

STRUCTURAL PROPERTIES AND THERMAL BEHAVIOR OF Li_2CO_3 – BaCO_3 SYSTEM BY DTA, TG AND XRD MEASUREMENTS

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Abstract

The binary system Li_2CO_3 – BaCO_3 was studied by means of differential thermal analysis (DTA), thermogravimetry (TG) and X-ray phase analysis. The composition of carbonate and CO_2 partial pressure influence on the thermal behavior of carbonate were examined. It was shown that lithium carbonate does not form the substitutional solid solution with barium carbonate, however the possible formation of diluted interstitial solid solutions is discussed. Above the melting temperature the mass loss is observed on TG curves. This loss is the result of both decomposition of lithium carbonate and evaporation of lithium in Li_2CO_3 – BaCO_3 system. Increase of CO_2 concentration in surrounding gas atmosphere leads to slower decomposition of lithium carbonate and to increase the melting point.

Keywords: barium carbonate, carbon dioxide, differential thermal analysis, lithium carbonate, phase diagram, solid solutions, thermogravimetry

Introduction

Metal carbonates are of great interest as an auxiliary phase in solid-state electrochemical CO_2 gas sensors [1–6]. The auxiliary phase material should exhibit the long-term stability of composition, structure and microstructure at elevated temperatures, and in different gaseous atmospheres. The stability of these properties, apart from other factors, is necessary to assume the long-term stability of sensor signal.

It has been experimentally found, that the sensors based on binary carbonates M_2CO_3 – $\text{M}'\text{CO}_3$ (where M and M' denote alkaline metal and alkaline-earth metal, respectively), exhibit much better long-time stability in comparison to sensors build of the simple carbonates [1, 2].

The studies of phase diagrams and the properties of binary carbonate systems were reported in several papers involving the following binary carbonates: Li–Ca [7, 8], Na–Ba [9], Na–Ca [8], K–Ca [8–10]. However, there are no available data for Li_2CO_3 – BaCO_3 . This system seems to be promising in the manufacture of high-

sensitive CO_2 gas sensors, because of the lowest affinity to water vapour of Li_2CO_3 in comparison to other alkaline metal carbonates.

The purpose of this work was to investigate the structural and thermal properties of Li_2CO_3 – BaCO_3 system in the whole range of composition.

Experimental

Sample preparation

The Li_2CO_3 (purity 99.99%) and BaCO_3 (99+%) (Sigma-Aldrich, both reagents of A.C.S. reagent grade) used as starting materials were dried to constant mass at 200°C (473 K), and stored over silica gel in desiccators until used. The binary carbonates were prepared by dry mixing of appropriate amounts of Li_2CO_3 and BaCO_3 and one-axis cold pressing in a pellet die (75 MPa). Prepared pellets were then heated (10 K min^{-1}) above the melting temperature (T_m) and cooled (10 K min^{-1}). Samples for DTA and TG measurements were melted directly in the DTA apparatus during the first run, as described below. Samples for X-ray diffraction measurements were prepared in the separate furnace, but in the same conditions (melting temperature, gas atmosphere) as in the case of samples used in DTA and TG experiments – the heating conditions (T_m) were derived from DTA and TG measurements. Obtained carbonates were crushed in an agate mortar to the form of fine powder, and stored over silica gel in desiccator until used for X-ray diffraction measurements.

Measurements

Differential thermal analysis (DTA) and thermogravimetry (TG) measurements were done using TA Instruments type SDT 2960, equipped with the mass spectrometer Balzers ThermoStar GSD 300 and DSC 2010 unit. Small pieces of previously mixed and pelleted carbonates were placed in alumina crucible (60 mm^3) and heated (10 K min^{-1}) above the melting temperatures (T_m), then cooled down (10 K min^{-1}). The first run was made in order to allow the possible reaction or mixing between carbonates to take place. After this first run sample was not removed from the apparatus, and the second run with the heating and cooling ratio 3 K min^{-1} was started and the DTA as well as TG data presented in this work were collected. The reference material used was the $\alpha\text{-Al}_2\text{O}_3$, the samples mass was about 50 mg ($\pm 5\text{ mg}$). All measurements were done in controlled atmosphere: in artificial air with different CO_2 partial pressures (0.03 and 1.25 vol% of CO_2). Such CO_2 pressures were selected because the 0.03 vol% is the natural level of carbon dioxide pressure in regular air, the 1.25 vol% of CO_2 was the highest CO_2 partial pressure used by us in the experiments concerning operation of electrochemical sensors based on Li_2CO_3 – BaCO_3 carbonates [6]. During all experiments the total gas flow rate was kept at constant level of $6\text{ dm}^3\text{ h}^{-1}$.

X-ray diffraction measurements were done using Seifert XRD-7 diffractometer with CuK_α filtered radiation in the 2θ range from 10 to 60° , with 0.05° step and sampling time 3 s. All X-ray diffraction measurements were done in air, at room temperature.

Results and discussion

XRD analysis

Diffraction patterns of studied Li_2CO_3 – BaCO_3 samples prepared in air (0.03 vol% CO_2) above melting temperature and cooled down, together with the data for pure Li_2CO_3 and pure BaCO_3 are presented in Fig. 1. Almost all reflexes observed for Li_2CO_3 – BaCO_3 compositions can be identified as either BaCO_3 or Li_2CO_3 . Only one unidentified reflex of very low intensity, for the sample containing 25 mol% of Li_2CO_3 , corresponding to $2\theta=40.6^\circ$ was found (not shown in Fig. 1). These results suggest, that lithium and barium carbonate do not form solid solutions within the wide range of composition. Such a conclusion seems to be justified taking into account differences in crystallographic structures (Li_2CO_3 – monoclinic, BaCO_3 – orthorhombic), ionic radii (Li^+ 59 pm, Ba^{2+} 136 pm) and valences of both ions. Such differences make hypothesis about formation of substituted solid solutions doubtful.

On the other hand, intensities of some reflexes change considerably, as shown in Fig. 1. The observed changes of relative intensities of some XRD reflexes after heating may result from microstructure changes or formation of very diluted interstitial solid solutions of lithium in barium carbonate.

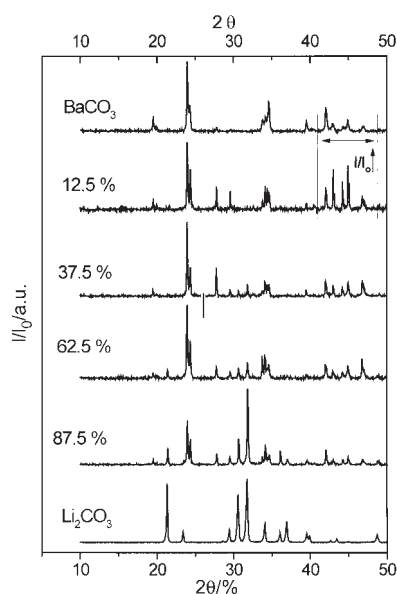


Fig. 1 XRD patterns of binary carbonates in the system Li_2CO_3 – BaCO_3 , together with the data obtained for pure Li_2CO_3 and BaCO_3 . The annotations describe the Li_2CO_3 content (mol%) in the sample

DTA analysis of the Li_2CO_3 – BaCO_3 system

Figures 2 and 3 show the DTA heating and cooling curves obtained for Li_2CO_3 – BaCO_3 carbonates during the second run. CO_2 concentration in surrounding gas atmosphere was 0.03 vol%. Well-developed endothermic (Fig. 2) and exothermic peaks (Fig. 3) correspond to melting and solidification, respectively. However, their position does not correspond to the same temperatures. There is about 40.0 ± 6.5 degrees of difference between minimum value on heating curves and maximum value on cooling curves. The DTA curve of the composition of 62.5 mol% Li_2CO_3 shows splitting of the exothermic peak into two. This splitting may result from the appearance of the lithium oxide as minority phase being the product of the decomposition of lithium carbonate.

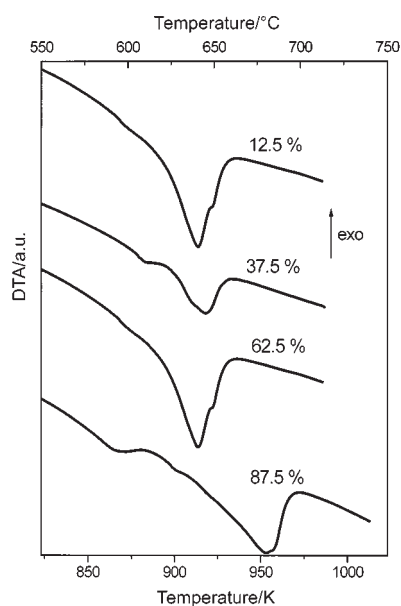


Fig. 2 DTA heating curves obtained for Li_2CO_3 – BaCO_3 carbonates, for the measurement done at 0.03 vol% of CO_2 . The annotations describe the Li_2CO_3 content (mol%) in the sample

Effect of CO_2 concentration on DTA and TG results

In order to determine the influence of CO_2 partial pressure on thermal stability of Li_2CO_3 – BaCO_3 carbonate as well as to explain the splitting of DTA peaks, the DTA and TG experiment in different CO_2 partial pressures was done. Figures 4 and 5 show the DTA dependence on the temperature during typical experiment, as described in Experimental Part. First run of heating-cooling (10 K min^{-1}) was done in order to homogenise the sample, the second run of heating-cooling (3 K min^{-1}) was done to collect the DTA data for pure Li_2CO_3 and 25 mol% Li_2CO_3 :75 mol% BaCO_3 sample. The measurements were done at atmospheres containing different CO_2 concentrations

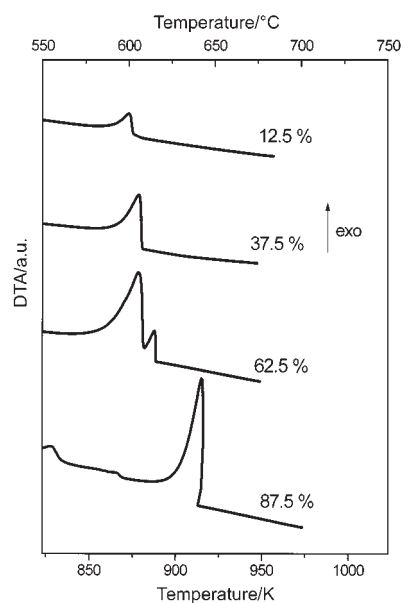


Fig. 3 DTA cooling curves obtained for Li_2CO_3 – BaCO_3 carbonates, for the measurement done at 0.03 vol% of CO_2 . The annotations describe the Li_2CO_3 content (mol%) in the sample

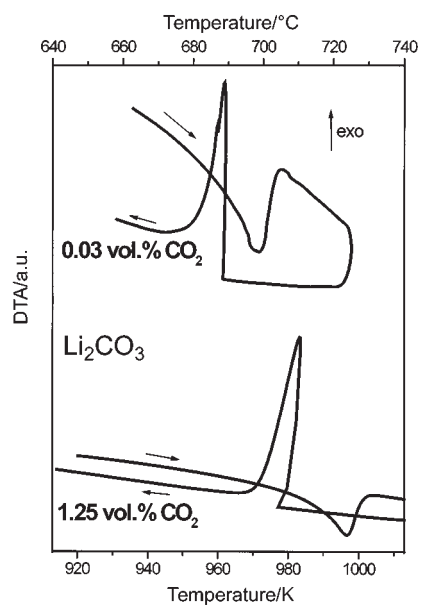


Fig. 4 DTA heating-cooling curves obtained for Li_2CO_3 for different CO_2 atmospheres (second run)

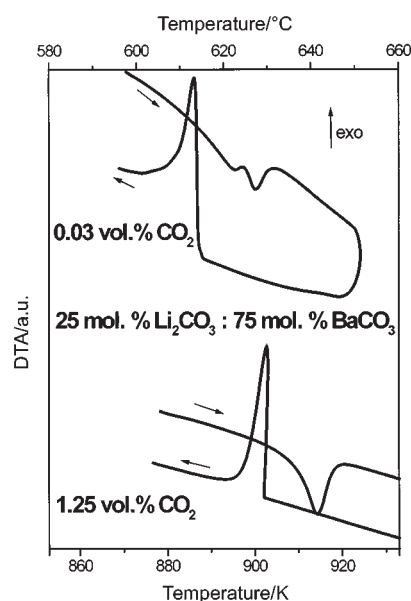


Fig. 5 DTA heating-cooling curves obtained for 25 mol% Li_2CO_3 :75 mol% BaCO_3 samples for different CO_2 atmospheres (second run)

(0.03 and 1.25 vol%). The broadening or even splitting of peaks, observed in case of 0.03 vol% concentration of CO_2 , disappears for higher concentration of CO_2 (1.25 vol%). This suggests that at low CO_2 pressure the decomposition of Li_2CO_3 occurs mainly according to the reaction:



Figures 6 and 7 illustrate the thermogravimetric results (TG) monitored simultaneously with the DTA curves shown in Figs 4 and 5. Left ordinate axes represent the mass loss (TG%) related to Li_2CO_3 , while right ordinate axes represent the degree of decomposition defined by the formula:

$$\text{Degree of decomposition} = \frac{\Delta m}{\Delta m_{\text{theoret}}} 100 \quad (2)$$

where Δm denotes experimental mass change, $\Delta m_{\text{theoret}}$ corresponds to the maximum value of mass change when total amount of lithium carbonate in the sample decomposes to lithium oxide.

As one can see, in both cases the mass loss occurs for molten samples, while for the solid samples the mass change is almost negligible. It is with agreement with the results obtained by Rode for pure Li_2CO_3 [11]. The increase of CO_2 partial pressure decreases the mass change at high temperature (above melting point). This mass change is partially reversible. The mass loss at higher CO_2 pressure due to decompo-

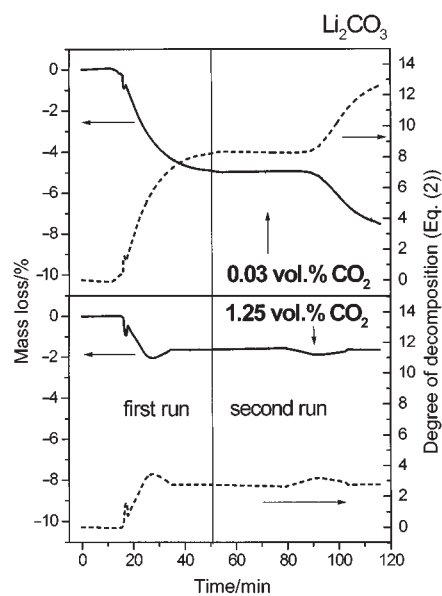


Fig. 6 The relative mass changes during heating-cooling cycles obtained for Li_2CO_3 for different CO_2 atmospheres (first and second run)

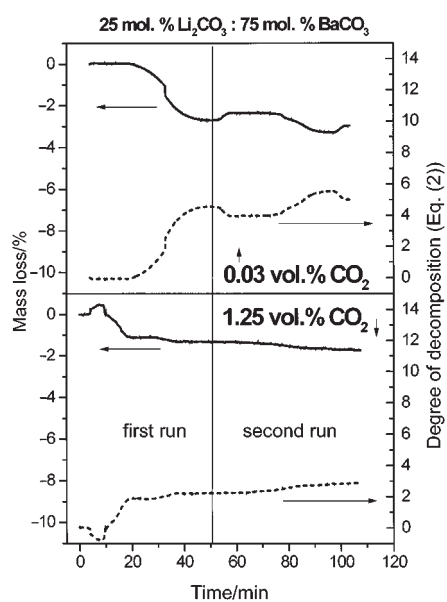


Fig. 7 The relative mass changes during heating-cooling cycles obtained for 25 mol% Li_2CO_3 :75 vol% BaCO_3 samples for different CO_2 atmospheres (first and second run)

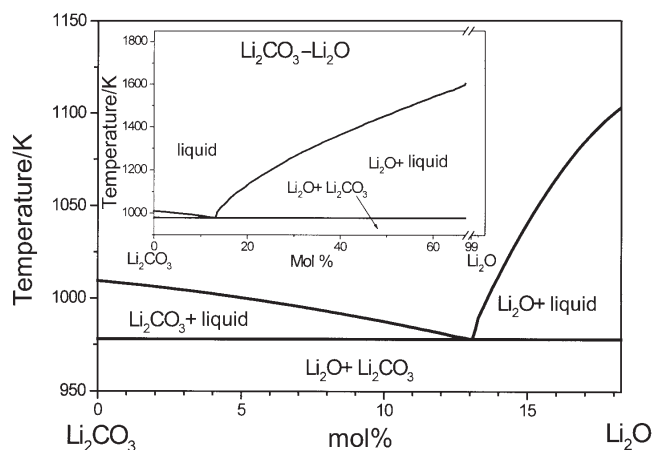


Fig. 8 Phase diagram of Li_2CO_3 – Li_2O . Figure prepared basing on the data from [13]

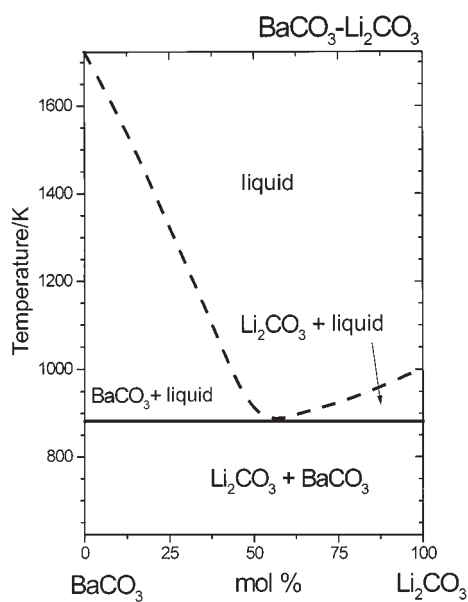


Fig. 9 Phase diagram of Li_2CO_3 – BaCO_3 system

sition of Li_2CO_3 is not completely stopped, as expected basing on thermodynamic data [12]. It may suggest that the evaporation of lithium at elevated temperatures take place in these cases. In the case of 25 mol% Li_2CO_3 :75 mol% BaCO_3 sample the mass loss is lower than that for pure lithium carbonate. It indicates that the presence of barium carbonate in the sample leads to stabilisation of Li_2CO_3 .

The comparison of DTA and TG curves monitored at 0.03 vol% CO_2 with these monitored at 1.25 vol% CO_2 indicates that the melting point temperature increases with the increase of CO_2 concentration while mass loss decreases for both samples. These effects can be explained taking into consideration the phase diagram of Li_2CO_3 – Li_2O (Fig. 8) [13]. The increase of CO_2 concentration in gas atmosphere shifts the equilibrium (1) towards the stabilisation of carbonate. On the other hand, the decrease of Li_2O content leads to the increase of the melting point in the system Li_2CO_3 – Li_2O .

Taking into account the XRD, DTA and TG results we can propose the phase diagram of the Li_2CO_3 – BaCO_3 illustrated in Fig. 9.

Conclusions

Lithium and barium carbonates do not form substitutional solid solutions in the whole range of studied compositions, however the reflexes intensity changes may suggest the appearance of diluted interstitial solutions (lithium in BaCO_3).

The lithium carbonate decomposition reaction is highly influenced by the CO_2 partial pressure and the sample composition: the increase of CO_2 partial pressure and the presence of BaCO_3 in the sample leads to the decrease of decomposition degree of sample (Li_2CO_3) as well as to the increase of melting temperature. These results may suggest that the Li_2O formed during partial decomposition of sample play an important role in mechanism of carbonate melting, probably by local eutectic formation. This reaction seems to occur on the sample surface: Li_2CO_3 – BaCO_3 system the amount of superficial lithium carbonate is lower than in the case of pure Li_2CO_3 .

The studied system Li_2CO_3 – BaCO_3 seems to be much more complex than other binary carbonates due to evaporation of lithium during partial decomposition of lithium carbonate to Li_2O above melting point temperature.

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