

## DTA STUDIES ON THE EFFECT OF IMPURITIES ON THE PHASE TRANSFORMATIONS OF BARIUM CARBONATE

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Orthorhombic ( $\gamma$ ) barium carbonate, undergoes a reversible transformation to hexagonal ( $\beta$ ) form around 1093 K which in turn undergoes a reversible transformation to cubic ( $\alpha$ ) form around 1253 K. Cationic impurities such as  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ , have been doped in pure barium carbonate and their effect on the kinetics and energetics of its transformations were studied. By using DTA technique, the enthalpy and energy of activation for the transformation of pure and doped samples of barium carbonate have been calculated and compared.

Barium carbonate undergoes two transformations one around 1093K from orthorhombic ( $\gamma$ )  $\rightarrow$  hexagonal ( $\beta$ ) form and the second around 1253K from hexagonal ( $\beta$ )  $\rightarrow$  cubic ( $\alpha$ ) form. Both these transformations are reversible and there is a considerable thermal hysteresis in these transformations. Although the thermal transformations of barium carbonate have been examined by some workers [1–3] there is limited information in the literature on the effect of impurities on the enthalpy, kinetics and energetics of these transformations. Such a study is of particular importance owing to the fact that impurities markedly affect the phase transformation of solids [4].

In the present investigation the kinetics and energetics of  $\gamma \rightarrow \beta$  and  $\beta \rightarrow \alpha$  transformations of barium carbonate with known amount of different impurity cations were studied and the values for enthalpy ( $\Delta H$ ) and energy of activation ( $E_a$ ), have been evaluated from the DTA data.

### Experimental

All the samples of pure and doped barium carbonate were prepared by hydrolysis of the trichloroacetate salts [5]. The procedure yielded pure samples and avoided unintentional incorporation of impurities. For the preparation of doped samples known amounts of impurity cations,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ , were taken in the form of carbonates or oxides along with the sample of pure barium carbonate before reacting with trichloroacetic acid. The impurity cations were chosen on the basis of their ionic size. All the chemicals used were of analytical grade.

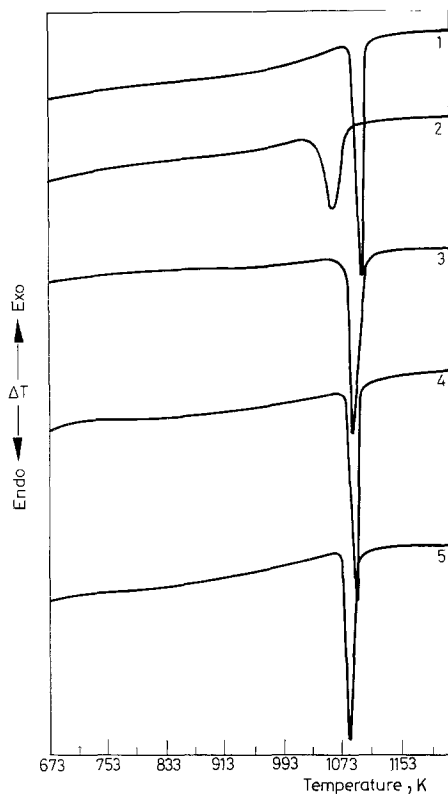


Fig. 1. DTA curves of (1) pure  $\text{BaCO}_3$ , (2)  $\text{BaCO}_3$  with 20% Ca, (3)  $\text{BaCO}_3$  with 10% Sr, (4)  $\text{BaCO}_3$  with 10% Zn and (5)  $\text{BaCO}_3$  with 10% Cd as impurities

Fisher differential thermo-analyzer Model 260, fitted with an automatic voltage stabilizer and a recorder, has been used for the DTA studies. The particle size of the sample was within 100 to 200 mesh (B.S.S.). Quartz crucible was used as sample holder with the sample size of about 100 mg. The curves were recorded at a heating rate of 10 K/min and also during uncontrolled cooling. (Cooling conditions were maintained similar for all the runs). The temperature was measured on a calibrated platinum *vs* platinum – rhodium thermocouple connected in series with the reference block thermocouple maintained at 273 K. Calcined  $\alpha$ -alumina was used as the reference material. The experiments were carried out under static air atmosphere. The activation energy was calculated following the method of Borchardt and Daniels [6].  $\Delta H$  values were computed by comparing the area under the peak for the doped samples with the orthorhombic(II)  $\rightarrow$  hexagonal(I) peak of pure potassium sulphate [7, 9] and also with orthorhombic (II)  $\rightarrow$  rhombohedral (I) peak of pure potassium nitrate [8, 9]. The values obtained from both the standards were comparable hence only the average values are reported.

### Results and discussion

The  $\Delta H$  values estimated from the peak areas may have an uncertainty of  $\pm 5$  per cent. The activation energy values obtained by employing the procedure of Borchardt and Daniels may have large uncertainties ( $\pm 15$  per cent), but the comparison of values in related system is valid [10].

#### *Orthorhombic ( $\gamma$ ) to hexagonal ( $\beta$ ) transformation*

The inception and peak temperatures for the forward transformation ( $T_i$  and  $T_p$ ), peak temperature during cooling ( $T'_p$ ), as well as the  $\Delta H$  and  $Ea$  values for the forward transformation for the pure and doped samples of barium carbonate are listed in Table 1.

It is evident from Table 1 that the incorporation of impurities affects  $T_i$ ,  $T_p$ ,  $T'_p$ ,  $\Delta H$  and  $Ea$  values. The  $Ea$  value for the various doped samples range from 840 to 3060 kJ/mole in comparison to 2160 kJ/mole for the pure barium carbonate. The variation in the value of  $\Delta H$  is also fairly large ranging from 9.7 to 16.4 kJ/mole compared to 13.5 kJ/mole for the pure barium carbonate.

As shown in Table 1, the hysteresis in the transformation temperatures of pure barium carbonate is  $\sim 53$  K. Hysteresis is a necessary consequence of the coexistence of two phases [11] and the magnitude of hysteresis is determined by the

Table 1

Values of  $T_i$ ,  $T_p$ ,  $T'_p$ ,  $\Delta H$  and  $Ea$  for orthorhombic ( $\gamma$ )  $\rightarrow$  hexagonal ( $\beta$ ) transformation of various doped samples of barium carbonate

S. No.	Impurity, atomic %	$T_i$ , K	$T_p$ , K	$T'_p$ , K	$\Delta H$ , kJ/mole	$Ea$ , kJ/mole	Ionic radii, nm
1	None	1077	1095	1042	13.5	2160	0.135
2	Ca (0.1)	1089	1103	1045	16.4	3060	
3	Ca (0.5)	1084	1100	1041	15.9	2970	
4	Ca (1.0)	1080	1097	1038	15.6	2020	0.099
5	Ca (5.0)	1052	1083	1028	14.0	1510	
6	Ca (10.0)	1021	1071	1024	12.7	900	
7	Ca (20.0)	1015	1058	1017	9.7	840	
8	Sr (0.1)	1078	1097	1046	15.9	2240	
9	Sr (1.0)	1072	1094	1043	15.4	1780	0.113
10	Sr (5.0)	1069	1091	1034	13.8	1470	
11	Sr (10.0)	1066	1084	1032	12.2	1100	
12	Zn (1.0)	1081	1095	1041	13.5	2720	
13	Zn (5.0)	1077	1093	1039	12.6	2300	0.074
14	Zn (10.0)	1071	1089	1033	11.6	1700	
15	Cd (0.1)	1074	1097	1045	15.1	2030	
16	Cd (1.0)	1074	1096	1045	14.4	1820	0.097
17	Cd (5.0)	1068	1092	1044	13.3	1622	
18	Cd (10.0)	1064	1080	1028	12.9	1240	

relative volumes of the high temperature and low temperature phases. The increased hysteresis ( $\sim 59\text{K}$ ) occurring by the addition of 1 atomic percent  $\text{Ca}^{2+}$  is likely to be due to the variation in  $\Delta V$  caused by the presence of smaller cations. However no crystallographic data are available on the low and high temperature forms of barium carbonate with these impurities.

As the impurity content is increased, a decrease is observed in  $T_i$ ,  $T_p$ ,  $T'_p$ ,  $\Delta H$  and  $Ea$  in case of all the cations studied, though the absolute magnitude of the decrease depends on the particular impurity cation. This may probably be attributed to their different ionic radii and electronic configuration.

#### *Hexagonal ( $\beta$ ) $\rightarrow$ cubic ( $\alpha$ ) transformation*

The hexagonal ( $\beta$ )  $\rightarrow$  cubic ( $\alpha$ ) transformation of doped samples of barium carbonate was also studied. The results indicate that the incorporation of impurities affect the inception and peak temperatures in a similar fashion. The  $\Delta H$  for this transformation was calculated for the pure sample to be 3.0 and 3.4 kJ/mole on the heating and cooling cycle respectively.

While the  $Ea$  and  $\Delta H$  values for the doped samples, could not be obtained accurately due to very small size of the peak, similar trend of variation in the transformation temperatures was observed as in the case of  $\gamma \rightarrow \beta$  transformation. In case of  $\text{Sr}^{2+}$  doped samples however, the transformation temperatures increased in the  $\beta \rightarrow \alpha$  transformation in contrast to the decrease observed in the  $\gamma \rightarrow \beta$  transformation.

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