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Thermodynamic determination and assessment of the CsF-ThF$_4$ system

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ABSTRACT

In this study we present a comprehensive thermodynamic description of the binary CsF-ThF$_4$ system. The phase equilibria of several intermediate compositions in this system have been determined using the DSC technique combined with a post-analysis using powder X-ray diffraction. Considering all the novel experimental data, a thermodynamic model for the CsF-ThF$_4$ system has been developed for the first time using the Calphad approach. The present model reproduces very well the measurements performed. Knudsen effusion mass spectrometry (KEMS) has further been used to investigate the vapour pressure over the molten CsF-ThF$_4$ salt and to determine the thermodynamic activities of CsF and ThF$_4$ in the liquid solution. As part of this study, the vaporization of pure CsF was examined and the results were compared with the literature showing a good agreement. Next, the vapour pressure of CsF-ThF$_4$ in the liquid solution was investigated by measuring three samples with compositions X ThF$_4$ = (0.4, 0.6, 0.8) mol/mol. A strong negative deviation from Raoult's law was observed for both species, more evident in case of CsF, and a good agreement with the predictions of our thermodynamic model was found. This article is a prerequisite for the assessment of the ternary LiF-CsF-ThF$_4$ system.

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1. Introduction

The molten salt reactor (MSR) was selected along with 5 other concepts as one of the most promising nuclear reactor types for the future fission reactor technologies by the Generation IV International Forum [1]. The nuclear fuel in this design is dissolved in a carrier salt and circulated in the core, therefore omitting the need for fuel rods and allowing higher temperature and therefore higher thermal efficiency. In addition, the design can be coupled with a thorium fuel cycle for a sustainable energy production, thorium being three times more abundant on Earth than uranium [2]. Current research efforts in Europe are focused on a ^{7}LiF-ThF$_4$ – UF$_4$ – PuF$_3$ liquid fuel for a fast spectrum reactor [3]. The present work reports the description of the CsF-ThF$_4$ system as ^{137}Cs is one of the major fission products, with a high yield of 7% [4]. Cesium has a high contribution to the environmental burden in case of a nuclear accident, and its potential release into the environment is a subject of primary concern for the safety of the general public. The knowledge of the phase equilibria during normal operating and off-normal conditions, and a thorough understanding of the release mechanism of cesium from the salt are therefore crucial. The vapour pressure indeed determines the driving force for radioactivity release in case of an accident with uncontrolled temperature increase. Furthermore, the reactor salt is a multi-component salt, optimised to have a lowest liquidus temperature in order to avoid freezing. Any higher evaporation of a component with respect to the others would lead to a change in composition of the fuel mixture and therefore change in its thermodynamic properties. An increase of the melting point could occur, which would result in lowering or even crossing of the safety margin. The only experimental data available to this date for the CsF-ThF$_4$ system are the phase diagram data of Thoma and Carlton [5] and the structural studies of the CsThF$_5$, CsTh$_3$F$_{13}$ and CsTh$_6$F$_{25}$ intermediate compounds by Underwood et al. [35,36,37].

The present work reports for the first time a complete thermodynamic assessment of the CsF-ThF$_4$ binary system, including phase diagram data, vapour pressures, and thermodynamic activities of the liquid solution using differential scanning calorimetry (DSC), X-ray diffraction (XRD) and Knudsen effusion mass spectrometry (KEMS). In addition, the experimental measurements have been used to develop a thermodynamic model for this system using the Calphad method [28,29].

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2. Experimental methods

2.1. Sample preparation

All samples were handled inside the dry atmosphere of an argon-filled glove box because of their high sensitivity to water and oxygen. The oxygen and moisture impurity content in this box was long-term under 1 ppm for oxygen and under 2 ppm for water. Samples of various compositions of the CsF-ThF_4 system were prepared from commercial CsF and in-house prepared ThF_4 end-members. The ThF_4 material was synthesized from oxide by the fluorination process at 873.15 K under argon flow. The thorium dioxide was obtained from thorium nitrate solution (available from JRC-Karlsruhe stock) by precipitation of thorium by oxalic acid, filtration of the formed oxalate and further thermal decomposition and conversion into oxide at 1073.15 K for 4 h under dynamic air atmosphere [6]. The conversion of oxides into fluorides is achieved by use of pure HF gas, where the following reaction is taking place [7].

$$ThO_2 + 4HF \rightarrow ThF_4 + 2H_2O \tag{1}$$

The purity of the starting material was assessed using differential scanning calorimetry and X-ray diffraction. The result obtained for ThF_4 (T_M = 1385.65 K) was in close agreement with the literature data (T_M = 1384.15 K) [8] confirming high purity of the starting material. To remove residual moisture from the commercial CsF, a drying procedure was applied for several hours at 673 K under argon flow using the flow rate of 0.5 L/min at 1 bar. The provenance and purity of the starting materials is shown in Table 1.

2.2. Differential scanning calorimetry

The melting points and the phase equilibria points were examined using the differential scanning calorimeter (DSC) detector of type SETARAM MDHTC96. The equipment consists of a furnace for heating and a detector for the measurement of the heat flow difference between sample and reference crucible. The reference crucible is kept empty and both crucibles are surrounded by a series of S-type thermocouples [9,10].

The alkali fluoride vapours become very corrosive at elevated temperatures and in order to avoid the damage to the platinum thermocouples in the calorimetric device, the encapsulation technique based on stainless steel crucible with inert Ni liner developed at JRC-Karlsruhe was used [11]. The whole experimental chamber is under argon atmosphere in order to avoid oxidation of the stainless steel container at high temperatures. Calibration of the temperature was applied to all measurements performed by DSC to compensate for the thermal gradient and time delay caused by the penetration of the heat through the crucible wall to the sample during the dynamic regime. The most frequent DSC calibrants are metals with high purity of known melting temperatures. Indium, aluminium, gold, lead, silver, copper, zirconium and tin were chosen as calibrants since they all have different melting points. These standard materials have been heated up at different rates from 2 K/min to 12 K/min, the melting temperatures have been measured and the difference between the measured and the theoretical melting temperature has been plotted as a function of the heating rate. These points were then fitted with a linear fit. The intercept and slope of this fit were further plotted as a function of the melting temperatures for all calibrants and fitted to obtain the full calibration relation.

The DSC measurements consisted of two cycles with 10 K/min heating ramp up to 1473 K, and successive cooling down to 373 K, with cooling rate of 10 K/min. The phase equilibria data were derived from the onset temperature from the second cycle, the first cycle allowing mixing of the end-members in the appropriate ratios. The DSC has a low uncertainty of ± 2 K, however, due to weak signals, the standard uncertainty on the temperature for the phase equilibria measurements was estimated to be ± 10 K.

2.3. Powder X-ray diffraction

The intermediate compound compositions in the CsF-ThF_4 phase diagram were characterized at room temperature by X-ray diffraction after the successive cycles in the DSC. The measurements were carried out using a Bruker D8 Bragg–Brentano X-ray diffractometer mounted inside a glovebox and equipped with a curved Ge monochromator (111), a copper tube (40 kV, 40 mA), and a LinxEye position sensitive detector. The data were collected by step scanning in the range $10^\circ < 2\theta < 120^\circ$, with an integration time of about 8 h, a count step of 0.02° (2θ), and a dwell of 5 s/step. Structural analysis was performed using the Powder Cell software (Version 2.4) and by Le Bail fit using the Fullprof2k suite [12].

2.4. Knudsen effusion mass spectrometry

Knudsen Effusion Mass spectrometry (KEMS) is a powerful tool for the determination of the thermodynamic properties at high temperatures based on the equilibrium between condensed and gaseous phases. It can be used for identification of the gas composition and its vaporising behaviour as a function of temperature by means of the conversion of the detected spectral ion intensity data into the corresponding vapour pressures of the species in the gaseous phase. This method can further be used for determination of other thermodynamic properties such as sublimation enthalpies, thermodynamic activities, and ionisation energies of gaseous species.

The KEMS apparatus used in this study is installed in a glove box to permit the handling of radioactive materials. The only commercially obtained part of the apparatus is the mass spectrometer. The KEMS system consists of a Knudsen effusion cell with tungsten crucible, which is placed in a vacuum chamber (10^{-6} -10^{-7} mbars), coupled to a QMG 422 quadrupole mass spectrometer from Pfeiffer Vacuum. Within the cell, in which the sample and the reference material are placed, the equilibrium is achieved between the gas and condensed phases. The cell is heated by tungsten coil heating elements under constant rate, while appropriate thermal insulation is achieved by tungsten shields. The cell temperature is externally controlled by a IMPAC IS12 pyrometer calibrated prior to the experiment based on melting points of known standard metals (Cu, Pt, Ag) showing at that point a plateau on the MS intensity curve. The uncertainty of the pyrometer is ±10 K [13,14]. Tungsten was chosen for the furnace heating elements as well as the material of the crucible due to its high melting point and negligible reactivity with the sample. The beam of

Table 1
The provenance and purity of all materials used in this study. DSC: Differential scanning calorimetry, XRD: X-ray diffraction.

Material	Supplier	Initial Weight Fr. Purity	Purification Method	Final Weight Fr. Purity	Analysis Method
CsF	Alfa Aesar	0.999	Drying	0.999	–
ThF_4	In-house made	–	Fluorination	0.999	DSC/XRD

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