CHAPTER - II

PRECURSOR ROUTE THROUGH HYDROLYSIS
OF DIETHYL OXALATE

C H A P T E R - I I

PRECURSOR ROUTE THROUGH HYDROLYSIS OF DIETHYL OXALATE
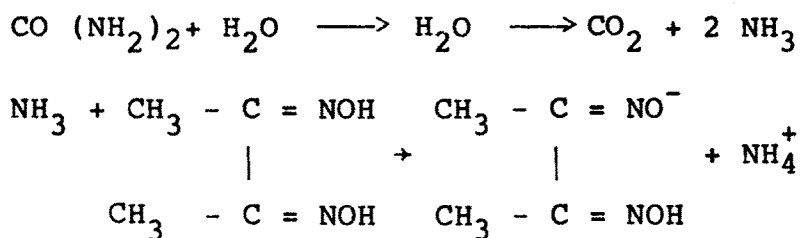
2.1 INTRODUCTION

Direct synthesis of ceramic mixed oxides is followed in solid state preparations. Sometimes there are specific disadvantages in this method, because of the chemical and thermodynamic stabilities, sluggishness of thermal decomposition reactions or requirement of very high temperature for thermal degradation of the starting materials. The desired starting materials in pure oxidic forms are unstable in cases like barium and strontium carbonates. The alternative to this is to follow chemical precursor routes in which hydroxides are precipitated and further ignited to mixed oxides. Hydroxide precipitates are generally gelatinous or slimy and carry with them adsorbed or occluded impurities.[1] A method involving preparation of pure and granular mixed oxides is desirable. Precipitation from homogeneous solutions (PFHS) technique therefore is suggested as a new method of the precursor formation. Hydrolytic liberation of the oxalate ion is studied in this chapter for preparation of cuprate superconductors.

2.2 PRECIPITATION FROM HOMOGENEOUS SOLUTION (PFHS TECHNIQUE)

The major part of the precipitation reaction is separation of a pure solid phase in a compact and dense form which can be filtered easily. In the PFHS technique the precipitant is not added as such, but is slowly generated by a homogeneous chemical reaction within the solution. During the process of precipitation the solvent remains homogeneous with respect to concentration of the ion being precipitated and the reagent; if the generating reaction rate is slow then the high supersaturation is avoided and gradual formation of solid takes place throughout the entire solution.

The PFHS technique was first reported in 1952 by Bickerdike and Willard in case of urea hydrolysis.[2]

$$CO\ (NH_2)_2 + H_2O \longrightarrow H_2O \longrightarrow CO_2 + 2\ NH_3$$

$$
NH_3 +
\begin{array}{c} CH_3 - C = NOH \\ | \\ CH_3 - C = NOH \end{array}
\rightarrow
\begin{array}{c} CH_3 - C = NO^- \\ | \\ CH_3 - C = NOH \end{array}
+ NH_4^+
$$

Urea was hydrolyzed to increase the pH gradually and precipitate nickel dimethylglyoximate.

Bordner and Gordon studied the thermogravimetric analysis of uranium 8-hydroxyquinolinate which were precipitated from homogeneous solution.[3] At the same time several kinetic studies were carried out in case of PFHS technique.

In PFHS technique different anions can be generated at a slow rate of the reaction such as hydroxides, phosphates, oxalates and sulphates.[4]

In the present study we have used oxalate ester as a precipitant. Initially the appropriate volumes of all nitrate solutions were taken and the diethyl oxalate was used as the source of oxalate ion. In case of oxalate anion the urea may be employed to raise the pH of the acid solution which contain hydrogen oxalate ion $HC_2O_4^-$, thus affording a method of slow generation of oxalate ion.

$$CO(NH_2)_2 + 2HC_2O_4^- + H_2O = 2NH_4^+ + CO_2 + 2C_2O_4^{2-}$$
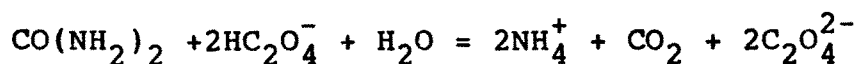
The best methods to precipitate magnesium[5] and zinc[6] are as oxalates from 85% acetic acid solution containing ammonium acetate and diethyl oxalate.

By using ethyl or methyl oxalates as source of oxalate ion, thorium[7] and the rare earth[8] ions can be precipitated. The compound dioxalylacetone has been used to liberate oxalate ions and precipitate thorium.[9]

Calcium can also be determined as an oxalate by precipitation from homogenous solution by cation release from the EDTA complex in the presence of oxalate ion.[10]
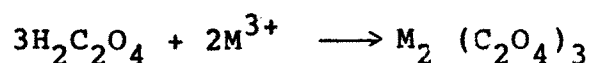
Dimethyl and diethyl oxalates can be hydrolysed to serve as reagents for generating oxalate ion :

$$(C_2H_5)_2C_2O_4 + 2 H_2O = 2 C_2H_5OH + 2H^+ + C_2O_4^{2-}$$
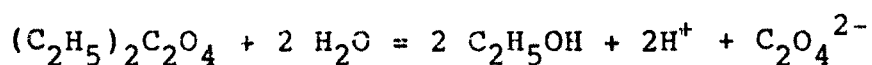
After hydrolytic decomposition the oxalate reacts with metal ion as follows

$$H_2C_2O_4 + M^{2+} \longrightarrow M (C_2O_4)$$

or

$$3H_2C_2O_4 + 2M^{3+} \longrightarrow M_2 (C_2O_4)_3$$

Diethyl oxalate is usually prefered because of its slower rate of hydrolysis.[11] Satisfactory results are obtained in case of diethyl oxalate with calcium, magnesium and zinc.

Some of the methods that have been used to generate various anions homogeneously are listed in Table 2.1.

Table 2.1   Applications of PFHS technique

Generated Anion	Reagent	Generation Reaction	Element precipitate
OH^-	Urea	$(NH_2)(O+3H_2O = CO_2+2NH_4 + 2OH^-$	Al,Ge,Th
PO_4^{3-}	Triethyl	$(C_2H_5O)_3PO+H_2O = 3C_2H_5CH+H_3PO_4$	Fe,Sn,Zn
$C_2O_4^{2-}$	Diethyl oxalate	$(C_2H_5O)_2C_2O_4+2H_2O = 2C_2H_5OH+H_2C_2$	Mg,Zn
SO_4^{2-}	dimethyl sulfate	$(CH_3O)_2SO_2+H_2O = 2CH_3OH+SO_4^{2-}+2H^+$	Ba,Cu,Sr
CO_3^{2-}	Trichloracetic acid.	$HC_2Cl_3O_2+2OH^- = CHCl_3+CO_3^{2-}+H_2O$	La,Pr

The PFHS technique is used where there is need for close control of the concentration of precipitating ion. Generally, the homogeneously formed solids occupy from one-tenth to twentieth, the volume of those formed by the classi cal procedure;[12] and precipitate formed is easy to filter and wash. Gorden[13] reported that precipitate of the hydrous aluminium oxide prepared from 0.1 gram of the element and 1 gram manganese salt by PFHS by hydrolysis of urea showed that only 0.2 mg of manganese remained as contaminant.

For avoiding the postprecipitation and coprecipitation pH values must be kept within narrow range during preci pitation. For example, to precipitate calcium oxalate in presence of magnesium ions or phosphate ions, the pH must be held as low as possible, consistant with enough $C_2O_4^-$ ion to precipitate the calcium. If the pH is too high, calcium phosphate may be coprecipitated or magnesium oxalate is post-precipitated.[14] Another advantage of close pH control in an operation is that by controlling the solubility of the precipitate, control of speed of precipitation is possible and hence control of the particle size.

It is known and observed that generally Y^{3+} and the rare earth ions such as trivalent La^{3+} give curdy or gelati-nous, bulky precipitate in direct oxalate precipitation. This type of precipitate is not very easy to handle. In case of La^{3+} and Y^{3+} if PFHS technique is applied this difficulty

is overcome and the precipitate is granular, microcrysta-
lline and easily filtrable.

The difference between curdy and crystalline preci-
pitates is that the curdy crystals do not grow beyond the
colloidal size and they adsorb considerable amounts of
impurities and even with repeated washings these impurities
are not removed completely.[15]

PFHS is a technique in which the precipitating ion
(oxalate ion $C_2O_4^{2-}$) is slowly liberated within the solution
by the hydrolysis of diethyl oxalate. In this technique
there is a uniform rate of reaction throughout the precipi-
tation process. Each oxalate ion initially catches a metal
ion and forms a nucleus of a crystal. After sometime with
further reaction more of the oxalate ions are released and
react with more metal ions and grow into a crystalline form.
This process of crystal growth takes place uniformly through
out the precipitation reaction hence the resultant product
is of uniform grain size. Generally the dilute solutions are
used for precipitation reaction so that grains are of proper
size for easy filtration.

It was found that barium ion is not completely preci-
pitated and hence 5% excess barium ion makes good the loss
due to incomplete precipitation.

The resultant metal oxlates or mixed metal oxalates
are very different in texture from those obtained by direct
precipitation or coprecipitation.

We have applied the PFHS technique to precipitate lanthanum, barium and copper and yttrium, barium, copper oxalates for 1,2,3 compounds and also applied for La-Ba-Sr-Cu and Y-Ba-Sr-Cu oxalates for 1,1,1,3 compounds. The individual oxalates were also prepared. Thus by hydrolytically generating oxalate ion from diethyl oxalate at 40-75°C homogeneous oxalate precursors required in the synthesis of candidate superconducting 1 2 3 and 1 1 1 3 compounds were prepared.

Mechanism of Precipitation

Mechanism of precipitation depends upon the relationship of particle size to supersaturation and stability of supersaturated solutions. This concept of relative supersaturation and its effect upon particle size was first described by Weimarn.[16] Particle size of the precipitate depends upon the various factors like temperature, rate of mixing of reagents, concentration of reagents and the solubility of precipitate.

Important Steps in Precipitate Formation

For the formation of solid phase from the solution two processes are involved. First step is the nucleation or nuclei formation and second step is particle growth.

(1) Nucleation - For any precipitate there is necessity of presence of minimum number of ions or molecules required to produce the stable second phase which is in contact with solution.

(2) <u>Particle Growth</u> - The second process that can occur during precipitation is the growth of particles which are already present in solution. This growth can only begin when the nuclei or other seed particles are present.

<u>Conditions of Precipitation</u>[17]

Number of general rules may be stated as follows :

(1) Precipitation should be carried out in dilute solution due regard being paid to the solubility of the precipitate.

(2) The reagents should be mixed slowly and with constant stirring. This will keep the degree of supersaturation small and will assist the growth of the crystals. A slight excess of the reagent is all that is generally required. In exceptional cases a large excess may be necessary. In some instances the order of mixing the reagent may be important. Precipitation may be effected under conditions which increase the solubility of the precipitate thus further reducing the degree of supersaturation.

(3) Precipitation is effected in hot solutions, provided the solubility and the stability of the precipitate permit to do so. Either one or both the solutions should be heated to just below the boiling point or other more favourable temperature. At the higher temperature :

(a) the solubility is increased with a consequent reduction in the degree of supersaturation.

(b) Coagulation is assisted and sol formation decreased.

(c) The velocity of crystallisation is increased thus leading to better form of crystals.

(4) Crystalline precipitates should be digested for as long as practical, preferably overnight, except in those cases where post precipitation may occur. As a rule, digestion on the steam bath is desirable. This process decreases the effect of co-precipitation and gives more readily filtrable precipitates. Digestion has little effect upon amorphous or gelatinous precipitates.

(5) The precipitate is still appreciably contaminated as a result of co-precipitation or other causes, the error may often be reduced by dissolving it in suitable solvent and then reprecipitated. The amount of foreign substance present in the second precipitation will be small and consequently the amount of the entrainment by the precipitate will also be small.

(6) If the precipitate should be washed with appropriate dilute solution of an electrolyte pure water may tend to cause peptisation.

Merits and Demerits of PFHS Technique

Eventhough the solid state reaction is quite a simple method for the preparation of ceramics it has certain disadvantages. For example, the reactants are mixed in grain size level which does not give homogeneous mixing and the reaction itself can be slow.

Chemical precipitation has certain disadvantages like uncertainty of the final composition due to the thermodynamic instability of the compound leading to partial precipitation, formation of gelatinous precipitate and the precipitation of several species of the non-uniform composition.

By using the coprecipitation method homogeneous mixing can be achieved. Precipitation from the homogeneous solution can be used in such cases when a uniform textured, pure homogeneous precipitate is obtained. This technique also affords a better control on stoichiometry.

Disadvantages of the method is that the decomposition of the oxalates passes through a carbonate formation step since some metal carbonates such as $BaCO_3$ and $SrCO_3$ do not easily decompose even at the recommended sintering temperature and long duration sintering is required.

Thus by considering the advantages and disadvantages of the PFHS technique it is concluded that this technique produces homogeneous and dense ceramics with the sharp super

conducting transition. The reaction in which the carbonates are not the starting materials or do not have intermediate carbonate formation may be therefore better choices.

2.3 HYDROLYSIS OF DIETHYL OXALATE

Diethyl oxalate undergoes hydrolysis reaction and makes available oxalate ion for reaction with metal ion involving following hydrolytic equilibria

$$
\begin{array}{ccc}
COOC_2H_5 & & COOH \\
| & \xrightarrow{\quad(H_2O)\quad} & | \\
COOC_2H_5 & K_1 & COOC_2H_5
\end{array}
$$

$$
\begin{array}{ccc}
COOC_2H_5 & & COOH \\
| & \xrightarrow{\quad(H_2O)\quad} & | \\
COOH & K_2 & COOH
\end{array}
$$
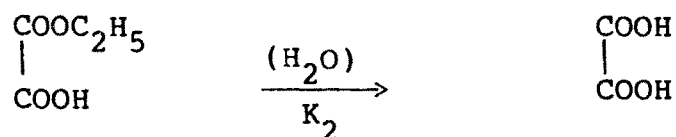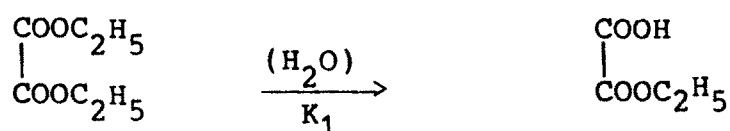
The ionization constants for these successive equilibria are $pK_1 = 1.27$, $pK_2 = 4.27$. Metal ions react with liberated oxalic acid giving $M(ox)$ and $M_2(ox)_3$ with M^{2+} and M^{3+} ions respectively. The hydrolytic reaction is slow and can be conveniently carried out in aqueous solution $60^{\circ}C$.

The kinetics of hydrolysis of diethyl oxalate in aqueous medium at $30^{\circ}C$, $40^{\circ}C$, $50^{\circ}C$, $60^{\circ}C$ has been studied by using acid-base titration method and the results are given in table 2.2 and rate data are given in Fig. 2.1.

The thermodynamic quantities like activation energy and frequency factor are calculated. The hydrolysis proceeds through a unimolecular, slow, rate determining first step followed by a rapid second step.
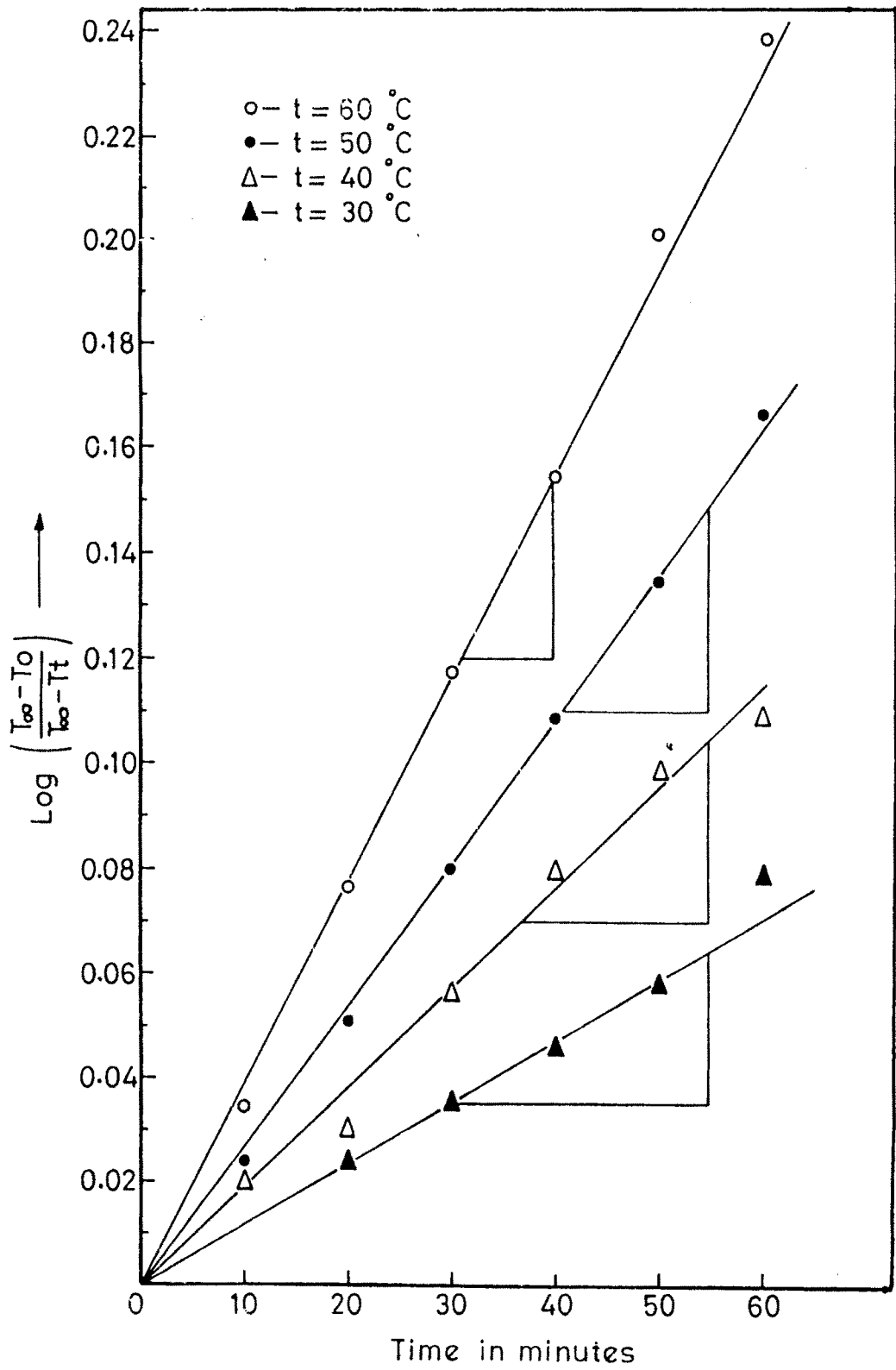
Fig.2·1 Kinetic data for the hydrolysis diethyl oxalate.

Table 2.2 : Rate data and thermodynamic parameters for hydrolysis of diethyl oxlate.

Temp.		Calculated	Graphical
$30^{\circ}C$	Mean k_1	2.766×10^{-3}	2.7636×10^{-3}
$40^{\circ}C$	Mean k_2	4.523×10^{-3}	4.606×10^{-3}
$50^{\circ}C$	Mean k_3	6.397×10^{-3}	5.680×10^{-3}
$60^{\circ}C$	Mean k_4	9.088×10^{-3}	8.956×10^{-3}
	Energy of Activation	9.592 Kcal	9.624 Kcal
	Frequency factor A	0.635×10^8	0.630×10^8

The studies indicate that oxalate formation by hydro-lytic dissociation of diethyl oxalate can be carried out at $60^{\circ}C$. Hence single metal ions or their mixtures were treated with sufficient excess of diethyl oxalate added, in small lots and simmering the solution over a sufficient length of time.

2.4 PREPARATIONS

(1) Yttrium Oxalate

About 13.7 g (0.05 mole) of the yttrium nitrate (99.99%) $Y(NO_3)_3 6H_2O$ was dissolved in distilled water. To this solution little nitric acid solution was added. Diethyl oxalate was used for the precipitation. The mixture was kept at $60^{\circ}C$ on hot plate. Addition of diethyl oxalate was

was made after 20 minutes interval. After some time tiny, white coloured oxalate particles appeared and as the diethyl oxalate was consumed by hydrolysis gradually, the precipitation enhanced. Six lots of diethyl oxalate were added for complete precipitation. The granular, heavy, white precipitate was allowed to settle overnight. It was filtered on Whatman No.1 filter paper. After washing with water and alcohol, the product was dried in air for 24 hours. The resulting‾ yttrium oxalate was used for the thermal analysis The yield was quantitative.

Duval[18] prepared yttrium oxalate by treating the nitrate with oxalic acid in slightly acidic form. While Wendlandt[19] used methyl oxalate for the precipitation.

(2) Lanthanum Oxalate

Lanthanum oxalate was prepared by using procedure similar to the one reported for yttrium oxalate.

About 22.5 g (0.05 mole) of lanthanum nitrate (99.99%) $La(NO_3)_3$ $7H_2O$ was dissolved in A.R. grade nitric acid and was heated to expell nitric acid and was dissolved in distilled water. Granular, microcrystalline lanthanum oxlate was obtained on hydrolysis of diethyl oxalate which was filtered and dried. The yield was quantitative.

(3) Barium Oxlate

About 13 g (0.05 mole) of barium nitrate (99.99%) $Ba(NO_3)_2$ was dissolved in distilled water and by precipita-

ting with deithyl oxalate the final product was obtained. The yield was quantitative.

(4) Strontium Oxalate

About 10.5 g (0.05 mole) of strontium nitrate (99.99%) $Sr(NO_3)_2$ was dissolved in distilled water. Granular white precipitate of strontium oxalate was obtained on hydrolysis of diethyl oxalate which was filtered and dried and used for thermal analysis. The yield was quantative.

Duval[20] prepared strontium oxalate in a solution conta ining acetic acid by adding the 10% aqueous solution of potassium oxalate drop by drop to the boiling solution of strontium chloride.

(5) Cooper Oxalate

About 12 g (0.05 mole) of copper nitrate (99.99%) $Cu(NO_3)_2$ $3H_2O$ was dissolved in distilled water. Granularblue precipitate of copper oxalate was obtained on hydrolysis of diethyl oxalate which was filtered and dried. The yield was quantitative.

Duval[21] prepared copper oxalate by using oxalic acid.

2.5 GENERAL PROPERTIES

(1) Yttrium Compounds

(a) Yttrium Oxalate

The formula of the yttrium oxalate was determined by estimating the yttrium containt by spectrophotometric method

by using Arsenazo.[22] Oxalate ion was estimated by dissolving the weighed quantity of the compound in acetic acid and estimating the oxalate ion as calcium oxalate.[23]

Yttrium oxalate Y_2 $(C_2O_4)_3$ $9H_2O$ is a microcrystalline, white coloured powder and slightly soluble in water. The solubility of yttrium oxalate is determined over wide range of oxalate concentration with pH range 0.5 to 4.6. The solubility product is 5.34 x 10^{-29} when the oxalate activity exceeds 10^{-3}M.[24]

The product yttrium oxalate analyses to 29.38% g Y, 53.75% of oxalate ion and 14.62% water of crystallization against the theoretical values Y 29.44%, oxalate 43.72% and water 14.57%.

(b) Yttrium Carbonate

Y_2 $(CO_3)_3$ $2H_2O$ is a white coloured powder soluble in acid.[25]

(c) Yttrium Oxide

Y_2O_3 is a white solid obtained by igniting the nitrate carbonate, oxalate or hydroxide. Its solubility in water at 29°C is 8 x 10^{-6} mole/litre[26] and the melting point is 2410°C.

(2)Lanthanum Compounds

(a) Lanthanum oxalate

The formula of lanthanum oxalate was determined by estimating lanthanum containt by spectrophotometric method

by using Alizarine as reagent[27] and oxalate ion was estimated as mentioned above.

$La_2(C_2O_4)_3$ 10 H_2O is a white coloured microcrystalline powder which is slightly soluble in water. The solubility of Lanthanum oxalate is of the order 10^{-28} as derived from the measurements in 0.02 to 0.1 N HCl at $20^{\circ}C$.[28]

The product $La_2(C_2O_4)_3$ 10 H_2O analyzes to 38.50% La, 36.62% oxalate and 24.25% water of crystallization against the theoretical values La 38.52%, La 36.60% oxalate and 24.26% of water.

(b) Lanthanum carbonate

$La_2(CO_3)_3$ $8H_2O$ is a white coloured powder soluble in acid. The density is 2.65.[29]

(c) Lanthanum oxide

La_2O_3 is a white solid, generally prepared by heating the hydroxides, nitrate, carbonate or oxalate and its density is 5.77.[29]

(3) Barium Compounds

(a) Barium oxalate

The formula of the barium oxalate was determined by estimating barium containt as barium sulfate by standard gravimetric procedures[30] and estimating the oxalate ion as mentioned above.

This is a white coloured microcrystalline powder which is slightly soluble in water.

The product BaC_2O_4, $1/2$ H_2O analyzes to 58.64% Ba, 37.52% oxalate ion and 3.84% of water of crystallization against the theoretical values Ba 58.60%, oxalate ion 37.55% and 3.84% water of crystallization.

(b) **Barium Carbonate**

$BaCO_3$ is a white coloured solid. Melting point is 811°C and boiling point 1450°C.[31]

(c) **Barium oxide**

BaO is usually a white, earthy, porous and probably amorphous solid which is soluble in methyl alcohol. Boiling point of BaO is about 2000°C.[32]

(4) **Strontium Compounds**

(a) **Strontium oxalate**

The formula of strontium oxalate was determined by estimating strontium gravimetrically as strontium sulfate[33] and oxalate ion as mentioned above.

$SrC_2O_4H_2O$ is a white coloured powder which is more soluble in water than the calcium oxalate. In presence of NH_4NO_3 NH_4Cl and ammonium acetate the solubility of strontium oxalate is increased 6.4, 5.4 and 9 times respectively.[34]

The product $SrC_2O_4H_2O$ analyses to 45.22%, Sr 45.3% of oxalate ion and 10.60% water of crystallization against

the theoretical value Sr 45.25% oxalate 45.41 and 10.62% H_2O.

(b) Strontium carbonate

$SrCO_3$ is a white coloured solid which is soluble in acid. Its melting point is $1340^\circ C$.[35]

(c) Strontium oxide

SrO is usually a white, porous solid with specific gravity in between 3 and 4. It is soluble in methyl alcohol.[32]

(5) Copper Compounds

(a) Copper oxalate

The formula of copper oxalate was determined by estimating copper containt with EDTA titration[36] and oxalate as mentioned above.

CuC_2O_4 1/2 H_2O is a bluish green coloured microcrystalline powder which is slightly soluble in water.

The product copper oxalate CuC_2O_4 0.5 H_2O analyzes to 37.81% Cu, 51.8% oxalate ion and 10.62% water of crystallization against the theoretical value 10.62% Cu, 51.7% oxalate and 10.62% of H_2O.

(b) Copper carbonate

Copper carbonate is a bluish coloured material which is soluble in NH_4OH.[37]

(c) Copper oxide

CuO is usually brownish black powder. Its melting point is 1064°C and specific gravity of CuO range from 6.130 to 6.451.[38]

2.6 I R SPECTRA OF OXALATES, CARBONATES AND OXIDES

The changes taking place in thermal analysis can be monitored by running I.R. spectra of starting, intermediate and end products in KBr pellates over the range 4000-200 cm^{-1}. In the thermal decomposition reactions of an oxalate the probable intermediate is a carbonate which finally decomposes to oxide. IR spectral data and assignments for all the five oxalates, carbonates and oxides are given in tables 2.3 to 2.5 and the spectra are shown in Figures 2.2 to 2.4.

In preparatory and analytical procedures in inorganic chemistry oxalate ion is a preferred anion because of many advantageous properties such as sparing solubility, quantitative precipitation, easy filtrability and suitability as intermediate in further ceramic production.

In the present study precursor oxalates are synthesized by PHFS technique. The candidate participating metals e.g. Y^{3+}, La^{3+}, Ba^{2+}, Sr^{2+} and Cu^{2+} and their turnary mixtures give characterizable compositions in which the oxalate ion behaves as a dianion. The IR spectral assignments for these salts are mainly with respect to carbonyl, metal-oxygen frequency and associated water. Thermal

Table 2.3 : IR spectral data for metal oxalates

$Y_2(C_2O_4)_3$	$La_2(C_2O_4)_3$	BaC_2O_4	SrC_2O_4	CuC_2O_4	Predominant mode
3000 - 3500	3455 3175 3085	3595 3530 3465	3575 3340 3075	3500-3300 3000-3300	Due to structural and adsorbed water
2895	2845	2995	2905	2955	-
2355	2355	2365	2345	2345	-
	1755				
1600	1600	1600	1600	1600	ν as (C = O)
-	-	1475	1470	1515	
1445	1485	1390	1455	1385	ν as(C-O) + ν(C-C)
1395 1315	1360 1315	1330 1317	1370 1315	1365 1315	ν s (C-O) + δ(O-C=O)
905	905	870	915	825	ν (C-O) + δ (O-C=O)
855 805	860 795	-	-	-	δ (O-C=O) + ν (M-O)
595	595	490	490	500	ν (MO) + ν (C-C)
495	495	-	-	-	ring def.~ ν (O-C=O)
-	-	395	400	385	ν (MO) + ring
380	380	-	-	-	δ (O-C = O)

FIG. 2·2 — INFRARED ABSORPTION SPECTRA

OF METAL OXALATES

TRANSMITTANCE

Y³⁺

La³⁺

Ba²⁺

Sr²⁺

Cu²⁺

4000   3000   2000   1400   800   200
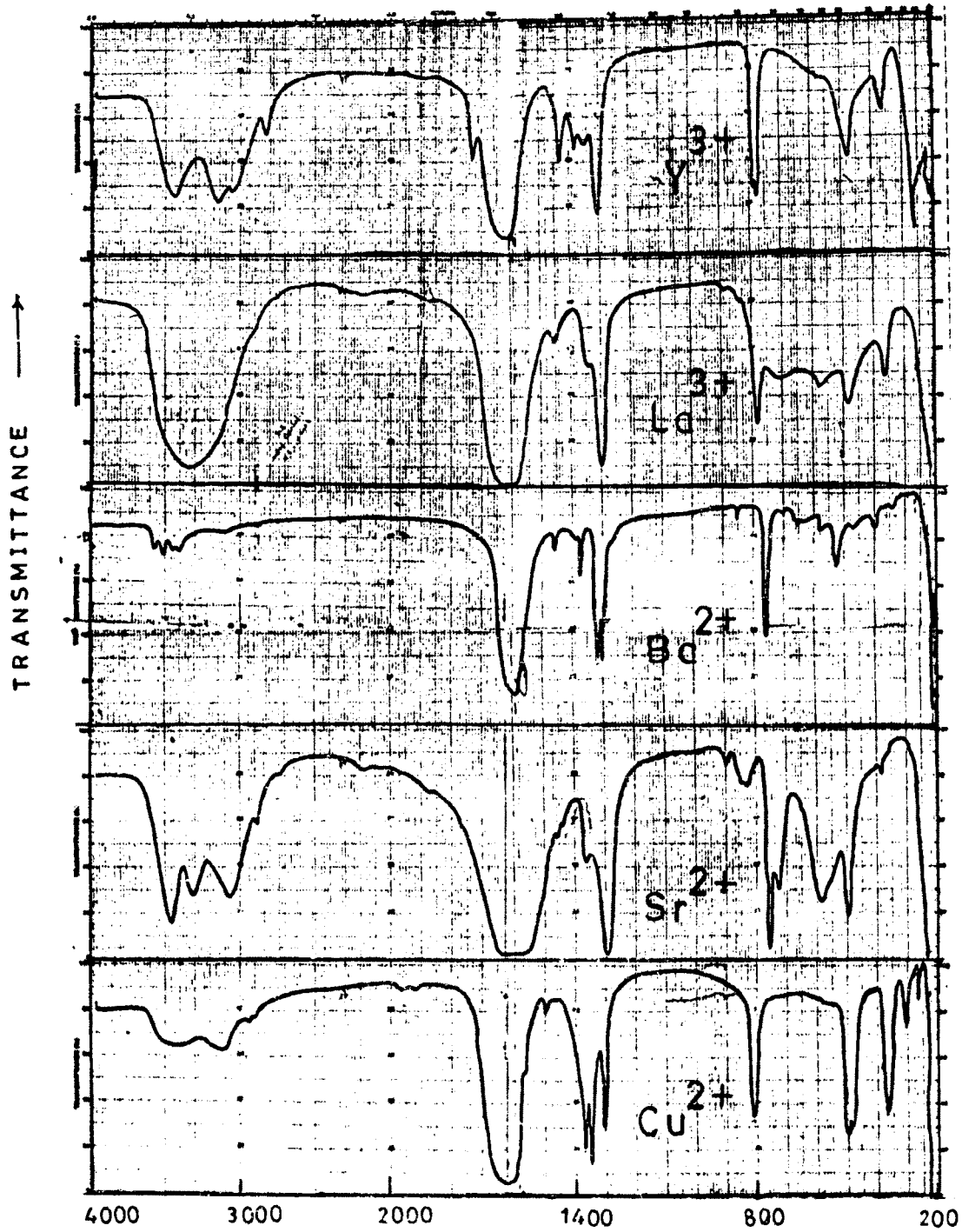
Table 2.4 : IR spectral data for metal carbonates

Y$_2$(CO$_3$)$_3$	La$_2$(CO$_3$)$_3$	BaCO$_3$	SrCO$_3$	CuCO$_3$	Predominant mode
3000-3500	3000-3500	3415	3435	3565 3537 3355	Due to structural or and adsorbed water
-	-	2700	2920	-	-
2325	2325	2423	2473	2315	-
-	-	-	-	1635	ν(O$_{II}$)
-	-	-	-	1555	
1300	1472	1455	1470	-	ν(CO$_{II}$) + ν(CO$_I$)
1600	1375	-	-	1315	
1075	1075	1055	1087	1115	δ(VO$_I$)+ν(CO$_{II}$)
840	850	-	855	875	δ(O$_{II}$(O$_{II}$)
745	435	681	703	775	
-	-	-	-	607	
-	-	-	-	435	ν(CO O$_I$)
-	-	-	-	320	ν(CO O$_I$) + ring def.

FIG. 2·3 — INFRARED ABSORPTION SPECTRA OF

METAL CARBONATES

TRANSMITTANCE

Y³⁺

La³⁺

Ba²⁺

Sr²⁺

Cu²⁺

4000   3000   2000   1400   800   200
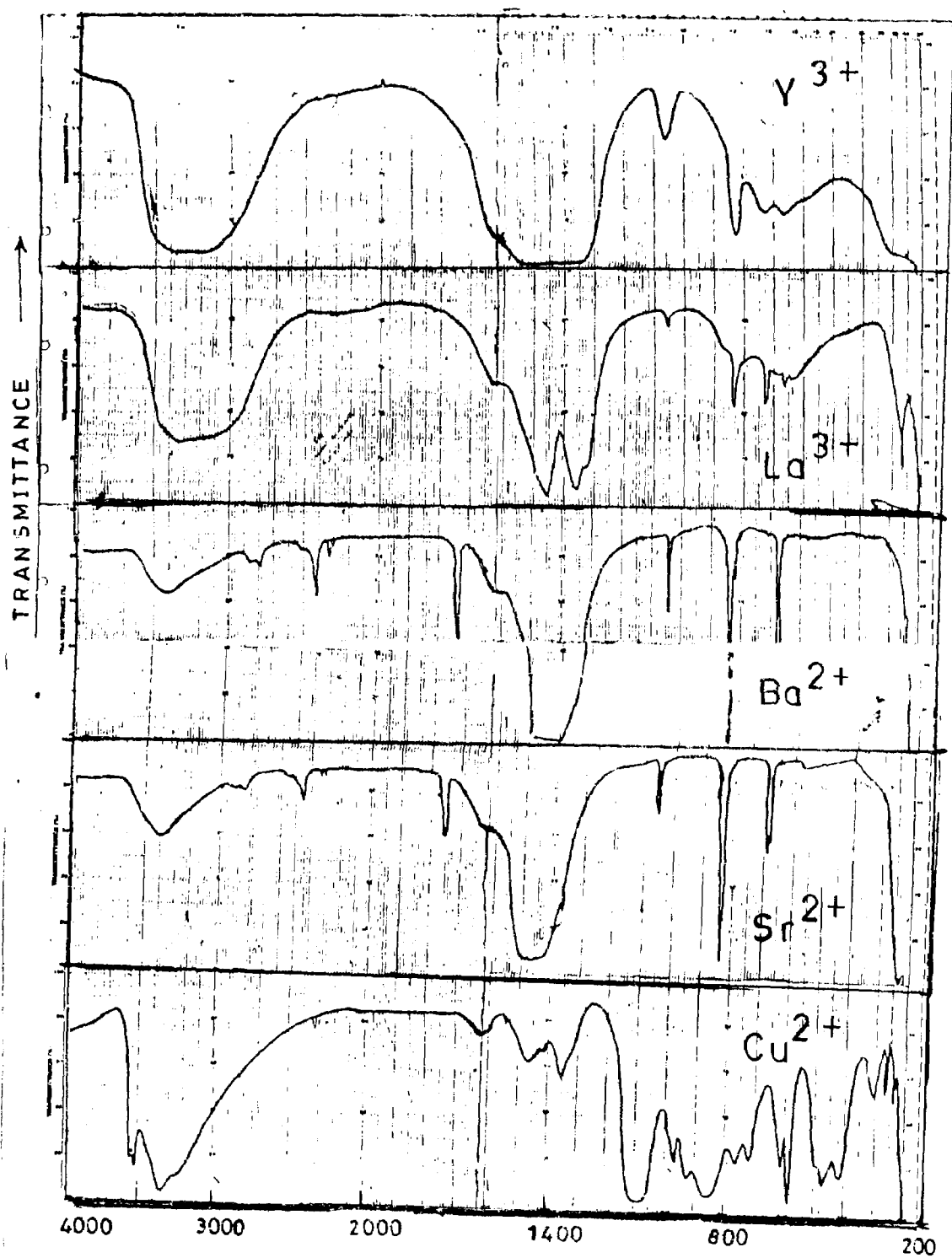
Table 2.5 : IR spectral data for metal oxides

Y_2O_3	La_2O_3	BaO	SrO	CuO	Predominant mode
3000-3500	3430	3000-3500	2915	-	Due to structural and adsorbed water.
2315	2475	2415	2455	-	-
1610	1730	1760	1765	-	$\nu\,(Co^{II})$
1340	1365	1400	1455	-	$\nu\,(CO_{II}) + \nu\,(Co_I)$
-	1085	-	-	-	
-	1055	1060	1065	-	$O = M = O$
-	1045	-	-	-	
-	870	-	-	-	
-	845	855	855	-	$\delta(O_{II}\,(O_{II})$
-	-	-	837	-	
-	725	685	695	-	
-	655	-	-	665	$\nu(M - O)$
-	625	-	-	615	
560	-	585	590	-	
400	-	-	520	-	

A
9714

FIG. 2·4 – INFRARED ABSORPTION SPECTRA

OF METAL OXIDES

TRANSMITTANCE →

Y³⁺

La³⁺

Ba²⁺

Sr²⁺

Cu²⁺

4000   3000   2000   1400   800   200
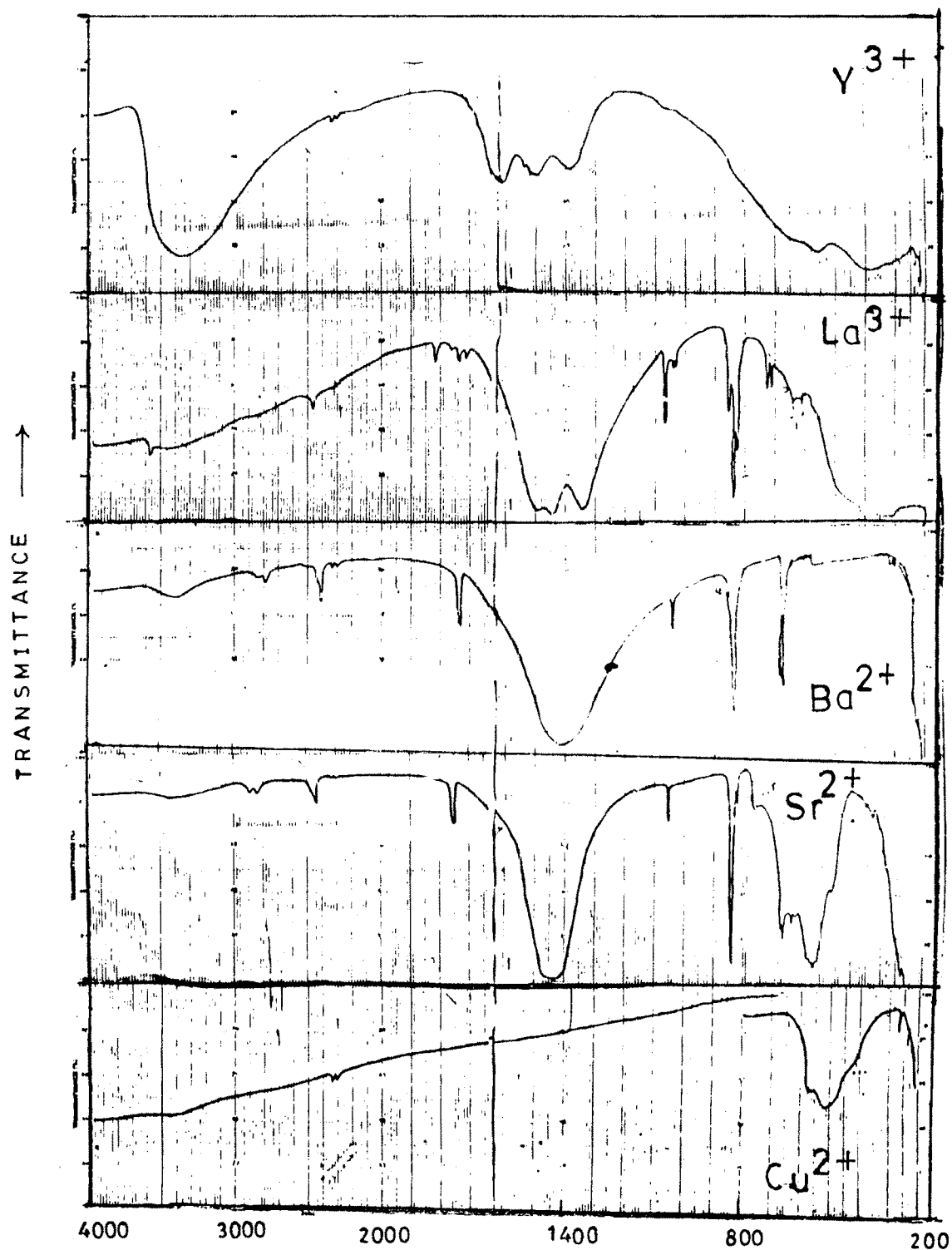
decomposition of oxalate in many cases passes through a carbonate formation finally giving oxides. The confirmation of the course of reaction may be followed by studying IR spectra at intermediate stages and end products. Complex kinds of thermal degradation reactions may lead to variable courses of reactions and therefore the confirmation of the course of oxalate decomposition yielding oxidic ceramics can be very conveniently traced by IR spectroscopy. Those oxalate which easily yield carbonates but are difficult to decompose further will show presence of carbonates and suitable measures can be exercised to overcome this difficulty.

Assignments in carbonates and oxide are also given. The complimentary information can be had from thermal analysis which gives weight loss data which can interpreted in terms of component lost or the residue left over at chosen temperatures. The IR spectra of residues confirm the findings.

2.7 THERMAL ANALYSIS OF METAL OXALATES AND METAL CARBONATES

The thermal analyses of metal oxalates and carbonates were carried out on a home made TGA unit over the temperature range- ambient to $1000^\circ C$. The heating rate was $30^\circ C$ per 10 minutes. In case of barium and strontium carbonate the decomposition even at $1000^\circ C$ was sluggish. Hence the final weight loss was found out by transferring a crucible

in a muffle furnace at $1300^{\circ}C$ where it was kept over 48 hours. The TGA curves of decomposition of oxalates and carbonates are traced in Fig. 2.5 and 2.6.

The profile of the thermal change speaks of all chemical changes during the heating cycle. Each weight loss was quantitatively analysed for the probable thermochemical changes and the weight loss was accounted for stoichiometric amount of the product lost. The cooling curve can also be plotted.

Metal oxalates in general show first step of dehydration reaction followed by loss of CO leaving the residue of carbonate. The carbonate further losses CO_2 quantitatively and leaves behind residue of metal oxide. However, a temperature at which the changes take place and the rate at which reaction proceeds are quite different for each compound and therefore interpretation of thermolysis of mixed oxalate can be interpreted on the basis of behaviour of the individual oxalate assuming nature of thermal changes completely additive.

Metal carbonates as discussed above show two or three-step-decomposition giving oxides. In ceramic methods the alkaline earth compounds used are the carbonates hence the study of carbonate is important. We have observed that in ceramic method the traces of carbonates in starting oxide materials are retained in the final product and in any pre-

cursor method if carbonate is an intermediate the same is the observation. Oxalate method is not free from this defect.

(1) Yttrium oxalate

In case of yttrium oxalate ~ 20 mg of the sample is taken in silica crucible and then subjected to thermal analysis. The formula of the precipitated yttrium oxalate is $Y_2(C_2O_4)_3 \ 9H_2O$. The hydrate water started to come off at $45^\circ C$ and upto 175°-$180^\circ C$ the curve is not horizontal because of instability of yttrium oxalate ions.

From $180^\circ C$-$300^\circ C$ the weight loss was observed. We found this level because of formation of the dihydrate. These observations are the same as Duval,[18] while Wendlandt[19] gives this dihydrate level within the range $180^\circ C$-$260^\circ C$. Then dihydrate begins to decompose at $300^\circ C$ and gives the break in curve at $410^\circ C$. The composition of the compound at $410^\circ C$ is $Y_2 \ (C_2O_4)$. And finally at $700^\circ C$ the formation of Y_2O_3 is complete. (Table 2.6)

(2) Lanthanum oxalate

$La_2 \ (C_2O_4)_3 \ 10 \ H_2O$ sample ~ 15 mg. is used for the thermal study. The water of hydration starts to come off at $125^\circ C$ and $300^\circ C$. It leads to $La_2(C_2O_4)_3 \ 2H_2O$. The dihydrate which immediately gives off water at $400^\circ C$ by the decomposition of oxalate gives the weight corresponding to the

formula $La_2O_3CO_2$. And $La_2O_3CO_2$ which decomposes above $700^\circ C$ to form La_2O_3.

Reaction	Temp.

$La_2(C_2O_4)_3$ $10H_2O$

$La_2(C_2O_4)_3$ $10H_2$ $\rightarrow$ $La_2(C_2O_4)_32H_2O$ + $8H_2O$ $160^\circ C$

$La_2(C_2O_4)_3$ $2H_2O$ $\rightarrow$ $La_2O_3CO_2$ + $3CO$ + $2CO_2$ + $2H_2O$ $400^\circ C$

$La_2O_3CO_2$ $\rightarrow$ La_2O_3 + CO_2 above $700^\circ C$.
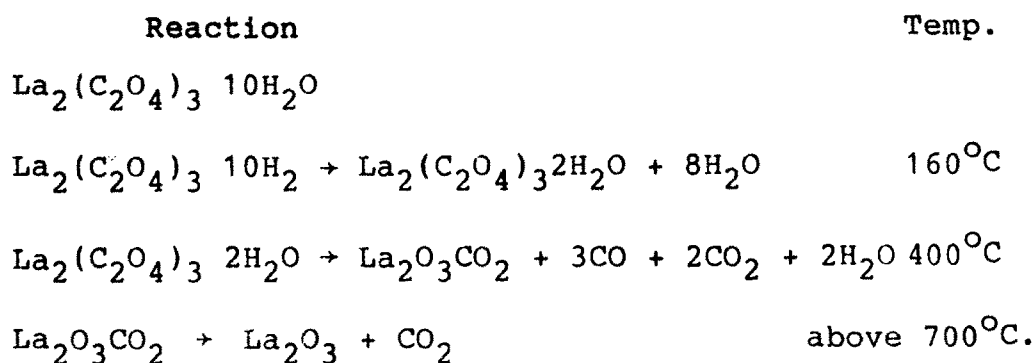
Our observations perfectly match with the observation of Padmanabhan, Sariya and Sundarm.[39]

Wendlandt[19] reported that the water of hydration begins to come of at $55^\circ C$. No intermediate hydrates are detected by observation. The oxide formation takes place at $800^\circ C$. (Table 2.7)

(3) **Barium oxalate**

$Ba_2C_2O_4$ $1/2$ H_2O is used for the thermal study. Complete loss of associated water molecule was observed at $125^\circ C$. And from this temperature upto $\sim 325^\circ C$ the horizontal plot is obtained due to formation of unhydrous barium oxalate. Then there is sudden change in temperature, carbon monoxide and carbon dioxide begin to come off.The complete formation of barium carbonate take at $462^\circ C$. Duval[40] observed complete formation of barium carbonate at $476^\circ C$.

Table 2.6   T.G.A. data for   Yttrium oxalate
complex.

Wt. of the sample taken for TGA : 20.0 mg.

Obs. No.	Temp. in ^{o}C	Time in min.	Weight in mg.	Change in wt. Δ W
1	32.5	10.0	20.0	
				0.8
2	62.5	20.0	19.2	
				1.2
3	100.0	30.0	18.0	
				1.6
4	125.0	40.0	16.4	
				0.6
5	162.5	50.0	15.8	
				0.0
6	200.0	60.0	15.8	
				0.0
7	225.0	70.0	15.8	
				0.0
8	262.5	80.0	15.8	
				0.0
9	300.0	90.0	15.8	
				0.2
10	325.0	100.0	15.6	
				0.4
11	362.0	110.0	15.2	
				0.4
12	400.0	120.0	14.8	
				0.0
13	430.0	130.0	14.8	
				1.2
14	462.5	140.0	13.6	
				0.9
15	500.0	150.0	12.7	
				0.7
16	525.0	160.0	12.0	
				0.5
17	550.0	170.0	11.5	
				0.7
18	575.0	180.0	10.8	
				0.8
19	600.0	190.0	10.0	
				0.8
20	625.0	200.0	9.2	
				0.7
21	650.0	210.0	8.5	
				0.6
22	675.0	220.0	7.9	
				0.5
23	700.0	230.0	7.4	
				0.0
24	725.0	240.0	7.4	

Table 2.7   T.G.A. data for Lanthanum oxalate
complex.

Wt. of the sample taken for TGA : 15.0 mg.

Obs. No.	Temp. in $^{\circ}C$	Time in min.	Weight in mg.	Change in wt. ΔW
1	32.5	10.0	15.0	
				0.0
2	62.5	20.0	15.0	
				0.0
3	100.0	30.0	15.0	
				0.0
4	125.0	40.0	15.0	
				0.6
5	162.5	50.0	14.4	
				0.6
6	200.0	60.0	12.8	
				0.8
7	225.0	70.0	12.0	
				0.0
8	262.5	80.0	12.0	
				0.0
9	300.0	90.0	12.0	
				0.8
10	325.0	100.0	11.2	
				2.2
11	362.0	110.0	9.0	
				1.4
12	400.0	120.0	7.6	
				0.0
13	430.0	130.0	7.6	
				0.0
14	462.5	140.0	7.6	
				0.0
15	500.0	150.0	7.6	
				0.0
16	525.0	160.0	7.6	
				0.1
17	550.0	170.0	7.5	
				0.1
18	575.0	180.0	7.4	
				0.2
19	600.0	190.0	7.2	
				0.2
20	625.0	200.0	7.0	
				0.1
21	650.0	210.0	6.8	
				0.2
22	675.0	220.0	6.7	
				0.3
23	700.0	230.0	6.5	
				0.0
24	725.0	240.0	6.3	
				0.1
25	750.0	250	6.3	
				0.0
26.	775.0	260.0	6.2	
				0.0
27.	800.0	270.0	6.2	

Table 2.8   T.G.A. data for Barium oxalate
            complex.

Wt. of the sample taken for TGA : 30.0 mg.

Obs. No.	Temp. in °C	Time in min.	Weight in mg.	Change in wt. ΔW
1	32.5	10.0	30.0	
				1.0
2	62.5	20.0	29.0	
				0.2
3	100.0	30.0	28.8	
				0.0
4	125.0	40.0	28.8	
				0.0
5	162.5	50.0	28.8	
				0.0
6	200.0	60.0	28.8	
				0.0
7	225.0	70.0	28.8	
				0.0
8	262.5	80.0	28.8	
				0.0
9	300.0	90.0	28.8	
				0.0
10	325.0	100.0	28.8	
				0.8
11	362.0	110.0	28.8	
				0.5
12	400.0	120.0	27.5	
				1.0
13	430.0	130.0	26.5	
				1.3
14	462.5	140.0	25.2	
				1.3
15	500.0	150.0	25.2	
				0.0
16	525.0	160.0	25.2	
				0.0
17	550.0	170.0	,,	
				,,
18	575.0	180.0	,,	
				,,
19	600.0	190.0	,,	
				,,
20	625.0	200.0	,,	
				,,
21	650.0	210.0	,,	
				,,
22	675.0	220.0	,,	
				,,
23	700.0	230.0	,,	
				,,
24	725.0	240.0	,,	

Table 2.9   T.G.A. data for Strontium oxalate
complex.

Wt. of the sample taken for TGA : 14.4 mg.

Obs. No.	Temp.in $^{\circ}C$	Time in min.	Weight in mg.	Change in wt. ΔW
1	32.5	10.0	24.4	
				0.6
2	62.5	20.0	23.8	
				0.8
3	100.0	30.0	23.0	
				0.8
4	125.0	40.0	22.2	
				0.8
5	162.5	50.0	22.1	
				0.1
6	200.0	60.0	22.1	
				0.0
7	225.0	70.0	22.1	
				0.0
8	262.5	80.0	22.1	
				0.0
9	300.0	90.0	22.1	
				0.0
10	325.0	100.0	22.1	
				0.0
11	362.0	110.0	22.1	
				0.0
12	400.0	120.0	22.1	
				0.9
13	430.0	130.0	22.1	
				1.7
14	462.5	140.0	19.5	
				1.1
15	500.0	150.0	18.4	
				0.0
16	525.0	160.0	18.4	
				0.0
17	550.0	170.0	''	
				''
18	575.0	180.0	''	
				''
19	600.0	190.0	''	
				''
20	625.0	200.0	''	
				''
21	650.0	210.0	''	
				''
22	675.0	220.0	''	
				''
23	700.0	230.0	''	
				''
24	725.0	240.0	''	

Table 2.10   T.G.A. data for Copper oxalate complex.

Wt. of the sample taken for TGA : 28.5 mg.

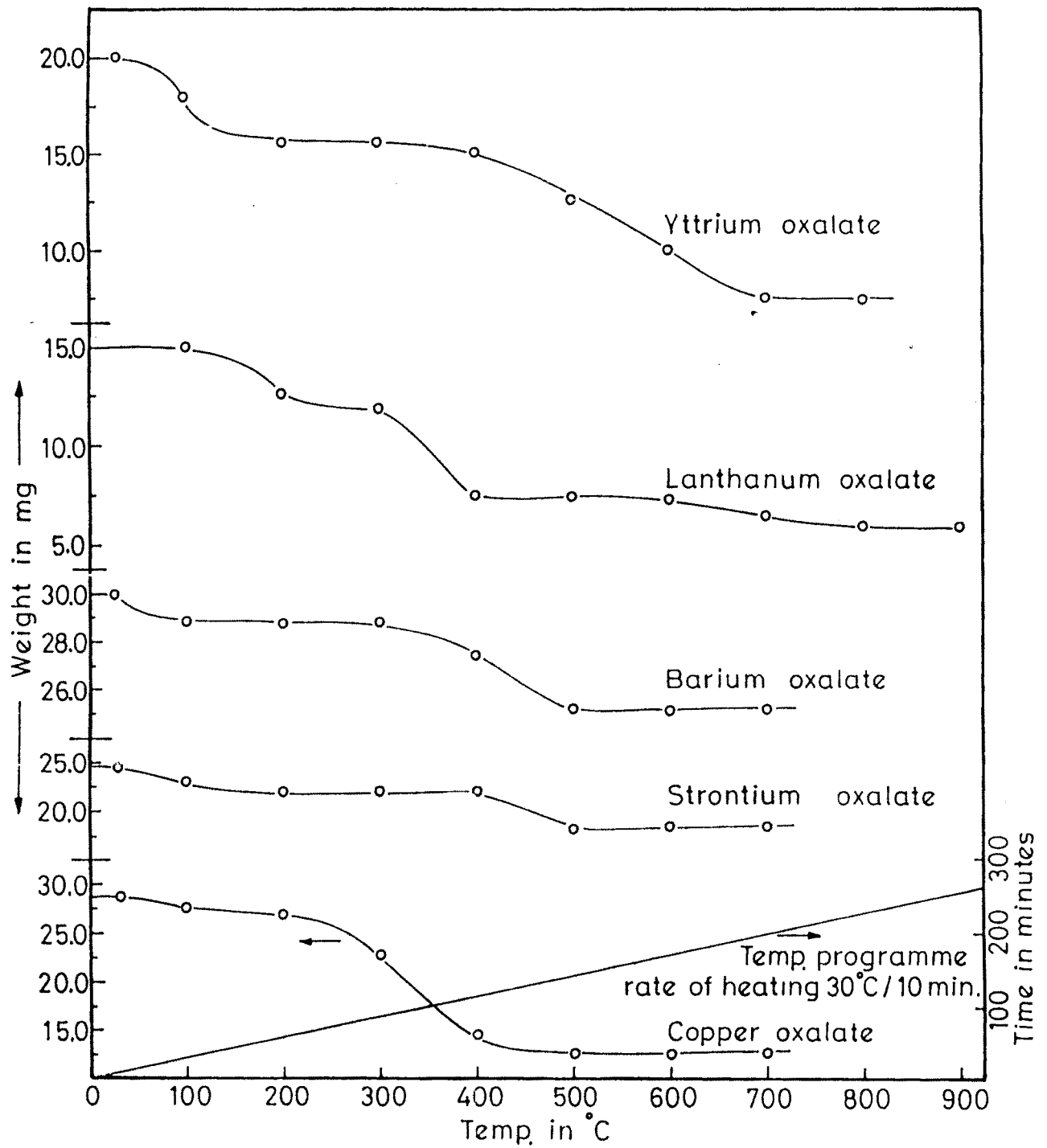| Obs. No.	Temp. in °C	Time in min.	Weight in mg.	Change in wt. ΔW
1	32.5	10.0	28.5	
				0.5
2	62.5	20.0	28.0	
				0.4
3	100.0	30.0	27.6	
				0.6
4	125.0	40.0	27.0	
				0.0
5	162.5	50.0	27.0	
				0.0
6	200.0	60.0	27.0	
				0.0
7	225.0	70.0	27.0	
				0.0
8	262.5	80.0	27.0	
				4.2
9	300.0	90.0	22.8	
				2.8
10	325.0	100.0	20.0	
				3.4
11	362.0	110.0	16.6	
				2.0
12	400.0	120.0	14.6	
				2.1
13	430.0	130.0	12.5	
				0.1
14	462.5	140.0	12.4	
				0.0
15	500.0	150.0	12.4	
				,,
16	525.0	160.0	,,	
				,,
17	550.0	170.0	,,	
				,,
18	575.0	180.0	,,	
				,,
19	600.0	190.0	,,	
				,,
20	625.0	200.0	,,	
				,,
21	650.0	210.0	,,	
				,,
22	675.0	220.0	,,	
				,,
23	700.0	230.0	,,	
				,,
24	725.0	240.0	,,	

Fig. 2·5   TGA   of   metal   oxalates

Dharmaprakash and P.Mohal Rao[41] studied the decomposition of barium oxalate and calcium oxalate (Table 2.8).

(4) Strontium oxalate

SrC_2O_4 H_2O begin to give off water from $25^\circ C$. And it gives formation of unhydrous oxalate within the range 103°-$400^\circ C$. The decomposition carbon monoxide and carbon dioxide takes place in the range of 400°-$510^\circ C$, and gives strontium carbonate. Our observation almost agrees with Duval[20] while Winkler[42] and Erdey and Paulik who give $132^\circ C$ as the dehydration temperature. (Table 2.9)

(5) Copper oxalate

CuC_2O_4 $1/2$ H_2O is used for thermal study. Water molecule begins to come off from $25^\circ C$ and after the complete dehydration the resulting unhydrous oxalate is stable from 125° to $262^\circ C$. Above $462^\circ C$ the black coloured copper oxide is formed. Ishii[43] reported that the limits of unhydrous oxalate were in the range 150° to $210^\circ C$ (Table 2.10).

(6) Yttrium carbonate

$Y_2(CO_3)$ $3H_2O$ is used for thermal study. $Y_2(CO_3)_3$ was obtained within the temperature range 225°-$300^\circ C$. Finally whitish coloured Y_2O_3 is obtained by heating the sample at $700^\circ C$. (Table 2.11). Fridman V. Moskina Gorokhov[44] reported the thermal decomposition of yttrium carbonate with yttrium fluoride.

(7) Lanthanum carbonate

$La_2 (CO_3)_3 H_2O$ is unstable upto $300^{\circ}C$. $La_2(CO_3)_3$ is stable in the range $300^{\circ}-400^{\circ}C$. CO_2 gas evolution starts from $550^{\circ}C$ and $La_2O_3CO_2$ is stable from 550° to $680^{\circ}C$. Finally La_2O_3 formation takes place at $770^{\circ}C$. (Table 2.12) These observations exactly match with the observations of Sklyarenko-Chubukov.[45]

(8) Barium carbonate

There is no change in weight from $25^{\circ}C$ to $1000^{\circ}C$ (Table 2.13) These observations exactly match with Duval's observations.[46]

(9) Strontium carbonate

It was observed that there is no change in weight from $250^{\circ}C$ to $1000^{\circ}C$ (Table 2.14). It is reported that the thermal decomposition of $BaCO_3$ takes place at about $1360^{\circ}C$.

(10) Copper carbonate

From $25^{\circ}C$ to $162^{\circ}C$ there is no change in weight on thermal analysis curve and from $162^{\circ}C-500^{\circ}C$ there is continuous change in weight and finally it gives copper oxide (CuO) above $500^{\circ}C$ (Table 2.15).

In all the above cases, results of thermal decomposition yield corresponding residual composition at appropriate temperatures. These were confirmed by withdrawing the samples

Table 2.11   T.G.A. data for   Yttrium Carbonate
complex.

Wt. of the sample taken for TGA : 13.0 mg.

Obs. No.	Temp.in ^{o}C	Time in min.	Weight in mg.	Change in wt. Δ W
1	32.5	10.0	13.0	
				0.0
2	62.5	20.0	13.0	
				0.0
3	100.0	30.0	13.0	
				0.0
4	125.0	40.0	13.0	
				0.4
5	162.5	50.0	12.6	
				0.4
6	200.0	60.0	12.2	
				0.4
7	225.0	70.0	11.8	
				0.0
8	262.5	80.0	11.8	
				0.0
9	300.0	90.0	11.8	
				0.4
10	325.0	100.0	11.4	
				0.4
11	362.0	110.0	11.0	
				0.7
12	400.0	120.0	10.3	
				0.8
13	430.0	130.0	9.5	
				0.9
14	462.5	140.0	8.6	
				0.4
15	500.0	150.0	8.2	
				0.3
16	525.0	160.0	7.9	
				0.3
17	550.0	170.0	7.6	
				0.2
18	575.0	180.0	7.4	
				0.1
19	600.0	190.0	7.3	
				0.0
20	625.0	200.0	7.3	
				0.1
21	650.0	210.0	7.2	
				0.0
22	675.0	220.0	7.2	
				0.1
23	700.0	230.0	7.1	
				0.0
24	725.0	240.0	7.1	

Table 2.12   T.G.A. data for   Lanthanum Carbonate complex.

Wt. of the sample taken for TGA : 6.4 mg.

Obs. No.	Temp. in $^{\circ}C$	Time in min.	Weight in mg.	Change in wt. ΔW
1	32.5	10.0	6.4	
				0.0
2	62.5	20.0	6.4	
				0.0
3	100.0	30.0	6.4	
				0.1
4	125.0	40.0	6.3	
				0.0
5	162.5	50.0	6.3	
				0.0
6	200.0	60.0	6.3	
				0.1
7	225.0	70.0	6.2	
				0.0
8	262.5	80.0	6.2	
				0.0
9	300.0	90.0	6.2	
				0.1
10	325.0	100.0	6.1	
				0.0
11	362.0	110.0	6.1	
				0.0
12	400.0	120.0	6.1	
				0.3
13	430.0	130.0	5.8	
				0.4
14	462.5	140.0	5.4	
				0.2
15	500.0	150.0	5.2	
				0.2
16	525.0	160.0	5.0	
				0.0
17	550.0	170.0	5.0	
				0.0
18	575.0	180.0	5.0	
				0.0
19	600.0	190.0	5.0	
				0.0
20	625.0	200.0	5.0	
				0.0
21	650.0	210.0	5.0	
				0.0
22	675.0	220.0	5.0	
				0.0
23	700.0	230.0	5.0	
				0.1
24	725.0	240.0	4.9	
				0.3
25	750.0	250.0	4.6	
				0.3
26	775	260.0	4.3	
				0.0
27	800	270.0	4.3	

Table 2.13 T.G.A. data for Barium Carbonate complex.

Wt. of the sample taken for TGA : 20.0 mg.

Obs. No.	Temp.in °C	Time in min.	Weight in mg.	Change in wt. ΔW
1	32.5	10.0	20.0	
				0.0
2	62.5	20.0	20.0	
				0.0
3	100.0	30.0	,,	
				,,
4	125.0	40.0	,,	
				,,
5	162.5	50.0	,,	
				,,
6	200.0	60.0	,,	
				,,
7	225.0	70.0	,,	
				,,
8	262.5	80.0	,,	
				,,
9	300.0	90.0	,,	
				,,
10	325.0	100.0	,,	
				,,
11	362.0	110.0	,,	
				,,
12	400.0	120.0	,,	
				,,
13	430.0	130.0	,,	
				,,
14	462.5	140.0	,,	
				,,
15	500.0	150.0	,,	
				,,
16	525.0	160.0	,,	
				,,
17	550.0	170.0	,,	
				,,
18	575.0	180.0	,,	
				,,
19	600.0	190.0	,,	
				,,
20	625.0	200.0	,,	
				,,
21	650.0	210.0	,,	
				,,
22	675.0	220.0	,,	
				,,
23	700.0	230.0	,,	
				,,
24	725.0	240.0	,,	

Table 2.14   T.G.A. data for   Strontium Carbonate
complex.

Wt. of the sample taken for TGA : 10.0 mg.

Obs. No.	Temp.in $^\circ$C	Time in min.	Weight in mg.	Change in wt. Δ W
1	32.5	10.0	10.0	
				0.0
2	62.5	20.0	10.0᠕	
				0.00
3	100.0	30.0	,,	
				,,
4	125.0	40.0	,,	
				,,
5	162.5	50.0	,,	
				,,
6	200.0	60.0	,,	
				,,
7	225.0	70.0	,,	
				,,
8	262.5	80.0	,,	
				,,
9	300.0	90.0	,,	
				,,
10	325.0	100.0	,,	
				,,
11	362.0	110.0	,,	
				,,
12	400.0	120.0	,,	
				,,
13	430.0	130.0	,,	
				,,
14	462.5	140.0	,,	
				,,
15	500.0	150.0	,,	
				,,
16	525.0	160.0	,,	
				,,
17	550.0	170.0	,,	
				,,
18	575.0	180.0	,,	
				,,
19	600.0	190.0	,,	
				,,
20	625.0	200.0	,,	
				,,
21	650.0	210.0	,,	
				,,
22	675.0	220.0	,,	
				,,
23	700.0	230.0	,,	
				,,
24	725.0	240.0	,,	

Table 2.15   T.G.A. data for   Copper Carbonate
             complex.

Wt. of the sample taken for TGA : 25.9 mg.

Obs. No.	Temp. in $^\circ$C	Time in min.	Weight in mg.	Change in wt. Δ W
1	32.5	10.0	25.9	
				0.0
2	62.5	20.0	25.9	
				0.0
3	100.0	30.0	25.9	
				0.0
4	125.0	40.0	25.9	
				0.0
5	162.5	50.0	25.9	
				0.8
6	200.0	60.0	25.1	
				0.9
7	225.0	70.0	24.2	
				2.2
8	262.5	80.0	22.0	
				1.7
9	300.0	90.0	20.3	
				1.1
10	325.0	100.0	19.2	
				1.2
11	362.0	110.0	18.0	
				0.8
12	400.0	120.0	17.2	
				1.2
13	430.0	130.0	16.4	
				0.8
14	462.5	140.0	15.2	
				0.4
15	500.0	150.0	14.8	
				0.0
16	525.0	160.0	14.8	
				0.0
17	550.0	170.0	14.8	
				,,
18	575.0	180.0	,,	
				,,
19	600.0	190.0	,,	
				,,
20	625.0	200.0	,,	
				,,
21	650.0	210.0	,,	
				,,
22	675.0	220.0	,,	
				,,
23	700.0	230.0	,,	
				,,
24	725.0	240.0	,,	
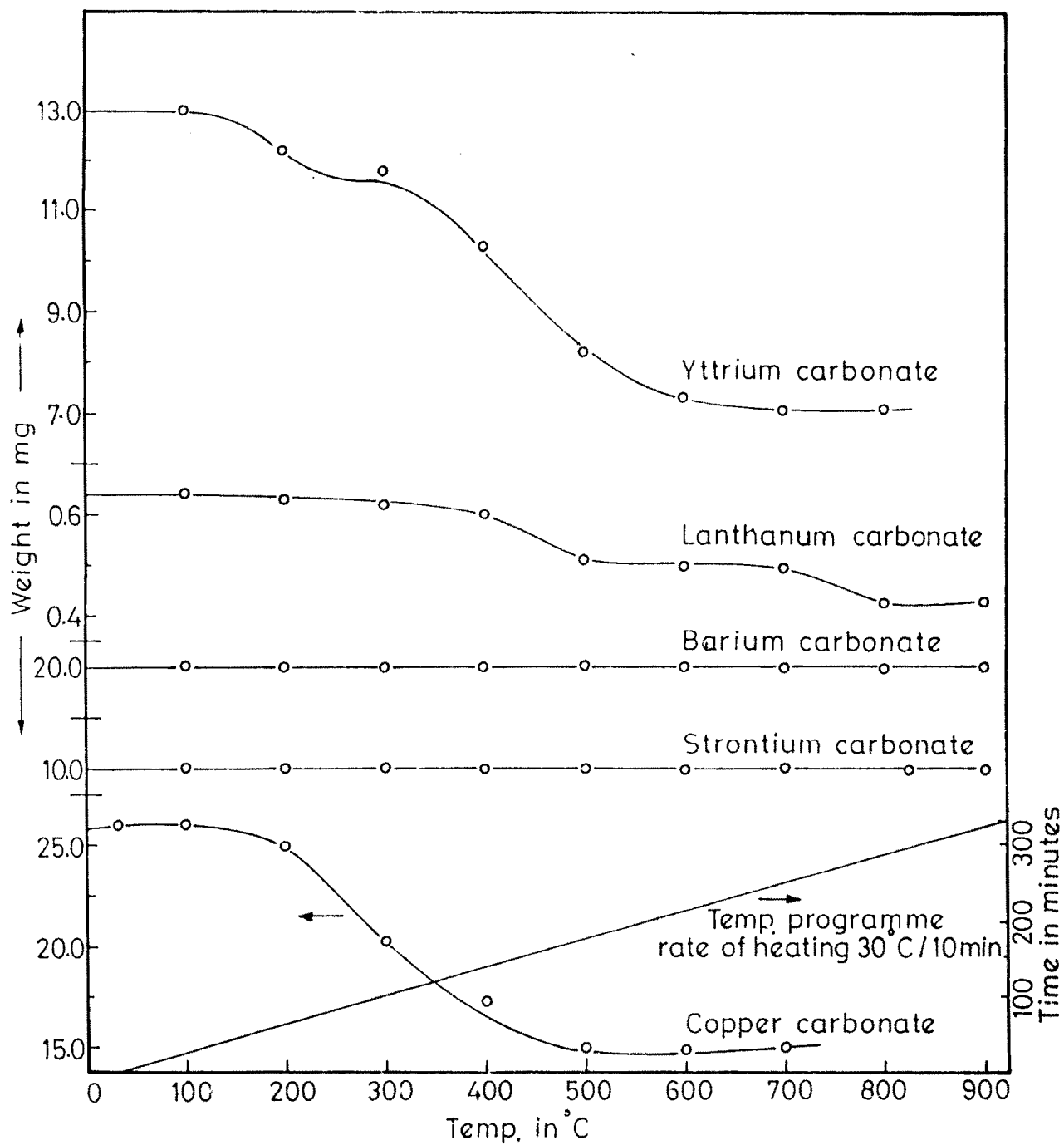
Fig. 2·6 T G A of metal carbonates

2.16 Chemical changes during thermal analysis.

Ytrrium oxalate $Y_2(C_2O_4)_3$ 9 H_2O

Weight of the sample taken : 20.0 mg

Temp.range	Expected wt.	Obtained wt.	Formula	Cause
25 - 162°C	Continuous change in wt.			loss of 7 H_2O mol.
162-300°C	15.8 mg	15.8 mg	$Y_2(C_2O_4)_3$ $2H_2O$	
300-400°C	Continuous change in wt.			loss of 2 H_2O mol.
400-425°C	14.8 mg	14.8 mg	$Y_2(C_2O_4)_3$	
425-700°C	Continuous change in wt.			(CO_2+CO)
Above 700°C	7.4 mg	7.5 mg	Y_2O_3	

Lanthanum Oxalate : $La_2(C_2O_4)_3$ $10H_2O$

Weight of the sample taken : 15.0 mg

Temp.range	Expected wt.	Obtained wt.	Formula	Cause
25 - 125°C	15.0 mg	15.0 mg	$La_2(C_2O_4)_3$ $10H_2O$	
125-225°C	Continuous change in wt.			Loss of 8 H_2O mol.
225-300°C	12.0 mg	12.0 mg	$La_2(C_2O_4)_3$ $2H_2O$	
300-400°C	Continuous change in wt.			
400-525°C	7.5 mg	7.5 mg	$La_2O_3CO_2$	$3CO+2CO_2$
525-775°C	Continuous change in wt.			
Above 775°C	6.7 mg	6.2 mg	La_2O_3	

Barium oxalate : BaC_2O_4 $1/2$ H_2O

Weight of the sample taken : 30.0 mg

Temp.range	Expected wt.	Obtained wt.	Formula	Cause
25 - 125°C	Continuous change in wt.			loss of H_2O
125-325°C	28.8 mg	28.8 mg	BaC_2O_4	
325-462°C	Continuous change in wt.			loss of CO_2+Co
462-700°C	25.2 mg	25.2 mg	$BaCO_3$	

Strontium oxalate : $SrC_2O_4H_2O$

Weight of the sample taken : 24.4 mg

Temp.range	Expected wt.	Obtained wt.	Formula	Cause
25 - 162°C	Continuous change in wt.			loss of H_2O
163-400°C	22.1 mg	22.1 mg	SrC_2O_4	
400-462°C	Continuous change in wt.			loss of CO_2+Co
462-700°C	18.6 mg	18.4 mg	$SrCO_3$	

Copper oxalate : CuC_2O_4 $1/2$ H_2O

Weight of the sample taken : 28.5 mg

Temp.range	Expected wt.	Obtained wt.	Formula	Cause
25 - 125°C	Continuous change in wt.			Loss of H_2O
125-262°C	27.0 mg	27.0 mg	CuC_2O_4	
125-462°C	Continuous change in wt.			Loss of CO_2+CO
Above 462°C	12.7 mg	12.4 mg	CuO	

Table 2.17 : Chemical changes during thermal analysis.

Yttrium carbonate : $Y_2(CO_3)_3 \cdot 3H_2O$

Weight of the sample taken : 13.0 mg

Temp.range	Expected wt.	Obtained wt.	Formula	Cause
125-225°C	Continuous change in wt.	Continuous change in wt.		Loss of H_2O mol.
225-300°C	11.8 mg	11.8 mg	$Y_2(CO_3)_3$	
300-700°C	Continuous change in wt.	Continuous change in wt.		Loss of $3CO_2$
Above 700°C	7.1 mg	7.1 mg	Y_2O_3	

Lanthanum carbonate : $La_2(CO_3)_3H_2O$

Weight of the sample taken : 6.4 mg

Temp.range	Expected wt.	Obtained wt.	Formula	Cause
125-300°C	Continuous change in wt.	Continuous change in wt.		Loss of 1 H_2O mol.
300-400°C	6.1 mg	6.1 mg	$La_2(CO_3)_3$	
400-550°C	Continuous changed in wt.	Continuous change in wt.		Loss of 2 CO_2
550-680°C	5.0 mg	5.0 mg	$La_2O_3CO_2$	
680-770°C	Continuous change in wt.	Continuous change in wt.		Loss of CO_2
Above 770°C	4.8 mg	4.3 mg	La_2O_3	

Barium carbonate - $BaCO_3$

Weight of the sample taken : 20.0 mg

Temp.range	Expected wt.	Obtained wt.	Formula	Cause
0 - 1000°C	20.0 mg No change in wt.	20.0 mg No change in wt.	$BaCO_3$	

Strontinum carbonate : $SrCO_3$

Weight of the sample taken : 10.0 mg

Temp.range	Expected wt.	Obtained wt.	Formula	Cause
0-1000°C	10.0 mg No change in wt.	10.0 mg No change in wt.	$SrCO_3$	-

Copper carbonate ($CuCO_3$

Weight of the sample taken : 28.5 mg

Temp.range	Expected wt.	Obtained wt.	Formula	Cause
25-162°C	Constant wt.	Constant wt.	$CuCO_3$	
162-500°C		Continuous change in wt.		Loss of CO_2
Above 500°C	14.7 mg	14.7 mg	CuO	

from the thermobalance crucible and analysing the quenched material by standard chemical analytical procedures and IR spectra.

Chemical changes in all the above thermal reactions are given in Tables 2.16 and 2.17.

2.8 GENERAL NATURE OF THE OXALATE PRECIPITATES

Low power optical microscopy gives the information about the crystallinity of the resultant metal oxalates. The photomicrographs of the oxalates of copper, lanthanum, yttrium, barium. Strontium obtained from PFHS technique are given as plates A and precipitates obtained from direct oxalate precipitation are given as Part B. It can be seen from all the photographs that uniform crystalline materials are obtained by PFHS and the precipitates obtained by direct method are either amorphous or irregular materials. Obviously with further treatment PFHS is expected to give purer and uniform textured material.

2.9 CONCLUSION

In order to get microcystalline uniform grained precursor components diethyl oxalate hydrolysis method was used and the physical form. of the resdultant oxalate is quite satisfactory. The study of barium and strontium oxalates indicated that even at sufficiently high temperature at which ceramic superconducting materials are prepared

Photomicrographs of metal oxalates

Sr.No.	Compound	Photomicrograph Numbers	
		Direct precipitation method	PFHS method
1.	Copper oxalate	1	6
2.	Lanthanum oxalate	2	7
3.	Yttrium oxalate	3	8
4.	Barium oxalate	4	9
5.	Strontium oxalate	5	10
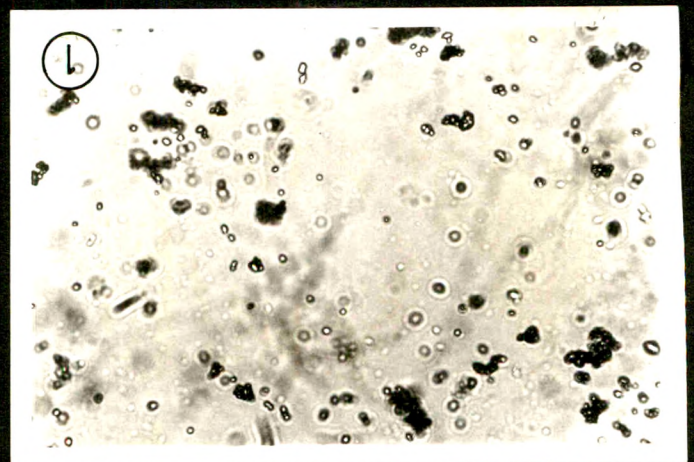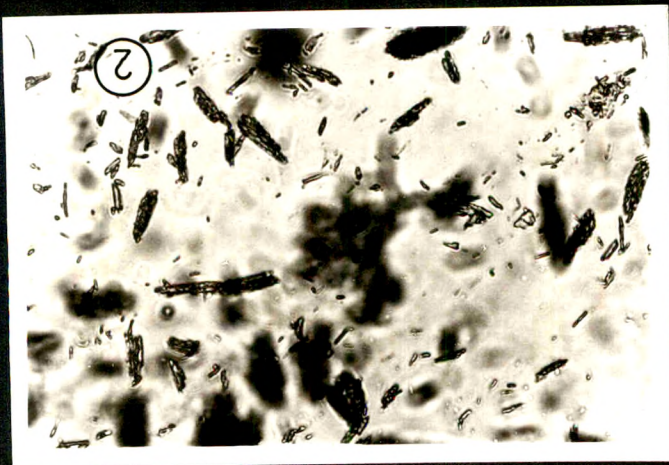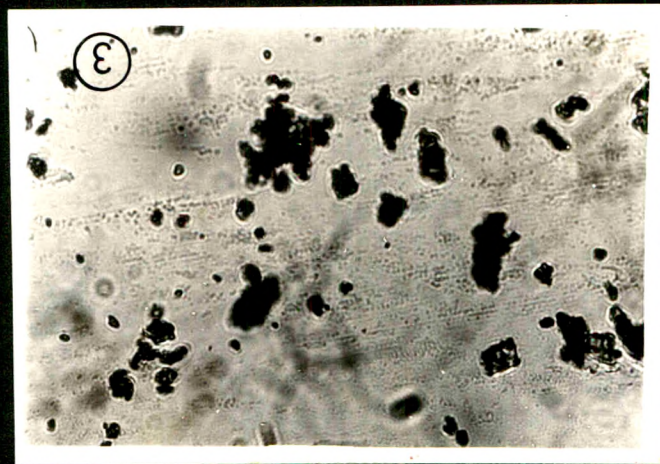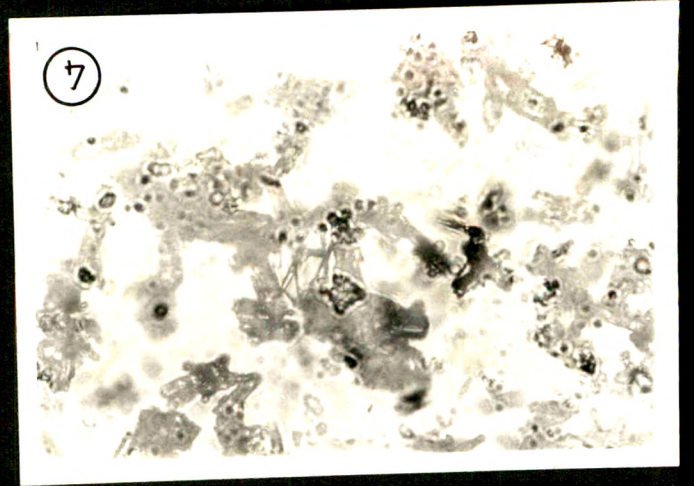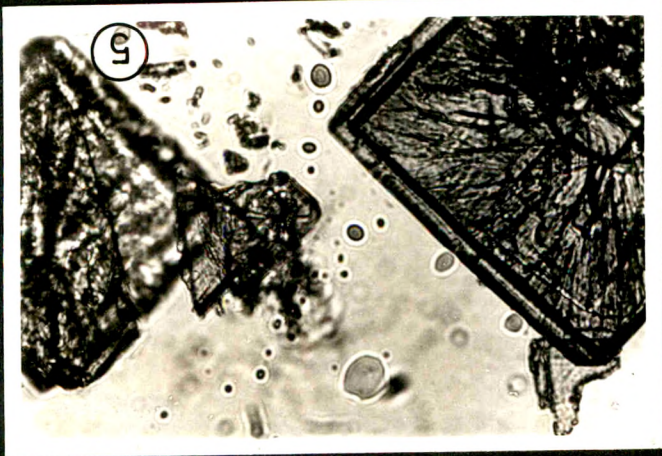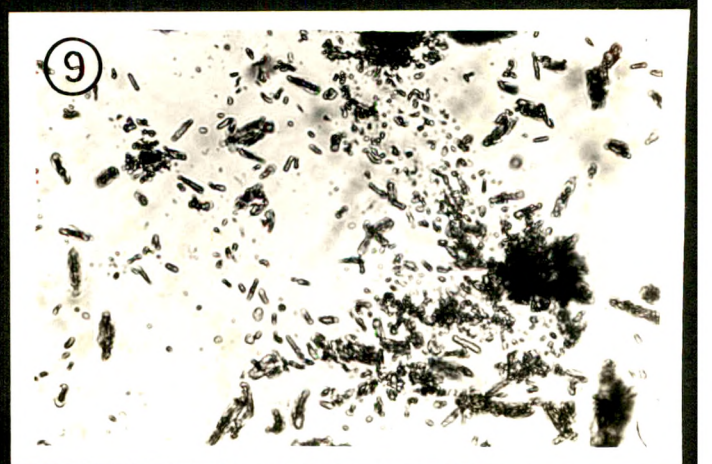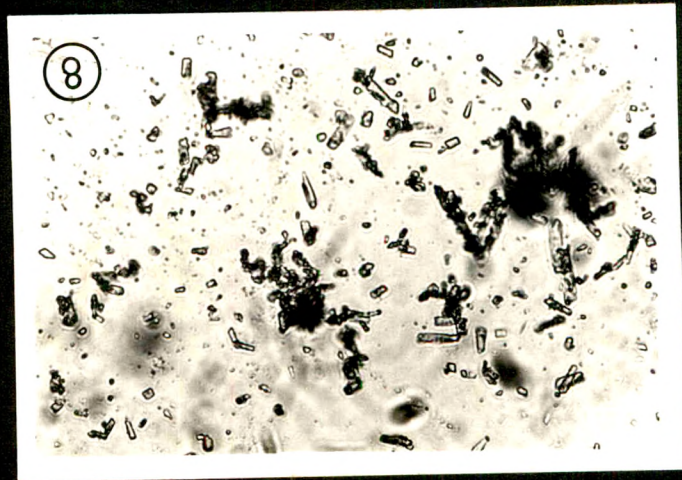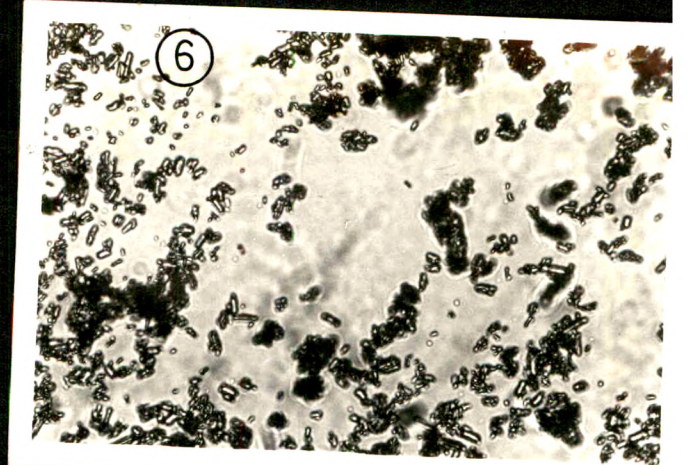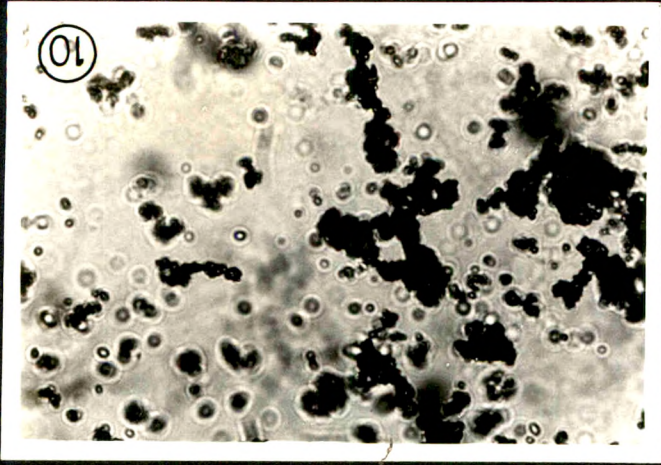
i.e. 950°C there is no indication of conversion of carbonate to oxide. Even prolonged heating for a very long period of 40 hours there is no sizabole conversion. These carbonates do not quantitatively yield oxides even at 1200°C on prolonged heating. It is, therefore, inferred that in any procedure in which starting material contains barium carbonate, strontium carbonate or produce barium or strontium carbonate may be avoided or the furnace treatment must be prolonged so that no trace of carbonate is left which must be ascertained by chemical analysis. In this respect it can be said that the oxalate method is not free from these drawbacks, since oxalates directly decompose into carbonate. Our study aims at indicating that hydrolytic generation of oxalate ions to give oxalate precursor is superior to direct oxalate precipitation by using oxalic acid.

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