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Ab initio calculation of excess properties of $La_{1-x}(Ln,An)_xPO_4$ solid solutions

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ABSTRACT

We used *ab initio* computational approach to predict the excess enthalpy of mixing and the corresponding regular/subregular model parameters for $La_{1-x}Ln_xPO_4$ (Ln=Ce,…, Tb) and $La_{1-x}An_xPO_4$ (An=Pu, Am and Cm) monazite-type solid solutions. We found that the regular model interaction parameter W computed for $La_{1-x}Ln_xPO_4$ solid solutions matches the few existing experimental data. Within the lanthanide series W increases quadratically with the volume mismatch between $LaPO_4$ and $LnPO_4$ endmembers ($\Delta V = V_{LaPO_4} - V_{LnPO_4}$), so that $W(\mathrm{kJ/mol}) = 0.618(\Delta V\ (\mathrm{cm^3/mol}))^2$. We demonstrate that this relationship also fits the interaction parameters computed for $La_{1-x}An_xPO_4$ solid solutions. This shows that lanthanides can be used as surrogates for investigation of the thermodynamic mixing properties of actinide-bearing solid solutions.

1. Introduction

Monazite-type phosphates are considered as potential nuclear waste forms for immobilization of minor actinides (Np, Am, Cm) and Pu [1,2]. Before these ceramic materials could be used in nuclear waste processing, their ability to incorporate actinides and the thermodynamic properties of the relevant solid solutions should be well characterized and understood. The excess enthalpy of mixing (the heat absorbed or released upon mixing of the pure endmembers) is the major thermodynamic property determining the stability of a solid solution. Within the regular and subregular models, this excess effect is described with polynomials containing adjustable coefficients, named the Margules interaction parameters. These parameters together with the solubility products or the standard Gibbs free energies of the endmembers are essential for modeling the thermodynamic stability of a solid solution phase [3]. However, it is usually very difficult to accurately measure the effects of mixing. For monazite-type phosphates experimental calorimetric data are available only for three solid solutions with the compositions of $La_{1-x}Ln_xPO_4$ (Ln=Nd, Eu, Gd) [4]. The uncertainties of the experimentally derived parameters constitute about 50% of the measured values. In view of the lack of experimental data here we performed systematic calculation of $La_{1-x}Ln_xPO_4$ (Ln=Ce,…, Tb) and $La_{1-x}An_xPO_4$ (An=Pu, Am and Cm) monazite-type solid solutions using the state-of-the-art *ab initio* methods of quantum chemistry. The aim of this study is to derive interaction parameters for a wide range of monazite-type solid solutions, which could be used for further geochemical modeling. We also wish to test structure–property relationships, which have been proposed for monazite-type ceramics in previous studies [2,4,5] and to check whether the results obtained for the solid solutions of lanthanides are transferable to lanthanide–actinide solid solutions.

2. Computational details

The *ab initio* calculations were performed with density functional theory (DFT) using a plane-wave Quantum-espresso package [6]. We applied the gradient-corrected PBEsol exchange correlation functional [7] with the plane wave energy cut-off of 50 Ryd. A recent study [8] has shown that this functional gives good structural parameters of monazite. The effects of the core electrons of Ln, An, O and P on the wave functions were modeled with the aid of ultrasoft pseudopotentials [9]. The $5s^2\ 5p^6 6s^2$ electrons of lanthanides and $6s^2\ 6p^6 6d^1 7s^2$ of actinides were treated explicitly. The $4f$ and $5f$ electrons of Ln and An were included into the core. This simplification is thought to be particularly valid for the description of excess

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properties of isostructural solid solutions, as many effects related to strong electronic correlations tend to cancel out. This is because the energy differences between materials that have similar ionic structures and electronic configurations are considered. As a $2\times2\times2$ supercell of monazite contains 192 atoms, the calculations were restricted to gamma point only. Our previous study of monazite systems [8] has shown that with this setup the energies are converged to within 0.1 kJ per mole of LnPO$_4$. This precision is sufficient for present needs.

Popa et al. [4] have shown that the excess enthalpies of the considered solid solutions can be well described with the subregular model:

$$\Delta H^E=[W_1(1-x)+W_2x]x(1-x)\cong Wx(1-x), \tag{1}$$

where W_1 and W_2 are the Margules parameters. When these parameters are similar (the solid solution is symmetric), the mixing can be described with the regular model, which requires a single parameter $W=(W_1+W_2)/2$. Here we assume that the excess Gibbs free energy is essentially equal to the excess enthalpy. Our test calculations performed on $La_{1-x}(La,Eu)_x PO_4$ solid solution with the aid of empirical interatomic potentials provided by Prof. J.D. Gale from Curtin University have shown that the contribution from the vibrational entropy to the excess free energy at 1000 K does not exceed 8% and thus could be neglected. The interaction parameters W_1 and W_2 were derived from the total energy differences of the model systems, using the Single Defect Method of Sluiter and Kawazoe [10]. The W parameters, which are equal to the slopes of the excess mixing function in the limits of $x=0$ and $x=1$ [10], can be estimated as the ratios of finite changes in the total energy and mole fraction of a supercell of a host endmember due to the insertion of a single substitutional defect (a cation representing the solute phase). In this study we computed the total energies of supercells with the composition of $La_{31}(Ln,An)(PO_4)_{32}$ and $La(Ln,An)_{31}(PO_4)_{32}$. The W_1 and W_2 parameters were computed from Eq. (1) by solving the following equations:

$$W_1\tfrac{31}{32}+W_2\tfrac{1}{32}=\tfrac{1}{32}\Big[E_{tot}(La_{31}(Ln,An)(PO_4)_{32}) - \tfrac{31}{32}E_{tot}(La_{32}(PO_4)_{32})-\tfrac{1}{32}E_{tot}((Ln,An)_{32}(PO_4)_{32})\Big] \tag{2}$$

$$W_1\tfrac{1}{32}+W_2\tfrac{31}{32}=\tfrac{1}{32}\Big[E_{tot}(La(Ln,An)_{31}(PO_4)_{32}) - \tfrac{31}{32}E_{tot}((Ln,An)_{32}(PO_4)_{32})-\tfrac{1}{32}E_{tot}(La_{32}(PO_4)_{32})\Big], \tag{3}$$

where $E_{tot}(La_{32}(PO_4)_{32})$ and $E_{tot}((Ln,An)_{32}(PO_4)_{32})$ are the total energies of 2 × 2 × 2 supercells of LaPO$_4$ and (Ln,An)PO$_4$ endmembers respectively. A similar approach has been recently successfully applied to estimation of interaction parameters of a range of solid solutions with barite- and aragonite-type structures [11].

The single defect method [10] suggests that the enthalpy of mixing in a disordered phase at any intermediate composition x can be predicted from the knowledge of the interaction parameters computed in the dilute limits. This assumption is tested here with the aid of a quasirandom structure (QRS). A QRS is used to represent an $(A_{1-x}B_x)R$ solid solution with a random distribution of exchangeable atoms using a supercell of possibly smaller size [12,13]. We note that in the original publication [12] the quasirandom structures were named SQS (special quasirandom structures). In this study we prefer to use a more general term (QRS) emphasizing that our procedure differs in some detail from the derivation procedure employed in Zunger et al. [12]. A simple approach of arranging A and B atoms randomly within a small cell does not usually result in good representation of the disordered state, as the cell composition, and its excess enthalpy can deviate quite strongly from the ensemble average. The efficient way of reducing fluctuations in the excess enthalpy is to impose control on the occurrence frequencies of clusters such as pairs, triplets, and quadruplets [12,13]. Our experience in modeling of solid solutions of silicates, carbonates and sulfates, where interactions between exchangeable atoms are mediated by anionic groups remaining inert to the process of mixing, suggests that the pair clusters give the most important contribution to the excess enthalpy [11,14,15]. Consequently, the present approach consisted in the search of a 2 × 2 × 2 supercell, in which the frequencies of AB pairs at all cation–cation distances deviated as little as possible from the product $x(1-x)$. The sequence of test structures was created by random swaps of La and Ln atoms in a 2 × 2 × 2 supercell of monazite with the composition of $La_{16}Ln_{16}(PO_4)_{32}$. The probabilities of LaLn pairs were monitored at 23 distances, which fall into the range of 4.11–10.87 Å. As the pairwise interactions at short distances are typically stronger, the squared misfit at each distance was weighted with a factor, which is proportional to the inverse of the squared distance. A QRS with a minimum misfit was found after performing of about 200 000 swaps. This QRS is visualized in Fig. 1. The atomic positions are given in the Supplementary Material. In this structure the probabilities of LaLn pairs deviate slightly from the theoretical (random) values only at the 16th and 20th distances. We assume that the contribution from these pairs to the enthalpy of ordering should be negligibly small, thus the excess enthalpy of this structure should closely match the enthalpy of mixing of a perfectly disordered solid solution. This assumption is confirmed in the next section, where a close agreement between the excess enthalpy of this structure and the enthalpy computed with Eq. (1) at $x=0.5$ is demonstrated. The excess enthalpy of the QRS, H^E_{QRS} and the relevant interaction parameter, W_{QRS}, are derived as

$$H^E_{QRS}=\tfrac{1}{4}W_{QRS}=E_{tot}(La_{16}(Ln,An)_{16}(PO_4)_{32}) -\tfrac{1}{2}\big(E_{tot}(La_{32}(PO_4)_{32})+E_{tot}((Ln,An)_{32}(PO_4)_{32})\big), \tag{4}$$

where $E_{tot}(La_{16}(Ln,An)_{16}(PO_4)_{32})$ is the total energy of the QRS supercell.

3. Results and discussion

The Margules parameters W_1 and W_2 obtained for the considered systems are given in Table 1. All solid solutions are closely described with the regular mixing model. The average asymmetry defined by the difference between W_1 and W_2 parameters is smaller than 1 kJ/mol. Interestingly, the sign of this difference

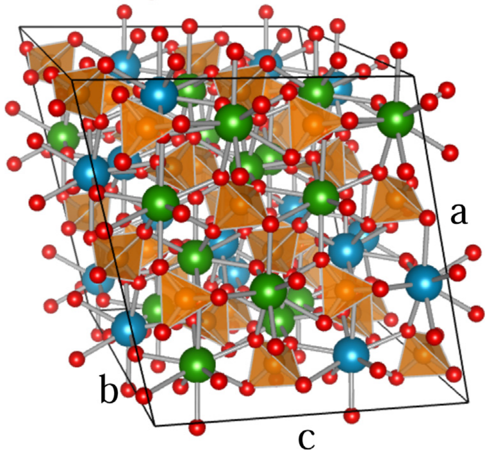

Fig. 1. The quasirandom structure of $La_{0.5}Ln_{0.5}PO_4$ monazite. The La and Ln/An cations are shown as blue and green spheres, respectively (for the color figure refer to the electronic version). PO$_4$ groups are shown as polyhedra. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)