Thermal decomposition of Gd-Mg oxalate and the effect of γ-irradiation

S C Moharana, J Praharaj & D Bhatta*
Department of Chemistry, Utkal University, Bhubaneswar 751004, India
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Decomposition of Mg and Gd oxalates, mechanical mixture and co-precipitated (unirrad. and irrad.) Gd-Mg oxalate has been studied by adopting rising temperature technique. The kinetics of the decomposition are investigated using thermogravimetry. The TG-DTA data exhibit two different stages of weight loss and endotherms, corresponding to individual components in the co-precipitate. Kinetic parameters for different stages are obtained by applying best fit models of solid state reaction in the Coats-Redfern's equation. Effects of irradiation and co-precipitation technique on the mechanism of decomposition of Gd-Mg ox have been studied.

Thermal decomposition of oxalates finds application in the synthesis of superconducting double or multicomponent oxides, used as precursors for high purity titanates, stanates, ferrites and zirconates of desired stoichiometry. Decomposition of mechanical mixture or co-precipitated oxalates of alkaline earth, rare earth and transition metals leads to synthesis of bulk monophasic multicomponent oxide structures, an essential component of High Temperature Ceramic Super Conductors (HTCS). Co-precipitation technique is widely used for separation of small quantity of rare earth elements from ore in which oxalate ion acts as most effective carrier. Decomposition of co-precipitated double oxalates of rare earth with alkaline earth metal and ammonium has been carried out. It has been reported that the component oxalates in the co-precipitate retain their identity during decomposition.

Absorption of ionizing radiation by a substance results in a variety of physico-chemical consequences depending on the nature of the system and the energy of incident radiation. Effect of irradiation on the individual and co-precipitated oxalates has been studied with particular emphasis on lanthanum and barium. Irradiation alters the on-set temperature of the decomposition as well as the kinetic parameters such as activation energy, velocity constant etc.

Decomposition of unirradiated and irradiated double oxalates of magnesium and gadolinium has been undertaken to explore the effect of co-precipitation and irradiation on the mechanism of the process as these are essential constituents of high Tc super conductors.

Materials and Methods

AR grade chemicals were used throughout the experiment.

The individual oxalates of magnesium and gadolinium were prepared following the earlier procedure and the co-precipitated Gd-Mg oxalate was prepared by adding ammonium oxalate (5% w/v) solution to the aqueous solution mixture of Mg(NO₃)₂ and Gd(NO₃)₃ (mole ratio 3:1). The pH of the solution was maintained at 5.5-6.5 by adding dilute ammonium hydroxide and the mixture was heated on a hot water bath for 2h, the precipitate was filtered, washed with distilled water several times and dried.

Compositional analysis was carried out by chemical methods and inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin-Elmer p-400). The water molecules present were determined from weight loss in the dehydration steps in the TG study. The co-precipitated oxalate has the stoichiometry Gd₀.₉Mg₁.₁₂(C₂O₄)₂.₄₈H₂O, which tallied with earlier data.

X-ray powder diffraction study was carried out using Philips PW1710 X-ray diffractometer with Cu Kα radiation, α-nickel filter.

Crystals of uniform mesh size were sealed in vacuum in glass ampoules and were exposed to Co γ-rays (450-850kGy) at room temperature at the dose rate of 29 kGy h⁻¹ as determined by Fricke dosimeter. Simultaneous TG-DTA data of different samples were recorded in a Shimadzu DTG – 50 thermal analyser at the heating rate of 10°C min⁻¹ in static air.
00°C using open alumina crucibles with α-
s reference material.

and Discussion

alysis:

d-values of co-precipitate (Table I) indicate 
 of peaks corresponding to those of 
um and magnesium oxalate with slight shift in 
 s suggesting the formation of co-precipitate 
 individual components retain their identity.

her d-values of co-precipitate compared to that 
 x may be due to partial substitution of Gd 3+ 
 Å) by Mg 2+ (r=0.780Å). The structure of co-
te is found to be different from that of Gd-ox

order of decomposition reaction is determined 
 the DTG plots following Horowitz and 

\[ n = \text{order} \]

eight fraction at temperature \( T_1 \) corresponding 
 peak.

of reactions of different samples lies 
0.42 (Gd-ox) to 7.3 (Gd-Mg-ox, stage-II). It 
 s from pure to coprecipitated and irradiated 
. The phenomena may be due to simultaneous 
ce of more number of related reactions in the 
temperature range in the coprecipitated and 
d samples.

osition of oxalates

drous Mg oxalate undergoes maximum 
oss at 450-540°C corresponding to a strong 
 at 510°C due to overlap of different s 
 v, decomposition of oxalate to 
te, the latter to oxide and oxidation of carbon 
e.

DTA curve for gadolinium oxalate decal 
consists of three endothermic peaks in the range 
220°C at about 110, 180 and 210°C respe 
which may arise due to dehydration of hydrated 
Two adjacent exotherms are found for the anh 
salt at 375 and 428°C respectively, the former 
 to decomposition of oxalate to carbonate a 
atter to oxidation and partial car 
decomposition resulting Gd 2O 3 (CO 3 ) 3- (ref 12) 
ing increasing temperature, the extent of decom 
of carbonate increases, thus increasing the value 
in subsequent oxidation steps exhibiting 
exotherms.

Decomposition of Gd-Mg oxalate (Fig. 1) pr 
through two endothermic DTA peaks at 39 
90°C and the TG curve constitutes two over 
sigmoidal regions, stage I (380-420°C) and si 
(440°-500°C) corresponding to anhydrous Gd-ox 
Gd-Mg-ox respectively. Decomposition temper 
Gd-ox shifts to a higher value (thus increa 
stability of the double salt), whereas that of 
shifts to a lower end in the co-precipitate 
mpurity cation in the solid solution distur 
symmetry of the oxalate ion, promoting its brea 
de composition of carbonate increases, thus increasing the value 
in subsequent oxidation steps exhibiting 
exotherms.

| 1—XRD data of co-precipitated and pure oxalates |
|---|---|---|---|---|---|
| d-values (Å) | Gd-Mg oxalate |
| 4.79 | 4.23 |
| 4.00 | 2.52 |
| 2.42 | 1.24 |

---(1)

![Fig. 1—TG-DTA curves for decomposition of (a) Mix 
mixture (Gd ox +Mg ox, 0.9:1.12 mol) (b) Gd-Mg oxalat](image-url)
formation of stronger C-O-Mg bonds compared to C-O-Gd bonds, inhibiting the decomposition of Gd-ox, the earlier initiation of exothermic decomposition of which enhances the decomposition of Mg-ox. Irradiation of mixed oxalate increases the peak temperature of Gd-ox but decreases that of Mg-ox. The phenomena may occur due to overcrowding of the former by the product species formed upon irradiation (cage effect), which prevents the release of evolved gases upon decomposition, thus shifting the peak temperature to a higher value. But in case of latter, though overall rate decreases, the increase in the rate of acceleratory stage due to increased point defects shifts the peak temperature to a lower value.

**Kinetic analysis**

As the decomposition of the co-precipitate occurs through two stages of weight loss (indicated by two overlapping sigmoidal regions in the TG curve) corresponding to Gd-ox and Mg-ox respectively, the kinetic analyses are carried out for each individual stage. The weight loss temperature plots are redrawn as fraction decomposed, $\alpha$, vs. temperature for application of suitable kinetic models (Fig. 2). The kinetic models applied for decomposition are summarized in Table 2.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Symbol</th>
<th>$g(\alpha)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avrami-Erofeev- Nuclei growth</td>
<td>$A_2$</td>
<td>$-\ln(1-\alpha)^{1/2}$</td>
</tr>
<tr>
<td>(n=2,3)</td>
<td>$A_3$</td>
<td>$-\ln(1-\alpha)^{1/3}$</td>
</tr>
<tr>
<td>Phase boundary movement</td>
<td>$R_3$</td>
<td>$1-(1-\alpha)^{1/2}$</td>
</tr>
<tr>
<td>(Cylindrical symmetry) (n=2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diffusion mechanism (n=3)</td>
<td>$D_3$</td>
<td>$[1-(1-\alpha)^{1/3}]^{1/2}$</td>
</tr>
</tbody>
</table>

![Fig. 2—Variation of fraction decomposed, $\alpha$, with Temp. for (a) Gd-Mg ox, (b) Irrad Gd-Mg ox (650 kGy) & (c) Gd ox + Mg ox, (0.9:1.42 mol).](image-url)
values of $\alpha$, for a particular component in the coprecipitate are higher than that in the mechanical mixture as well as individual salts. In case of Gd-ox, though irradiation increases the value at lower temperatures, reverse phenomena take place at higher temperatures. But for Mg-ox, $\alpha$ decreases throughout the process.

In order to ascertain the nature of nucleation and nuclei growth taking place during decomposition, the data are analysed in the light of theories of different solid state reaction models like Avrami Erofeev ($A_2$ and $A_3$) nuclei growth and phase boundary movement (Cylindrical symmetry) ($R_2$) and diffusion mechanism ($D_3$) etc.

The kinetic parameters are determined in the specified temperature ranges using Coats-Redfern's Eqn. (ref 15),

$$\log \left[ \frac{g(\alpha)}{T^2} \right] = \log (AR/\beta E) - \frac{E}{2.303} \frac{RT}{E} \quad ... (2)$$

where, $A =$ Pre exponential factor, $R =$ Universal gas constant, $\beta =$ Rate of heating.

$E =$ Energy of activation and $T =$ Absolute temperature

The values of $g(\alpha)$ are chosen for various rate determining steps (Table 2) and $\log \left[ \frac{g(\alpha)}{T^2} \right]$ is plotted against $1/T$ (Fig. 3 and 4). It is indicated that the best possible mechanisms for decomposition of Gd-ox and Mg-ox are $D_1$ and $A_2$ respectively which are also exhibited by the components in the coprecipitate as seen from the linearity of the plots obtained by best fitting data to the highest co-efficient of the linear regression analysis.

Activation energy, $E$ and $\log A$ are determined using Eq.2, rate constant from Arrhenius eq. and the entropy change, $\Delta S$ by applying Eq.(3), (ref 16)

$$\Delta S = R \ln (Ah/kT_s) \quad ... (3)$$

where, $h =$ Planck's constant, $k =$ Boltzmann's constant and other terms have their usual meaning.

It is evident from the data that the activation energy for gadolinium decreases but that for magnesium increases by coprecipitation but reverse phenomenon takes place upon irradiation.

The kinetic parameters for different samples are as follows:

![Fig. 3—Variation of $\log \left[ \frac{g(\alpha)}{T^2} \right]$ vs $1/T$ for (a) Gd-Mg-ox (b) Irrad. Gd-Mg-ox (650 kGy) and (c) Gd-ox+Mg-ox (0.9:1.12 mol) ($R_2$ mechanism) (Stage -I).](image)

![Fig. 4—Variation of $\log \left[ \frac{g(\alpha)}{T^2} \right]$ vs $1/T$ for (a) Gd-Mg-ox (b) Irrad. Gd-Mg-ox (650 kGy) and (c) Gd-ox+Mg-ox (0.9:1.12 mol) ($R_2$ mechanism) (Stage -II).](image)
The decrease in the energy of activation and increase in the rate of reaction on coprecipitation, in case of Gd-ox may arise due to introduction of defects and dislocations into lattice by the incorporation of foreign ions, Mg$^{2+}$. The enhancement in the rate of reaction for Mg-ox may be resulted due to similar circumstances as in the case of Gd-ox, but increase in

| Table 3—Kinetic parameters for decomposition of (i) Gd$_2$(C$_2$O$_4$)$_3$, (ii) Mg C$_2$O$_4$, (iii) mechanical mixture Gd-ox + Mg-ox (0.9:1.12 mol) (iv) unirrad and (v) irradi. Gd-Mg-ox |
|---|---|---|---|---|---|---|---|---|---|---|
| React Temp (K) | Samples | $T_c$(K) | Mechanism | $E\pm$5 kJmol$^{-1}$ | Log $A$ (A/s$^{-1}$) | $k\pm0.5 \times 10^{12}$ (s$^{-1}$) | $\Delta$E$\pm$0.002 kJ mol$^{-1}$ | $r^2$ |
| Pure oxalates |
| 653-713 | Gd-ox | 648 | R$_2$ | 249 | 15.84 | 0.051 | 0.9864 |
| | | | D$_3$ | 525 | 35.04 | 0.411 | 0.9882 |
| 693-813 | Mg-ox | 785 | A$_2$ | 100 | 4.15 | -0.174 | 0.9735 |
| | | | A$_3$ | 63 | 1.44 | -0.225 | 0.9703 |
| | | | R$_2$ | 184 | 9.41 | -0.073 | 0.9734 |
| Mixed oxalates (Stage-I) |
| 688-705 | Mech. Mixture | 700 | R$_2$ | 471 | 32.63 | 0.373 | 0.9762 |
| | | | D$_3$ | 980 | 69.80 | 1.080 | 0.9820 |
| 653-693 | Gd-Mg-ox | 665 | R$_2$ | 209 | 13.45 | 0.006 | 0.9425 |
| | Unirrad | | D$_3$ | 431 | 29.95 | 0.232 | 0.9543 |
| 645-704 | Irrad. (kGy) | 450 | D$_3$ | 232 | 15.25 | 0.240 | 0.9790 |
| | | | R$_2$ | 482 | 33.89 | 0.397 | 0.9760 |
| 643-713 | 650 | 667 | D$_3$ | 536 | 38.82 | 0.109 | 0.9904 |
| | | | R$_2$ | 233 | 15.58 | -0.112 | 0.9847 |
| 629-693 | 850 | 660 | D$_3$ | 228 | 15.16 | 0.038 | 0.9698 |
| | | | R$_2$ | 581 | 42.45 | 0.561 | 0.9302 |
| Mixed oxalates (Stage-II) |
| 753-783 | Mech. Mixture | 773 | A$_2$ | 148 | 7.55 | -0.108 | 0.9941 |
| | | | A$_3$ | 93 | 3.69 | -0.182 | 0.9940 |
| | | | R$_2$ | 278 | 16.18 | 0.057 | 0.9942 |
| 713-773 | Gd-Mg-ox | 763 | A$_2$ | 163 | 8.99 | -0.081 | 0.9824 |
| | Unirrad | | A$_3$ | 105 | 4.81 | -0.160 | 0.9818 |
| | | | R$_2$ | 303 | 18.50 | 0.101 | 0.9705 |
| 708-772 | Irrad. (kGy) | 450 | 750 | A$_2$ | 142 | 8.22 | -0.095 | 0.9757 |
| | | | A$_3$ | 97 | 4.25 | -0.171 | 0.9783 |
| | | | R$_2$ | 232 | 15.25 | 0.040 | 0.9790 |
| 733-783 | 650 | 748 | A$_2$ | 142 | 7.50 | -0.071 | 0.9842 |
| | | | A$_3$ | 96 | 4.05 | -0.175 | 0.9681 |
| | | | R$_2$ | 215 | 14.98 | 0.099 | 0.9688 |
| 698-762 | 850 | 743 | A$_2$ | 128 | 6.72 | -0.124 | 0.9858 |
| | | | A$_3$ | 107 | 5.14 | -0.154 | 0.9323 |
| | | | R$_2$ | 192 | 10.89 | 0.044 | 0.9950 |
the energy of activation may be attributed to kinetic compensation effect\textsuperscript{17}.

\textit{Role of irradiation}

Energetic radiations like γ-rays, X-rays etc. affect the various physico-chemical parameters of the crystal, as a consequence of excitation and ionisation followed by rupture of the chemical bonds in the anions\textsuperscript{5,18}. The damaged entities thus generated lead to the formation of point defects & additional nucleation centres which grow in size and number with increasing radiation dose\textsuperscript{19} and produce sufficient strain and fracture the crystal lattice. Vacancies are also generated in the lattice\textsuperscript{5} as

\begin{equation}
\text{M} \text{C}_2\text{O}_4 \rightarrow \text{M} \text{C}_2\text{O}_4,_{n} \text{n}+n \text{O}
\end{equation}

where, M = divalent metal,

\begin{itemize}
  \item \text{□} = an oxygen vacancy
  \item \text{n} = number of oxygen vacancies
\end{itemize}

It has also been reported that upon irradiation with γ-rays, defects and dislocations generated in the lattice get annealed (radiation annealing.)\textsuperscript{18}. Thus the ordered structure of the crystal is restored with molecular reconstruction upon irradiation\textsuperscript{20}. The product species so generated cover the reactant surfaces (cage effect)\textsuperscript{14} thus acting as a barrier for further decomposition to proceed. The decrease in the reaction rate of the co-precipitate upon irradiation may be attributed to the above phenomena in which in addition to strengthening of bonds and cage formed in the lattice, unreactive radicals are created resulting decrease in the number of decomposition centres, consequently the reaction rate. Though irradiation decreases reaction rates for both the components it increases the energy of activation of Gd-ox in the coprecipitate whereas reverse phenomenon occurs for Mg-ox. The former may be ascribed to cage effect and the latter to kinetic compensation phenomenon\textsuperscript{17}.

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\textbf{References}