Phase transformation studies on pure and doped strontium carbonate*

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MS received 21 November 1979 ; revised 3 January 1980

Abstract. The orthorhombic-hexagonal transformation of strontium carbonate is a reversible reconstructive transformation. Cationic impurities like K^+ , Ca^{2+} , Ba^{2+} , Cd^{2+} , Y^{3+} , La^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+} , Dy^{3+} , Ho^{3+} , Bi^{3+} , Zr^{4+} doped in pure strontium carbonate affect the kinetics and energetics of the transformation.

Keywords. Phase transformations ; strontium carbonate ; orthorhombic-hexagonal transformation.

1. Introduction

The orthorhombic-hexagonal transformation of strontium carbonate is a reversible reconstructive transformation involving a change in the primary coordination—the transformation is therefore expected to be sluggish and associated with high activation energy (Rao and Rao 1967). Although the orthorhombic-hexagonal transformation of pure strontium carbonate has been examined by several workers (Lander 1951; Gruver 1950; Baker 1962; Smykatz-Kloss 1964) there is limited information in the literature on the effect of impurities on the enthalpy, kinetics and energetics of the transformation. We have investigated this aspect. Such a study is of particular importance, as the incorporation of foreign ions can give rise to controlled electronic disorders, i.e., valency change or controlled atomic disorder, i.e. cation vacancy, etc.; these changes markedly effect phase transformation of solids (Subba Rao *et al* 1968; Rao and Mehrotra 1978). In the present investigation, the kinetics and energetics of orthorhombic-hexagonal transformation of strontium carbonate with known amounts of different impurity cations have been studied. The values for enthalpy of transformation (ΔH) and energy of activation (E_a), for pure and different impurity doped samples of strontium carbonate have been evaluated from differential thermal analysis (DTA) data.

2. Experimental

Samples of pure and doped strontium carbonate were prepared by hydrolysis of the trichloroacetate salts (Rao and Yoganarasimhan 1965). The procedure yielded

* Paper presented at the Annual Convention of Chemists held at Andhra University, Waltair, December 1978.

pure samples and avoided unintentional incorporation of impurities. For the preparation of doped samples, known amounts of impurity cations (K^+ , Ca^{2+} , Ba^{2+} , Cd^{2+} , Y^{3+} , La^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+} , Dy^{3+} , Ho^{3+} , Bi^{3+} , Zr^{4+}) were taken in the form of carbonates or oxides along with the sample of pure strontium carbonate before reacting with trichloroacetic acid. The impurity percentage indicated in different cases are those which were added at the time of preparation. The impurity cations were chosen on the basis of their ionic size. All the chemicals used were of analytical grade.

Fisher differential thermo-analyser Model 260, fitted with an automatic voltage stabiliser and a recorder, has been used for the DTA studies. The particle size of the sample was within 100 to 200 mesh (BSS). Quartz crucibles were used as sample and reference holders with the sample amount of about 100 mg. The curves were recorded at a heating rate of $10^\circ/\text{min}$. Cooling curves were recorded at uncontrolled cooling rate. The temperature was measured on a calibrated platinum-platinum rhodium thermocouple with reference junction at 0°C . Calcined α -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 (1957). ΔH values were computed by comparing the area of transformation peak for the doped samples with the orthorhombic (II)-hexagonal (I) transformation peak of pure potassium sulphate (Majumdar and Roy 1965; Rao and Rao 1966).

3. Results and discussion

The ΔH values estimated from peak areas may have an uncertainty of $\pm 5\%$. The activation energy values obtained by employing the procedure of Borchardt and Daniels may have large uncertainties ($\pm 10\%$), but the comparison of values in related systems would be valid (Rao and Rao 1966; Rao and Mehrotra 1979). The temperature at the starting point of the DTA peak for the forward transformation, forward transformation peak temperature and backward transformation peak temperature, ΔH value for the forward transformation (ΔH_f), ΔH value for the backward transformation (ΔH_r) and E_a value of the forward transformation (E_a) for the pure and doped samples of strontium carbonate are listed in table 1.

It is evident from table 1 that the incorporation of impurities affects peak temperature forward transformation, forward transformation peak temperature, backward transformation, ΔH and E_a values. The E_a value for the various doped samples range from 840 to 2860 kJ/mole as compared to 2540 kJ/mol for the pure strontium carbonate. The variation in the values of ΔH_f and ΔH_r is also fairly large ranging from 13.4 to 24.3 kJ/mole and 13.0 to 21.8 kJ/mole respectively as compared to 20.9 and 18.8 kJ/mole for the pure strontium carbonate when potassium sulphate is taken as standard. It may be pointed out that the values reported here may not be the absolute values but are sufficient to indicate the trend of variation in similar systems.

As shown in table 1, the thermal hysteresis in the transformation of pure strontium carbonate is $\sim 65^\circ$. Hysteresis is a necessary consequence of the coexistence of two phases (Ubbelohde 1957) and the magnitude of hysteresis is determined by the relative volumes of the high temperature and low temperature phases (Rao

Table 1. Impurity effects on the phase transformation of strontium carbonate.

Impurity ⁺ (%)	Transformation temperature			ΔH_f kJ/mole	ΔH_r kJ/mole	E_a kJ/mole	Ionic radii (nm)
	Forward °C	Forward peak °C	Backward peak °C				
None	909	930	865	20.9	18.8	2540	0.113
K (1.0)	921	939	880	23.0	20.5	2860	
K (5.0)	918	935	876	21.8	20.1	2600	0.133
K (10.0)	913	932	871	21.3	19.7	2380	
Ca (1.0)	903	925	858	18.4	16.3	2200	
Ca (5.0)	892	918	846	15.5	15.1	1720	0.099
Ca (10.0)	867	907	823	13.4	13.0	840	
Ba (1.0)	909	927	860	18.8	17.6	2340	
Ba (5.0)	901	919	848	16.8	16.3	2080	0.135
Ba (10.0)	889	906	837	15.1	14.6	1600	
Cd (1.0)	909	930	864	20.1	17.6	2210	
Cd (5.0)	905	924	859	18.4	16.7	1900	0.097
Cd (10.0)	898	920	853	16.7	16.3	1730	
Y (1.0)	908	928	865	21.3	18.8	2510	
Y (5.0)	912	934	869	22.6	19.7	2660	0.093
Y (10.0)	917	940	875	23.4	20.9	2850	
La (5.0)	919	943	876	24.3	21.8	2820	0.115
Nd (5.0)	916	938	874	23.9	20.9	2730	0.108
Sm (5.0)	913	936	873	22.6	20.5	2640	0.104
Gd (5.0)	912	933	870	21.8	19.3	2570	0.102
Dy (5.0)	912	931	865	21.8	18.8	2560	0.099
Ho (5.0)	910	929	862	20.5	18.0	2480	0.097
Li (5.0)	906	924	861	20.1	17.6	2230	0.108
Zr (5.0)	914	935	876	22.2	21.3	2750	0.080

+ Impurity concentrations are in at.%,

and Rao 1966). The increased ($\sim 72^\circ\text{C}$) and the decreased ($\sim 59^\circ\text{C}$) hysteresis, occurring by the addition of 5 at.% Ca^{2+} and K^+ , is likely to be due to the variation in ΔV caused by the presence of smaller and bigger cations respectively. Unfortunately, no crystallographic data are available on the low and high temperature forms of strontium carbonate with these impurities.

In the case of K^+ doped samples the E_a and ΔH values increase for 1 at.% impurity compared to that for pure strontium carbonate. On further increase in impurity content, both E_a and ΔH values decrease regularly but still the values are higher than that for pure strontium carbonate. The forward and backward transformation temperatures follow the trend of ΔH values. With the increase in Ca^{2+} and Ba^{2+} impurity from 1 to 10 at.% both E_a and ΔH values decrease regularly. The transformation temperatures follow the trend of ΔH and E_a values, in both the cases. A similar trend is observed in the case of Cd^{2+} doped samples. On increasing Y^{3+} impurity content from 1 to 10 at.% both E_a and ΔH values increase regularly. The transformation temperatures follow the trend of ΔH and E_a values respectively.

In the case of lanthanide-doped samples, E_a and ΔH values decrease regularly from lanthanum to holmium as the ionic radii decrease (for the same at.% impurity, i.e. 5%).

A perusal of the data given in table 1 for the doped samples in general shows that as the E_a values increase the starting point of the peak also shifts to a higher temperature and with the increase in ΔH values the transformation temperatures increase.

The variation of the forward and backward transformation temperatures and E_a of the transformation with impurities is understandable (Rao and Rao 1967; Sharp 1972), but no reasoning can be put forward for the variation in the ΔH values with impurities. It seems likely that for Ca^{2+} ion impurity doped samples the lower ΔH values may be due to the fact that the orthorhombic-hexagonal transformation in this case occurs over wider temperature range causing broad and shallow DTA peaks. Accordingly, the ΔH values are low when the transformation temperature values are low.

The present findings reveal that if the oxidation state of the impurity cations is the same, but the ionic radii are different, the trends in the variation of E_a and ΔH values are similar, although there is a contrast in their behaviour when the absolute values of E_a and ΔH are considered. It is also observed that K^+ and Y^{3+} impurities affect the transformation characteristics in a different manner; this may partly be due to the effect of cation and anion vacancies produced by +1 and +3 ions but these effects are difficult to assess from the present investigation. In the case of lanthanide doped samples, forward and backward transformation peak temperature, ΔH and E_a values increase with the size of the impurity cation (for the same percentage of the impurity).

Acknowledgement

Financial assistance from the University Grants Commission, New Delhi, is gratefully acknowledged.

References

- Baker E H 1962 *J. Chem. Soc.* p. 2525
- Borchardt H J and Daniels F 1957 *J. Am. Chem. Soc.* **79** 41
- Gruver R M 1950 *J. Am. Ceram. Soc.* **33** 96
- Lander J 1951 *J. Am. Chem. Soc.* **73** 5794
- Majumdar A J and Roy R 1965 *J. Phys. Chem.* **69** 1684
- Rao C N R and Rao K J 1967 in *Progress in solid state chemistry* ed. H Reiss (New York : Pergamon Press) **4** 31
- Rao C R M and Mehrotra P N 1978 *Can. J. Chem.* **56** 32
- Rao C R M and Mehrotra P N 1979 *Thermochim. Acta* **29** 180
- Rao K J and Rao C N R 1966 *J. Mater. Sci.* **1** 238
- Rao M S and Yoganarasimhan S R 1965 *Am. Mineral.* **50** 1489
- Sharp J H 1972 in *Differential thermal analysis* ed. R C Mackenzie (New York : Academic Press) **2** 66
- Smykatz-Kloss W 1964 *Beitr. Miner. Petrogr.* **9** 481
- Subba Rao G V, Natarajan M and Rao C N R 1968 *J. Am. Ceram. Soc.* **51** 179
- Ubbelohde A R 1957 *Rev. Chem. Soc.* **11** 246