Study of phase equilibria in LiCl-KCl-PrCl$_3$ pseudo-ternary system

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A B S T R A C T

The pseudo-ternary phase diagram of LiCl-KCl-PrCl$_3$ has been investigated to understand the interaction of PrCl$_3$ with LiCl-KCl molten salt medium by differential thermal analysis (DTA) technique and characterization of the coexisting phases in the solid state using X-ray diffraction (XRD). The results of these experiments showed that the LiCl-KCl-PrCl$_3$ system consists of two quasi-ternary sections, namely (1) LiCl-KCl-K$_2$PrCl$_5$ section which has a ternary eutectic temperature of 591 $\pm$ 4 K and approximate eutectic composition of 55.1 mol% LiCl-39.6 mol% KCl-5.3 mol% K$_2$PrCl$_5$ and (2) LiCl-K$_2$PrCl$_5$-PrCl$_3$ section having a ternary eutectic temperature of 654 $\pm$ 7 K and approximate eutectic composition of 46.8 mol% LiCl-32.2 mol% K$_2$PrCl$_5$-21.0 mol% PrCl$_3$. A pseudo-ternary peritectic reaction at 762 $\pm$ 1 K is observed at 22.3 mol% LiCl-39.6 mol% KCl-38.1 mol% K$_2$PrCl$_5$. Isothermal sections at selected temperatures and the polythermal liquidus projection with isothermal contours are drawn over the ternary phase field.

1. Introduction

Molten LiCl-KCl eutectic is used as liquid electrolyte medium in the pyrochemical reprocessing of spent metallic fuel [1]. In this process, spent metallic fuel is dissolved in molten salt in the soluble chloride form and the fuel materials are selectively separated from fission products (FPs) by electrorefining [2,3]. Spent metallic fuel primarily includes actinides, rare earth elements, noble metals, alkali and alkaline earth elements, etc. The buildup of the anodically dissolved fission products in the molten salt medium with time, could lead to the formation of high melting ternary or higher order compounds and result in the progressive increase of the liquidus temperature of the salt medium [4]. The increase in liquidus temperature can influence the pyrochemical process parameters adversely. Praseodymium being one of the major FP elements [5], it is necessary to understand the interaction of PrCl$_3$ in the LiCl-KCl medium and hence the study of phase equilibria in the LiCl-KCl-PrCl$_3$ pseudo-ternary system is essential.

2. Literature survey

The LiCl-KCl binary phase diagram is a simple eutectic system. Korin and Soifer [6] reported the binary eutectic temperature as 627.5 K and the composition as 58.7 mol% LiCl and 41.3 mol% KCl in this system, based on their study using differential scanning calorimetry and also considering the data reported earlier by several authors. Basin

et al. [7] studied the phase diagram of LiCl-KCl system by thermal analysis technique and combining the method of oscillation phase analysis [8]. They reported the eutectic temperature as 625 K and composition as 58.2 mol% LiCl and 41.8 mol% KCl. Liquidus temperatures, eutectic temperature, and composition reported by Basin et al. [7] are in close agreement with those reported by previous investigators. In the present work, the phase diagram reported by Basin et al. [7] is considered for the construction of the pseudo-ternary phase diagram of the LiCl-KCl-PrCl$_3$ system. The LiCl-KCl binary phase diagram reported by Basin et al. [7] is showed in Fig. 1.

Kim and Okamoto [9] investigated the LiCl-PrCl$_3$ binary phase diagram using differential thermal analysis (DTA) and X-ray diffraction (XRD). They reported this phase diagram to be a simple eutectic type having the eutectic temperature as 737 $\pm$ 1 K and the composition as 30.6 mol% PrCl$_3$ – 69.4 mol% LiCl. Earlier, Qiao et al. [10,11] investigated this system using DTA. They further assessed and optimized this binary system. They reported the system as simple eutectic having a eutectic temperature of 739 K and eutectic composition of ca. 30 mol% PrCl$_3$ – 70 mol% LiCl. Gong et al. [12] carried out thermodynamic optimization of this binary system by PARROT program using the reported experimental data [9–11]. The liquidus temperatures reported by Qiao et al. [10,11] are about 30–40 K lower in the PrCl$_3$ rich region than the values reported by Kim and Okamoto [9]. Qiao et al. [10,11] determined the liquidus temperatures during the cooling runs of DTA experiments. However, the rare earth containing salt systems are known for supercooling. Hence, the lower values of the
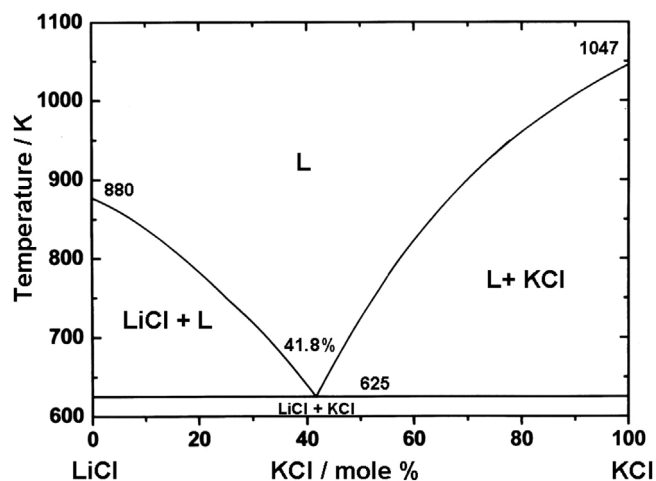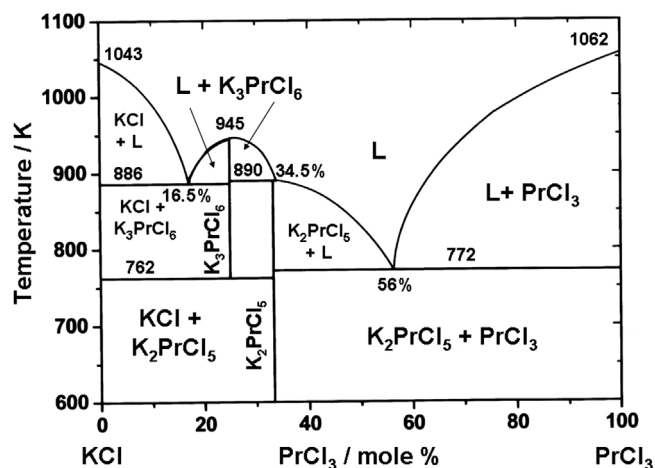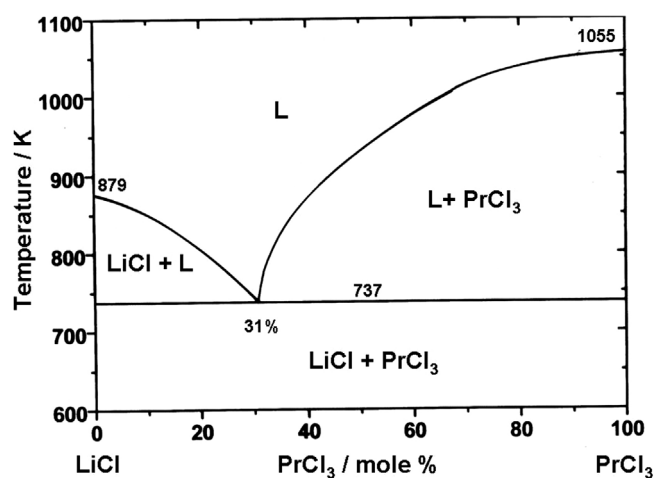
Fig. 1. LiCl–KCl pseudo binary phase diagram [7].

Fig. 2. LiCl–PrCl$_3$ pseudo binary phase diagram [9].

Fig. 3. KCl–PrCl$_3$ pseudo binary phase diagram [13].

the DSC analysis of five samples containing < 17 mol% PrCl$_3$, they reported the ternary eutectic temperature at 625 K. Further, they characterized LiCl and K$_2$PrCl$_5$ by XRD for the samples containing > 17 mol% PrCl$_3$. They observed the solidus temperature as 681 K based on the DSC analysis of three samples. They reported a step increase in the solidus and liquidus temperatures for the sample containing 17 mol % PrCl$_3$ (50.9 mol% LiCl- 36.1 mol% KCl – 17 mol%PrCl$_3$), which falls on the isopleth connecting LiCl-KCl $_{eutectic}$ and PrCl$_3$ and attributed this to the existence of the LiCl and K$_2$PrCl$_5$ pseudo-binary line. This implies that the compound K$_2$PrCl$_5$ melts congruently; and must undergo eutectic reaction with K$_3$PrCl$_6$, also. In contrast, Seifert et al. [13] reported the peritectic decomposition of K$_2$PrCl$_5$ at 890 K, which implies that LiCl and K$_2$PrCl$_5$ are expected to form a non-binary join instead of a pseudo-binary eutectic. In view of the above discrepancies reported in literature, the LiCl-KCl-PrCl$_3$ ternary phase diagram needs a thorough investigation. Further, data on the primary and secondary crystallization temperatures as well as the crystallizing phases and liquidus temperatures over the ternary phase field are not available. In this context, a detailed phase diagram study on the LiCl-KCl-PrCl$_3$ system was taken up in the author's laboratory by DTA technique supported by XRD characterization of the coexisting phases in the solid state.

3. Experimental

3.1. Materials

Details of the chemicals used in the study are given in Table 1. Anhydrous lithium chloride (99.995% pure, packed in sealed glass ampoules under argon, M/s Alfa Aesar, USA) and praseodymium chloride (99.99% pure, packed in sealed glass ampoules under argon, M/s Aldrich, Germany) were used in this work. Anhydrous potassium chloride (99.995% pure on the metals basis, M/s Alfa Aesar, Germany) was further purified by heating it up to its melting point in a quartz crucible, which in turn was placed inside a quartz vessel in a stream of dry HCl saturated argon gas. The details of salt purification are described elsewhere [16]. The purified salt was placed inside a secondary containment vessel and stored inside an argon atmosphere glove box used for handling molten sodium. The purity of these starting compounds, viz. LiCl, KCl, and PrCl$_3$ were examined by carrying out DTA studies. Sharp endotherms in the DTA traces of LiCl, KCl, and PrCl$_3$ were obtained and the melting points of LiCl, KCl and PrCl$_3$ were found to be 878 K, 1045 K, and 1051 K, respectively. The observed melting points of LiCl, KCl and PrCl$_3$ were in agreement with the data reported in the literature [7,9–13,17–21].

liquidus temperatures may probably be attributed to the supercooling effect in the DTA samples. Therefore, the phase diagram reported by Kim and Okamoto [9] is considered as more accurate and used in the present ternary phase diagram construction. The LiCl-PrCl$_3$ binary phase diagram reported by Kim and Okamoto [9] is showed in Fig. 2.

Seifert et al. [13] reported the KCl-PrCl$_3$ binary phase diagram. It is the only work available in the literature. They reported two ternary compounds, viz. K$_2$PrCl$_5$ and K$_3$PrCl$_6$ in this system. The author reported K$_2$PrCl$_5$ to be stable from 573 K and undergoes peritectic decomposition to K$_3$PrCl$_6$ and liquid containing 34.5 mol% PrCl$_3$ – 65.5 mol% KCl at 890 K. According to them, it undergoes a eutectic reaction with PrCl$_3$ at 772 K having a eutectic composition of 56 mol% PrCl$_3$ – 44 mol% KCl. They also reported K$_3$PrCl$_6$ to be stable above 762 K and to be congruently melting. They reported a eutectic reaction between K$_3$PrCl$_6$ and KCl at 886 K and the eutectic composition as 16.5 mol% PrCl$_3$ – 83.5 mol% KCl. Gaune-Escard et al. [14] observed the formation temperature of K$_3$PrCl$_6$ as 768 K from differential scanning calorimetry studies and reported it to be congruently melting at 944 K. The KCl-PrCl$_3$ binary phase diagram reported by Seifert et al. [13] is showed in Fig. 3.

Literature data on the LiCl-KCl-PrCl$_3$ system is limited. Nakamura and Kurata [15] reported the partial phase diagram of the isopleth connecting LiCl-KCl $_{eutectic}$ and PrCl$_3$ (up to 25 mol% PrCl$_3$) by investigations involving thermal analysis, visual observation, electro-motive force measurement and powder X-ray diffraction methods. For the samples containing < 17 mol% PrCl$_3$, they identified LiCl, KCl, and K$_2$PrCl$_5$ as coexisting phases below the solidus temperature. Based on