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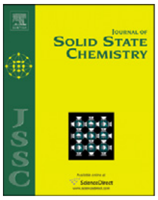

Synergistic use of Knudsen effusion quadrupole mass spectrometry, solid-state galvanic cell and differential scanning calorimetry for thermodynamic studies on lithium aluminates

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ABSTRACT

Three ternary oxides $LiAl_5O_8(s)$, $LiAlO_2(s)$ and $Li_5AlO_4(s)$ in the system Li–Al–O were prepared by solid-state reaction route and characterized by X-ray powder diffraction method. Equilibrium partial pressure of $CO_2(g)$ over the three-phase mixtures $\{LiAl_5O_8(s)+Li_2CO_3(s)+5Al_2O_3(s)\}$, $\{LiAl_5O_8(s)+5LiAlO_2(s)+2Li_2CO_3(s)\}$ and $\{LiAlO_2(s)+Li_5AlO_4(s)+2Li_2CO_3(s)\}$ were measured using Knudsen effusion quadrupole mass spectrometry (KEQMS). Solid-state galvanic cell technique based on calcium fluoride electrolyte was used to determine the standard molar Gibbs energies of formations of these aluminates. The standard molar Gibbs energies of formation of these three aluminates calculated from KEQMS and galvanic cell measurements were in good agreement. Heat capacities of individual ternary oxides were measured from 127 to 868 K using differential scanning calorimetry. Thermodynamic tables representing the values of $\Delta_fH^0(298.15\,K)$, $S^0(298.15\,K)$ $S^0(T)$, $C^0_p(T)$, $H^0(T)$, $\{H^0(T)-H^0(298.15\,K)\}$, $G^0(T)$, $\Delta_fH^0(T)$, $\Delta_fG^0(T)$ and free energy function (fef) were constructed using second law analysis and FACTSAGE thermo-chemical database software.

1. Introduction

Lithium–aluminum–oxygen system has four ternary oxides: $LiAl_5O_8(s)$, $LiAlO_2(s)$, $Li_3AlO_3(s)$ and $Li_5AlO_4(s)$; however, $Li_3AlO_3(s)$ is reported to be unstable above 670 K [1,2]. Among these oxides, $LiAlO_2(s)$ has gained importance for its potential use as breeder material in the irradiation blanket for future nuclear fusion reactors due to its chemical and thermal stability as well as less radiation damage [3]. This oxide exists in three possible allotropes, hexagonal α-$LiAlO_2$ up to 673 K, monoclinic β-$LiAlO_2$ from 673 to 1073 K and tetragonal γ-$LiAlO_2$, the most stable form at temperature greater than 1073 K. This aluminate is also used as an inert and non-conductive ceramic matrix to contain molten carbonate electrolyte between the anode and the cathode of molten carbonate fuel cells due to its high mechanical and thermal stability [3–5]. This aluminate is also expected to be less reactive with cladding materials presently used in fusion reactors due to lower vapor pressures and higher melting points than solid Li_2O. Many researchers have carried out the preparation, decomposition and thermal studies of $LiAlO_2(s)$ [6,7] but studies on other aluminates in Li–Al–O system are very scarce. Ikeda et al. [1] have studied the vaporization and thermo-chemical stability of lithium aluminates using high-temperature Knudsen effusion mass spectrometry. Many researchers have reported the enthalpy and heat capacity values of $LiAlO_2$ from 298 to 1700 K [8]. Kleykamp [8] has reported the heat capacity of $LiAlO_2(s)$. In this study, thermodynamic properties of $LiAl_5O_8(s)$, $LiAlO_2(s)$ and $Li_5AlO_4(s)$ were determined using Knudsen effusion quadrupole mass spectrometry (KEQMS), solid-state galvanic cell based on CaF_2 solid electrolyte and differential scanning calorimetry (DSC).

2. Experimental

2.1. Materials preparation

Ternary oxides, $LiAl_5O_8(s)$, $LiAlO_2(s)$ and $Li_5AlO_4(s)$, were prepared using conventional solid-state reaction route using pre-heated powder samples of $Li_2CO_3(s)$ and $Al_2O_3(s)$ (LEICO Industries Inc., mass fraction 0.9999). The individual powders were weighed according to their stoichiometric ratios and mixed homogeneously using an agate mortar and pestle and the resultant powder samples were pelletized using a steel die at a pressure of 100 MPa. The pellets were initially heated at 900 K for 50 h in air in a re-crystallized alumina crucible and then cooled, reground and again pelletized. These pellets were then heated at

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1150 K for 48 h. The resultant samples were characterized by X-ray powder diffraction (XRD) technique using DIANO XRD with Cu-$K\alpha$ radiation and graphite monochromator and found to be pure crystalline phases of $LiAl_5O_8$(s), γ-$LiAlO_2$(s) and β-Li_5AlO_4(s).

Three-phase mixtures {$LiAl_5O_8$(s)+Li_2CO_3(s)+5Al_2O_3(s)}, {$LiAl_5O_8$(s)+2Li_2CO_3(s)+5$LiAlO_2$(s)} and {$LiAlO_2$(s)+2Li_2CO_3(s)+Li_5AlO_4(s)} for KEQMS were prepared by homogeneously mixing the individual pre-heated compounds in stoichiometric ratios and pelletized using a steel die and then sintered at 700 K to remove moisture. The sintered pellets were broken into small pieces and loaded inside the Knudsen cell.

According to the phase relations in the Li_2O–Al_2O_3 pseudo-binary system, phase mixtures: {2$LiAl_5O_4$(s)+5Al_2O_3(s)+2LiF(s)}, {5$LiAlO_2$(s)+$LiAl_5O_4$(s)+4LiF(s)} and {Li_5AlO_4(s)+$LiAlO_2$(s)+4LiF(s)} were also prepared by homogenously mixing the pre-heated individual powders and pelletized using a steel die at a pressure of 100 MPa and sintered at 800 K for 10 h under moisture and hydrogen-free oxygen atmosphere. These sample pellets were then used for solid-state galvanic cell experiments. Powder samples of $LiAl_5O_8$(s), $LiAlO_2$(s) and Li_5AlO_4(s) were used for DSC.

2.2. Knudsen effusion quadrupole mass spectrometry (KEQMS)

The Knudsen effusion mass spectrometric technique is one of the most informative methods for vaporization processes and thermodynamic properties of high-temperature systems. Generally, for thermodynamic measurements, traditional magnetic sector mass spectrometer attached to Knudsen effusion system is preferable among quadrupole and time-of-flight mass spectrometers. Murray et al. [9] have shown that thermodynamic data obtained by Knudsen effusion technique using magnetic sector spectrometer and quadrupole mass spectrometer are in good agreement for pure chromium and chromium–silicon samples. However, quadrupole mass spectrometer has no significant advantages over magnetic mass spectrometer but they are very compact and relatively inexpensive. Stolyarova et al. [10] have reported that quadrupole mass spectrometer coupled to Knudsen cell can effectively be used for thermodynamic studies at high temperature.

In this study, a residual gas analyzer (RGA) coupled to Knudsen effusion system was used for equilibrium partial pressure measurements. An RGA is a quadrupole mass spectrometer in which the ionizer is immersed in the gas to be analyzed, and the ionizer is characterized by an open construction in which the gas may enter and leave in all directions. It is assumed that the gas is homogenous and that changes in the gas density with time occur slowly enough such that the instrument is always in equilibrium with the gas. This instrument can be used to identify the kind of molecules present in the gaseous phase and, when calibrated, can be used to determine concentrations or partial pressures [11–13] of individual species.

The KEQMS used in this study is an in-house designed Knudsen vacuum chamber and arranged in such a way that it allows reciprocally perpendicular molecular beam from the Knudsen effusion cell. The Knudsen vacuum chamber was heated to the desired temperature using resistance heater. The temperature near the Knudsen cell was measured using a pre-calibrated (ITS-90) chromel–alumel thermocouple. The Knudsen cell used was made of 15 mol% calcia stabilized zirconia (CSZ) with a thin cylindrical orifice of dia 0.8 mm and height 0.2 mm at the centre of the lid. This setup is used only for partial pressures measurements of permanent gaseous species such as CO, O_2, N_2, CO_2, etc. and not for condensable vapor species. A shutter is placed between the ionizer and the Knudsen effusion chamber such that it does not come into the path of the molecular flow. The shutter isolates the Knudsen effusion cell while recording the background signal.

The detected signal (I_i^+) measured using Faraday cup detector is related to the partial pressure of the vapor species (p_i) by

$$p_i = K_{\text{inst}} I_i^+ T/(\sigma_i a_i) \tag{1}$$

where K_{inst} is the instrumental constant, I_i^+ is the measured ion current in ampere, T is the absolute temperature near the Knudsen cell, σ_i is the electron impact cross-section and a_i isotopic abundance of the specific ion. Eq. (1) can be represented as

$$\ln p_i = \ln K_{\text{inst}} + \ln(I_i^+ T) - \ln \sigma_i - \ln a_i \tag{2}$$

For permanent gaseous species such as CO_2 at mass, $m = 44$, $\ln \sigma = -45.52$ at 30 eV [14] and the isotopic abundance as 100%, Eq. (2) can be expressed as

$$\ln P_i = \ln K_{\text{inst}} + \ln(I_i^+ T) + 45.52 \quad (\text{for } i = \text{CO}_2) \tag{3}$$

2.2.1. Calibration of KEQMS

Prior to calibration of the instrument, the background signals were monitored by heating the Knudsen chamber with empty Knudsen cell at different temperatures from ambient to 1161 K at pressure level $\sim 1\times10^{-5}$ Pa. The background signals as a function of temperature are shown in Fig. 1. It is evident from the figure that the background signals corresponding to H_2^+, N_2^+, CO^+ and CO_2^+ do not change appreciably with change in temperature. During experiments, the actual signals were obtained by subtracting the ion intensities due to background.

The instrument calibration constant (K_{inst}) was determined by measuring the ion intensities of CO_2^+ over the phase mixtures of {$CaCO_3$(s)+CaO(s)}, {$SrCO_3$(s)+SrO(s)}, {$BaCO_3$(s)+BaO(s)} and {Li_2CO_3(s)+Li_2O(s)}. Three different ionization energies (30, 50 and 70 eV) were used to measure the ion intensities of CO_2^+ to check the linearity of pressure measurements. However, 30 eV is sufficient to ionize all types of gaseous molecules; hence, the actual experiments were carried out at ionization energy of 30 eV. Prior to actual measurement, a particular phase mixture (mass ~1 g) was loaded inside the Knudsen cell and then heated at 700 K for 4 h under high vacuum to remove the moisture and other unwanted gaseous species.

2.2.2. Partial pressure measurements of CO_2(g) over equilibrium phase mixtures

Huang et al. [15] have reported the thermodynamic data of $Na_4Fe_6O_{11}$(s) by measuring the partial pressure of CO_2(g) over {2Na_2CO_3(s)+3Fe_2O_3(s)} phase mixture using Knudsen effusion mass spectrometry from 918 to 1013 K. Similar approach was adopted in this study to determine the Gibbs energies of formation of $LiAl_5O_8$(s), $LiAlO_2$(s) and Li_5AlO_4(s) by measuring the partial pressure of CO_2(g) over the equilibrium phase mixtures {$LiAl_5O_8$(s)+Li_2CO_3(s)+5Al_2O_3(s)}, {$LiAl_5O_8$(s)+2Li_2CO_3(s)+5$LiAlO_2$(s)} and {$LiAlO_2$(s)+2Li_2CO_3(s)+Li_5AlO_4(s)}.

The ion intensities of CO_2^+ over these equilibrium phase mixtures were measured using KEQMS. For each measurement, two sets of experiments were carried out and the ion intensities for other gaseous species were in background level during the measurement. Subsequently, partial pressures of carbon dioxide, $p(CO_2)$ over the phase mixture were obtained using Eq. (3). After the mass spectrometric measurements, the resultant phase mixtures were analyzed by XRD technique and found to be the mixture of corresponding lithium aluminate, lithium carbonate and alumina. Therefore, it was assumed that the following equilibrium reactions were established inside the Knudsen cell under experimental conditions:

$$Li_2CO_3(s) + 5Al_2O_3(s) = 2LiAl_5O_8(s) + CO_2(g) \tag{4}$$