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Relationship between the thermodynamic excess properties of mixing and the elastic moduli in the monazite-type ceramics

Piotr M. Kowalski[a,b,*], Yan Li[a,b]

[a] Institute of Energy and Climate Research (IEK-6), Forschungszentrum Jülich, Wilhelm-Johnen-Strasse, 52425 Jülich, Germany
[b] JARA High-Performance Computing, Schinkelstrasse 2, 52062 Aachen, Germany

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A B S T R A C T

Using *ab initio* quantum chemistry we computed the excess thermodynamic properties and the elastic moduli for a series of monazite-type single substitution solid solutions ($Ln_{1-x}Ln_xPO_4$). We found that the Margules interaction parameters of all the solid solutions can be described by a simple function of the endmembers volume mismatch ΔV, i.e. $W(\text{kJ/mol}) = 0.616(\Delta V(\text{cm}^3/\text{mol}))^2$. We show that the obtained relationship could be also derived by considering the strain energy resulting from the substitution of cations of different sizes, knowing the Young's modulus and the volumes of endmembers. This indicates that the strain resulting from the structural incorporation of cations is a major factor responsible for arising of the excess properties in monazite-type ceramics. Our results show thus a way to estimate the excess thermodynamic properties of solid solutions from the structural and elastic parameters, namely the endmembers volumes and the Young's modulus, which could be easily measured or computed.

1. Introduction

Naturally occurring monazites contain up to 32 wt.% ThO_2 and 16 wt.% UO_2 without significant radiation damage to their crystalline structure [1] which makes monazite-type ceramics potentially suitable for the conditioning of long-lived radionuclides such as minor actinides (Np, Am, Cm) or Pu [2–5]. Although reactor- or weapon-grade plutonium is a fissile material that could be used as nuclear fuel, its immobilization in ceramic waste forms is considered as a solution to the threat of nuclear weapon proliferation. Moreover, there exist Pu-bearing waste streams and stocks of separated civilian Pu unsuitable for reuse as nuclear fuels, requiring immobilization prior to geological disposal [6]. Monazites are considered as potential ceramic nuclear waste forms due to high potential waste load, chemical and structural flexibility, various synthesis routes and high corrosion resistance [7,3–5,8]. However, before these ceramics could be used in nuclear waste management their physical and chemical properties, most importantly the thermodynamic parameters and stability upon incorporation of actinides [9–11], dissolution and corrosion behaviour [12,13] and resistance to radiation damage [14–16], have to be well characterized and understood. Characterization of properties of solid solutions are very important in that aspect. This is because ceramics consisting of a mixture of radionuclides with host matrix cations are usually considered for the nuclear waste conditioning and disposal purposes [7,17–20].

The excess enthalpy of mixing, H^E, is one of the major parameters used in the assessment of stability of a solid solution [21]. It describes the heat absorbed or released upon formation of a solution and for the monazite-type ceramics it is represented by a regular solid solutions model so $H^E = Wx(1-x)$, where W is the Margules interaction parameter [22,23,9]. H^E is an important thermodynamic parameter that determines the formation of a miscibility gap and potential phase separation [21,24], which from the perspective of a solid-solution-type ceramic waste form is an undesired behavior. Since H^E represents the excess energy of mixing it is usually a small quantity of up to a few kJ/mol which is also the level of uncertainty of the available calorimetric methods. Therefore it is usually very difficult to measure the H^E values accurately. As a consequence, the experimental data are available only for the $La_{1-x}Ln_xPO_4$ solid solutions with Ln = Nd, Eu and Gd but have high uncertainties of ~50% [22]. On the other hand the Margules interaction parameters can be derived by *ab initio* atomistic simulations which also allows for investigation of the mechanisms producing the excess properties in the considered solid solutions [9].

Our recent calculations of the $La_{1-x}(Ln/An)_xPO_4$ (Ln=La, Ce,...and Dy, An=Pu, Am and Cm) solid solutions demonstrated that the Margules interaction parameter increases quadratically as a function of the unit-cell volume mismatch between the

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[*] Corresponding author at: Institute of Energy and Climate Research (IEK-6), Forschungszentrum Jülich, Wilhelm-Johnen-Strasse, 52425 Jülich, Germany.
E-mail address: p.kowalski@fz-juelich.de (P.M. Kowalski).

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endmembers. In general there are many cases of such a behavior known in the literature, although the underlying reasons are not fully understood [25]. There is an agreement that the main contributor to the excess properties is the strain energy arising from the incorporation of cations which sizes differ from the size of the cations that form the matrix. In addition there may be also chemical energy contribution arising for instance from the change in Coulombic interaction when mixing cations of different charge or from the change in the type of bonding in the system (covalent vs. ionic) [25]. However, having cations of the same +3 charge and very similar bonding in the considered monazite-type solid solutions we do not expect either of the effects to be important and thus one can suspect that the strain energy is the dominant factor that determines the excess enthalpy of mixing.

In this paper we report the results of systematic calculations of the Margules interaction parameters of all the monazite-type single substitution solid solutions. The main aims of these studies have been to check if the relationship between the Margules interaction parameters and the volume difference of endmembers derived by Li et al. [9] for the $La_{1-x}(Ln/An)_xPO_4$ solid solution case describes in general the excess thermodynamic properties of all monazite-type solid solutions that involve the mixture of any two Ln^{3+} cations and if it does, to find a physical explanation of this phenomenon. Assuming that the main contribution to the thermodynamic excess properties comes from the strain we attempted a derivation of the excess enthalpies of mixing from the elastic moduli by considering the strain energy produced by mixing of cations of different sizes. The Young's, bulk and shear moduli required to estimate the strain energy were also systematically computed for a series of monazites and compared with the available experimental data. The resulting elastic properties-based estimates of the Margules interaction parameters are then compared with the independent *ab initio* results.

2. Computational methods

The *ab initio* calculations were performed with plane-wave Quantum-ESPRESSO package [26] using density functional theory with the PBEsol exchange correlation functional [27] which was shown to produce good structures and energetics of monazites [28]. The computational setup is identical to the one used in our previous studies of monazite-type solid solutions [9]. We applied the energy cutoff of 50 Ryd and the core electrons were modeled by the ultrasoft pseudopotentials [29]. The modeled monazite-type ceramics were represented by 192 atoms containing 2 × 2 ×2 supercells and the structures of the 50:50 solid solutions were modeled with the quasi random structures (QRS) [30] constructed by Li et al. [9]. We assumed the regular solid solutions model where the excess enthalpy H^E is described by a single Margules interaction parameter W as $H^E = W \cdot x \cdot (1-x)$ [31,21,22]. The experimental and atomistic modeling studies have shown that this model describes well the monazite-type solid solutions [22,9]. Having the energies of the supercells the Margules interaction parameter is computed as:

$$W = \frac{1}{8}E_{tot}(Ln^{a}{}_{16}Ln^{b}_{16}(PO_4)_{32}) - \frac{1}{16}(E_{tot}(Ln^{a}{}_{32}(PO_4)_{32}) + E_{tot}(Ln^{b}_{32}(PO_4)_{32})), \tag{1}$$

where $E_{tot}(Ln^{a}_{16}Ln^{b}_{16}(PO_4)_{32})$ is the total energy of the QRS supercell and $E_{tot}(Ln^{a,b}{}_{32}(PO_4)_{32})$ are the total energies of the supercells that represent the Ln^aPO_4 and Ln^bPO_4 endmembers, where a and b superscripts indicate different Ln cations. The uncertainties of the computed interaction parameters are mainly a consequence of the quality of the applied computational method. Because we have already shown that the applied PBEsol exchange-correlation functional results in very good prediction of the structural and thermodynamic parameters of monazites [28,10] we assume that these uncertainties are rather small. The reported here good match between the Margules interaction parameters calculated *ab initio* and derived considering the strain energy, which is also estimated from the experimental data, indicates that the computational errors are rather small.

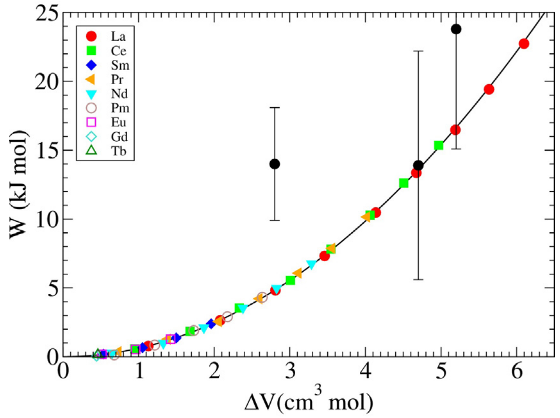

Fig. 1. The Margules interaction parameters W derived here for the $Ln_{1-x}Ln_xPO_4$ (Ln=La, Ce,. . .and Dy) solid solutions plotted as a function of the unit-cell volume mismatch, ΔV. The line represents the $W(\mathrm{kJ/mol}) = 0.616(\Delta V(\mathrm{cm^3/mol}))^2$ fit to the computed data. The experimental data (filled circles with error bars) comes from Popa et al. [22]. We note that the experimental error bars could be underestimated [9].

The elastic moduli were computed from the stiffness–strain relationship following the procedure outlined in Wang et al. [32] by derivation of the compliance tensor constructed by inversion of the computed stiffness matrix. In order to get the value of the effective elastic moduli we applied the Voigt-Reuss-Hill averaging scheme [33].

3. Results

Our previous *ab initio* calculations of the $La_{1-x}Ln_xPO_4$ (Ln =Ce, Sm,. . ., and Dy) solid solutions demonstrated that the Margules interaction parameter increases quadratically as a function of the endmembers volume mismatch ΔV, namely $W(\mathrm{kJ/mol}) = 0.618(\Delta V(\mathrm{cm^3/mol}))^2$ [9]. Interestingly, Li et al. [9] found that this relationship is also valid for the analogous solid solutions with actinides ($La_{1-x}An_xPO_4$). The Margules interaction parameters computed in the scope of the current studies for a series of the $Ln_{1-x}Ln_xPO_4$ solid solutions (Ln=La, Ce,. . ., and Dy) are shown in Table 1 and illustrated in Fig. 1. It is clear that the interaction parameters derived here follow the same trend as derived for the $La_{1-x}Ln_xPO_4$ solid solution. Fitting the parabola to all the data given in Fig. 1 we obtained $W = 0.616\Delta V^2$, thus relationship that is well consistent with the one derived previously for La:(Ln, An) solid solutions. This apparent property-structure correlation obtained for all the considered monazite-type solid solutions requires further explanation.

Assuming that the major contributor to the excess properties of a monazite-type solid solution is the strain energy resulting from the incorporation of different sizes cations into the crystalline lattice, the Margules interaction parameters could be estimated from the elastic energy arising from the incorporation of the larger/smaller size cation into a given crystalline lattice [34,35,25]. The Hook's law relates the Young's modulus to the force F required to cause a stain in an element of material in the following way:

$$E = \frac{Fl_0}{A_0 \Delta l}, \tag{2}$$