Composition dependent order-disorder transition in $\text{Nd}_x\text{Zr}_{1-x}\text{O}_{2-0.5x}$ pyrochlores: a combined structural, calorimetric and *ab initio* modeling study

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Abstract

The order-disorder phase transition in the $\text{Nd}_x\text{Zr}_{1-x}\text{O}_{2-0.5x}$ system is studied by complementary techniques which include wet chemical synthesis of a series of compositions with various Nd/Zr ratios with the final annealing at 1873 K, X-ray diffraction, oxide melt solution calorimetry and *ab initio* thermodynamic modeling. Our structural data indicate the transition from ordered to disordered pyrochlore at $x \sim 0.31$ at a temperature of 1873 K. Our calorimetric data show a transition enthalpy of ~ 30 kJ/mol, which corresponds to an entropy of disordering of ~ 16 J/K/mol. The latter value is significantly smaller than the configurational entropy of transition computed under the

assumption of complete disorder in a fluorite phase, indicating a substantial degree of order remaining in the fluorite phase at the temperature of synthesis. The considered phases are computed ab initio using a series of specialquasi-random structures that emulate the complete or partial disorder. The results of our calculations and thermodynamic modeling are in good agreement with the measured lattice parameters, the Nd content at the order-disorder transition, and the measured formation and transformation enthalpies. Thus our combined experimental and modeling results provide valuable insight into the disordering of this pyrochlore phase and of other pyrochlore materials.

1 Introduction

Pyrochlore compounds ($A_2B_2O_7$) have wide applications and are of interest [1] as thermal barrier coatings [2, 3], as solid oxide ion conductors [4], as quantum spin liquid materials [5-7] and as candidate materials for the immobilization of radionuclides [8-11]. Particularly important is the ability of certain pyrochlore compounds to sustain self-irradiation without becoming amorphous. Indeed, natural analogues of pyrochlores can accommodate up to 30 wt.% UO_2 and up to 9 wt.% ThO_2 while preserving their crystalline structure over geological time periods of millions of years [8, 12-14]. Various experimental techniques such as actinide-doping [15-21], dissolution studies [22-24], thermochemical measurements [25-29] and ion beam irradiation [30-40], as well as atomistic simulations [38, 41-47] have been used to characterize properties of these materials that are relevant to nuclear waste management. It has been noted that the radiation resistance, which is observed for some classes of pyrochlores, e.g. the zirconates, is correlated with the formation of a disordered defect fluorite phase[8].

Consequently, many studies have focused on this order-disorder transition (e.g. [8, 37, 48]). It has also been observed that pyrochlores can be transformed to the defect fluorite phase by applying pressure [49] or temperature [37, 48, 50], by irradiation [38, 51] and by compositional changes [52-57]. The last route is of special interest as it allows following the disordering process under more easily accessible experimental conditions. The present study investigates the structural and thermodynamic effects associated with the order-disorder transition in $\text{Nd}_x\text{Zr}_{1-x}\text{O}_{2-0.5x}$ by complementary techniques: X-ray diffraction, solution calorimetry and *ab initio* thermodynamic modeling. In this study the modeling approach of Jiang et al. [48] based on the assumption of a completely random distribution of cations in the defect fluorite phase is extended to non-stoichiometric compositions. The recent finding of weberite-type short range order in the defect fluorite [58] is addressed here by computing models which assume fluorite and partially disordered weberite-type atomic distribution in the defect fluorite phase.

The coordination polyhedra of the pyrochlore and defect fluorite structure are shown in Figure 1. The general formula of a stoichiometric pyrochlore is $A_2B_2X_6YZ$. The eight-fold coordinated *A* site (16d) is usually occupied by a III-valent rare earth element, while the six-fold coordinated *B* site (16c) is commonly occupied by a 3d, 4d or 5d transition metal or a IVa group element. The oxygen atoms commonly adopt the *X* (48f) and the *Y* (8b) sites, whereas the latter site can also be occupied by hydroxyl groups. The *Z* (8a) position is vacant. In comparison to the fluorite structure, whose composition can be conveniently written as A_4X_8 , pyrochlore misses one eighth of the anions. The presence of two different cation species with different valences creates the possibility of cation ordering and a change in the structure. In fully disordered pyrochlore the *A* site is coordinated by six *X* and two *Y* anions, while the *B* site is coordination by *X* anions only

(Figure 1a). The *X* position is four-fold coordinated by two *A* and two *B* cations, whereas the *Y* site is four-fold coordinated solely by *A* cations. The vacant site *Z* is surrounded by four *B* cations.

In the ideal defect fluorite structure (Figure 1b), which represents a fully disordered fluorite, the oxygen vacancy occupies the *X*, *Y* and *Z* sites (8c) of the original pyrochlore structure which reduces the two cationic pyrochlore sites to one cationic site (4a) with an average coordination number of seven. Weberite, which is suggested as a model of the defect fluorite structure at the local scale [58], represents another type of an ordered arrangement of III- and IV-valent cations and the vacancies, which is derivable from the defect fluorite, but which deviates significantly from that of pyrochlore. In weberite the *A*-site of fluorite splits unequally into *A*, *B* and *C* cation sublattices, such that the *A*- and *B*-sublattices are occupied predominantly by III- and IV-valent cations, while in the *C*-sublattice both the III- and IV-valent cations are mixed at random [58]. We refer to this structure as weberite, being aware of the fact that an “ideal weberite” does not contain cationic site mixing. The general formula of the weberite, which can be viewed as a polymorph of the ideal pyrochlore, can be written as ABC_2X_7Z , where the *X*- and *Z*-sublattices are occupied by the oxygen atoms and vacancies, respectively. As weberite contains a fully disordered cationic sublattice *C*, its average degree of order is intermediate between those of pyrochlore and fluorite.

Stoichiometric $Ln_2Zr_2O_7$ (*Ln* = lanthanide) pyrochlores have been subjected to detailed thermodynamic investigations, such as differential scanning calorimetry (DSC), adiabatic calorimetry and oxide melt solution calorimetry [25-29]. Saradhi et al. [59] measured the enthalpy and entropy differences between stoichiometric $Eu_2Zr_2O_7$ pyrochlore and the disordered fluorite structures of the same composition. The disordering entropy of

17.8 J/K/mol, estimated from the measured transition enthalpy (H_{tr}) of 37.8 ± 3.1 kJ/mol [59] and the transition temperature (T_{tr}) of 2128 K [60] assuming $H_{tr} = T_{tr} \cdot S$, is significantly lower than the configurational entropy of fully disordered defect fluorite of 48.1 J/K/mol [48]. This observation supports the finding of significant short range ordering in the nominally disordered phase [58]. The predictions of enthalpy differences between the ordered and disordered phases have also been made for hafnate and zirconate pyrochlores [1, 48, 61, 62].

Little attention has been given to thermochemical effects associated with the composition dependent transformation from pyrochlore to disordered fluorite. Guo et al. [53] reported thermal conductivity, thermal diffusivity and heat capacity measurements on $Nd_xZr_{1-x}O_{2-0.5x}$ with x in the range of 0.1 - 0.5. For compounds with $x \leq 0.3$, a defect fluorite structure was observed, while compositions with $x > 0.3$ showed the pyrochlore structure. The thermophysical properties reported for both structures did not show any structure-dependent breaks. To the best of our knowledge there have been no observations made yet regarding the enthalpy changes in this system as a function of composition.

Several properties of pyrochlore compounds relevant to the order-disorder transition have been investigated by atomistic modeling. Force field and *ab initio* simulations were applied for the calculation of defect formation energies [37, 38, 45, 46, 63] and for the investigation of defect annealing processes [41]. Vanpoucke et al. [64] studied the relative stability of the pyrochlore and defect fluorite phases. The temperature and pressure effects on the order-disorder transition were also studied [48, 49, 65]. Minervini et al. [66] investigated the effect of disorder on the structural parameters, while Xiao et al. [67] modeled the amorphization induced by electronic excitations. The molecular

dynamics technique was used to simulate the order-disorder transition and the amorphization of pyrochlore [43, 68, 69]. Chartier et al.[42] simulated radiation damage cascades in $\text{La}_2\text{Zr}_2\text{O}_7$. Some of these studies indicated that the transition to the defect fluorite is caused by an accumulation of cationantisite defects (e.g. [43]), while others showed that the transformation could be correlated with the low energetic costs of formation of combined cation and anion defects [46] or with the energetic favorability of the anion Frankel pair defect formation [45]. Jiang et al. [48] and Li et al.[45]modeled the temperature driven order-disorder transition in pyrochlores assuming perfect order and perfect disorder in the pyrochlore and defect fluorite phases, respectively. Although these studies have shown that under these assumptions it appears possible to predict reasonable values of the order-disorder transition temperatures in pyrochlores of variable compositions, the data of Shamblin et al. [58] indicate that the short range ordering in the disordered phase could significantly alter the corresponding enthalpy and entropy effects. This conclusion can be further supported noting that the disordering enthalpy of ~ 38 kJ/mol measured for $\text{Eu}_2\text{Zr}_2\text{O}_7$ [59] is markedly lower than the values of the order of 100 kJ/mol, which were obtained in previous atomistic simulation studies [1, 45, 48, 59, 61]. These results indicate that further experimental and thermodynamic modeling studies are needed to understand the structural states of pyrochlore compounds under specified temperature, pressure and composition parameters and to rationalize the noted contradiction.

Here a combination of experimental and *ab initio* atomistic simulation tools is applied to pyrochlore compounds in the $\text{Nd}_x\text{Zr}_{1-x}\text{O}_{2-0.5x}$ system. The transition to the defect fluorite structure has been initiated by gradual replacement of Nd by Zr. Although significant experimental and modeling effort has been put into observing, explaining and predicting

the structural stability at various chemical compositions, here we study for the first time the composition-induced transition from pyrochlore to defect fluorite in the $\text{Nd}_x\text{Zr}_{1-x}\text{O}_{2-0.5x}$ system by complementary experimental and atomistic simulation approaches, which allow for a more detailed characterization of the disordering process.

2 Materials and Methods

2.1. Synthesis

The sample powders were synthesized via a wet chemical co-precipitation route involving the hydroxides in liquid ammonia according to Chen [70]. The different chemical compositions were achieved by mixing appropriate amounts of the aqueous solutions of the starting materials $\text{Nd}(\text{NO}_3)_3$ and ZrOCl_2 . A detailed description is given by Finkeldei et al.[23]. The precipitated, washed and ground hydroxides were calcined in air for 2 h at 873 K in an alsint[®] sintering crucible. A second grinding step was applied before the powders were sintered for 30 h at 1873 K. The heating and cooling rate was 5.3 K/min. After sintering the powders were ground thoroughly.

An additional set of samples synthesized under the same conditions was subjected to shorter sintering times of ~5 h. This set of samples was used solely for the XRD characterization.

2.2. Structural and chemical characterization

X-ray diffraction - XRD measurements were carried out from 10 to 130° 2 θ using a D4 instrument (θ -2 θ geometry) from Bruker AXS GmbH. Samples were measured on a slit sample holder. The ZrO_2 - Nd_2O_3 powder patterns were evaluated by a detailed analysis

of Bragg reflection shapes. The lattice parameter was determined via the Nelson-Riley method [71, 72].

Energy dispersive X-ray analysis - The Nd/Zr ratios of the five powders, which were used for the high temperature calorimetry were measured via EDX using a FEI Quanta 200F.

2.3. High temperature oxide melt solution calorimetry

The enthalpies of formation, ΔH_f° , of seven pyrochlore and defect fluorite samples were measured by high temperature oxide melt solution calorimetry using a Calvet-type custom built isoperibol calorimeter [73-75]. Sodium molybdate ($3 \text{ Na}_2\text{O} \cdot 4 \text{ MoO}_3$) at 973 K was the solvent, which was prepared according to [76] using MoO_3 (Fisher, 99.5 % purity) and $\text{Na}_2\text{MoO}_4 \cdot 2 \text{ H}_2\text{O}$ (Emdmillipore, 99.5 % purity) as reagents. The calorimeter was calibrated by measuring the heat content of $\alpha\text{-Al}_2\text{O}_3$ pellets [75]. To remove possible residual water, all samples were preheated to 1073 K for at least 8 h. Approximately 5 mg pellets, weighed accurately on a microbalance, were dropped from room temperature into 20 g solvent (973 K). To assure an oxidative environment, a constant flow of O_2 was bubbled through the solvent with a flow rate of 9.8 mL/min. This method enhances the dissolution rate and prevents local saturation of the melt [75]. Oxygen was also flushed through the calorimeter chamber (43 mL/min) to ensure a stable environment above the solvent. The measured heat effect upon dropping a pellet, called the enthalpy of drop solution, was obtained by integrating the heat flow curve using CALISTO software provided by Setaram. This methodology has been used extensively on similar materials [73-75, 77]. The difference in enthalpy of drop solution

between reactants and products gives the enthalpy of reaction; i.e. formation from binary oxides, at room temperature.

2.4. Computational approach

The *ab initio* density functional theory calculations were performed using the quantum-ESPRESSO code [78]. We used PBE [79] and PBEsol[80] exchange-correlation functionals and ultrasoft pseudopotentials to represent the core electrons of the computed atoms [81]. Two slightly different exchange-correlation functionals were applied because PBE gives better energetics and PBEsol – a simple modification of PBE – results in improved structural properties [80], which will be also demonstrated in this study. The 5s5p6s electrons of Nd atoms, the 4s4p4d5s electrons of Zr atoms and the 2s2p electrons of O atoms were treated explicitly. In regular calculations the 4f electrons were described with a pseudopotential, the so-called “*f*-in-core” approach. The plane wave energy cutoff was set at 50 Ryd and in each calculation the cell parameters and the ionic positions were relaxed to equilibrium positions. Therefore, the forces acting on the atoms were smaller than 0.005 eV/Å and the final pressure was 0 GPa with a tolerance of 0.01 GPa. The pyrochlore and defect fluorite were modeled using a 2x2x2 pyrochlore supercell containing between 88 and 92 atoms, depending on the Nd content. The same approach was used in the computation of the order-disorder transition temperature and the defect formation energies in a series of pyrochlores of different compositions [45]. The weberite structures were modeled with supercells twice the size than pyrochlore and defect fluorite structures. In [45, 82-84] we showed that the DFT+*U* approach with the Hubbard *U* parameter derived from the linear response method [85] predicts the structural parameters and the reaction enthalpies of various *f*-

elements compounds that are in much better agreement with experimental measurements than DFT. This is because of the explicit accounting for the *f*-electrons correlations by the DFT+*U* method and direct *ab initio* computation of the Hubbard *U* parameter, which represents the strength of these electronic correlations. Therefore, in the present study both the “*f*-in-core” as well as DFT+*U* calculations were applied in parallel, and in order to assess the strength of electronic correlations the DFT+*U* results are treated as correction to the DFT. Our linear response calculations [85] resulted in the Hubbard *U* value of 5 eV for both phases. This value is adopted in all calculations. We note that many of the previous atomistic simulations studies were performed with force field methods (e.g. [37, 38, 41-43, 66, 68, 69]). Recent *ab initio* calculations of defect formation energies in pyrochlores [45, 86] show that the force field calculations [38, 66] severely overestimate the defect formation energies in pyrochlores, which rationalizes our choice of computational approach.

The $\text{Nd}_x\text{Zr}_{1-x}\text{O}_{2-0.5x}$ pyrochlore, defect fluorite and weberite were represented by special quasi-random structures [87]. These structures were specially designed to emulate the intrinsic disordering in pyrochlore, weberite and fluorite. The structure of an ideal ordered pyrochlore can be conveniently described with four sublattices, the Zr and Nd atoms separately reside in the Zr- and Nd-sublattices, while the oxygen atoms and vacancies reside within the O- and O-vac-sublattices, respectively. In a non-stoichiometric pyrochlore, when two Nd atoms are substituted with two Zr atoms, an additional oxygen atom is introduced for electroneutrality into the formerly vacant 8a site. We assumed that the introduced Zr and O atoms distribute themselves randomly on the Nd and O-vac-sublattices, respectively. This implies that the configurational entropy of a non-stoichiometric Zr-rich pyrochlore is only associated with the Nd- and O-vac-sublattices, while the Zr- and O-sublattices remain fully occupied. This model is illustrated in Figure 2.

The defect fluorite phase is modeled by specialquasi-random structures designed under the assumption of full randomness over the whole cationic and anionic sublattices, respectively [45, 88]. The weberite-type disordered structures [58] are modeled assuming that the extra Zr atoms, substitute equally all Nd sites within A and C sublattices, while the excess oxygen atoms are randomly distributed over the O-vacancy sublattice. We note that Stanek et al. [89] considered an alternative charge compensation mechanism to oxygen inclusion/removal for the non-stoichiometric compositions. By performing force-field calculations, which should be validated by the *ab initio* data [45], they proposed that four Nd^{3+} cations could be substituted by three Zr^{4+} cations and a cation vacancy for the formation of non-stoichiometric compositions. Our *ab initio* calculations suggest that such a mechanism is by 0.4 eV less energetically favorable. Thus, although other charge-balancing schemes cannot be excluded, our *ab initio* calculations, the performance of our model in reproducing the calorimetric data (section 3.3) and the results of previous studies [53] point toward the oxygen-driven charge compensation mechanism.

3 Results and Discussion

3.1. Structural characterization by X-ray diffraction

The crystal structures of samples with various chemical compositions were subjected to a detailed investigation. Previous studies [90-93] suggested the investigated range of $x = 0.23 - 0.52$ for $\text{Nd}_x\text{Zr}_{1-x}\text{O}_{2-0.5x}$ to cross three different stability fields of the ZrO_2 - Nd_2O_3 phase diagram. The compositions with the lowest Nd-content crystallize in the defect fluorite structure. More Nd-rich compositions enter a narrow two-phase region where defect fluorite and pyrochlore coexist. A further increase of the Nd_2O_3 mole

fraction corresponds to the single-phase pyrochlore stability field. Figure 3a shows representative patterns of samples with $x = 0.25$, 0.31 and 0.50 . Typical reflections of the pyrochlore and defect fluorite structure are indexed in Figure 3a. The presence of the pyrochlore phase is revealed by the appearance of the superstructure reflections $(311)_{PY}$, $(331)_{PY}$ and $(511)_{PY}$ (Figure 3a). The sample with $x = 0.25$ appears to be single phase defect fluorite, while that with $x = 0.50$ appears to be single phase pyrochlore. The asymmetric reflection in the $x = 0.31$ sample (Figure 3c) can be fitted with two overlapping Gaussian functions, the first belonging to pyrochlore and the second to defect fluorite. This sample reveals peak splitting, which is consistent with the two-phase co-existence.

The lattice constants of both phases are very similar ($2a_{DF} = 10.465 \text{ \AA}$ and $a_{PY} = 10.487 \text{ \AA}$ for defect fluorite and pyrochlore, respectively). Therefore, the separation of the peaks in the XRD pattern becomes difficult. The problem of determining the phase boundaries of the two-phase region with low lanthanide oxide content is well known [94-96]. For a wide class of zirconia-lanthanide oxide system the two-phase region spans only over 2 - 3 mol % Ln_2O_3 . This is also the case for our system, where the two-phase region was observed in the range of $x = 0.32 - 0.33$. Nevertheless, all XRD reflections of the samples with $x = 0.31$ and 0.33 were successfully fitted with two Gaussian functions. Figure 3b shows the fit for the sample with $x = 0.25$.

With increase in Nd_2O_3 content the XRD reflections shift to smaller 2θ values (Figure 3a). This effect is associated with the substitution of the smaller Zr^{4+} cation by the larger Nd^{3+} cation (0.72 nm and 1.109 nm, respectively [97]). The dependence of the lattice parameter on the chemical composition is shown in Figure 4. The defect fluorite lattice parameters are doubled for a better comparison with the pyrochlore lattice parameters.

Our results are in good agreement with previous experimental data [90-93]. Within the single-phase regions the lattice parameter a increases linearly with increasing Nd content. For the two-phase samples ($x = 0.31$ and 0.33), the lattice parameter of each phase is independent of the Nd content as shown by the horizontal dashed lines in Figure 4.

3.2. Thermochemistry

The drop solution enthalpy (ΔH_{ds}) is the sum of the heat content of the sample and the heat released or acquired during its dissolution in a solvent. Appropriate thermochemical cycles (see Table 1) are used to determine enthalpies of formation from the oxides ($\Delta H_{f,ox}^\circ$) (see Table2). To enable this calculation, ΔH_{ds} measured values of this study and ΔH_{ds} literature values of Nd_2O_3 and ZrO_2 [29, 98] as well as the standard formation enthalpies of the oxides [99] are needed.

Both the pyrochlore and the defect fluorite samples show exothermic dissolution. The time for the calorimetric signal to return to its baseline value was about 60 minutes which is longer than usual for this technique [100, 101] and may suggest slower dissolution of the sample. Therefore, in order to reduce the error associated with the longer time of signal collection, possibly caused by random baseline fluctuations, we increased the number of runs of each composition up to 14. The ΔH_{ds} uncertainty was between 2.6 to 5.7 kJ/mol depending on the sample (Table2).

Table 1: Thermochemical cycle for $Nd_xZr_{1-x}O_{2-0.5x(s,298)}$ solid solution ΔH° determination from oxides and elements. The data marked with ^a are taken from [29], ^b from [28] and ^c from [99]. The subscripts correspond to: _s = solid, ₂₉₈ = 298 K, ₉₇₃ = 973 K, _{sln} = solution, _{ds} = drop solution, _{cr} = crystalline, _g = gaseous.

Reaction		ΔH (kJ/mol)
$4^*Nd_xZr_{1-x}O_{2-0.5x(s,298)} \rightarrow 4^*x NdO_{1.5(sln,973)} + 4^*(1-x) ZrO_{2(sln,973)}$	(1) $\Delta H_{ds}Nd_xZr_{1-x}O_{2-0.5x}$	see Table2
$Nd_2O_{3(cr,298)} \rightarrow Nd_2O_{3(sln,973)}$	(2) $\Delta H_{ds}Nd_2O_3$	- 163.4 ± 3. 4 ^a
$ZrO_{2(cr,298)} \rightarrow ZrO_{2(sln,973)}$	(3) $\Delta H_{ds}ZrO_2$	19.5 ± 0.9 b
$2^*Nd_{(s,298)} + 1.5 O_{2(g,298)} \rightarrow 2^*NdO_{1.5(s,298)}$	(4) $\Delta H_f^\circ Nd_2O_3$	-1807.9 ± 1.0 ^c
$Zr_{(s,298)} + O_{2(g,298)} \rightarrow ZrO_{2(s,298)}$	(5) $\Delta H_f^\circ ZrO_2$	-1100.6 ± 1.7 ^c
$x 0.5Nd_2O_{3(s,298)} + 1-x ZrO_{2(s,298)} \rightarrow Nd_xZr_{1-x}O_{2-0.5x(s,298)}$	(6) $\Delta H_{f,ox}^\circ 4^*Nd_xZr_{1-x}O_{2-0.5x}$	see Table2
$\Delta H(6) = -\Delta H(1) + 4^*x 0.5\Delta H(2) + 4^*(1-x) \Delta H(3)$		
$4^*(x)0.5 Nd_{(s,298)} + 4^*(1-x) Zr_{(s,298)} + 4^*(2-0.5x) O_{2(g,298)} \rightarrow 4^*Nd_xZr_{1-x}O_{2-0.5x(s,298)}$	(7) $\Delta H_{f,el}^\circ 4^*Nd_xZr_{1-x}O_{2-0.5x}$	see Table2
$\Delta H(11) = 4^*0.5(x) \Delta H(4) + 4^*(1-x) \Delta H(5) + \Delta H(6)$		

Table 2: The enthalpies of drop solution ($\Delta H_{ds, 973}$) in $3\text{Na}_2\text{O} \cdot 4\text{MoO}_3$ at 973 K for defect fluorite and pyrochlore samples with molar fraction of Nd and Zr ($\chi(\text{Nd})$, $\chi(\text{Zr})$) (normalized to 7 oxygen in formula), x in the chemical formula $\text{Nd}_x\text{Zr}_{1-x}\text{O}_{2-0.5x}$, the structure type (DF: defect fluorite, PY: pyrochlore), and the calculated enthalpies of formation from oxides ($\Delta H_{f, ox, 298}$) using the thermochemical cycle in Table 1.

$\chi(\text{Nd})$	$\chi(\text{Zr})$	x	structure type	$\Delta H_{(ds, 973)}$ (kJ/mol)	$\Delta H_{(f, ox)}^\circ$ (kJ/mol)
0.88	2.83	0.24	DF	-57.0 ± 2.7	39.02 ± 2.7
1.08	2.68	0.29	DF	-62.3 ± 2.9	23.74 ± 2.8
1.14	2.64	0.30	DF	-71.4 ± 4.0	27.25 ± 3.4
1.43	2.42	0.37	PY	-44.7 ± 3.3	-27.68 ± 3.1
1.65	2.25	0.42	PY	-47.5 ± 5.7	-45.63 ± 4.4
2.08	1.93	0.52	PY	-57.7 ± 3.0	-73.77 ± 3.3
2.06	1.95	0.51	PY	-74.6 ± 5.2	-55.12 ± 4.3

Figure 5 shows the results of $\Delta H_{(f, ox)}^\circ$ from defect fluorite (red circles) and pyrochlore (blue squares) at 298 K. The single data point from Navrotsky and Ushakov[27] which corresponds to a stoichiometric $\text{Nd}_2\text{Zr}_2\text{O}_7$ pyrochlore (yellow triangle) is in good agreement with the data observed in the present study. The $\Delta H_{(f, ox)}^\circ$ value of -122.7 ± 6.8 kJ/mol from Bolech et al. [26] for $\text{Nd}_2\text{Zr}_2\text{O}_7$ pyrochlore falls off the trend significantly. This discrepancy could be explained by experimental differences, e.g. no flushing and no bubbling of the solvent with O_2 during the measurement in [26], as already noted by Navrotsky and Ushakov[27].

The $\Delta H_{(f, ox)}^\circ$ data sets obtained for the pyrochlore and defect fluorite structures vary approximately linearly with the composition (see **Figure 5**). The linear fits for pyrochlore

and defect fluorite are parallel within the range of uncertainty and differ about 30 kJ/mol, with a less exothermic enthalpy for the defect fluorite than for the pyrochlore. Thus we can associate the value of 30 kJ/mol with the enthalpy of disordering and phase transition.

3.3. Atomistic Modeling

Figure 6 shows the computed lattice parameters of the $\text{Nd}_x\text{Zr}_{1-x}\text{O}_{2-0.5x}$ pyrochlore, defect fluorite and weberite phases as functions of the composition. The DFT-PBE approach systematically overestimates the lattice parameter, which is a known feature of the PBE functional. However, the experimentally observed slope of the lattice parameter vs. the Nd content function is well reproduced. The results obtained with the PBEsol functional are in much better agreement with the experimental data, as it is usually observed for this functional [79]. Our calculations predict the lattice parameters of the pyrochlore, defect fluorite and weberite structures to be very similar, which is also observed in our XRD data (Figure 4).

The computed formation enthalpies of pyrochlore, defect fluorite and weberite phases are compared to the measured values in Figure 7. It is known that energy differences predicted by DFT could systematically differ from the experimental values (see [48]). In case of *f*-element-bearing materials, and pyrochlore in particular, these offsets come mainly from the electronic correlations that are not well captured by the standard DFT methods [45]. The formation enthalpies computed with the PBE functional show offsets from the PBE+*U* calculations of -0.2 kJ/mol, +15.6 kJ/mol and +4.9 kJ/mol for stoichiometric pyrochlore, defect fluorite and weberite, respectively. Despite this

apparent deficiency of the DFT relative to the DFT+ U method, it very accurately reproduces the experimental value for stoichiometric $\text{Nd}_2\text{Zr}_2\text{O}_7$ of Navrotsky et al.[27]. The computed value (-70.8 kJ/mol) falls within uncertainties of the published value (71.6 ± 3.3 kJ/mol[27]). We note also that DFT fits well all measured formation enthalpies of the samples from the pyrochlore domain. This suggests that the electronic correlation effects do not affect the result in this case. On the other hand, a more significant offset is observed for the defect fluorite and weberite. We thus assumed that these offsets result from the correlation of f -electrons [45] and calibrated the computed DFT formation enthalpies by applying the corrections that reflect the difference between the DFT and DFT+ U results obtained for the stoichiometric case, weighted by the number of f -electrons (number of Nd atoms). We checked that the corrected formation enthalpies are consistent with the DFT+ U calculations. This confirms that f -electrons correlations are responsible for the discussed offsets.

As shown in Figure 7 the computed formation enthalpies of the pyrochlore phase are in excellent agreement with the experimental data over the entire Nd content range. This indicates that the proposed model (Figure 2) adequately describes the pyrochlore phase. On the other hand the predicted formation enthalpies of defect fluorite are about 10 kJ/mol more exothermic than the measured data which fall into the defect fluorite domain. On the modeling side this rather small energy difference could be attributed to uncertainties of the applied methods, including DFT and the limited size of the special quasi-random structures [102]. On the other hand, the assumption of complete disorder of the cationic and anionic sublattices, implemented within the constructed special quasi-random structures, certainly oversimplifies the real structure of defect fluorite [58]. We note that the measured enthalpy values fall between the enthalpy limits of the defect

fluorite and weberite structures. At the order-disorder transition composition the trends representing fluorite and weberite deviate by ~ 30 kJ/mol. With the increase in the fraction of Nd the enthalpy difference increases. The formation enthalpy of the stoichiometric weberite of 31.6 kJ/mol is by ~ 72 kJ/mol less exothermic than that of the defect fluorite, while the difference in the formation enthalpies between stoichiometric weberite and pyrochlore is ~ 39.8 kJ/mol. We note that the last value is close to the disordering enthalpy of 37.8 ± 3.1 kJ/mol measured by Saradhi et al. [59] for the $\text{Eu}_2\text{Zr}_2\text{O}_7$ composition. The disordering enthalpy for the $\text{Eu}_2\text{Zr}_2\text{O}_7$ system, computed assuming an ideal defect fluorite structure of disordered fluorite, is 72 kJ/mol [48]. This is much higher than the value reported by Saradhi et al. [59]. The independent measurement of the disordering enthalpy for the $\text{Eu}_2\text{Zr}_2\text{O}_7$ system by Saradhi et al. [59] thus supports the finding of significant short-range order in the disordered fluorite phase as reported by Shamblin et al [58]. The computed formation enthalpies of weberite are significantly less exothermic (by ~ 10 kJ/mol) than the measured enthalpies of the disordered fluorite. In general the formation enthalpies measured here for defect fluorite samples are located between the results predicted for defect fluorite and weberite structures. This suggests that at these compositions the structure of defect fluorite is short range ordered according to the weberite scheme, but this ordering is incomplete. The extent of this ordering can be approximately estimated from the free energies of the participating phases.

The Gibbs free energy difference between two phases can be estimated according to

$$\Delta G = \Delta H - T\Delta S_{\text{conf}} \quad (1)$$

wherein our case ΔH is the DFT-calculated enthalpy difference between special quasi-random structures that emulate the disordered phase and pyrochlore, while ΔS_{conf} is the

difference in the configurational entropies of the two phases. Here, we neglect contributions from the vibrational entropy, assuming that they are similar for both phases. The same approach was used in previous studies for a prediction of the critical temperatures of order-disorder transition in pyrochlores [45, 48].

The configurational entropy S_{ideal} per mole of a site, in which A and B atoms are randomly distributed, is given by the ideal mixing model:

$$S_{\text{ideal}} = -R(x_A \ln x_A + x_B \ln x_B) \quad (2)$$

where R is the gas constant and x_A and x_B are the mole fractions of A and B atoms in a given structural site. The entropy of the defect fluorite phase is the sum of the ideal mixing entropies of the cationic and anionic sublattices. The configurational entropy of the pyrochlore phase is solely combined of the ideal mixing entropies of Nd- and O-vac-sublattices. The configurational entropies of pyrochlore (S_{PY}), fully disordered defect fluorite (S_{DF}) and weberite (S_{WB}), assuming the applied disordering models are computed as follows:

$$\begin{aligned} S_{\text{PY}} &= -3R\{2x \ln(2x) + (1 - 2x) \ln(1 - 2x)\} \\ S_{\text{DF}} &= -4R\left\{x \ln(x) + (1 - x) \ln(1 - x) + \frac{x}{2} \ln\left(\frac{x}{4}\right) + \left(2 - \frac{x}{2}\right) \ln\left(1 - \frac{x}{4}\right)\right\} \\ S_{\text{WB}} &= -2R\{x \ln(x) + (1 - x) \ln(1 - x) + (1 - 2x) \ln(1 - 2x) + (2x) \ln(2x)\} \end{aligned} \quad (3)$$

The computed S_{conf} values are visualized in Figure 8a and listed in Table 3. The entropy of the fully disordered defect fluorite always exceeds the entropy of the partially ordered pyrochlore or weberite. It is interesting to note that the entropy for the $\text{Eu}_2\text{Zr}_2\text{O}_7$ phase of 17.8 J/mol/K, which is computed from the measured enthalpy of disordering [59] and the measured temperature of this transition [60], appears to be much more consistent with

the entropy of the stoichiometric weberite (11.5 J/mol/K) (Figure 8a, red filled square) than of the fully disordered fluorite. This supports the finding of Shamblin et al. [58] that the weberite-type structure is a better representation of the disordered pyrochlore at the local scale. The entropy of the order-disorder transition at the Nd fraction of $x = 0.31$ of 16 J/mol/K estimated from the experimental data obtained here is much smaller than the entropy difference between the defect fluorite and pyrochlore. This again indicates substantial ordering in the disordered fluorite phase. Assuming that the configurational entropy of pyrochlore is well reproduced by our model, the experimentally constrained transition entropy indicates the entropy of the disordered phase of ~ 33 J/mol/K, which falls between the values predicted for weberite and defect fluorite. Similarly, the measured formation enthalpies fall between the formation enthalpy sequences computed with the defect fluorite and weberite models. Both results indicate that at the transition composition the structure of defect fluorite has a certain degree of short range order according to the weberite structural scheme.

Accordingly, the degree of short range order can be defined as the fraction of weberite-type domains within the disordered matrix of defect fluorite. Although this definition does not fully reflect the nature of short range ordering, and the size of these domains is not constrained, we believe that such a model can approximately emulate the thermodynamic effect of this partial ordering phenomenon. The fraction of weberite-type domains, n_{WB} , at a given temperature can be estimated from a two-state model:

$$\frac{n_{DF}}{n_{WB}} = e^{\frac{-\Delta G}{kT}}, n_{DF} + n_{WB} = 1 \quad (4)$$

where ΔG is the free energy range due to the weberite-defect fluorite transition. These fractions for selected Nd concentrations and $T = 1873$ K are listed in Table 3. The

resulting entropy ($T = 1873$ K) is plotted in Figure 8a. The two-state model predicts the transition entropy of ~ 15 J/K/mol, which is in good agreement with the experimentally constrained value. The enthalpy isotherm is plotted in Figure 7. It reproduces well the experimental data that fall into the defect fluorite domain.

The order-disorder transition temperature for stoichiometric $\text{Nd}_2\text{Zr}_2\text{O}_7$ can be computed by solving self-consistently equations (1), assuming $\Delta G = 0$, and (4) by selecting an initial value of n_{WB} and T , by evaluating the free energy of the disordered phase (DP) as $G_{\text{DP}} = n_{\text{DF}}G_{\text{DF}} + n_{\text{WB}}G_{\text{WB}}$ and taking $\Delta G = G_{\text{DP}} - G_{\text{PY}}$. This procedure results in a transition temperature of $T = 2405$ K, which is in good agreement with the experiment [61]. The order-disorder transition temperatures computed assuming different models of disordered pyrochlore are compared in Table 4 with the measured value [1, 61]. However, consistent with previous studies [45, 48], the experimental transition temperature could be reasonably well estimated assuming the defect fluorite structure. On the other hand, the same calculation with the weberite structure results in a much higher transition temperature of 3452 K. This suggests that if weberite correctly characterizes the ordering scheme of the disordered phase, the degree of short range ordering is likely to be incomplete.

Table 3: The configurational entropy S_{conf} in J/K/mol in pyrochlore (PY), defect fluorite (DF), weberite (WB) and the two-state weberite/defect fluorite model (DF/WB) with fractional concentrations n_{WB} and n_{DF} derived assuming $T = 1873$ K.

X	PY	DF	WB	DF/WB	n_{WB}	n_{DF}
0.50	0.0	48.1	11.5	27.4	0.57	0.43
0.44	9.4	45.7	17.7	30.1	0.56	0.44

0.38	14.0	42.7	20.4	31.2	0.52	0.48
0.33	15.9	40.3	21.2	31.1	0.48	0.52
0.31	16.5	38.9	21.3	30.8	0.46	0.54
0.30	16.7	38.3	21.3	30.7	0.45	0.55

Table 4: The order-disorder transition temperature for stoichiometric pyrochlore predicted assuming different phases of the disordered pyrochlore and different disordering enthalpies. The experimental value is provided for comparison [1, 61].

Phases	$\Delta S_{\text{conf}}(\text{J/K/mol})$	$T_{\text{O-D}}(\text{K})$
PY-DF	48.1	2310
PY-WB	11.5	3452
PY-WB/DF (two-state)	38.1	2405
Exp		2573±50

Figure 8b shows the difference in the free energies between the pyrochlore and defect fluorite, in which the fraction of weberite corresponds to 1873 K. Our calculations predict the free energy difference to cross the zero line at $x = 0.295$. This composition is consistent with the measured Nd transition content of 0.312 (at $T = 1873 \text{ K}$), indicating a good predictive capability of the two-state model. Thus, although the two-state model certainly oversimplifies the nature of the short range ordering in defect fluorite we think that it fulfills its role by indicating the importance of this phenomenon in the order-disorder transition in pyrochlore. A more detailed understanding of the short range phenomenon in the disordered phase requires more elaborated thermodynamic modeling and further experimental investigation.

4 Summary and conclusions

We investigated the composition induced order-disorder transition in the $\text{Nd}_x\text{Zr}_{1-x}\text{O}_{2-0.5x}$ pyrochlore with a combination of complementary experimental and atomistic modeling techniques and provide a refined understanding of the disordering process in this material. The obtained XRD data show a continuous decrease in the lattice parameters with an increasing substitution of Nd by Zr. The transition from the pyrochlore to the defect fluorite phase is located at $0.30 < x < 0.33$. The drop solution calorimetric measurements of the enthalpy formation allowed an estimation of the enthalpy and entropy changes at the order-disorder transition of 30 kJ/mol and 16 J/K/mol, respectively, at the synthesis temperature of 1873 K. The state-of-the-art *ab initio* calculations performed on the specially designed quasi-random structures allowed the prediction of the lattice parameters of the $\text{Nd}_x\text{Zr}_{1-x}\text{O}_{2-0.5x}$ phases and the formation enthalpies of the pyrochlore phase which are in excellent agreement with the measured values. The experimental formation enthalpies of the disordered phase fall between the values predicted for defect fluorite and weberite. The ordering isotherm can be reproduced by a simple two-state model of defect fluorite and weberite. This model predicts the transition at $x = 0.3$, which is in very good agreement with the transition composition derived from our XRD data. Our results thus suggest that the defect fluorite phase is not completely disordered. This conclusion is consistent with recent findings of weberite-type short range ordering in defect fluorite. A more detailed understanding of the disordered structures would require more elaborated statistical-thermodynamic modeling as well as further experimental effort. Nevertheless, the good performance of the *ab initio* methods in describing the enthalpy effects associated with different ordering structures is encouraging, as it offers a possibility to estimate standard thermodynamic

properties of various experimentally challenging actinide-bearing pyrochlore matrices that are currently discussed in the nuclear waste management context. This is an important finding, which could provide approaches to be applied for more straightforward modeling of thermodynamic equilibria involving pyrochlores of variable compositions at various temperatures.

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Figure captions

Figure 1: Schematic representation of the cationic coordination polyhedra of (a) the pyrochlore and (b) defect fluorite structure with the oxygen vacancies as white spheres.

Figure 2: Model of the partial disordering of a $\text{Nd}_x\text{Zr}_{1-x}\text{O}_{2-0.5x}$ pyrochlore. The $2 \times 2 \times 2$ supercell contains 32 cation and 8 O-vac sites. The cationic sites are divided into the two Nd- and Zr-sublattices. The excess Zr atoms are randomly distributed in the Nd-sublattice and the additional O atoms are randomly distributed on the O-vac-sublattice. The parameter k corresponds to the number of excess Zr atoms introduced into the Nd-sublattice.

Figure 3: Representative powder XRD pattern of $\text{Nd}_x\text{Zr}_{1-x}\text{O}_{2-0.5x}$ with $x = 0.25$ (green), 0.31 (blue) and 0.50 (red). For $x = 0.31$ the defect fluorite and pyrochlore crystal structure coexist, whereas for 0.25 and 0.50 a single defect fluorite or pyrochlore phase are obtained. For each of the three chemical compositions of (a) in (b-d) the (662) pyrochlore and (331) defect fluorite reflections are plotted with the corresponding Gaussian fit function. Adapted from [103].

Figure 4: Lattice parameter a for various chemical compositions. The lattice parameters of the defect fluorite structure were multiplied by two for better comparison with the pyrochlore samples. The vertical dashed lines indicate the phase boundaries of the pyrochlore (PY) (right) and defect fluorite (DF) (left) crystal structure respectively, as it was determined from the samples sintered at 1873 K for at least 5 h. The uncertainty is within the size of the symbols.

Figure 5: Enthalpy of formation ($\Delta H_{f, \text{ox}, 298\text{K}}$) for the various pyrochlore and defect fluorite compositions. Red circles: defect fluorite structure, blue squares: pyrochlore structure, yellow triangle: stoichiometric $\text{Nd}_2\text{Zr}_2\text{O}_7$ pyrochlore, taken from [27].

Figure 6: The computed and the measured lattice parameters of $\text{Nd}_x\text{Zr}_{1-x}\text{O}_{2-0.5x}$ pyrochlore (PY), defect fluorite (DF) and weberite (WB). Note the improvement of the computed values when the PBEsol function is used.

Figure 7: The computed formation enthalpies of $\text{Nd}_x\text{Zr}_{1-x}\text{O}_{2-0.5x}$ pyrochlore (green), defect fluorite (red) and weberite (blue). The dashed lines represent the 3rd order polynomial fits to the *ab initio* data. The thick dashed red line represents the result of the two-state model of disordered phase computed at $T = 1873$ K. The *ab initio* results are compared with the experimental data (black squares).

Figure 8:(a) The configurational entropies of $\text{Nd}_x\text{Zr}_{1-x}\text{O}_{2-0.5x}$ pyrochlore (green), defect fluorite (red), weberite (blue) and disordered pyrochlore modeled by two-state model assuming $T = 1873$ K (red dashed). The double arrow indicates the configurational entropy difference measured here. The red filled square indicates the entropy measured for the $\text{Eu}_2\text{Zr}_2\text{O}_7$ system [59], (b) the computed free energy differences between $\text{Nd}_x\text{Zr}_{1-x}\text{O}_{2-0.5x}$ pyrochlore and the disordered phase represented by the two-state model of defect fluorite and weberite computed for a transition temperature of $T = 1873$ K.

(a)

O (8b)

(b)

O-vac (8c) O (8c)

Zr sublattice

Nd sublattice

k=2

O-vac sublattice

Zr sublattice

Nd sublattice

k=4

O-vac sublattice

Zr sublattice

Nd sublattice

k=6

O-vac sublattice

Zr sublattice

Nd sublattice

k=16

O-vac sublattice