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KINETICS OF THE DECOMPOSITION OF CALCIUM CARBONATE IN THE PRESENCE OF Bi_2O_3

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Abstract

Former studies concerning the formation of the compounds in the pseudobinary systems of Bi_2O_3–MO type (M = Ca, Sr, Ca+Sr) have shown that the reaction which occurs with the highest rate is that between Bi_2O_3 and CaO. In the present work $CaCO_3$ was used as CaO source. We carried out an investigation of the thermal decomposition of $CaCO_3$ in the presence of Bi_2O_3 in comparison with the decomposition of pure $CaCO_3$.

The presence of Bi_2O_3 exerts a complex influence on the $CaCO_3$ decomposition acting on the nucleation as well as on the diffusion of CO_2. The decomposition of the samples with low Bi_2O_3 content follows the mechanism of a contracting sphere. A change from surface nucleation to bulk nucleation is recorded for higher amounts of Bi_2O_3.

Keywords: Bi_2O_3, $CaCO_3$ decomposition, kinetics

Introduction

Bi-based superconducting materials belong to the oxidic system Bi_2O_3–SrO–CaO–CuO. Taking into account that calcium and strontium oxides give solid solutions in the whole range of compositions the system can be considered as pseudoternary and described by the formula Bi_2O_3–(Sr,Ca)O–CuO. From the ternary diagram given in Fig. 1 we can see that the location of the superconducting phases corresponds to compositions rich in alkaline-earth oxides.

Previous investigations in the oxidic systems of Bi_2O_3–MO and CuO–MO type (M=Ca, Sr, Ca+Sr) have shown that in nonisothermal conditions the components of systems containing Bi_2O_3 and CaO exhibit much higher reactivity than those of the systems containing SrO and CuO [1].

This paper aims an investigation of the thermal decomposition of $CaCO_3$ in the presence of Bi_2O_3 in comparison with the decomposition of pure $CaCO_3$. The nonisothermal kinetic parameters of the thermal decomposition have been determined.

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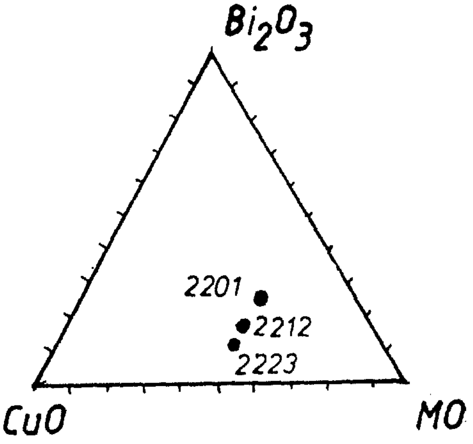

Fig. 1 The location of the superconducting phases in the pseudoternary system Bi_2O_3–MO–CuO (M=Ca+Sr)

Experimental

Powders of calcium carbonate (Merck) and Bi_2O_3 (Carlo Erba) have been used. The mixtures have been obtained by dry homogenization (1 h).

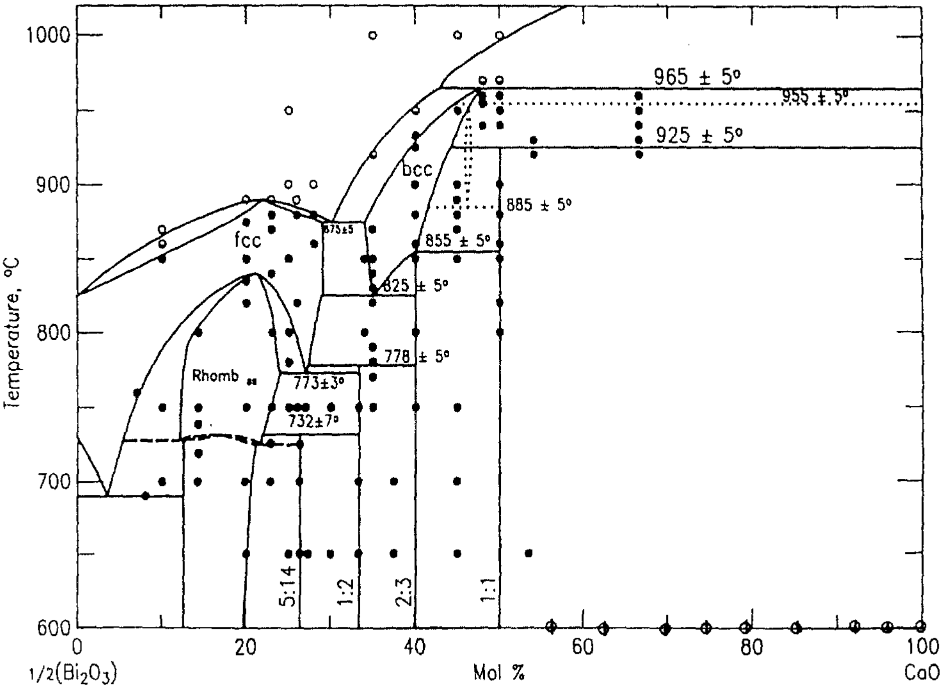

Fig. 2 The phase diagram of the Bi_2O_3–CaO system [2]

Figure 2 shows the most recent phase diagram of the binary system Bi_2O_3–CaO [2],where the investigated compositions are marked on the abscissa.

The heating curves have been recorded in static air atmosphere in the temperature range 20–880°C by help of a MOM Budapest type Paulik-Paulik-Erdey derivatograph OD-102 at a heating rate of 2.7 K min^{-1}.

The phase composition of the samples obtained through the nonisothermal treatment has been established by X-ray measurements. A HZG-3 X-ray diffractometer with the radiation K_α of cobalt was used.

In order to perform a kinetic analysis of the decomposition a versatile program written in BASIC language by Dragoe and Segal was used [3]. The program allows to calculate the nonisothermal kinetic parameters by help of three integral methods namely Coats-Redfern [4], Flynn-Wall [5] for constant heating rate and a variant of Coats-Redfern method modified by Urbanovici and Segal [6]. The optimum values of the kinetic parameters correspond to a minimum mean square deviation of the regression straight line with respect to the experimental points. The program allows the simulation of the TG curve in α–T coordinates using the kinetic parameters obtained by help of Coats-Redfern method, as well as to put on it the experimental points and thus to check the accuracy of the determined parameters.

Results and discussion

The molar compositions of the investigated mixtures located in the area corresponding to rich contents in CaO of the phase diagram are listed in Table 1. The table lists equally the temperatures of the endothermic peak on the DTA curve corresponding to the thermal decomposition and the phase composition of the samples resulted from the nonisothermal treatment. The presence of Bi_2O_3 decreases the peak temperature from 840°C to 790°C.

Table 1 Thermal analysis data phase composition for the investigated samples

Sample	Composition/mol%		T_{endo}/	Phase composition
	CaO	1/2(Bi_2O_3)	°C	at 880°C
1	100.00	0.00	840	CaO
2	95.94	4.06	825	CaO, C_{mon}
3	92.14	7.86	825	CaO, C_{mon}
4	85.39	14.61	825	C_{mon}, CaO
5	79.50	20.50	815	C_{mon}, CaO
6	74.67	25.33	815	C_{mon}, CaO
7	69.95	30.05	805	C_{mon}
8	62.46	37.54	795	C_{mon}
9	56.41	43.59	790	C_{mon}

C_{mon} = C-centered monoclinic $Ca_6Bi_7O_{16.5}$

The X-ray diffractograms show the lines of CaO thus confirming the occurence of the CaCO$_3$ decomposition. As seen from the inspection of Table 1, at higher contents of Bi$_2$O$_3$ besides CaO, a well crystallized binary compound corresponding to the C-centered monoclinic phase 'C_{mon}' reported by Burton *et al.* [2] has been identified. Starting with the composition 7 (Table 1) this compound is the only which was identified.

The 'C_{mon} ' is characterized by the composition Ca$_6$Bi$_7$O$_{16.5}$ and it was identified in the Bi$_2$O$_3$–CaO system at temperatures higher than 900°C [2]. Its formation in the mixtures investigated by us at temperatures lower than 900°C is probably due to the high reactivity of CaO resulted through the decomposition of CaCO$_3$.

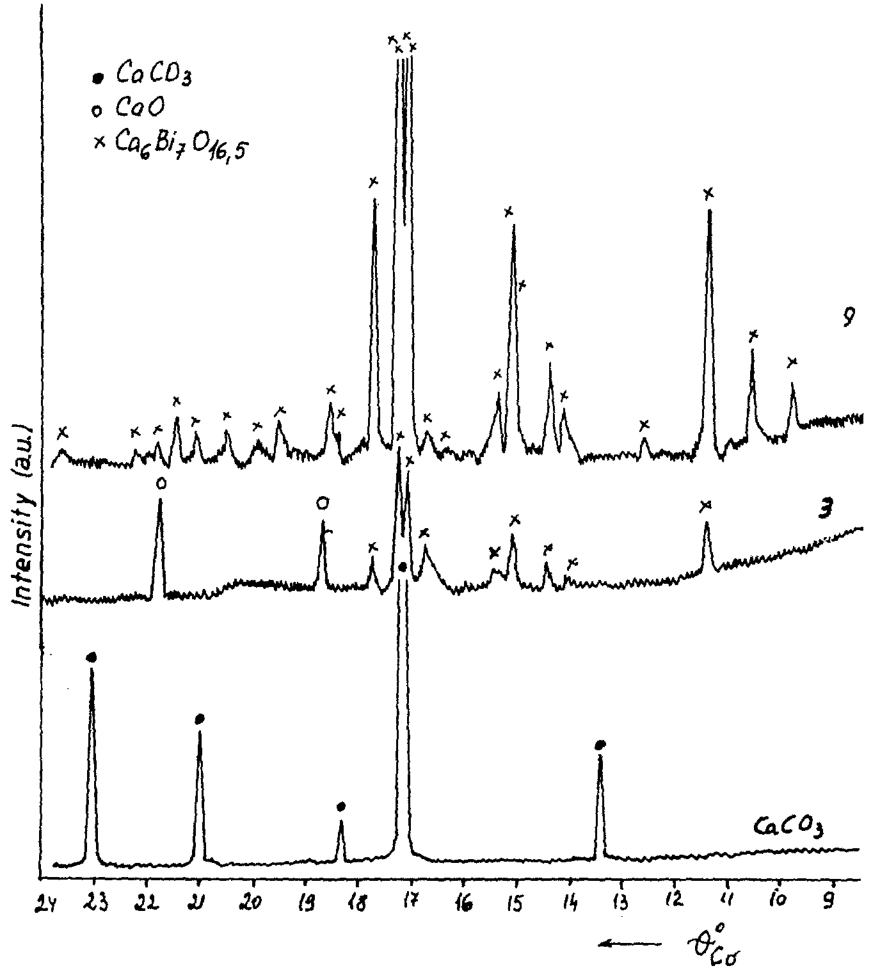

Fig. 3 The diffractograms of CaCO$_3$ as well as of two significant mixtures (3 and 9).

Figure 3 shows the X-ray diffractograms for pure $CaCO_3$ and two significant mixtures.

Table 2 lists the values of the nonisothermal kinetic parameters for the decomposition of pure $CaCO_3$ and in the presence of Bi_2O_3.

The inspection of the table shows a satisfactory agreement among the values of the kinetic parameters obtained by the three applied integral methods.

As seen from the inspection of this table, the decomposition of pure calcium carbonate occurs according to the contracting sphere model with a value of the reaction order which equals 0.6 quite close to 2/3. The obtained values are in good agreement with the literature data [7–9]. The presence of Bi_2O_3 in mixture with calcium carbonate determines changes in the value of the kinetic parameters of the decomposition.

For a better characterization of the investigated mixtures reactivity, the rate constants at 780°C have been calculated according to the Arrhenius equation (Table 3). Table 3 contains only the results obtained using the Coats-Redfern method.

Table 3 Values of the kinetic parameters for the investigated mixtures obtained using the Coats-Redfern method and the rate constants calculated at 780°C

Sample	E/kJ mol^{-1}	A/s^{-1}	n	k/s^{-1}
1	188 (±2)	$(9.3\pm2.4)10^{5}$	0.60(±0.02)	$(4.1\pm0.8)10^{-4}$
2	197 (±4)	$(27.6\pm13.4)10^{5}$	0.56(±0.04)	$(4.8\pm1.2)10^{-4}$
3	199 (±2)	$(41.3\pm11.0)10^{5}$	0.54(±0.02)	$(5.8\pm1.4)10^{-4}$
4	184 (±4)	$(6.0\pm3.1)10^{5}$	0.56(±0.02)	$(4.6\pm1.2)10^{-4}$
5	177 (±2)	$(3.7\pm1.1)10^{5}$	0.57(±0.02)	$(6.1\pm1.5)10^{-4}$
6	180 (±2)	$(4.3\pm1.7)10^{5}$	0.59(±0.04)	$(5.3\pm1.3)10^{-4}$
7	189 (±3)	$(19.9\pm8.5)10^{5}$	0.67(±0.05)	$(8.1\pm1.5)10^{-4}$
8	192 (±3)	$(27.5\pm9.5)10^{5}$	0.82(±0.02)	$(10.4\pm2.0)10^{-4}$
9	201 (±2)	$(144\pm60)10^{5}$	0.86(±0.04)	$(14.2\pm2.0)10^{-4}$

Simultaneous change of the activation energy, E, and the preexponential factor, A, values with Bi_2O_3 content, namely an increase until 7.86% mol $1/2(Bi_2O_3)$ (sample 3) followed by a decrease until 20.5% mol $1/2(Bi_2O_3)$ (sample 5) and a new important increase for the remaining samples has been recorded.

The activation energy exhibits a minimum value for the sample with 20.5% mol $1/2(Bi_2O_3)$. Under such conditions on the surface of the crystalline particles an important number of fast-growing nuclei are generated and a reaction interface which moves toward the center is thus formed. This model accounts for the value obtained for the reaction order close to 0.6 (contracting sphere model).

At higher concentrations of Bi_2O_3 the value of the reaction order tends to unity and the activation energy increases considerably. Due to the higher

Table 2 Values of the kinetic parameters for the investigated mixtures

Sample	Coats-Redfern			Flynn-Wall			Coats-Redfern modified		
	E/ kJ mol^{-1}	*A*/ s^{-1}	*n*	E/ kJ mol^{-1}	*A*/ s^{-1}	*n*	E/ kJ mol^{-1}	*A*/ s^{-1}	*n*
1	188±2	(9.3±2.4)10^5	0.60±0.02	194±2	(2.3±0.6)10^6	0.58±0.02	190±2	(1.2±2.1)10^6	0.60±0.02
2	197±4	(2.8±1.3)10^6	0.56±0.04	202±2	(7.2±2.5)10^6	0.54±0.04	199±4	(4.3±2.2)106	0.55±0.05
3	199±2	(4.1±1.1)10^6	0.54±0.02	204±2	(9.5±3.4)10^6	0.52±0.02	201±2	(5.8±1.8)106	0.52±0.02
4	184±4	(6.0±3.1)10^5	0.56±0.02	190±4	(1.6±0.6)10^6	0.54±0.02	187±3	(1.0±2.2)106	0.58±0.02
5	177±2	(3.7±1.1)10^5	0.57±0.02	183±2	(1.0±2.1)10^6	0.55±0.02	180±2	(5.6±1.0)105	0.56±0.02
6	180±2	(4.3±1.7)10^5	0.59±0.04	185±2	(1.1±2.7)10^6	0.56±0.03	182±2	(6.0±1.6)105	0.57±0.03
7	189±3	(2.0±0.8)10^6	0.67±0.05	194±3	(4.5±2.0)106	0.65±0.05	191±4	(2.8±1.3)10^6	0.65±0.05
8	192±3	(2.8±1.0)10^6	0.82±0.02	196±3	(8.1±2.2)10^6	0.78±0.03	194±3	(4.2±1.0)106	0.78±0.02
9	201±2	(14.4±6.0)10^6	0.86±0.04	207±2	(28.5±4.0)106	0.83±0.05	204±3	(19.0±2.4)10^6	0.84±0.04

amounts of Bi_2O_3 which surround the crystalline grains of $CaCO_3$ and thus hinder the diffusion of CO_2, the partial pressure of CO_2 in the reacting system increases facilitating the reverse reaction. The nucleation could now occur statistically in the bulk of the crystalline grains thus accounting for the increase of the reaction order toward unity.

The minimum value of the activation energy does not correspond to a minimum of the rate constant, due to the fact that the preexponential factor decreases with the Bi_2O_3 contents too (compensation effect). The observed oscillations in the first portion of the curve $k=f(Bi_2O_3$ content) are close to the experimental errors (Table 3). An important increase of the reactivity of $CaCO_3$ is determined by higher amounts of Bi_2O_3 (samples 7–9).

Conclusions

The presence of Bi_2O_3 has a complex influence on the decomposition of $CaCO_3$ acting on the nucleation as well as on the diffusion of CO_2.

The decomposition of the samples with low Bi_2O_3 content occurs according to a contracting sphere mechanism. A change from surface nucleation to bulk nucleation is recorded for higher amounts of Bi_2O_3.

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