2 \cdot 4H_2O \xrightarrow{303-453\text{ K}} PbZrO(C_2O_4)_2 + 4H_2O \quad (1)$$

$$2PbZrO(C_2O_4)_2 \xrightarrow{453-593\text{ K}} Pb_2Zr_2O_5CO_3 + 4CO + 3CO_2 \quad (2)$$

$$Pb_2Zr_2O_5CO_3 \xrightarrow{603-723\text{ K}} 2PbZrO_3 + CO_2 \quad (3)$$

All the decomposition steps are endothermic reactions except the last which is initially endothermic followed by an exothermic band. This exothermic band does not correspond to any weight loss, as seen from the TG curve, and is probably due to the transition from one crystalline state of $PbZrO_3$ to another.

These authors also calculated the apparent activation energy and order of reaction for the second and last decomposition reactions in a nitrogen atmosphere employing the graphical method of Coats and Redfern. The order of reaction for these decomposition steps is found to be unity [41]. The heats of reaction from DSC curves for different decomposition steps were also evaluated.

Decomposition of lanthanum zirconyl oxalate

Reddy and Mehrotra [70] investigated the thermal behaviour of lanthanum zirconyl oxalate. The decomposition of this oxalate is complex process and takes place is six steps

$$La_2(ZrO)_2(C_2O_4)_5 \cdot 10H_2O \xrightarrow{RT-423\text{ K}} La_2(ZrO)_2(C_2O_4)_5 \cdot 4H_2O + 6H_2O \quad (1)$$

$$La_2(ZrO)_2(C_2O_4)_5 \cdot 4H_2O \xrightarrow{423-498\ K} La_2(ZrO)_2(C_2O_4)_5 + 4H_2O \qquad (2)$$

$$La_2(ZrO)_2(C_2O_4)_5 \xrightarrow{498-548\ K} \underset{(\mathbf{I})}{La_2(ZrO)_2(C_2O_4)_3(CO_3)_2} + 2CO \qquad (3)$$

$$La_2(ZrO)_2(C_2O_4)_3(CO_3)_2 \xrightarrow{548-673\ K} \underset{(\mathbf{II})}{La_2Zr_2O_4(C_2O_4)_2CO_3} + 2CO_2 + CO \qquad (4)$$

$$La_2Zr_2O_4(C_2O_4)_2CO_3 \xrightarrow{673-773\ K} \underset{(\mathbf{III})}{La_2Zr_2O_6CO_3 \cdot CO} + 2CO_2 + CO \qquad (5)$$

$$La_2Zr_2O_6CO_3 \cdot CO \xrightarrow{773-1073\ K} La_2Zr_2O_7 + CO_2 + CO \qquad (6)$$

The dehydration of the hydrate takes place in two steps between room temperature and 498 K giving the anhydrous oxalate. This reaction is shown as one endotherm in the DTA curves.

The decomposition of oxalate is a multiple process. The first step in the oxalate decomposition occurs at 498–548 K and the weight loss corresponds to the loss of two moles of carbon monoxide. The IR spectrum of the solid obtained isothermally at 523 K indicates the presence of the oxalato–carbonate complex (**I**). The decomposition of the oxalato–carbonate (I) intermediate occurs at 548–673 K. The IR spectrum of this residue also shows bands belonging to both oxalate and carbonate groups. Further decomposition of the oxalato–carbonate intermediate (**II**) takes place between 673 and 773 K resulting the formation of carbonate intermediate. The band at 2340 cm^{-1} in the IR spectrum of the carbonate is attributed to the presence of carbon dioxide adsorbed on the solid. DTA suggests that these two changes in the oxalate decomposition are of a complex nature. There is an endothermic peak around 643 K, immediately followed by an exothermic band. The latter peak may be due to the domination of the oxidation of carbon monoxide evolved in air over the oxalate decomposition. The IR spectrum of the residue obtained isothermally at 773 K for 4 h indicates the presence of carbonate.

The decomposition of the carbonate occurs at 773–1073 K, liberating one mole each of CO and CO_2. This change occurs in DTA at around 1133 K. The X-ray powder diffraction pattern data of the end product heat at 1273 K for several hours indicates that it belongs to the cubic system with $a = 10.680$ Å. The end product is identified as $La_2Zr_2O_7$.

CONCLUSIONS

Studies on the thermal behaviour of a majority of titanyl and zirconyl oxalates have been discussed in this review. The different interpretations given by different workers, however, particularly the incorrect identification of intermediates by earlier workers due to the lack of sufficient techniques, has led to confusion regarding the chemical nature of various intermediates formed during the thermal decomposition. This made it difficult to establish any straightforward relationship between the thermal behaviour of the complex and its chemical composition. However, bearing in mind recent investigations using advanced techniques for the identification of intermediate products and the correlation of thermal stability data, and ignoring the interpretation of earlier workers, we can arrive at some conclusion regarding the general schemes for the decomposition of simple and complex titanyl and zirconyl oxalates.

There are two major decomposition steps for the simple titanyl and zirconyl oxalate, viz. the dehydration of the hydrate and the decomposition of the oxalate to the oxide. The dehydration of the hydrate takes place in two steps. The second step overlaps the oxalate decomposition and results in the formation of oxide.

$$\mathrm{MO(C_2O_4)\cdot}n\mathrm{(H_2O)} \rightarrow \mathrm{MO(C_2O_4)\cdot}(n-x)\mathrm{H_2O} + x\mathrm{H_2O} \tag{1}$$

$$\mathrm{MO(C_2O_4)\cdot}(n-x)\mathrm{H_2O} \rightarrow \mathrm{MO_2} + (n-x)\mathrm{H_2O} + \mathrm{CO} + \mathrm{CO_2} \tag{2}$$

Both decomposition steps are endothermic reactions. The oxalate decomposition is endothermic even in air because it takes place in an atmosphere of water vapour. There is a small exotherm followed by the endotherm of oxalate decomposition, unaccompanied by any mass loss. This is attributed to the transition of oxide from one crystalline state to another.

The decomposition of most complex titanyl and zirconyl oxalates proceeds through four major decomposition stages, viz. dehydration, decomposition of oxalate to oxalate–carbonate intermediate, decomposition of oxalato–carbonate intermediate to carbonate and finally the decomposition of carbonate to the mixed metal oxide, $\mathrm{AMO_3}$. Further, the dehydration of some of the complex oxalates is completed in two or more steps. This is either due to the absorption of an extra water molecule by the oxalate or may be due to the difference in the dehydration rate.

$$\mathrm{AMO(C_2O_4)_2}(n+x)\mathrm{H_2O} \underset{-x\mathrm{H_2O}}{\rightarrow} \mathrm{AMO(C_2O_4)_2\cdot}n\mathrm{H_2O} \tag{1a}$$

$$\mathrm{AMO(C_2O_4)_2\cdot}n\mathrm{H_2O} \underset{-n\mathrm{H_2O}}{\rightarrow} \mathrm{AMO(C_2O_4)_2} \tag{1b}$$

$$2\mathrm{AMO(C_2O_4)_2} \underset{-\mathrm{(CO/CO_2)}}{\rightarrow} \mathrm{A_2M_2O}_x\mathrm{(C_2O_4)}_y\mathrm{(CO_3)}_z \tag{2}$$

$$\mathrm{A_2M_2O}_x\mathrm{(C_2O_4)}_y\mathrm{(CO_3)}_z \underset{-\mathrm{(CO+CO_2)}}{\rightarrow} \mathrm{A_2M_2O_5CO_3} \tag{3}$$

$$\mathrm{A_2M_2O_5CO_3} \underset{-\mathrm{CO_2}}{\rightarrow} 2\mathrm{AMO_3} \tag{4}$$

where $x+y+z=6$.

The formation of the oxalato–carbonate complex intermediate is identified from the IR spectrum of the residue obtained by isothermal heating of the samples. The complex intermediate shows bands for both oxalate and carbonate groups. However, in some cases the oxalato–carbonate intermediate could not be isolated due to its highly unstable nature and the formation of this intermediate is sometimes not even observed from the thermogram. Further, in a few cases, a certain amount of the carbon dioxide evolved during the oxalate decomposition is retained in the solid surface of the carbonate intermediate, and therefore the formation of an additional carbonate intermediate with entrapped carbon dioxide, $A_2M_2O_5CO_3(CO_2)_x$, is also observed.

All the decomposition steps are endothermic reactions except the oxalate decomposition in an air atmosphere which is represented by an exothermic band in some compounds and endothermic in others, even in air. The comparatively low temperature for the side reaction of carbon monoxide to occur, and the relatively high water vapour (released during dehydration) pressure during the decomposition are the likely reasons why, in some cases, the oxalate decomposition remains endothermic in air. In a few complexes an extra exothermic peak, unaccompanied by any mass loss, is observed following the last decomposition step. This indicates the ordering process of the final decomposition product.

Only a little work has been done [38,41,50,51,62] in the area of thermal decomposition kinetics for the decomposition reactions of titanyl and zirconyl oxalates. In all cases the second and/or last decomposition reaction followed first-order kinetics.

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