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NaCl-ThCl₄-PuCl₃**

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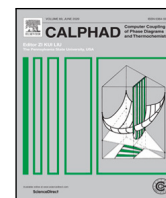
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A promising fuel for fast neutron spectrum Molten Salt Reactor: NaCl-ThCl₄-PuCl₃

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ABSTRACT

Chloride salts are considered a good alternative to fluoride salts as fuel carrier in the Molten Salt Fast Reactor concepts. The NaCl–ThCl₄–PuCl₃ fuel salt solution seems very promising, with low melting temperature eutectic compositions, and the potential to be used in a breeder and burner type of reactor design. This work focuses on the first thermodynamic modeling assessment of the ThCl₄–PuCl₃ binary system and the NaCl–ThCl₄–PuCl₃ ternary system, using the CALPHAD (Computer Coupling of Phase Diagrams and Thermochemistry) method and the quasichemical formalism in the quadruplet approximation. The investigated system shows potential for a high flexibility with respect to composition at operating temperatures, which can be beneficial to accommodate the requirements on other essential fuel properties (e.g. neutronic and thermo-hydraulic).

1. Introduction

Fast neutron spectrum Molten Salt Reactors (MSRs) are considered very promising for the production of energy in the future. MSRs give the access to a more compact and safer source of nuclear energy thanks to the use of a molten salt as nuclear fuel and coolant, that shows a number of advantageous physico-chemical properties. Fast MSR designs are well adapted to operate with a thorium bearing fuel (i.e. with fertile material), and offer a potential solution to recycle and transmute some of the large stock of plutonium and minor actinides (e.g. Np, Am, Cm) accumulated over the years in the spent fuel of the current generation of Light Water Reactors or in high-enriched military stockpiles [1]. To this date, fluoride salts are considered for most of MSR designs including for instance the LiF–ThF₄–²³³UF₄ salt mixture of the European Molten Salt Fast Reactor (MSFR) [2]. This is largely due to the experience gained during the Molten Salt Reactor Experiment (MSRE) carried out between 1965 and 1969 at the Oak Ridge National Laboratory [3], which was the first thorough demonstration of a civilian Molten Salt test Reactor. Recently, the interest in the use of chloride salts is also rising as an appealing alternative for fast neutron spectra reactors [4]. The latter allow in particular operation with fuel at lower temperatures compared to reactors operated on a fluoride fuel salt mixture [5].

Examples of chloride salt mixtures under consideration are NaCl–PuCl₃ [6], or NaCl–PuCl₃–MgCl₂ [7]. The chloride fuel salt mixture NaCl–ThCl₄–PuCl₃ is a still relatively unexplored, but an appealing option. Previous experimental characterization by Vorobei et al. has

demonstrated relatively low melting temperatures (598 K and 603 K, respectively) for the eutectic 46.5 NaCl - 35 ThCl₄ - 18.5 PuCl₃ and 58.5 NaCl - 23 ThCl₄ - 18.5 PuCl₃ compositions [8]. Furthermore, this solution shows multiple advantages, related to a rich neutron economy [9] and the intrinsic value of its three end-member compounds.

The sodium chloride (NaCl) based salt is a quasi unlimited resource, commonly called rock salt; it is available in multiple geological deposits and in the ocean, and represents an interesting alternative to lithium, a scarce resource already in high demand [10]. As a fertile isotope, thorium-232 is considered for the fuel cycle of the next generation of nuclear reactors (the Generation IV systems). The use of thorium is particularly interesting for countries with limited access to uranium resources and/or which have abundant sources of thorium such as India [10]. Moreover, the associated fuel cycle produces less long-lived actinide waste compared to the traditional U/Pu fuel cycle. Plutonium used as fissile material is considered in multiple Generation IV designs as experience has already been gained in current Light Water Reactors operating with MOX (Mixed-Oxide) fuel and in prototype and demonstration Sodium-cooled Fast Reactors such as the Russian BOR-60, Japanese Monju Reactor or French Superphenix [11–13]. It has intrinsic fissile quality, particularly ²³⁹Pu, which shows a better neutron economy than the uranium isotopes [14]. The global stockpile of separated plutonium (weapons grade and civilian) was estimated at (505 ± 10) metric tons worldwide in 2014 by the International Panel

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on Fissile Materials [1]. Integration and re-use of plutonium in Molten Salt Reactor concepts is thus an appealing option, including for the recycling of future plutonium waste streams generated by the current Light Water Reactors.

A thermodynamic model the NaCl-ThCl₄-PuCl₃ ternary system has not yet been reported in the literature. Thermodynamic assessments of the three binary constituting sub-systems (NaCl-PuCl₃, NaCl-ThCl₄ and ThCl₄-PuCl₃) are reported in this work followed by an extrapolation and optimization of the ternary system based on available phase diagram information. The excess Gibbs energy of the liquid solution has been expressed using the modified quasichemical formalism in the quadruplet approximation.

2. Thermodynamic modeling

The thermodynamic models reported herein were developed using the FactSage software version 8.2 and the OptiSage Optimizer [15], and are based on the CALPHAD (CALCulation of PHase Diagrams) method [16,17]. The optimization of the different parameters of the Gibbs energy functions for all phases present in the systems was based on available phase diagram and mixing enthalpy data [8,18–23].

2.1. Gibbs energies of pure compounds

The Gibbs energy of pure compounds is expressed by:

$$G(T) = \Delta_f H_m^o(298.15) - S_m^o(298.15) \cdot T + \int_{298.15}^T C_{p,m}(T) dT - T \int_{298.15}^T \frac{C_{p,m}(T)}{T} dT \quad (1)$$

where $\Delta_f H_m^o(298.15)$ is the standard enthalpy of formation and $S_m^o(298.15)$ is the standard entropy of the pure compound at standard pressure and reference temperature 298.15 K. $C_{p,m}$ is the heat capacity expressed as:

$$C_{p,m}(T) = a + bT + cT^2 + dT^{-2} + eT^3 \quad (2)$$

In this work, the thermodynamic data for NaCl(cr,l) were taken from the IVTAN database [24] with an exception for the heat capacity of the liquid phase, which was recently revised by van Oudenaren et al. [25]. The ThCl₄(cr,l) functions were taken from the recommendations by Rand et al. [26] and by Capelli and Konings [27]. The occurrence of a polymorphic transition between an α -ThCl₄, low-temperature metastable tetragonal phase (space group I4₁/a), and a high temperature form β -ThCl₄ (tetragonal, space group I4₁/amd) was observed by Chiotti et al. at 679 K [27,28]. This transition was included by Ocádiz et al. in their thermodynamic assessment of the NaCl-ThCl₄ system [29]. However, the α metastable phase is not apparent in the experimental phase diagram investigations of the latter system, nor that of ThCl₄-PuCl₃ [8]. Only Mason et al. reported its observation when using a very slow cooling rate [30]. The inclusion of this phase in the modeling of ThCl₄-PuCl₃ appeared rather challenging in relation with the existence of a (Th,Pu)Cl₄ solid solution at low PuCl₃ content. Since the extent of such a solid solution is also unknown for the α modification, it was decided not to include the α form in the assessment of the ternary system (Table 1).

As for the only intermediate compound described in this work, Na₂ThCl₆, the Neumann-Kopp approximation was used [31] based on the heat capacities of the end-member compounds, while the other thermodynamic functions were taken from the optimization by Ocádiz et al. of the NaCl-ThCl₄ binary system [29]. PuCl₃(cr,l) functions were selected from the review by Capelli and Konings [27]. The enthalpy of formation and melting point are the very few experimental data available for this compound [32,33]. The standard entropy and heat capacity are based on estimations by comparison with the uranium and lanthanides trichlorides [34–36]. All the thermodynamic data used in this work are summarized in Table 1.

2.2. Solid solution

One solid solution was included in the ThCl₄-PuCl₃ system on the ThCl₄-rich side of the phase diagram (Fig. 3), based on the data of Vorobei et al. [8]. A two-sublattice polynomial model was used to describe the solution, to be consistent with the formalism used for other solid solutions in the JRC molten salt database [38]. In this case, the considered cationic species on the first sublattice are Th⁴⁺ and Pu³⁺, and the anionic species on the second sublattice is Cl-, meaning the end-member compositions correspond to the ThCl₄ and PuCl₃ stoichiometries, respectively. The Gibbs energy function $G(T)$ of the solid solution is described by the equation:

$$G(T) = X_{Th(IV)} \cdot G_{m,Th(IV)}^o + X_{Pu(III)} \cdot G_{m,Pu(III)}^o + X_{Th(IV)} RT \ln X_{Th(IV)} + X_{Pu(III)} RT \ln X_{Pu(III)} + \Delta G_m^{xs} \quad (3)$$

where $G_{m,Th(IV)}^o$ and $G_{m,Pu(III)}^o$ are the molar Gibbs energies of the pure end-members, $X_{Th(IV)}$ and $X_{Pu(III)}$ their site molar fraction, R the universal gas constant and ΔG_m^{xs} is the excess Gibbs energy. The excess Gibbs energy can be expressed by:

$$\Delta G_m^{xs} = \sum_{i,j} y_{Th(IV)}^i \cdot y_{Pu(III)}^j \cdot L_{i,j} \quad (4)$$

where $L_{i,j}$ is an interaction coefficient which can depend on temperature T described by the equation:

$$L_{i,j} = A + BT \quad (5)$$

and where $y_{Th(IV)}$ and $y_{Pu(III)}$ are the equivalent site fractions of the end-member species, described as charge equivalent site fractions. In this case, the equivalent site fractions $y_{Th(IV)}$ and $y_{Pu(III)}$ are defined by:

$$y_{Th(IV)} = \frac{4X_{Th(IV)}}{4X_{Th(IV)} + 3X_{Pu(III)}} \quad (6)$$

$$y_{Pu(III)} = \frac{3X_{Pu(III)}}{4X_{Th(IV)} + 3X_{Pu(III)}} \quad (7)$$

The optimized excess energy parameters, obtained via optimization in the OptiSage - Calphad Optimizer (version 1.0.0) of FactSage and subsequent manual iteration, are given by the following equation:

$$\Delta G_{(Th(IV),Pu(III))Cl}^{xs} = y_{Th(IV)}^2 y_{Pu(III)} \cdot (43699.7 - 43.1384 \cdot T) / \text{J.mol}^{-1} \quad (8)$$

In addition, to avoid the formation of a solid solution on the PuCl₃ rich side of the phase diagram, the Gibbs energy of the PuCl₃ end-member of the solid solution had to be destabilized according to:

$$G_{PuCl_3}(ss) = G_{PuCl_3} + 5000 / \text{J.mol}^{-1} \quad (9)$$

2.3. Liquid solutions

To describe the liquid solution, the modified quasichemical model in the quadruplet approximation was used [39,40]. A quadruplet is defined by two anions and two cations symmetrically dispatched around an axis. Two interactions are considered, the First Nearest Neighbor (FNN) interaction which describes the interaction cation–anion and the Second Nearest Neighbor (SNN) interaction which describes the interactions between the two closest ions in the same sublattice. This model is particularly well adapted for the description of ionic liquids as it allows to choose the composition of maximum short-range ordering in a binary system by varying the ratio between the cation–cation coordination numbers $Z_{AB/ClCl}^A$ and $Z_{AB/ClCl}^B$. Short-range ordering is defined by the quadruplet approximation and includes the SNN interactions between each cation and each anion. In a simple representation

Table 1

Thermodynamic data for end-members and intermediate compound used in this work for the thermodynamic assessment. Standard enthalpy of formation $\Delta_f H_m^\circ$ (298.15 K), standard entropy S_m° (298.15 K) and heat capacity coefficient of pure compounds $C_{p,m}(T/K)/(J.K^{-1}.mol^{-1}) = a + b.T + c.T^2 + d.T^{-2} + e.T^3$. Optimized data are shown in **bold**.

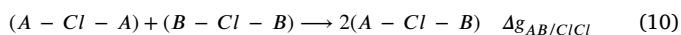
Compound	$\Delta_f H_m^\circ$ (298.15 K) (kJ.mol ⁻¹)	S_m° (298.15 K) (J.K ⁻¹ .mol ⁻¹)	$C_{p,m}(T/K)/(J.K^{-1}.mol^{-1}) = a + b.T + c.T^2 + d.T^{-2}$				T(K)	Ref.
			a	b	c	d		
NaCl _(cr)	-411.260	72.15	47.72158	0.0057	1.21466·10 ⁻⁵	-882.996	298.15–1074	[25,37]
NaCl _(l)	-390.853	83.30249	68	-	-	-	298.15–2500	[25]
PuCl _{3(cr)}	-959.600	161.4	91.412	0.03716	-	27400	298.15–6000	[27]
PuCl _{3(l)}	-931.116	170.46	144	-	-	-	298.15–6000	[27]
ThCl _{4(cr)}	-1186.300	183.499	120.293	0.0232672	-	-615050	298.15–6000	[26,27]
ThCl _{4(l)}	-1149.716	197.71	167.4	-	-	-	298.15–2500	[26,27]
Na ₂ ThCl _{6(cr)}	-2051.540	328.0	215.73616	0.0346672	2.42932·10 ⁻⁵	-616815.992	298.15–1074	[29]

Table 2

Cation–cation and anion–anion coordination numbers of the liquid solution.

A	B	$Z_{AB/ClCl}^A$	$Z_{AB/ClCl}^B$	$Z_{AB/ClCl}^Cl$
Na ⁺	Na ⁺	6	6	6
Th ⁴⁺	Th ⁴⁺	6	6	1.5
Pu ³⁺	Pu ³⁺	6	6	2
Na ⁺	Th ⁴⁺	3	6	2
Na ⁺	Pu ³⁺	3	6	2.4
Th ⁴⁺	Pu ³⁺	3	6	1.09

where A and B are two cations and Cl, the anion, the following reaction is obtained:



where $\Delta g_{AB/ClCl}$ is the parameter of the Gibbs energy change associated with the SNN exchange reaction described as:

$$\Delta g_{AB/ClCl} = \Delta g_{AB/ClCl}^0 + \sum_{i \geq 1} g_{AB/ClCl}^{i0} \chi_{AB/ClCl}^i + \sum_{j \geq 1} g_{AB/ClCl}^{0j} \chi_{BA/ClCl}^j \quad (11)$$

where $\Delta g_{AB/ClCl}^0$ and $g_{AB/ClCl}^{ij}$ are possibly dependent on temperature, but independent of composition, and optimized to fit as best as possible the experimental data available on a given system. The dependence on composition is given by the term $\chi_{AB/ClCl}$ defined as:

$$\chi_{AB/ClCl} = \frac{X_{AA}}{X_{AA} + X_{AB} + X_{BB}} \quad (12)$$

where X_{AA} , X_{AB} and X_{BB} represent the different cation–cation pair fractions. To maintain electro-neutrality in the system, the anion–anion coordination should be determined. The following equation is applied after the selection of cation–cation coordination numbers:

$$\frac{q_A}{Z_{AB/ClCl}^A} + \frac{q_B}{Z_{AB/ClCl}^B} = 2 \cdot \frac{q_{Cl}}{Z_{AB/ClCl}^{Cl}} \quad (13)$$

with q_i representing the charges of the different ions and $Z_{AB/ClCl}^{Cl}$ is the anion–anion coordination number. These choices are based on the optimization of the systems in order to get the maximum short range ordering and highest excess Gibbs energy at a composition usually close to the lowest eutectic in the phase diagram. The coordination numbers selected in this work are listed in Table 2.

The optimized excess Gibbs energy of the liquid solutions of respectively the NaCl–PuCl₃ and ThCl₄–PuCl₃ binary systems are given by the following equations:

$$\Delta g_{NaPu/ClCl} = -8450 - 3220 \chi_{NaPu/ClCl} - 5658 \chi_{PuNa/ClCl} \quad / \text{J.mol}^{-1} \quad (14)$$

$$\Delta g_{PuTh/ClCl} = -5360 - 5050 \chi_{ThPu/ClCl} + 8.7 \cdot T \cdot \chi_{PuTh/ClCl} \quad / \text{J.mol}^{-1} \quad (15)$$

as optimized in this work, whereas the equation for the NaCl–ThCl₄ is taken from Ocadiz et al. [29]:

$$\Delta g_{NaTh/ClCl} = -27700 - 7500 \chi_{NaTh/ClCl} - 14000 \chi_{ThNa/ClCl} \quad / \text{J.mol}^{-1} \quad (16)$$

2.4. Liquid solution for the ternary system

The ternary diagram of the NaCl–ThCl₄–PuCl₃ system was established from the three binary sub-systems described above, using the Kohler/Toop interpolation [41]. The latter is an asymmetric extrapolation model for which two groups of symmetry are considered: monovalent NaCl with a tendency to remain as dissociated ionic liquid, and tetravalent ThCl₄ and trivalent PuCl₃ which are more susceptible to form molecular species in the melt. The optimized ternary excess parameters of the system are presented below:

$$\Delta g_{NaTh(Pu)/ClCl}^{001} = -21700 \quad / \text{J.mol}^{-1} \quad (17)$$

$$\Delta g_{ThPu(Na)/ClCl}^{001} = 10500 \quad / \text{J.mol}^{-1} \quad (18)$$

$$\Delta g_{PuNa(Th)/ClCl}^{001} = 39500 \quad / \text{J.mol}^{-1} \quad (19)$$

3. Results

3.1. NaCl–PuCl₃ system

This model is an update of the model developed by Beneš and Konings [7], necessary because of a different choice of the thermodynamic data for solid and liquid NaCl as discussed in Section 2.1. The adjustment was only minimal. The system calculated in this work shows a very good agreement with the experimental thermodynamic data measured with a combination of thermal and differential thermal analysis techniques by Bjorklund et al. [18], as shown in Fig. 1. The eutectic equilibrium is calculated at a composition of $X_{PuCl_3} = 0.385$ and at a temperature $T = 725$ K. The eutectic equilibrium proposed by Bjorklund et al. is slightly lower in composition ($X_{PuCl_3} = 0.360$), and was based on the extrapolation of the liquidus curve. The present value is considered accurate considering the good fit with the rest of the experimental data. The comparison between invariant equilibria calculated in the model and the literature dataset is presented in Table 3.

Mixing enthalpy data have not been reported in the literature for the NaCl–PuCl₃ system, but have been predicted by Yin et al. [42] using an empirical method proposed by Davis [46], based on the linear extrapolation of the ionic parameters of cations with same charge as Pu³⁺. The estimated mixing enthalpy value at a composition of $X_{PuCl_3} = 0.5$ and a temperature of 1123 K is shown in Fig. 2 together with the computed values in the present CALPHAD model and that of Beneš and Konings. The mixing enthalpy calculated in this work is generally slightly lower than the two previous works but the minimum energy is found around the same composition of maximum short-range ordering ($X_{PuCl_3} = 0.423$ with a corresponding mixing enthalpy value of -6969 J.mol⁻¹). A more recent work by Schorne-Pinto et al. [19] used a semi-empirical method, building on the method of Davis, and based on the previous estimation of the composition of maximum short range ordering and value of mixing enthalpy at that particular composition by comparison with data on known systems. With this method, the minimum in the mixing enthalpy has been calculated at -7193 J.mol⁻¹

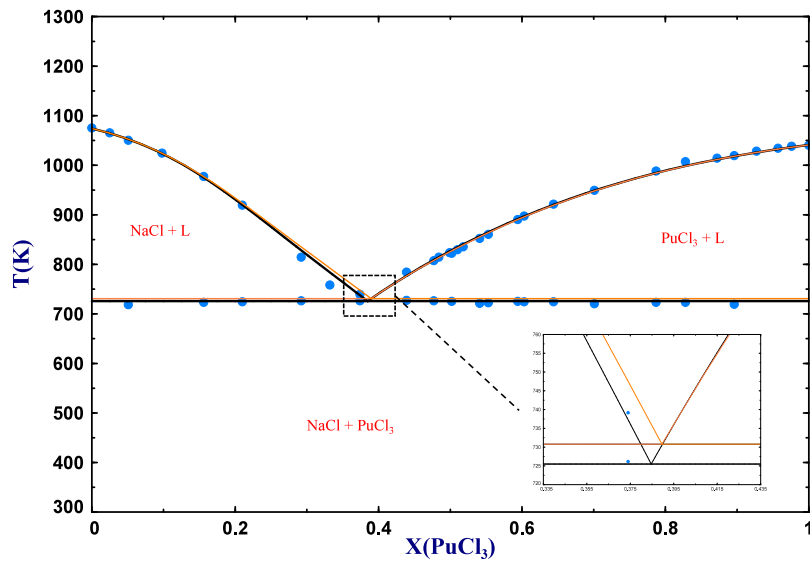


Fig. 1. NaCl-PuCl₃ phase diagram calculated in this work (—) and ● data from Bjorklund et al. [18]. The phase diagram (—) shown in orange is calculated from the previous model of Beneš and Konings [7].

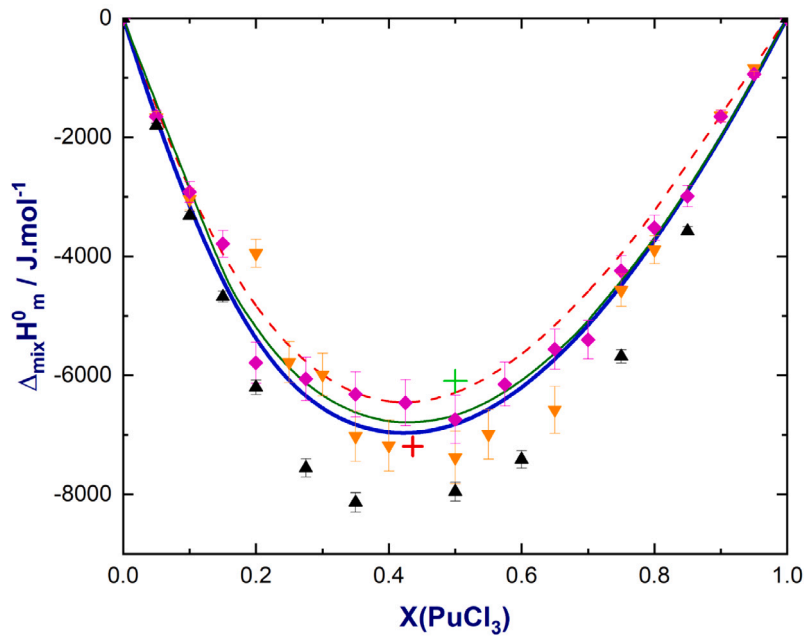


Fig. 2. Mixing enthalpy of the NaCl-PuCl₃ system calculated at 1123 K in this work (—), compared with values calculated from the model by Beneš and Konings [7] (---). Empirical evaluated values from model (---) and for the mixing enthalpy at $X_{\text{PuCl}_3} = 0.5$ (●) by Yin et al. [42]. The mixing enthalpy estimated at the composition of maximum short range ordering at 1123 K (◆) by Schorne-Pinto et al. [19]. The data are moreover compared to the experimental data of the mixing enthalpy of NaCl-NdCl₃ at 1124 K (◆) by Gaune-Escard et al. [43], NaCl-UCl₃ at 1113 K (▼) by Matsuura et al. [44] and NaCl-LaCl₃ at 1173 K (▲) by Papatheodorou and Ostvold [45].

for a composition of $X_{\text{PuCl}_3} = 0.436$, in close agreement with the values optimized in the present work. Furthermore, a comparison is made with the experimental mixing enthalpies data of three analogous systems: NaCl-NdCl₃ [43], NaCl-UCl₃ [44], and NaCl-LaCl₃ [45]. With a similar ionic radius and the same oxidation state, those systems are expected to yield mixing enthalpy values very close to each other. According to the theory of Hong and Kleppa [47], the magnitude of the mixing enthalpy value is related to the so-called relative ionic potential of the cations Na⁺ and Pu³⁺/U³⁺/Nd³⁺/La³⁺ given by the formula:

$$\Delta_{IP} = Z_1/r_1 - Z_2/r_2 \quad (20)$$

where Z_1 and Z_2 are the oxidation states, and r_1 and r_2 the ionic radii of the cations. The corresponding mixing enthalpy values are

thus expected in the same range, more specifically in the order La < U < Pu < Nd given the Shannon ionic radii of La³⁺ (1.032 Å), U³⁺ (1.025 Å), Pu³⁺ (1 Å) and Nd³⁺ (0.98 Å) in six-fold coordination. The good agreement with this trend for the mixing properties of the NaCl-PuCl₃ system lends support to the predictive capability of the model developed in this work (Fig. 2).

3.2. ThCl₄-PuCl₃ system

The model proposed in this work (Fig. 3) is based on the only experimental data set available in the literature, by Vorobei et al. from 1971 [8], who used differential thermal analysis [48]. It shows a good agreement with the liquidus transition data and the eutectic equilibrium, calculated at a composition of $X_{\text{PuCl}_3} = 0.323$ and temperature $T =$

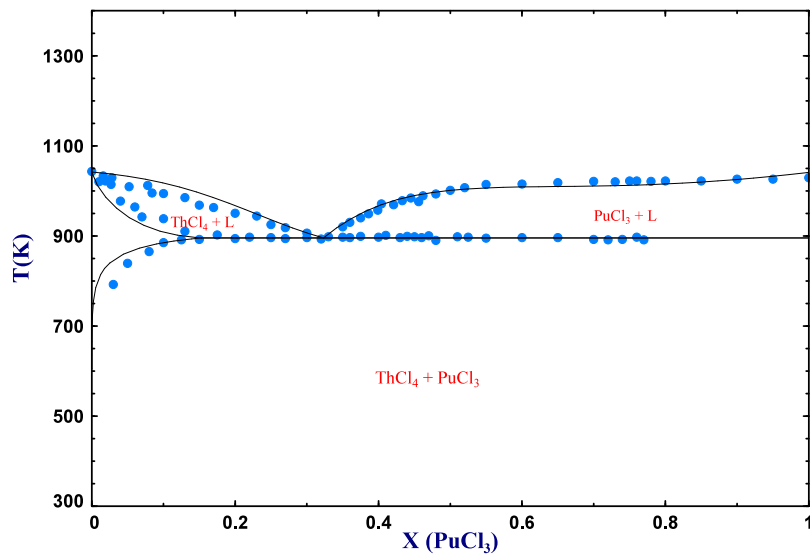


Fig. 3. Phase diagram of the ThCl₄-PuCl₃ system modeled in this work. (●) Data from Vorobei et al. [8].

Table 3

Invariant equilibria calculated in this work in the NaCl-PuCl₃, ThCl₄-PuCl₃ and NaCl-ThCl₄ systems compared to the reference data provided in the literature.

System	Invariant reaction	Equilibrium	Phase diagram calculated and literature data							
			This study		Bjorklund et al. [18]		Beneš and Konings [7]			
NaCl-PuCl ₃	NaCl + PuCl ₃ = L	Eutectic	X(PuCl ₃)	T (K)	X(PuCl ₃)	T (K)	X(PuCl ₃)	T (K)		
			0.385	724	0.360	726	0.383	725		
ThCl ₄ -PuCl ₃	ThCl ₄ + PuCl ₃ = L	Eutectic	This study		Vorobei et al. [8]					
			X(PuCl ₃)	T (K)	X(PuCl ₃)	T (K)				
			0.323	895	0.32–0.33	893				
NaCl-ThCl ₄	NaCl = L	Congruent melting	Ocádiz Flores et al. [29]		Tanii et al. [20]		Oyamada [21]		Vokhmyakov [22]	
			X(ThCl ₄)	T(K)	X(ThCl ₄)	T (K)	X(ThCl ₄)	T (K)	X(ThCl ₄)	T (K)
			0	1074	0	1074	–	–	0	1097
			0.251	667	–	639	0.255	633	0.26	667
			0.333	710	0.333	708	0.333	708	0.333	729
	Na ₂ ThCl ₆ = L	Congruent melting	0.461	660	–	637	0.45	648	0.49	686

895 K, in the interval of composition defined in the reference data at $X_{\text{PuCl}_3} = 0.32\text{--}0.33$.

The extent of the (Th,Pu)Cl₄ solid solution as calculated in this work is slightly less than reported experimentally. The present model provides the best compromise we could reach between the fitting of the solid solubility limit, the solidus and liquidus curves in the ThCl₄ rich region, and the composition of the eutectic equilibrium. We recommend performing complementary measurements to confirm and/or better define the phase equilibria on the ThCl₄ rich side. The maximum extent of the solid solution is calculated at $X_{\text{PuCl}_3} = 0.154$ at a temperature of 895 K in good agreement with the experimental data of Vorobei et al. [8]. The calculated and the literature data are compared in Table 3.

3.3. NaCl-ThCl₄ system

This model (Fig. 4) has been developed by Ocádiz Flores et al. in their work on the ACl-ThCl₄ (A = Li, Na, K) systems [29]. Three different works have been used as reference data [20–22]. The choice was made not to include the stoichiometric compound, NaThCl₅, considering that only one study reports it [49], and by analogy with NaCl-UCl₄ for which no such intermediate compound is reported. The choice to include only the β phase for ThCl₄ does not affect the agreement with the phase diagram data obtained with the different datasets, as summarized in Table 3.

3.4. Ternary assessment

Based on the three models of the binary systems as detailed above and the addition of ternary excess parameters, the ternary phase diagram was optimized for the first time (Fig. 5). The system is characterized by two ternary eutectics, which is in agreement with the only experimental study of this system realized by Desyatnik et al. [23]. The experimental details on the measurement conditions of the melting temperatures are not shared by the authors except for a standard uncertainty of ± 2 K. A comparison between the calculated and the experimentally observed invariant equilibria is made in Table 4. The model presented in this work shows a good agreement in terms of composition and temperature for the eutectic 1. Small discrepancies are observed in the composition of the eutectic 2: its position on the cotectic line between the primary crystallization fields of NaCl and Na₂ThCl₆ was selected as the best compromise that could be reached with the experimental data. Furthermore, the calculated eutectic in the pseudo-binary section (2 NaCl + ThCl₄)-PuCl₃ shows a good match with the temperature and composition measured by Desyatnik et al. [23], confirming the accuracy of the model presented here (Fig. 6).

4. Discussion

The relatively low temperatures around the ternary eutectics calculated here make the NaCl-ThCl₄-PuCl₃ system a promising choice for technological applications. In other chloride fuel salt mixtures in which plutonium was included, such as NaCl-UCl₃-PuCl₃, even an addition of

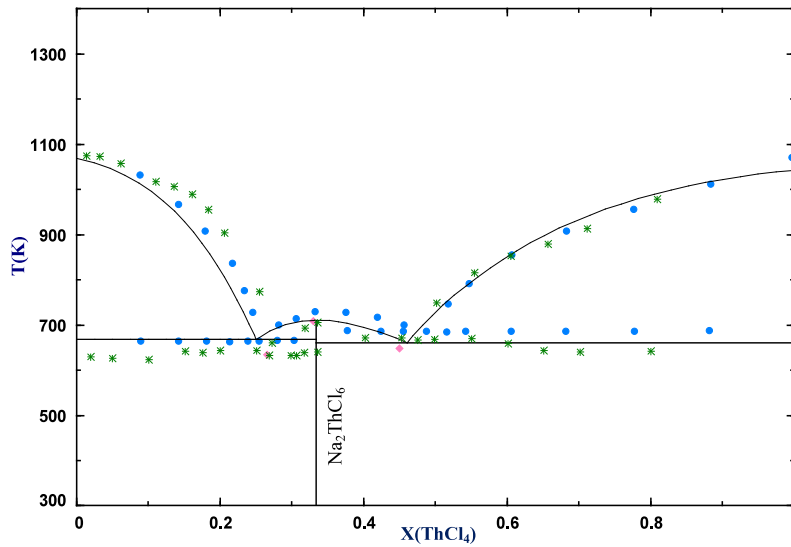


Fig. 4. NaCl-ThCl₄ calculated phase diagram by Ocádiz-Flores et al. [29], but excluding the low temperature metastable α phase. (*) Data from Tanii et al. [20], (●) data from Oyamada [21] and (◆) data from Vokhmyakov et al. [22].

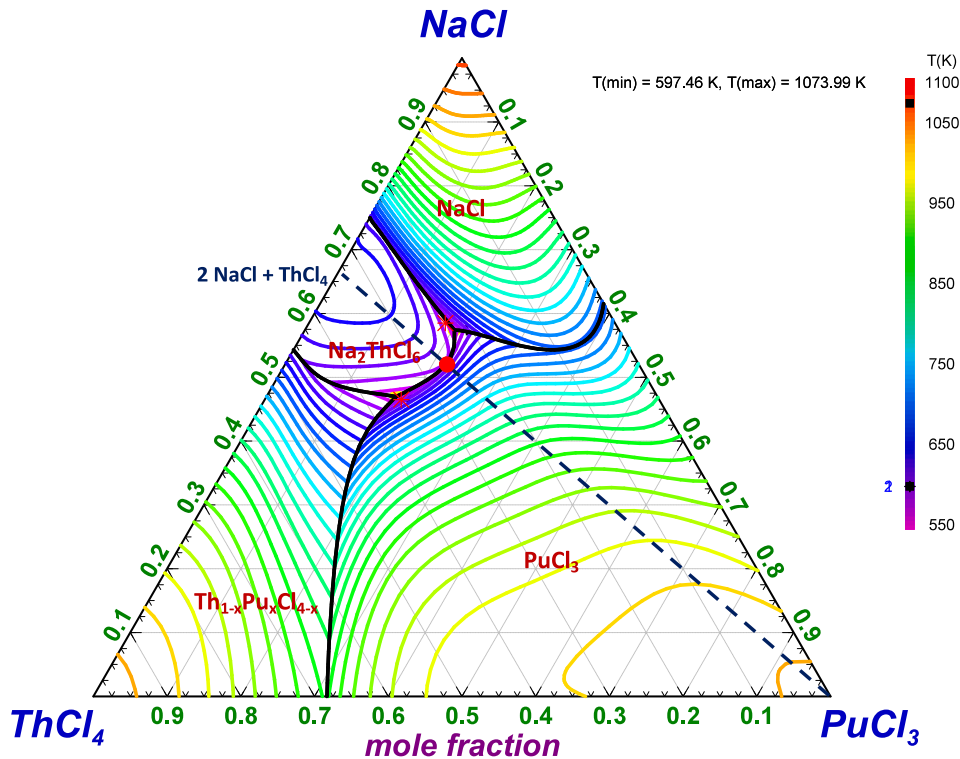


Fig. 5. Liquidus projection of the NaCl-ThCl₄-PuCl₃ system assessed in this work from 550 K to 1100 K with an increment of 20 K. Primary crystallization fields are indicated in the figure: NaCl; Na₂ThCl₆; Th_{1-x}Pu_xCl_{4-x}; PuCl₃. (*) Positions of the ternary eutectics and (●) the eutectic on the (2 NaCl + ThCl₄)-PuCl₃ pseudo-binary section measured by Desyatnik et al. [23].

Table 4

Invariant equilibria calculated in this work and comparison with the experimental data of Desyatnik et al. [23].

Compound	T(K)	X (NaCl)	X(ThCl ₄)	X(PuCl ₃)	Ref.
Ternary eutectic 1	597	0.470	0.354	0.176	This work [23]
	598	0.465	0.350	0.185	
Ternary eutectic 2	598	0.574	0.223	0.203	This work [23]
	603	0.585	0.230	0.185	
Eutectic on the Na ₂ ThCl ₆ -PuCl ₃ pseudo-binary section	628	0.521	0.261	0.218	This work [23]
	643	0.520	0.260	0.220	

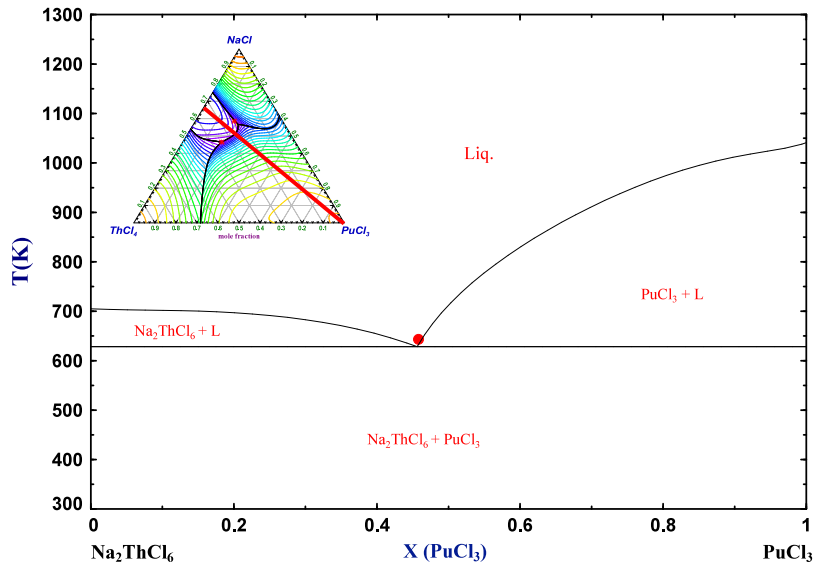


Fig. 6. Calculated pseudo-binary phase diagram of the Na_2ThCl_6 - PuCl_3 system. (●) The position of the eutectic on the pseudo-binary section from Desyatnik et al. [23].

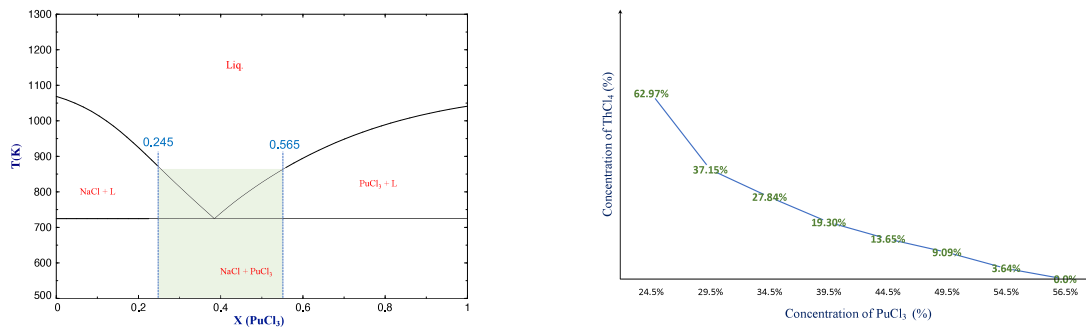


Fig. 7. Phase diagram of the NaCl - PuCl_3 system with the composition area of safety with the minimum inlet temperature minus 50 K (873 K) superposed in green (left), and curve of the maximal safe molar concentration* of ThCl_4 in the ternary solution NaCl - ThCl_4 - PuCl_3 as a function of the concentration of PuCl_3 . *Maximum concentration ensuring melting temperature of the ternary solution below 873 K.



Fig. 8. Chart of the maximal safe molar concentration* of PuCl_3 in the ternary solution NaCl - ThCl_4 - PuCl_3 as function of the concentration of ThCl_4 according to the ternary model. *Maximum concentration ensuring melting temperature of the ternary solution below 873 K.

MgCl_2 did not allow to reach a comparable range [7], with a quaternary eutectic at $T = 696.5$ K (62.9 NaCl - 16.5 MgCl_2 - 1.1 UCl_3 - 19.5 PuCl_3), nor the introduction of KCl that does not show quaternary eutectic melting temperatures lower than $T = 774.3$ K (22 NaCl - 33 KCl - 38 UCl_3 - 7 PuCl_3) [42]. The substitution of uranium by thorium

as fertile compound avoids the introduction of another chloride salt which could to some extent act as a neutron poison.

In terms of safety concerns, this system exhibits an interesting margin with respect to the operating minimal inlet temperature investigated for the MSFR, i.e 923 K [5]. Supposing a required margin of

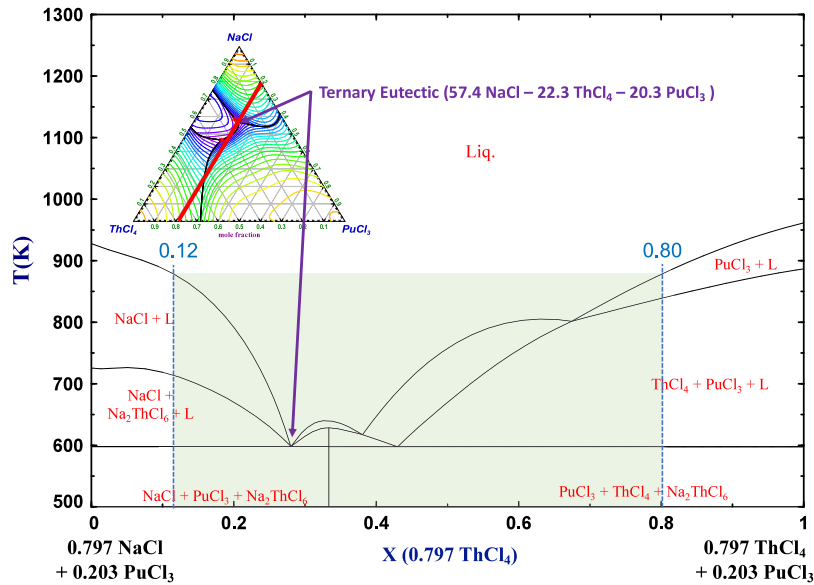


Fig. 9. Calculated pseudo-binary phase diagram of the 79.7 (NaCl-ThCl₄) + 20.3 PuCl₃ system, intercepting the ternary eutectic determined in Section 3.4. The green area represents the range of compositions with a liquidus transition below the minimum safety temperature of operation (T = 873 K).

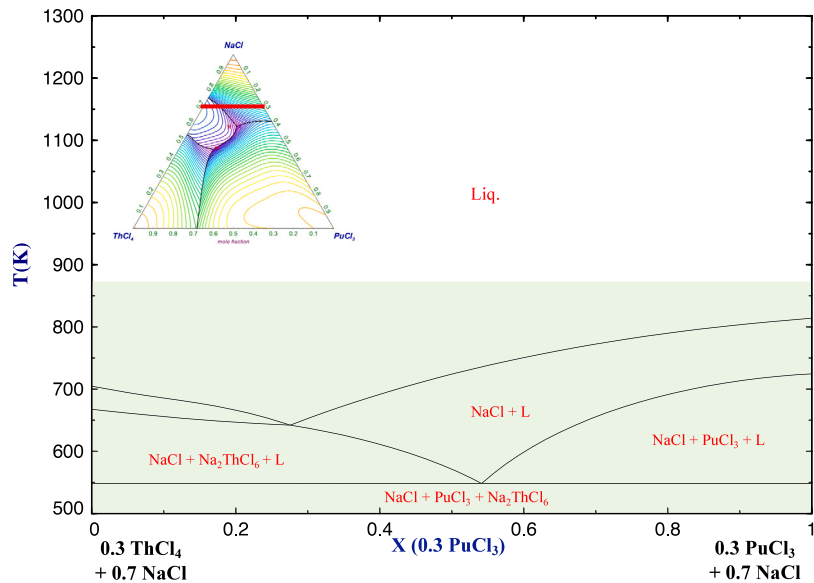


Fig. 10. Phase diagram of the pseudo-binary 30 (ThCl₄-PuCl₃) + 70 NaCl system with the composition area of safety with the minimum inlet temperature minus 50 K (873 K) superposed in green.

at least 50 K (873 K), the composition range of stability of the liquid is large, as illustrated below. This allows to consider a large panel of compositions for the fuel and to tailor its composition based on other requirements such as for instance neutronic or thermo-hydraulic properties.

The different fast spectrum chloride MSR concepts are designed to accommodate a high content of plutonium. For example, TerraPower’s Molten Chloride Fast Experiment project based its fuel on the binary system NaCl-PuCl₃ at the eutectic composition 64 NaCl - 36 PuCl₃ [6], and the equilibria defined by Bjorklund et al. [18]. The safe area of operation as defined above is shown in Fig. 7 (left) on the NaCl-PuCl₃ phase diagram optimized in this work, with an eutectic transition at a composition 61.5 NaCl - 38.5 PuCl₃. On this figure, we see that the interval of “safe” plutonium chloride concentrations extends between X_{PuCl₃} = 0.245 and 0.565. A calculation is then performed in the ternary melt of the maximum concentration of ThCl₄ (as a substitute for NaCl)

allowed if one wants to remain below the safety temperature for different fixed concentrations in PuCl₃ in the interval defined previously (i.e. between X_{PuCl₃} = 0.245 and 0.565, as shown in Fig. 7 (right)). It is observed that with high concentration of PuCl₃, the corresponding concentration of ThCl₄ becomes very limited. Fig. 8, showing the range of PuCl₃ concentration allowed to remain below the safe temperature as function of the concentration in ThCl₄, confirms this evolution. A “safe” area can be observed at the composition 40 (NaCl-PuCl₃) + 60 ThCl₄ between X_{PuCl₃} = 0 and X_{PuCl₃} = 0.28, which offers only a very limited margin with the safety temperature, thus could not be recommended. The detailed computed pseudo-binary sections are presented in the Supplementary data.

A pseudo-binary phase diagram passing through the ternary eutectic (57.4 NaCl - 22.3 ThCl₄ - 20.3 PuCl₃) at fixed PuCl₃ content is moreover shown in Fig. 9. It demonstrates a large interval of “safe” composition ranging from X_{ThCl₄} = 0.0956 (0.12 multiply by 0.797 ThCl₄) to X_{ThCl₄} = 0.638 (0.80 times 0.797 ThCl₄).

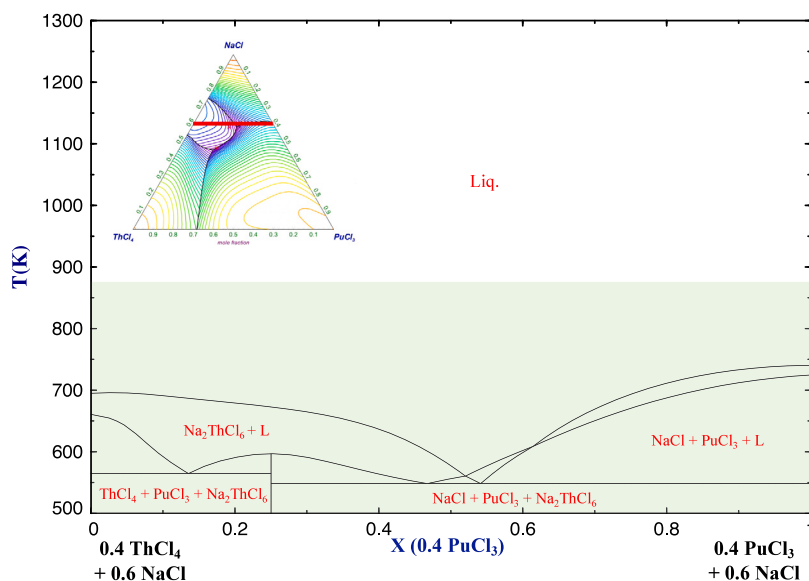


Fig. 11. Phase diagram of the pseudo-binary 40 (ThCl_4 - PuCl_3) + 60 NaCl system with the composition area of safety with the minimum inlet temperature minus 50 K (873 K) superposed in green.

The potential of this fuel is finally illustrated by the computation of the pseudo-binary systems at the constant concentration of 70% (Fig. 10) and 60% NaCl (Fig. 11). With fixed concentrations of heavy metal chloride (ThCl_4 + PuCl_3) of respectively 30% and 40%, all possible combinations between these two compounds in the ternary solution are meeting the safety requirements. The flexibility proposed by these systems is a major advantage that allows to optimize other necessary properties in order to get the most adapted fuel for a MSR.

An experimental study of the thermodynamic phase transition data of the mentioned key compositions appears essential, however, to validate the present model and for the development of this potential fuel in the framework of the fast neutron spectrum MSR. The evolution of the chemical composition of the fuel upon fission of plutonium (and uranium-233 generated from the fertile thorium), should also be monitored carefully as well as its impact on the thermo-physical properties. A more comprehensive picture of the fuel salt chemistry should then include the melts $\text{NaCl-ThCl}_4\text{-UCl}_3$ and $\text{NaCl-ThCl}_4\text{-UCl}_4$ as well as the extrapolation to the higher order system $\text{NaCl-ThCl}_4\text{-PuCl}_3\text{-UCl}_3\text{-UCl}_4$.

5. Conclusion

A thermodynamic assessment of the $\text{NaCl-ThCl}_4\text{-PuCl}_3$ system is reported for the first time based on the modified quasichemical formalism in the quadruplet approximation, including the modeling of the different binary constituting sub-systems. Two ternary eutectic transitions have been calculated at the compositions 47.0 NaCl - 35.4 ThCl_4 - 17.6 PuCl_3 and 57.4 NaCl - 22.3 ThCl_4 - 20.3 PuCl_3 at temperatures of 597 K and 598 K, respectively. This melt could be an interesting option as fuel for the fast neutron spectrum MSR concept as it offers a low melting temperature over a very wide range of composition, allowing flexibility in the choice of the final composition to accommodate neutronics, thermohydraulic and other requirements.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No novel experimental data was generated in the research described in the article.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.calphad.2022.102496>.

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