THERMODYNAMIC PROPERTIES OF THE MELT OF THE NaI – CeI_3 SYSTEM

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Introduction

In the work presented here the determination of the chemical activities of the components NaI and CeI_3 for the complete composition range of the NaI-CeI_3 system is described as well as the partial pressures of the identified gaseous species.
The obtaiened thermochemical data are important for fundamental research for the chemistry of molten salts and applied physical chemistry for the development of metal halide lamps. Metal halide lamps have achieved a widespread acceptance due to their high luminous efficiency and good colour quality. At the beginning of their developement these lamps were used for outdoor lighting e.g. the lighting of sportsfields. Since several years metal halide lamps are also used for indoor lighting and for the head lights of automobiles. The lamps contain a salt melt which in part vaporize under operating conditions. Important constituents of the melt are for example DyI_3, CeI_3, TmI_3, and NaI.

Experimental

Twelve NaI-CeI_3 samples with the compositions x_{NaI}= 0, 0.201, 0.351, 0.400, 0.496 (two independent runs), 0.554, 0.601, 0.700, 0.800, 0.898, and 1 were prepared by melting together NaI(s) and CeI_3(s) under argon atmosphere in sealed quartz ampoules. The pure salts were supplied by Alfa Aesar, USA with a purity of 99.9 mass% for CeI_3 and 99.5 mass% for NaI.

Results

The vapor of the system NaI-CeI_3 was investigated under equilibrium conditions in the temperature range from 728 K to 923 K by using Knudsen Effusion Mass Spectrometry with a one compartment Knudsen cell. The partial pressures of the abundant species were determined. The essential identified gaseous species are listed in Table 1. Na^+ is generated by fragmentation from the neutral precursors NaI(g) and $NaCeI_4$(g). For all of the investigated compositions the temperature dependence of the partial pressures of the gaseous species were determined from the measured ion intensities. Figure 1 shows the partial pressures of the vaporizing species over the x_{NaI}= 0.5 mixture. Based on the partial pressure measurements the thermodynamic activities were determined for four different temperatures (823K, 873K, 898K, 923K). Figure 2 shows the thermodynamic activieties for NaI(l) and CeI_3(l) as function of the melt composition at 923K. The vertical lines represent the phase boundaries between the two phase fields and the full miscibility range. Figure 3 shows the same dependency for 1173 K, which has been determined by extrapolating the temperature dependences of the thermodynamic activity for the different compositions. Comparing the plots in figure 2 and figure 3 points up the shift of the miscibility range of the liquid components NaI(l) and CeI_3(l) as a function of temperature, which is consistent with the phase diagram. The latter has also been determined by us using Differential Thermal Analysis (DTA). From the activities the enthalpies of mixing were determined.

Reactands in Knudsen Cell
NaI(l) + CeI_3(l)
T-Range
728 K – 923 K
Identified Ions in Mass Spectrum
Na^+, NaI^+, Na_2I^+, ($Na_2I_2^+$) Ce^+, CeI^+, CeI_2^+, CeI_3^+ ($NaCeI^+$), $NaCeI_2^+$, $NaCeI_3^+$, $NaCeI_4^+$ $Na_2CeI_4^+$

Table 1: Ion Species in the vapor of NaI-CeI_3 (50/50)

Fig. 1: Partial pressures above a mixture of molten NaI-CeI_3 (50/50)

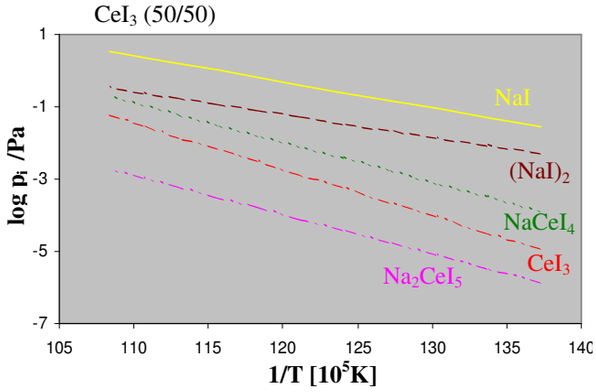

Fig. 2: Measured activities in the system NaI-CeI_3 at 923K

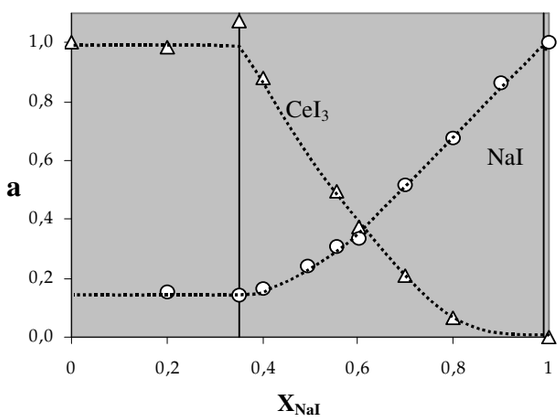

Fig. 3: Activities at 1173K, extrapolated from the temperature dependence of the measured values