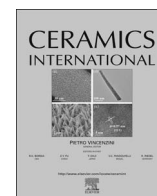




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Coupled phase diagram experiments and thermodynamic optimization of the binary Li_2O - MgO and Li_2O - CaO systems and ternary Li_2O - MgO - CaO system

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ABSTRACT

A key phase diagram study of the Li_2O - MgO and Li_2O - CaO systems at 1 atm was performed using equilibration/quenching experiments and differential scanning calorimetry measurements with sealed 90Pt-10Rh crucibles. In particular, the eutectic temperatures of both systems and the solubility of Li_2O in solid MgO and CaO were properly measured for the first time. The eutectic temperatures of the Li_2O - MgO and Li_2O - CaO systems were determined to be $1696 \pm 6 \text{ K}$ ($1423 \pm 6^\circ\text{C}$) and $1617 \pm 6 \text{ K}$ ($1344 \pm 6^\circ\text{C}$), respectively. A solubility of 2.6 mol% (1.9 wt%) Li_2O in solid MgO was measured at 1743 K (1470°C) and no detectable solubility of Li_2O in solid CaO was determined. The present experimental results were employed for the thermodynamic modeling of the binary Li_2O - MgO and Li_2O - CaO systems. The phase diagrams for the binary Li_2O - MgO and Li_2O - CaO systems were constructed for the first time, and the phase diagram of the ternary Li_2O - MgO - CaO system was predicted from the binary descriptions.

1. Introduction

The Li_2O -containing oxide systems have gained importance due to their wide applications as functional ceramics and flux components for metallurgical processes. The applications associated with the Li_2O - Na_2O - K_2O - CaO - MgO - Al_2O_3 - SiO_2 system include, for example, steelmaking [1], glassmaking [2,3], solid state electrochemistry [4–7], mineralogy [8], oxidative dehydrogenation catalysis [9–11], and thermal shock resistant ceramics [12,13] amongst others. The accurate understanding of the binary Li_2O - MgO and Li_2O - CaO systems are in particular essential for the catalysis of methane oxidation [14] and MgO -based refractories [15–17]. Moreover, the phase equilibria in the multicomponent Li_2O - MgO - and Li_2O - CaO - containing systems are very complex [18] and the available phase diagram and thermodynamic property data are often limited.

The thermodynamic database is developed using the CALculation of PHase Diagram (CALPHAD) methodology which can be a good and efficient tool to provide accurate and consistent thermodynamic property and phase diagram information. The Gibbs energies of all phases can be obtained by a critical evaluation and optimization of all available and reliable thermodynamic data and phase diagram data. This optimization commences from the unary, moving on to the binaries and then to ternary and higher

order systems. The optimized Gibbs energy descriptions of the phases are stored in a computerized database. This database can be accessed by a thermodynamic software with a Gibbs energy minimization routine to calculate any complex phase diagrams and chemical reactions. Hence, to have a better predictive ability in the higher order systems it is necessary to well constrain the lower-order system.

Keeping in mind the huge industrial application, a thermodynamically consistent database for the Li_2O - Na_2O - CaO - MgO - Al_2O_3 - SiO_2 system is being developed at McGill University. The authors [19] already optimized the Li - O system containing Li_2O , and Li_2O_2 phase, and Li_2O - SiO_2 system. In the present study, the experimental study and optimization of the Li_2O - MgO and Li_2O - CaO systems were performed. As the available experimental phase diagram data for both Li_2O - MgO system [9,20] and Li_2O - CaO system [21,22] are limited to the subsolidus region, key phase diagram experiments were performed to reveal the eutectic temperatures of the binary Li_2O - MgO and Li_2O - CaO systems. The thermodynamic optimizations of the two binary systems were then performed using the CALPHAD method to obtain accurate phase diagrams of the binary systems. The phase diagram of the Li_2O - CaO - MgO system was finally predicted based on the present optimizations and a previous description of the CaO - MgO system

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[23]. All the thermodynamic calculations in the present study were performed using the FactSage thermodynamic software [24].

2. Key phase diagram experiments

Quenching experiments and differential scanning calorimetry (DSC) measurements were performed in the Li_2O - MgO and Li_2O - CaO systems to determine the eutectic reaction temperatures of both systems and the solubility of Li_2O in solid CaO and MgO .

2.1. Starting materials

Reagent grade powders of Li_2O (99.9 wt%), MgO (99.998 wt%) and CaO (99.95 wt%) from Alfa Aesar (USA) were used to prepare the starting materials. To avoid the possible contamination of the starting materials by carbonates such as CaCO_3 , MgCO_3 and Li_2CO_3 , pure oxides were employed. Prior to the equilibration experiments, X-ray diffraction (XRD) analyses of all the reagents were conducted to confirm their purities. Due to the hygroscopic nature of the reagents, each of them was first dried overnight (12 h) at 773 K (500 °C) in a ST-1700C furnace (Sentro Tech, Strongsville, OH, USA; inner dimensions: 10 cm × 10 cm × 10 cm) equipped with MoSi_2 heating elements. The dried powders were then cooled down in a desiccator and stored in a drying oven at 393 K (120 °C). Batches of 2 g of starting materials were prepared by mixing appropriate proportions of each powder in an agate mortar filled with isopropyl alcohol ($\text{H}_2\text{O} < 0.02$ vol%) or cyclo-hexane (0 vol% H_2O) for 1 h. The alcohol was driven off under a hot lamp and the mixtures were stored in a drying oven at 393 K (120 °C). Due to the high volatility of Li_2O , all the experiments were carried out using sealed 90Pt-10Rh capsules. The sealed capsules were prepared from 90Pt-10Rh tubes (O.D. = 3.2 mm, I.D. = 2 mm) of 6–10 mm in length. One side was closed with a three-corner weld using a tungsten electrode. About 15–20 mg of starting materials were taken out from the drying oven and tightly packed into each 90Pt-10Rh capsule. The other side of the capsule was then welded after removing air as much as possible by crimping the capsule tube. As a small amount of Li_2O always evaporated during the high temperature experiments, the capsules would always bulge during the experiments. Without the crimping of capsules, we experienced frequent capsule leakages for the alkali oxide containing experiments. The integrity of the weld was checked using an optical microscope before/after each of the quenching experiment and DSC analysis.

2.2. Equilibration/quenching experiments

The equilibration/quenching experiments were conducted in the ST-1700C Sentro Tech furnace (Strongsville, OH, USA). Pt30Rh-Pt6Rh (type B) thermocouples were used to measure the temperature which was kept within ± 1 K with a PID controller. The equilibration temperatures in the present study were 1643 K (1370 °C) and 1743 K (1470 °C). The accuracy of the furnace temperature was checked by melting diopside ($\text{CaMgSi}_2\text{O}_6$) at 1665 K (1392 °C).

Several 90Pt-10Rh capsules, which were placed in a porous alumina boat, were equilibrated at the same time at the target temperatures for 2 h. After equilibration, the samples were quenched in a bath filled with ice-cold water. Samples showing any hints of leakage were rejected, so only a few experiments were successful for each target temperature. In particular, experiments with higher than 0.2 mol fraction Li_2O in the starting sample were always unsuccessful, so the only experiments reported in this study were the ones performed with a starting material made of 0.2 mol fraction Li_2O . The 90Pt-10Rh capsules were used because pure Pt capsules are known to react with Li_2O [22].

After quenching, the encapsulated samples were cast in epoxy and polished for phase analysis. To avoid any moisture pick-up during polishing, lapping oil was used as the polishing media. Then, the samples were cleaned in an ultrasonic bath using 2-propanol (<

0.01 vol% H_2O) or cyclo-hexane (0 vol% H_2O) for less than 10 s. The samples were then carbon-coated for Electron-probe micro-analysis (EPMA).

Phase composition analysis was carried out using wavelength dispersive spectrometry (WDS) and backscattered electron (BSE) images. EPMA analyses were conducted with the JEOL (Tokyo, Japan) 8900 probe at McGill University. An accelerating voltage of 15 kV was used with 20 nA beam current, a spot size of 1 or 5 μm (depending on the size of the phases), and counting times of 20 s on peaks and 10 s on backgrounds. Raw data were processed with the ZAF corrections using periclase (Mg) and diopside (Ca). As Li cannot be quantitatively analyzed by EPMA, the Li content was estimated by assuming the total of each analysis to be 100 wt% and by subtracting the content of Mg or Ca from it. This method is admittedly not perfect but it was the only one available for the authors in the present experiment; the error associated with the Li content can then be attributed to the cumulative errors coming from the preparation and analysis of the other oxides. The equilibrium phases were also identified by XRD using the Bruker Discover D8 X-ray diffractometer (Wisconsin, USA) with a Co-K α source equipped with HiSTAR area detector at McGill University. All the peaks recorded in the XRD scans were identified with the Powder Diffraction Files (PDF) of the International Centre for Diffraction Data (ICDD) using the Bruker AXS DIFFRAC.EVA (Bruker AXS, Karlsruhe, Germany, 2000) software package.

2.3. DSC analysis

DSC and TGA measurements were performed in the binary Li_2O - MgO and Li_2O - CaO systems using the Jupiter STA 449 F3 thermal analyzer (NETZSCH Instruments, Selb, Germany) at McGill University. Temperature and sensitivity calibrations were conducted with the melting and polymorphic transition temperatures and associated enthalpy changes of biphenyl ($\text{C}_{12}\text{H}_{10}$), benzoic acid ($\text{C}_7\text{H}_6\text{O}_2$), rubidium nitride (RbNO_3), potassium perchlorate (KClO_4), caesium chloride (CsCl), potassium chromate (K_2CrO_4), barium carbonate (BaCO_3), and diopside ($\text{CaMgSi}_2\text{O}_6$).

90Pt-10Rh capsules were used for the DSC experiments. The capsule size was slightly shorter (~ 6 mm in length) than the one used in the quenching experiments (~ 10 mm in length) in order to fit on the sensor of the DSC-TGA sample carrier. Heating and cooling rates of 10 K min^{-1} were employed in a flowing argon atmosphere with a gas flow rate of 20 mL min^{-1} . The samples were first heated up to 1573 K (1300 °C) and held for 1 h and then heated again to 1823 K (1550 °C) followed by cooling at 10 K min^{-1} to room temperature. A second cycle was then initiated by reheating the same sample to 1823 K (1550 °C) and subsequently by cooling down to room temperature with the same heating and cooling rate of 10 K min^{-1} . The second heating and cooling cycles were employed to collect the DSC data. Thermogravimetric analysis (TGA) was performed simultaneously with each DSC measurement to record any mass loss related to the leakage of a capsule; samples showing such losses were rejected. Two samples with the same composition were tested to confirm the reproducibility of the experimental results.

The sensitivity of DSC measurements with sealed Pt capsules was verified using pure lithium metasilicate (Li_2SiO_3 – 99.9 wt%, Alfa Aesar, Massachusetts, USA) and diopside ($\text{CaMgSi}_2\text{O}_6$ used by Konar et al. [18], prepared by Hudon et al. [25]). The melting temperature of Li_2SiO_3 and $\text{CaMgSi}_2\text{O}_6$ sample in a sealed Pt capsule was measured to be at 1488 K (1215 °C) and 1670 K (1397 °C), respectively. These results are close to the reported melting temperatures of Li_2SiO_3 at 1486 K (1213 °C) [19] and $\text{CaMgSi}_2\text{O}_6$ at 1665 K (1392 °C) [26]. Hence, the maximum error of measurement is ± 5 K (± 5 °C) from the preliminary Pt capsule tests with reference materials. This analysis confirms that samples sealed in this type of Pt capsules can be used for DSC experiments without interfering with the heat incidents.

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