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ROLE OF RARE EARTH (RE) SEMICONDUCTORS ON THE DECOMPOSITION OF BARIUM BROMATE

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Barium bromate decomposes in the solid state through various stages: (i) initial gas evolution, (ii) induction period, (iii) slow linear reaction, (iv) acceleratory and decay stages. Rare earth semiconductors (p-type), Gd_2O_3 and Dy_3O_3 facilitate the acceleratory and decay stages without affecting the induction and linear periods. The extent of decomposition is higher in the case of mixture than that of the pure salt. The data are discussed in the light of theories of Prout—Tompkins and Avarami-Erofeev mechanisms exploring that nucleation occurs in a chain branching manner and there is two dimensional growth of nuclei.

Keywords: barium bromate, rare earth, semiconductors

Introduction

Solid state decomposition of many inorganic molecular ions and the role of irradiation, doping and admixture thereon has been reported by workers in different laboratories [1–5]. But the effect of rare earth oxides with incomplete d and f shells are yet to be studied as the theory of electron-phonon interaction in these systems is still quite far from completion [6]. The difficulties encountered are due primarily to the dual role of the $d(f)$ electrons in the formation of the phonon spectrum. The present study throws light on the influence of rare earth semiconductors, Gd_2O_3 and Dy_2O_3 with unstable valency of the $d(f)$ shells on the decomposition of barium bromate with a view to find out an insitu mechanism for the process.

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Experimental

Solid solutions, (10.0% w/w) of barium bromate with rare earth oxides, Gd_2O_3 and Dy_2O_3 were prepared by adding required amount of the latter to the former and grinding thoroughly by an agate mortar and pestle. Decomposition study was undertaken gasometrically at 573.0 K and 583.0 K by using a pre-evacuated glass apparatus. The fractional decomposition, $\alpha(= p/p_f)$ was calculated from pressure values where 'p' is the pressure of oxygen liberated at time 't' and p_f, the final pressure on completion of the reaction.

Results and discussion

Decomposition isotherms are represented in Fig. 1 suggesting that the process occurs through induction period, linear, acceleratory and decay stages. The process is catalysed by adding rare earth oxides and the values at different time intervals are given in Table 1.

The initial gas evolution ($\alpha \approx 0{,}06$) which is due to release of occluded air from the accessible interior of the crystal remains unaffected by adding the additives. So does the induction period. The linear reaction stage is represented by

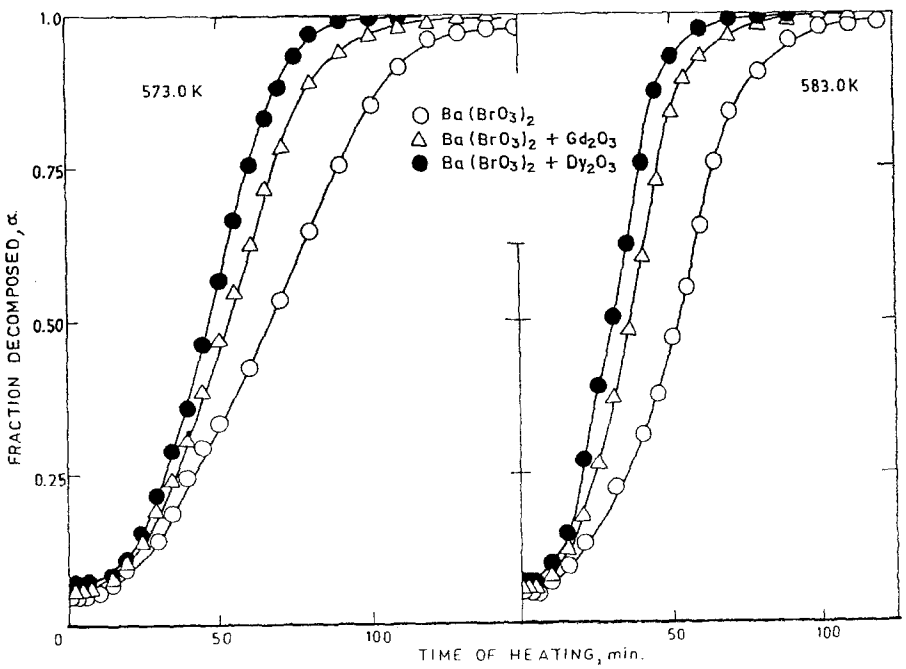

Fig. 1 Effect of rare earth semiconductors on the thermal decomposition of barium bromate

$$\alpha = K_1 t + C \quad (1)$$

where K_1 is the rate constant and C is a constant term. The duration of the linear stage gradually decreases with increasing temperature and almost vanishes at the highest temperature studied, i.e., 588.0 K as the surface decomposition occurs in this stage due to growth of the nuclei, generated in the initial period is very fast [7].

Table 1

Substance	Fractional decomposition (α)		
	50 min.	70 min	90 min
$Ba(BrO_3)_2$	0.33	0.53	0.74
$Ba(BrO_3)_2 + Gd_2O_3$	0.45	0.72	0.92
$Ba(BrO_3)_2 + Dy_2O_3$	0.57	0.88	0.99

Data on the sigmoidal regime are best explained in the light of Prout-Tompkins [8] relationship

$$\log\left(\frac{\alpha}{1-\alpha}\right) = K_{2,3}t + C \quad (2)$$

and, Avrami-Erofeev mechanism [9]

$$[-\log(1-\alpha)]^{1/n} = K_4\ K_5\ t + C \quad (3)$$

where K_2, K_3, K_4 and K_5 are the rate constants in the accelaratory and decay periods which are enhanced by using the rare earth oxides as shown in Table 2.

Table 2

Substance	$K_2 \cdot 10^2$ min^{-1}	$K_3 \cdot 10^2$ min^{-1}
$Ba(BrO_3)_2$	1.72	2.50
$Ba(BrO_3)_2 + Gd_2O_3$	2.98	4.48
$Ba(BrO_3)_2 + Dy_2O_3$	3.47	5.26

Applicability of Eq. (2) explore that nucleation occurs in a chain branching manner and is facilitated in the presence of semiconducting oxides.

The data are also well fitted to Avrami-Erofeev mechanism with n = 2, suggesting that there is two dimensional growth of nuclei during decomposition which is enhanced by the admixtures, Gd_2O_3 and Dy_2O_3.

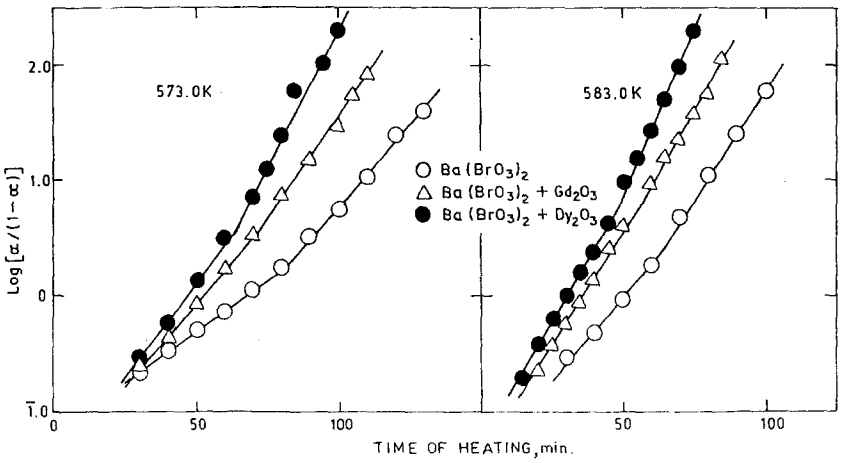

Fig. 2 The Prout-Tompkins relationship in pure and catalyst mixture of barium bromate

Mechanism

Barium bromate decomposes as

$$Ba(BrO_3)_2 \rightarrow BaBr_2 + O_2 \quad (4)$$

The catalytic effect of rare earth oxides on the thermal decomposition of barium bromate may be explained in the light of electron transfer mechanism [10, 11].

$$BrO_3^- + e \rightarrow BrO_2^- + O^-_{(ads)} \quad (i)$$

$$O^-_{(ads)} \rightarrow O_{(ads)} + e \text{ (solid oxide)} \quad (ii)$$

$$O_{(ads)} + O_{ads} \rightarrow O_2 (g) \quad (iii)$$

$$O_{ads} + O^- (ads) \rightarrow O_2 (g) + e \text{ (solid additive)} \quad (iv)$$

where step (ii) may be rate limiting. The BrO_2^- formed in step (i) may undergo further decomposition to give rise to Br^- and O_2.

Though decomposition is accelerated by the admixtures, Gd_2O_3 and Dy_2O_3, the effect is more prominent in the case of latter than that of the former which may arise due to the fact that in the rate determining step (ii), dysprosium accept electrons more easily from O^-_{ads} comparing to gadolinium as the catalytic activity of these oxides increases with decrease in basicity of the metal ion [12]. On the assumption that adsorbed oxygen generated in the step (i) by withdrawing an electron from the catalyst thus increasing the number of positive holes, a *p*-type

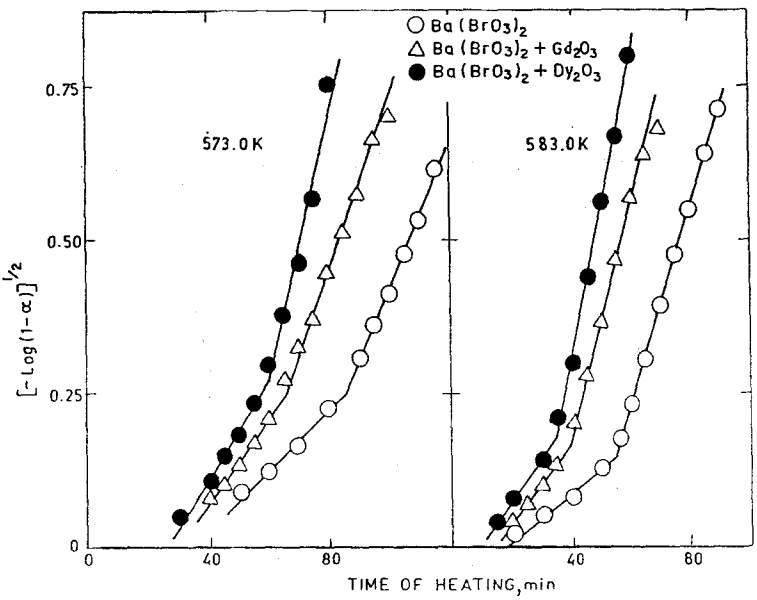

Fig. 3 The Avrami-Erofeev relationship in pure and catalyst mixture of barium bromate

semiconductor would be more conductive in oxygen atmosphere as in the present study. The presence of positive holes in the *d*-orbitals of Gd_2O_3 and Dy_2O_3 would favour step (ii) because it will accept electrons from the adsorbed oxide ion thus enhancing the decomposition. The catalytic activity of metal oxides on thermal decomposition is enhanced as the ionic radii (r_i) of the metal ion is decreased [12]. Basicity of the metal ion decreases with decreasing ionic radii. Gd^{3+} is more basic than Dy^{3+}, hence in the r. d. step (ii) the latter can accept electrons more favourably than the former thus resulting higher decomposition.

Both the rare earth oxides facilitate nucleation and nucleus growth resulting rapid decomposition thus reducing the energy of activation ($E\pm$ 5 kJ·ml^{-1}. Values for pure crystals as well as mixtures are represented in Table 3.

Table 3

Substance	E_A	E_D
$Ba(BrO_3)_2$	185.0	172.0
$Ba(BrO_3)_2 + Gd_2O_3$	148.0	128.0
$Ba(BrO_3)_2 + Dy_2O_3$	133.0	108.0

E_A and E_D are the activation energies for the acceleratory and decay processes respectively.

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Zusammenfassung — Bariumbromat zersetzt sich im festen Zustand über verschiedene Schritte: (i) anfängliche Gasentwicklung, (ii) Induktionsperiode, (iii) langsame lineare Reaktion, (iv) Beschleunigungs- und Abschlußschritt. Seltenerdenhalbleiter (vom *p*-Typ) erleichtern die Beschleunigungs- und Abschlußschritte, ohne die Induktions- und die lineare Periode zu beeinflussen. Das Ausmaß der Zersetzung ist im Falle von Gemischen höher als bei reinen Salzen. Die Angaben wurden im Hinblick auf die Mechanismentheorien von Prout-Tompkins und Avarami-Erofeev besprochen, die besagen, daß die Keimbildung auf kettenverzweigende Weise erfolgt und daß ein zweidimensionales Keimwachstum stattfindet.