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# Studies on the binary system Li<sub>2</sub>CO<sub>3</sub>-BaCO<sub>3</sub>

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## Abstract

The binary system  $Li_2CO_3$ -BaCO<sub>3</sub> was studied by means of heating-cooling curves, differential thermal analysis (DTA), thermogravimetry (TG), X-ray phase analysis and infrared spectroscopy. There is an eutectic at 609 ( $\pm$  4)°C and about 55 mol% Li<sub>2</sub>CO<sub>3</sub>. It was shown that lithium carbonate does not form substitutional solid solutions with barium carbonate, however, the possible formation of dilute interstitial solid solutions is suggested. © 2001 Elsevier Science B.V. All rights reserved.

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#### 1. Introduction

The binary systems  $M_2CO_3$ -M'CO<sub>3</sub> (where M and M' denote alkaline metal and alkaline-earth metal, respectively), are of great interest as an auxiliary phase in electrochemical CO<sub>2</sub> gas sensors [1–6] and elsewhere as a component of CO<sub>2</sub> resistivity gas sensors [7].

The studies of phase diagrams of these systems were the subject of several papers involving the following binary carbonates: Li–Ca [8,9], Na–Ba [10], Na–Ca [9], K–Ca [9–11]. However, there are no available data among them about Li<sub>2</sub>CO<sub>3</sub>–BaCO<sub>3</sub>, the most promising system in the manufacture of high-sensitive CO<sub>2</sub> gas sensors [2,3,5,6]. This work reports the results of our studies for the Li<sub>2</sub>CO<sub>3</sub>–BaCO<sub>3</sub> system in air atmosphere that is

essential in constructing electrochemical sensors for the determination of  $CO_2$ .

## 2. Experimental

## 2.1. Sample preparation

Nine samples covering a whole range of compositions of the system  $Li_2CO_3$ -BaCO<sub>3</sub> were examined in this work. The  $Li_2CO_3$  (purity 99.99%) and BaCO<sub>3</sub> (99 + %) from Sigma-Aldrich (both reagents of A.C.S. reagent grade) used in this work as starting materials were dried to constant weight at 200°C (473 K), and stored over silica gel in desiccators until used. The H<sub>2</sub>O content in Li<sub>2</sub>CO<sub>3</sub> derived from TG measurements before drying was less than 0.5 wt%, and negligible in the case of BaCO<sub>3</sub>. The binary carbonates were prepared by dry mixing of appropriate amounts of Li<sub>2</sub>CO<sub>3</sub> and BaCO<sub>3</sub>, one-axis cold pressing in a

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pellet die (75 MPa) and subsequent heating (10 K/min) in an artificial air flow (6 dm<sup>3</sup>/h), above the melting temperature  $T_{\rm M}$ , kept for 10 min, and slowly cooled. The heating conditions ( $T_{\rm M}$ ) for binary carbonates were derived from DTA and TG measurements, as described below. The heating of pressed samples was done in alumina boats, no chemical reaction between the alumina and carbonates were milled in an agate mortar to form fine powders, and stored over silica gel in a desiccator until used for further experiments.

# 2.2. DTA and TG measurements

DTA and TG measurements were performed in TA Instruments Derivatograph System, type SDT 2960, equipped with the mass spectrometer Balzers Thermostar GSD 300 and DSC 2010 unit. All experiments were done in alumina 60 mm<sup>3</sup> crucibles. It was not possible to use platinum crucibles because of high reactivity between Pt and carbonates, especially above the carbonate melting point. High purity  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was used as a reference material. Typical measurements were done with heating ratio 10 or 3 K/min in the flow of artificial air with flow ratio  $6 \text{ dm}^3/\text{h}$ . The sample weight was about 50 mg ( $\pm 5 \text{ mg}$ ), and time, sample weight, temperature and temperature differences were computer recorded simultaneously during the experiment.

Apart from the standard DTA and TG measurements, the heating-cooling measurements consisting of several heating-cooling cycles were performed, with the same experimental conditions as described above (heating-cooling ratio, gas type and gas flow rate, etc.). In the case of each heating-cooling measurement, the first cycle differed from the following ones. In the first heating cycle, the sample was the appropriate mixture of simple carbonates and the changes of thermal properties during the melting of the simple carbonates were observed. The following cycles were the observations of thermal properties of binary carbonate, with different properties than the carbonate mixture. The sample was not removed from derivatograph until all cycles were measured.



Fig. 1. DTA and TG results for BaCO<sub>3</sub> during heating (10 K/min).

## 2.3. XRD measurements

XRD measurements were done on SEIFERT XRD-7 diffractometer with Cu–K<sub> $\alpha$ </sub> filtered radiation. The X-ray diffraction patterns of the powdered carbonate samples (simple and binary) were typically measured in  $2\theta$  range from  $10^{\circ}$  to  $80^{\circ}$ , with a step of  $0.05^{\circ}$ , and sampling time of 3 s, although some more detailed experiments were also performed, where necessary. All X-ray diffraction measurements were done in air, at room temperature.

# 2.4. IR measurements

A Fourier spectrometer BIO-RAD, type FTS 60 V was used to collect IR spectra. The resolution was  $4 \text{ cm}^{-1}$ , measuring range  $400-4000 \text{ cm}^{-1}$  (MIR). The spectra were obtained using typical technique of KBr pellets.

## 3. Results and discussion

#### 3.1. DTA and TG analysis of pure components

Fig. 1 illustrates DTA and TG results monitored for BaCO<sub>3</sub> during heating in air with the rate 10 K/ min within the temperature range 25°C (298 K)– 1390°C (1663 K). BaCO<sub>3</sub> exhibits three crystallographic structures—rhombohedral (natural witherite),  $\beta$ -hexagonal and  $\alpha$ -cubic form. The temperatures of phase transformation in BaCO<sub>3</sub> are collected in Table 1. The observed endothermic peaks on the DTA curve in Fig. 1 at the temperature range 811–827°C (1084–1100 K) and 961–971°C (1234–1244 K) may correspond to the

Table 1 Temperatures of phase transformations in BaCO<sub>3</sub>

Temperature of	References	
γ-β	β–α	
1083	1253	[12]
1079	1241	[13]
1084	1255	[14]
1084	1234	This work

 $\gamma$ - $\beta$  and  $\beta$ - $\alpha$  phase transition, respectively. As seen from Table 1, the determined temperatures of the phase transition well agree with literature data [12–14]. Above 877°C (1150 K) a drop of the mass is observed on the TG curve. Firstly, the loss of the mass is very sluggish (between 877–1000°C), then the sudden weight change is observed (1000– 1240°C) and finally establishing of the equilibrium is observed. The entire drop of the mass within the temperature range 25 (298 K)–1390°C (1663 K) is equal to 21.4%. This figure is close to the theoretical change of the mass (22.3%) corresponding to the following decomposition reaction:

$$BaCO_3(s) \rightarrow BaO(s) + CO_2(g) \uparrow$$
. (1)

The determined decomposition temperature of BaCO<sub>3</sub> can be compared with that determined from the thermodynamic data. Fig. 2 illustrates the dependence of  $\Delta G$  of the reaction (1) as a function of temperature for several concentrations



Fig. 2.  $\Delta G$  of the decomposition BaCO<sub>3</sub> versus temperature for several concentrations of CO<sub>2</sub>.

(expressed in ppm) of CO<sub>2</sub> in the gas phase. Assuming that  $p(CO_2)$  in the experiment conditions was equal to 35 Pa [15], the decomposition,  $T_d$  temperature corresponding to  $\Delta G$  ( $T_d$ , 35 Pa)=0 is 893°C (1166 K). This value corresponds well with the observed early stage change of the mass in the TG curve.

The behavior of lithium carbonate during heating is a subject of controversial reports. Some authors claim that there are no thermal reactions before fusions begin at about 697°C (970 K) [16-18]. On the other hand, other authors postulate phase transition at 405–415°C (678–688 K) [19], 410°C (683 K) [20]. Barin [21] reports two polymorphic phase transitions at 350°C (623 K) and  $410^{\circ}C$  (683 K) with enthalpies of transformations 0.561 and 2.238 kJ/mol, respectively. Fig. 3 shows DTA and TG curves determined during heating of Li<sub>2</sub>CO<sub>3</sub> in the temperature range 25 (298 K)–777°C (1050 K). As seen in the inset of this figure, no thermal effects have been observed at the postulated phase transitions temperatures. It may be due to the rather small heat of phase transition [20,21]. The sharp peak near  $727^{\circ}C$  (1000 K)

corresponds to melting. There is also disagreement in literature concerning the melting point of  $Li_2CO_3$ . According to Barin [21]  $Li_2CO_3$  melts at 998 K. Other authors report values: 700°C (973 K) [16,20], 712°C (985 K) [22], 723°C (996 K) [17] 725°C (998 K) [18], 728°C (1001 K) [19].

Fig. 4 presents differential thermal analysis curves in the coordinate systems:  $\Delta T$  (right axis) and T (left axis) versus time for  $Li_2CO_3$  during subsequent heating and cooling runs. Two sharp peaks corresponding to melting and solidification can be observed. However, temperature ranges of these peaks differ considerably. First one begins at 694°C (967 K) and achieves extreme value at  $732^{\circ}C$  (1005 K), the second one begins at  $675^{\circ}C$ (948 K) and its extreme value is at 679°C (952 K). This difference may be explained analyzing a TG curve. As seen in Figs. 3 and 5, the loss of about 3% weight accompanies the melting process. The more detailed studies of the decomposition process of Li<sub>2</sub>CO<sub>3</sub> described elsewhere [23] and X-ray analysis showed that the weight loss results mainly by CO<sub>2</sub> liberation during decomposition of Li<sub>2</sub>CO<sub>3</sub> into lithium oxide and carbon dioxide.



Fig. 3. DTA and TG results for Li<sub>2</sub>CO<sub>3</sub> during heating (10 K/min).



Fig. 4. Dependence  $\Delta T$  and T on time during consecutive heating and cooling procedures for Li<sub>2</sub>CO<sub>3</sub>.



Fig. 5. DTA and TG results for Li<sub>2</sub>CO<sub>3</sub> during consecutive heating and cooling procedures.

The Li<sub>2</sub>O formed decreases the melting temperature of lithium carbonate, because in the binary system: Li<sub>2</sub>O-Li<sub>2</sub>CO<sub>3</sub> a eutectic mixture (containing 13 mol% of Li<sub>2</sub>O,  $T_{melt} = 705^{\circ}$ C) exists [24]. Rode [25] reports, that decomposition of  $LiCO_3$  takes place at 728°C (1001 K) i.e. soon after the fusion of solid lithium carbonate ( $T_{melt} = 723$ °C). These processes are probably responsible for



Fig. 6. DTA and TG results for Li<sub>2</sub>CO<sub>3</sub>-BaCO<sub>3</sub> (50 mol% Li<sub>2</sub>CO<sub>3</sub>) during consecutive heating and cooling procedures, first run.



Fig. 7. DTA and TG results for Li<sub>2</sub>CO<sub>3</sub>-BaCO<sub>3</sub> (50 mol% Li<sub>2</sub>CO<sub>3</sub>) during consecutive heating and cooling procedures, second run.

observed shift of the peaks on the  $\Delta T$  curve shown in Fig. 5.

# 3.2. DTA and TG analysis of binary Li<sub>2</sub>CO<sub>3</sub>-BaCO<sub>3</sub> system

Figs. 6 and 7 illustrate by way of example, DTA and TG curves for the Li<sub>2</sub>CO<sub>3</sub>-BaCO<sub>3</sub> mixture containing 50 mol% Li2CO3 recorded in two consecutive runs involving heating and cooling. The shape of the presented curves is similar to that for  $Li_2CO_3$ . The DTA for the first run (Fig. 6) on the heating part of the curve has sharp minimum beginning at 622°C (895 K) and minimum value at 653°C (926K). On the other hand, on cooling there is sharp exothermic peak beginning at 623°C (896 K) and achieving maximum value at 615°C (888 K). After this run, the 0.938% loss of weight (in relation to total mass of the sample) is observed. Assuming that this loss corresponds only to the decomposition of Li<sub>2</sub>CO<sub>3</sub> component, we can conclude that 3.44% of Li<sub>2</sub>CO<sub>3</sub> was decomposed. The second run (Fig. 7) exhibits much lower loss of weight 0.258% per total mass and 0.95% per mass of Li<sub>2</sub>CO<sub>3</sub>. It is interesting to mention that the sharp peak on the heating part of DTA curve observed in Fig. 6, now splits in two.

Figs. 8 and 9 show DTA curves for all the studied compositions during heating and cooling, respectively. Well developed endothermic (Fig. 8) and exothermic peaks (Fig. 9) correspond to melting and solidification, respectively. However, their position does not correspond to the same temperatures. There is about  $40.0 \pm 6.5^{\circ}$ C difference between minimum value on heating curves and maximum value on cooling curves.

# 3.3. XRD analysis

Fig. 10 shows X-ray diffraction patterns of the studied samples after heating in air above the melting temperature  $T_{\rm M}$  and cooling down. Taking into account the positions of peaks, almost all peaks observed for Li<sub>2</sub>CO<sub>3</sub>–BaCO<sub>3</sub> compositions can be identified as either BaCO<sub>3</sub> or Li<sub>2</sub>CO<sub>3</sub>. No shift in reflex positions was observed. There is only one exception: for the melted sample a small reflex for the sample containing 25 mol% Li<sub>2</sub>CO<sub>3</sub>

corresponding to  $2\theta = 40.6^{\circ}$  can be observed. On the other hand, the intensities of reflections change considerably. For example, low intensity peaks in the  $2\theta$  range of  $40-50^{\circ}$  observed for pure BaCO<sub>3</sub> assume higher relative intensities for the samples containing Li<sub>2</sub>CO<sub>3</sub>.

A more detailed X-ray analysis was performed using SiO<sub>2</sub> powder as an internal standard. Six samples containing 25, 50 and 75 mol% of Li<sub>2</sub>CO<sub>3</sub> just mixed with BaCO<sub>3</sub>, as well as melted, were ground with the constant mass (20 wt%) of  $\alpha$ quartz SiO<sub>2</sub>. Such a method allowed us to compare the reflex intensities coming from the mixed and melted (binary) carbonates. Figs. 11–13 illustrate the results. We observed, that samples after thermal treatment (melting) exhibit better developed peaks with higher intensities corresponding



Fig. 8. DTA curves during heating for Li<sub>2</sub>CO<sub>3</sub>–BaCO<sub>3</sub> compositions (12.5–100 mol% Li<sub>2</sub>CO<sub>3</sub>).



Fig. 9. DTA curves during cooling for  $Li_2CO_3$ -BaCO<sub>3</sub> compositions (12.5–100 mol%  $Li_2CO_3$ ).

to  $LiCO_3$  phase, than the mixtures of both carbonates.

The intensities as well as the  $d_{hkl}$  values observed and normalized, with respect to SiO<sub>2</sub> reflections were collected in Table 2. As seen, there are no visible changes in  $d_{hkl}$  between the sets of samples before and after annealing. Only small decrease of  $d_{hkl}$  for the reflection (102) of BaCO<sub>3</sub> may be noticed. These results suggest, that Li<sub>2</sub>CO<sub>3</sub> and BaCO<sub>3</sub> does not form solid solutions within wide ranges of concentrations. Such a conclusion seems to be justified taking into account the differences in crystal structures (Li<sub>2</sub>CO<sub>3</sub>—monoclinic, BaCO<sub>3</sub>—orthorhombic), ionic radii (Li<sup>+</sup> 59 ppm,  $Ba^{2+}$  136 ppm) and valencies of both ions. Such



Fig. 10. XRD diffraction patterns (Cu  $K_{\alpha}$ ) for Li<sub>2</sub>CO<sub>3</sub>–BaCO<sub>3</sub> compositions (0–100 mol% Li<sub>2</sub>CO<sub>3</sub>).

differences suggest hypothesis about formation of substituted solid solutions is very unlikely. The mentioned increase of  $d_{hkl}$  for BaCO<sub>3</sub> phase, if it is real, may indicate the formation of very diluted interstitial solid solutions of lithium in BaCO<sub>3</sub>. However, the observed increase is close to the uncertainty of the XRD method, thus the possibility of formation of these solid solutions should be verified by other methods. We have chosen MIR spectroscopy as such a method.

#### 3.4. Infrared spectroscopy

The model of  $CO_3^{2-}$  anions isolated by cations, was used in this paper for interpretation of IR spectra. Isolated, planar  $CO_3^{2-}$  anion has symmetry  $D_{3h}$  [26]. The absorption bands characteristic



Fig. 11. XRD diffraction patterns (Cu  $K_{\alpha}$ ) for Li<sub>2</sub>CO<sub>3</sub>-BaCO<sub>3</sub> (25 mol% Li<sub>2</sub>CO<sub>3</sub>) and SiO<sub>2</sub>, a-mixture of powders, b-after fusion.

of intermolecular  $CO_3^{2-}$  anion vibrations are located within 1800–400 cm<sup>-1</sup> region [27]. Four vibrations of  $CO_3^{2-}$  anion are [26–29]:

- (i) symmetric stretching vibrations ca.  $1065 \text{ cm}^{-1}$ ( $v_1$ )—Raman active;
- (ii) bending out of plane vibrations at 880– $850 \text{ cm}^{-1}$  (v<sub>2</sub>)—IR active;
- (iii) asymmetric stretching vibrations in the region of  $1450-1410 \text{ cm}^{-1}(v_3)$ —IR and Raman active;

(iv) bending in-plane vibrations at 720–680 cm<sup>-1</sup> ( $v_4$ )—IR and Raman active.

Fig. 14 presents MIR spectra of pure  $Li_2CO_3$ and  $BaCO_3$  and their mixtures before and after melting. On the spectrum of  $BaCO_3$  we can observe absorption bands, which may be ascribed to the intermolecular  $CO_3^{2-}$  anion vibrations, which are only slightly shifted in respect to vibrations of free ion: 1449 cm<sup>-1</sup> ( $v_3$ ), 857 cm<sup>-1</sup>



Fig. 12. XRD diffraction patterns (Cu K<sub> $\alpha$ </sub>) for Li<sub>2</sub>CO<sub>3</sub>-BaCO<sub>3</sub> (50 mol% Li<sub>2</sub>CO<sub>3</sub>) and SiO<sub>2</sub>, a-mixture of powders, b-after fusion.

 $(v_2)$  and  $694 \text{ cm}^{-1}$   $(v_4)$ . There is also a small peak at  $1060 \text{ cm}^{-1}$  corresponding to the  $v_1$  vibration. The spectrum of Li<sub>2</sub>CO<sub>3</sub> shows four mentioned bands corresponding to intermolecular vibrations of isolated anion. The twofold degeneracy of the normal modes  $v_3$  and  $v_4$  is removed due to decrease of symmetry of crystal lattice lithium carbonate in relation to the symmetry of ideal CO<sub>3</sub><sup>2-</sup> anion. The double band corresponding to  $v_3$  vibrations is here observed at 1503 and 1478 cm<sup>-1</sup>. On the other

hand, the band due to  $v_4$  vibrations splits into two components, and moreover shifts towards lower wave numbers, which maxima are at 509 and 422 cm<sup>-1</sup>. Also, the  $v_1$  vibration becomes active giving a small band at 1088 cm<sup>-1</sup>. The vibration  $v_2$ gives a sharp band at 863 cm<sup>-1</sup>.

Both studied carbonates give flat characteristics within  $4000-1800 \text{ cm}^{-1}$  (not shown in Fig. 14). It suggests the lack of OH<sup>-</sup> anions and molecules of water in their crystal structure.



Fig. 13. XRD diffraction patterns (Cu K<sub> $\alpha$ </sub>) for Li<sub>2</sub>CO<sub>3</sub>-BaCO<sub>3</sub> (75 mol% Li<sub>2</sub>CO<sub>3</sub>) and SiO<sub>2</sub>, a-mixture of powders, b-after fusion.

The comparison of spectra  $Li_2CO_3$ -BaCO<sub>3</sub> specimens before and after fusion indicates structural changes during fusion. The shape of the band corresponding to the mode  $v_3$  is affected for fused samples in relation to not fused mixtures of the same composition. The band broadens, and additional bands appear on the part corresponding to higher wavenumbers. This effect is characteristic of differentiation in bonds C–O length in the  $CO_3^{2-}$  anion. The structural changes during fusion are also suspected by observed changes of band intensities. It may be noticed that the increase of this band intensity occurs, which corresponds to predominant component. This suggests, that part of ions which are in minority incorporate into crystal lattice of the predominant component. Analogously, as it was observed for pure components, there is lack of the bands characteristic of  $OH^-$  and  $H_2O$  groups in fused mixtures. Table 2

Comparison of XRD data for Li<sub>2</sub>CO<sub>3</sub>-BaCO<sub>3</sub> (25 mol%, 50 mol% and 75 mol% of Li<sub>2</sub>CO<sub>3</sub>) before and after annealing

Reflection B: BaCO <sub>3</sub> L: $Li_2CO_3$ Q: $SiO_2$	25 mol% Li <sub>2</sub> CO <sub>3</sub>		50 mol% Li <sub>2</sub> CO <sub>3</sub>		75 mol% Li <sub>2</sub> CO <sub>3</sub>	
(4	Mixture	Annealed	Mixture	Annealed	Mixture	Annealed
Observed intensities (arbitrary units)						
B (111)	457	468	389	548	465	484
<b>B</b> (102)	197	355	165	322	197	259
L (-202)	33	32	34	83	82	187
L (002)	37	41	48	256	125	200
Q (101)	176	210	168	327	254	258
Normalized intensities (arbitrary units)						
<b>B</b> (111)	2.60	2.23	2.32	1.68	1.83	1.88
B(102)	1.12	1.69	0.98	0.98	0.78	1.00
L(-202)	0.19	0.15	0.20	0.25	0.32	0.72
L (002)	0.21	0.20	0.29	0.78	0.49	0.78
Observed $d_{hkl}$ (nm)						
<b>B</b> (111)	0.3714	0.3720	0.3726	0.3720	0.3714	0.3723
B(102)	0.3664	0.3657	0.3675	0.3660	0.3657	0.3663
L(-202)	0.2921	0.2917	0.2925	0.2917	0.2915	0.2919
L (002)	0.2812	0.2813	0.2819	0.2812	0.2812	0.2815
Q (101)	0.3341	0.3341	0.3351	0.3343	0.3338	0.3346
Corrected $d_{hkl}$ (nm)						
B (111)	0.3716	0.3722	0.3716	0.3719	0.3719	0.3719
B(102)	0.3666	0.3658	0.3664	0.3658	0.3661	0.3658
L(-202)	0.2922	0.2918	0.2918	0.2916	0.2918	0.2916
L (002)	0.2813	0.2814	0.2813	0.2811	0.2814	0.2813
Q (101)	0.3342	0.3342	0.3342	0.3342	0.3342	0.3342

## 3.5. Phase diagram of Li<sub>2</sub>CO<sub>3</sub>: BaCO<sub>3</sub> system

Based on the presented results we propose the schematic phase diagram of  $Li_2CO_3$ : BaCO<sub>3</sub> system, shown in Fig. 15.  $Li_2CO_3$  and BaCO<sub>3</sub> form the eutectic at about 55 mol% of  $Li_2CO_3$  with the melting temperature of 609 ( $\pm 4$ )°C. No other phases than  $Li_2CO_3$  and BaCO<sub>3</sub> were detected in the investigated temperature range. The possible formation of intersitial solutions is not shown in this diagram. Based on our results, it is not possible to determine the phase composition in the temperature range above solidus line (609°C). It could be done for example by X-ray diffraction high temperature measurements. Taking into account the decomposition of  $Li_2CO_3$  and possible evaporation of formed  $Li_2O$  (composition changes

and corrosive properties of  $Li_2O$ ) such an experiment seems to be very difficult to perform.

# 4. Conclusions

In this work, the results of DTA, TG, XRD and IR measurements of  $Li_2CO_3$ : BaCO<sub>3</sub> system were presented. Based on XRD results it can be suggested that  $Li_2CO_3$  and  $BaCO_3$  do not form substituted solid solutions over a wide range of composition. There is a eutectic at 609 ( $\pm$  4)°C and about 55 mol% of Li<sub>2</sub>CO<sub>3</sub>.

The observed intensity increase of some X-ray peaks coming from BaCO<sub>3</sub>, the slight splitting of DTA peaks, as well as the modification of IR spectra in the case of binary carbonates compared



Fig. 14. IR spectra for Li<sub>2</sub>CO<sub>3</sub>–BaCO<sub>3</sub> (0–100 mol% Li<sub>2</sub>CO<sub>3</sub>), physical mixtures-solid lines and samples after fusion—dashed lines.

with simple carbonates, may suggest the formation of very diluted interstitial solid solutions especially of lithium in BaCO<sub>3</sub>. This hypothesis has to be verified, because the observed changes in X-ray diffraction and modification of IR spectra may be caused by the crystallinity changes, and the splitting of DTA peaks can be caused by the Li<sub>2</sub>O-Li<sub>2</sub>CO<sub>3</sub> formation.

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Fig. 15. Phase diagram of Li<sub>2</sub>CO<sub>3</sub>–BaCO<sub>3</sub> system.

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