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Lattice Enthalpies, Polarizabilities and Shear Moduli of Lanthanide Orthophosphates $LnPO_4$

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Abstract

Lattice energies $\Delta_L H^\theta$ of lanthanide orthophosphates, $LnPO_4$ (Ln=Ce-Lu, excluding Pm) have been determined from the Born-Haber cycle and compared with those calculated by other methods. The Born-Haber cycle results in close values of $\Delta_L H^\theta$ to those obtained after an empirical equation proposed by Glasser and Jenkins. It has been found that: (i) the partial derivative of the lattice enthalpies to the molar volumes corresponds by dimension and magnitude to the shear moduli of these crystals; (ii) these moduli differ for the monazite- and xenotime-type structures of $LnPO_4$. Molar polarizabilities have been calculated for three $LnPO_4$ with monazite structure, Ln=Ce, Nd, Sm, and for three $LnPO_4$ with xenotime structure, Ln=Tb, Dy, Yb.

Keywords: Lanthanide orthophosphates, lattice enthalpies, shear moduli, molar polarizabilities

1. Introduction

Lanthanide orthophosphates, $LnPO_4$ (Ln = Ce-Lu), are naturally occurring lanthanide compounds within the rare earth series ($REPO_4$). $LnPO_4$ are crystals with the highest thermal stability among the compounds in the binary system $Ln_2O_3 – P_2O_5$ and valuable fundamental properties. For example, the first half of the lanthanide orthophosphates have melting points in the temperature range 2173–2373 K and five groups of applications: optical devices based on the 4f-4f transitions of Ln^{3+}, ionic conductors, geochronology, coatings, and matrices for radioactive wastes.[1–3]

$LnPO_4$ crystallize in two closely related structure types: monoclinic monazite (with space group $P\,2_1/n$), for Ce to Eu, and tetragonal zircon (xenotime) ($I\,41/amd$), for Ho to Lu; $GdPO_4$, $TbPO_4$, and $DyPO_4$ exist in both structure types.[1,2] Each unit cell contains four formula units $LnPO_4$ (Z = 4). The transformations of certain xenotime-type $LnPO_4$ (Ln = Tb, Ho, Er, Tm) to the scheelite ($I\,41/a$) or monazite structure have been studied by high-pressure high-temperature and inelastic neutron scattering.[4]

$LnPO_4$ have been also synthesized on nanoscale, e.g. Ln^{3+}: $GdPO_4$ nanorods as bioprobes for optical and magnetic imaging[5] or one-dimensional nanostructures Eu^{3+}: $LnPO_4$.[6]

The changes of the standard enthalpy (CSE) of formation of lanthanide orthophosphates from lanthanide oxides have been estimated by electronic structure calculations.[7] The results, however, needed a scaling factor in order to achieve a systematic adequacy compared to the alkaline earth carbonates, silicates, and sulfates. The discrepancy has been explained with overestimated electronic total energy derived from the density functional calculations. It has been concluded in the same study that the simplest ionic model and localized charges should reproduce more accurately the mentioned energy characteristics.

A confirmation of the ionic model follows from a study of the electronic structure of $LnPO_4$ by near edge x-ray absorption fine structure spectroscopy which reveals that all lanthanide ions are in (3+) – valence state.[8] The Ln^{3+}-state in $LnPO_4$ has been also achieved for the particular cases of cerium and praseodymium by appropriate stepwise decomposition and reduction in the solid-state syntheses.[3]

The energetics of $LnPO_4$ is important for the systematic studies of this series of compounds, including their thermodynamic stability. The thermodynamic properties of the monazite-type series of $LnPO_4$ are still not very well studied[9] and the stability limits of the same series have been correlated with models based only on geometric criteria.[1]

The amount of energy per mole that binds the ions in the crystal lattice of $LnPO_4$ is among those basic characteristics of these compounds. The purpose of the present work is to determine the lattice enthalpies of $LnPO_4$ by the Born-Haber thermochemical cycle and to relate these quantities to certain mechanical properties and molar polarizabilities.

2. Method

2. 1. Lattice Enthalpies

The lanthanide orthophosphates $LnPO_4$ have a defined stoichiometry and structure with assumed integral charges of the ions in the lattice. Hence, the lattice enthalpies $\Delta_L H^\theta$ can be determined by the Born-Haber cycle after eq. (1) below. The CSE of formation of $LnPO_4$ from oxides, $\Delta_{f,\,ox}H^\theta(LnPO_4)$, has been included to the cycle:

$$\begin{aligned} &-\Delta_{f,\,ox}H^\theta(LnPO_4) - (1/2)\Delta_f H^\theta(Ln_2O_3) - \\ &(1/2)\Delta_f H^\theta(P_2O_5) + \Delta_s H^\theta(Ln) + \Delta_s H^\theta(P) + \\ &+ 2\,\Delta_d H^\theta(O\text{–}O) + \Delta_i H^\theta(Ln) + \Delta_i H^\theta(P) + \\ &+ 4\Delta_{eg} H^\theta(O) - \Delta_L H^\theta(LnPO_4) = 0, \end{aligned} \tag{1}$$

where the following notation has been used:[10] the left-hand side subscript to each enthalpy pertains to, respectively: d-dissociation, eg-electron gain, f-formation, i-ionization, L-lattice, and s-sublimation; the right-hand side superscript ($^\theta$) designates “under standard conditions”: temperature $T = 298.15$ K, pressure $P = 101325$ Pa. The CSE are related to the corresponding energies of dissociation, electron gain, ionization, sublimation, and potential energy of the lattice according to the formulae, respectively:

$$\begin{aligned} &\Delta_d H^\theta = -\Delta_d U^\theta - (5/2)RT,\ \Delta_{eg} H^\theta = \\ &= -[\Delta_{eg} U^\theta - 5RT],\ \Delta_i H^\theta = \Delta_i U^\theta + n(5/2)RT, \\ &n = 3 \text{ for Ln, or } n = 5 \text{ for P, } \Delta_s H^\theta = \\ &= \Delta_s U^\theta + (5/2)RT; \end{aligned} \tag{2}$$

$$\begin{aligned} &LnPO_4(s) \rightarrow Ln^{3+}(g) + P^{5+}(g) + 4\ O^{2-}(g), \\ &\Delta n(g) = +\ 6 \text{ mol; } \Delta_L H^\theta = -\Delta_L U^\theta + 6\ (5/2)\ RT. \end{aligned} \tag{3}$$

The equations of each step (physical or chemical change) of the cycle are presented in Table 1. The data used in the calculations of $\Delta_L H^\theta$ are given in Table 2 and Table 3. The sign of the CSE must be reversed if the actual process takes place in the opposite direction. The overall sum of CSE is equal to zero for a closed path of changes starting and ending at the same state. The final step of the cycle is the formation of lanthanide orthophosphate in solid phase, $LnPO_4(s)$, from a gas of separated ions. This process is reverse in direction to that one in the definition of lattice energy as displayed in the first of eqs. (3).

2. 2. Molar Polarizations

The molar polarization P_m of a substance can be obtained by the Debye equation:

$$P_m = \frac{\varepsilon_r - 1}{\varepsilon_r + 2} V_m,\ \ V_m = \frac{M}{\rho}. \tag{4}$$

Experimental relative permittivity $\varepsilon_r = \varepsilon/\varepsilon_o$, molar mass $M/10^{-3}$ kg mol^{-1}, and density $\rho/10^3$ kg m^{-3} are needed in the determination of a molar polarization.

P_m has a dimension of m^3 mol^{-1}, i.e. the same as the molar volume V_m. Polarization of ionic solids arises almost exclusively from ionic polarizabilities which in turn originate from displacements of cations and anions in opposite directions by the applied electric field.

3. Results and Discussion

3. 1. Lattice Enthalpies

The lattice enthalpies obtained in this study are presented in Table 4. The values of the CSE of $LnPO_4$ lattice determined by the Born-Haber cycle vary in a narrow range, less than ± 0.8 % to their mean value within the lanthanide series. The deviations quoted in the same table should be considered as minimal since four out of nine quantities included in eq. (1) for determination of $\Delta_L H^\theta$ have been reported with standard deviations.

Table 1. Born – Haber cycle for lanthanide orthophosphates, $LnPO_4$

No	Equation of the process in each step	ΔH^θ
1.	$LnPO_4(s) \rightarrow (1/2)Ln_2O_3(s) + (1/2)P_2O_5(s)$	$-\Delta_{f,\,ox}H^\theta$
2.	$(1/2)Ln_2O_3(s) + (1/2)P_2O_5(s) \rightarrow Ln(s) + P(s) + 2O_2(g)$	$-(1/2)\Delta_f H^\theta$ (Ln_2O_3), (P_2O_5)
3.	$Ln(s) + P(s) + 2O_2(g) \rightarrow Ln(g) + P(s) + 2O_2(g)$	$\Delta_s H^\theta(Ln)$
4.	$Ln(g) + P(s) + 2O_2(g) \rightarrow Ln(g) + P(g) + 2O_2(g)$	$\Delta_s H^\theta(P)$
5.	$Ln(g) + P(g) + 2O_2(g) \rightarrow Ln(g) + P(g) + 4O(g)$	$2\Delta_d H^\theta(O_2)$
6.	$Ln(g) + P(g) + 4O(g) \rightarrow Ln^{3+}(g) + 3e^- + P(g) + 4O(g)$	$\Delta_i H^\theta(Ln)$
7.	$Ln^{3+}(g) + 3e^- + P(g) + 4O(g) \rightarrow Ln^{3+}(g) + 3e^- + P^{5+}(g) + 5e^- + 4O(g)$	$\Delta_i H^\theta(P)$
8.	$Ln^{3+}(g) + P^{5+}(g) + 4O(g) + 8e^- \rightarrow Ln^{3+}(g) + P^{5+}(g) + 4O^{2-}(g)$	$4\Delta_{eg} H^\theta(O)$
9.	$Ln^{3+}(g) + P^{5+}(g) + 4O^{2-}(g) \rightarrow LnPO_4(s)$	$-\Delta_L H^\theta$

Table 2. Changes of standard enthalpies of phosphorus and oxygen

ΔH^θ / kJ mol^{-1}	Value	Reference
$\Delta_i H^\theta$ (P)	17101.9	[11]
$\Delta_s H^\theta$ (P-white)	12.4	[12]
$\Delta_f H^\theta$ (P_2O_5)	– 1493.0	[13]
$\Delta_d H^\theta$ (O)	498.36 ± 0.17	[11]
$\Delta_{eg} H^\theta$ (O)	715.4	[10]

$\Delta_L H^\theta$ obtained in this work are compared in Table 4 with an empirical equation for lattice potential energy $\Delta_L U$, i.e. U_{POT},[14] in the following form:

$$U_{POT} = A\, I \left(\frac{2I}{v_m}\right)^{1/3} \qquad (5)$$

where A = 121.39 kJ mol^{-1} nm is an electrostatic factor, $I = ½\, \Sigma\, n_i\, z_i^2$ is the ionic strength with n_i being the number of ions with charge z_i per formula and v_m is the molecular volume in nm^3; the values of v_m are given in Table 4.

According to eq. (3), both quantities $\Delta_L H^\theta$ and $\Delta_L U$ are related by factors proportional to RT = 2.48 kJ mol^{-1} at T = 298.15 K, i.e. by 37.2 kJ mol^{-1}. The latter presents only 0.14% of the mean value of $\Delta_L H^\theta$ in the series. The values derived here by the Born – Haber cycle are less than 1.5% higher than those in the last column of Table 4 as determined by the empirical eq. (5), except for $GdPO_4$(m), $TbPO_4$(m), and $LuPO_4$(x) which are lower by 0.15 %, 0.5%, and 0.12%, respectively. It has been pointed out that eq. (5) used to obtain the last column in Table 4 results in estimates with certainty ± 7% compared to the known values.[14]

Table 3. Standard enthalpy changes of formation of lanthanide orthophosphates and sesquioxides, and of sublimation and ionization of lanthanide metals (all in kJ mol^{-1})

$LnPO_4$ [a]	$-\Delta_{f,\,ox}H^\theta$ [2]	$-\Delta_f H^\theta(Ln_2O_3)$ [11]	$\Delta_s H^\theta$(Ln) [11]	$\Delta_i H^\theta$(Ln) [16]
$CePO_4$(m)	317.2 ± 4.8	1796.2	422.6	3541.7 ± 9.9
$PrPO_4$(m)	312.2 ± 5.0	1809.6	355.6	3646.1 ± 9.9
$NdPO_4$(m)	312.0 ± 2.2	1807.9	327.6	3715.8 ± 38.6
$SmPO_4$(m)	301.8 ± 2.1	1823.0 ± 3.0	206.7	3887.7 ± 38.6
$EuPO_4$(m)	286.8 ± 1.8	1651.4 ± 12.1	175.3	4054.3 ± 10.9
$GdPO_4$(m)	296.2 ± 1.3	1819.6 ± 12.1	397.5	3768.1 ±19.3
$TbPO_4$(x)	286.1 ± 1.9	1865.2 ± 7.5	388.7	3808.7 ± 19.3
$TbPO_4$(m)	283.5 ± 1.8			
$DyPO_4$(x)	283.9 ± 1.7	1863.1 ± 7.5	290.4	3916.3 ± 37.4
$HoPO_4$(x)	278.8 ± 2.4	1880.7 ± 4.8	300.8	3941.5 ±19.3
$ErPO_4$(x)	275.6 ± 1.9	1897.9 ± 1.9	317.1	3952.4 ± 19.3
$TmPO_4$(x)	268.0 ± 2.0	1888.7 ± 5.9	232.2	4062.7 ± 17.4
$YbPO_4$(x)	269.6 ± 2.4	1814.6	152.1	4212.6 ± 2.5
$LuPO_4$(x)	263.9 ± 1.9	1878.2	427.6	3905.5 ± 38.7

[a] (m) – monazite structure, (x) – xenotime structure

Table 4. Molecular (v_m) and molar (V_m) volumes and lattice energies of lanthanide orthophosphates

$LnPO_4$	$v_m/10^{-30}$ m^3 [a]	$V_m/10^{-6}$ m^3 mol^{-1}	$\Delta_L H^\theta$/kJ mol^{-1} this work [b]	U_{POT} / kJ mol^{-1} [c]
$CePO_4$(m)	75.156	45.260	26899 ± 15	26493
$PrPO_4$(m)	74.114	44.632	26938 ± 15	26616
$NdPO_4$(m)	73.026	43.977	26978 ± 41	26748
$SmPO_4$(m)	71.384	42.988	27027 ± 42	26951
$EuPO_4$(m)	70.539	42.480	27061 ± 12	27058
$GdPO_4$(m)	69.975	42.140	27091 ± 27	27131
$TbPO_4$(x)	73.180	44.070	27135 ± 25	26729
$TbPO_4$(m)	68.964	41.531	27133 ± 25	27263
$DyPO_4$(x)	72.318	43.551	27141 ± 43	26835
$HoPO_4$(x)	71.500	43.058	27181 ± 24	26937
$ErPO_4$(x)	70.715	42.586	27213 ± 22	27036
$TmPO_4$(x)	70.051	42.186	27226 ± 23	27121
$YbPO_4$(x)	69.353	41.765	27242 ± 5	27212
$LuPO_4$(x)	68.773	41.416	27255 ± 41	27288

[a] values calculated with data from Ref. [2] ; [b] the minimal deviations are indicated (see text); [c] determined after an empirical equation proposed by Glasser and Jenkins.[14]

The molecular and molar volumes of $LnPO_4$ given in Table 4 have been calculated in this study by means of the structural data obtained from recent X – ray diffraction studies.[2] Unit cell volumes of $LnPO_4$ have been also given[15] or compiled for the monazite-type structure only.[1]

A comparison of the lattice enthalpies of $LnPO_4$ obtained in the present work with the lattice energies for the same compounds found by the density functional calculations reveals that the latter are 8–9 % higher than the former; this comparison is based on the graph "lattice energy – lanthanide ionic radius".[7]

It is noteworthy that the values of the lattice enthalpies $\Delta_L H^\theta$ presented here are determined from experimental values of CSE included in eq.(1) and independent on the types of pair interactions, mechanisms of summation, structural properties, etc.

The graphs of lattice enthalpies vs. molar volumes of $LnPO_4$ (with CSE of formation of $LnVO_4$ from oxides) are presented in Figure 1 (monazite structure) and Figure 2 (xenotime structure). The straight lines have regression coefficients: $R^2 = 0.9984$ and $R^2 = 0.9935$, for $LnPO_4$(m) and $LnPO_4$(x) respectively. Their slopes are negative, $(\partial\Delta_L H^\theta/\partial V_m) = -60.6 \times 10^6$ kJ m^{-3}, or $(\partial\Delta_L H^\theta/\partial V_m) = -60.6 \times 10^9$ Pa for the monazite structure of $LnPO_4$, and $(\partial\Delta_L H^\theta/\partial V_m) = -49.1 \times 10^6$ kJ m^{-3}, or $(\partial\Delta_L H^\theta/\partial V_m) = -49.1 \times 10^9$ Pa for the xenotime structure of $LnPO_4$. The negative sign of the slope accounts for the trend of changes of lattice enthalpies vs. molar volumes within the light and heavy lanthanide orthophosphates. Hence, lower approximate limits have resulted for the shear moduli of $LnPO_4$(m), $G \approx 61$ GPa, and $G \approx 49$ GPa for $LnPO_4$(x).

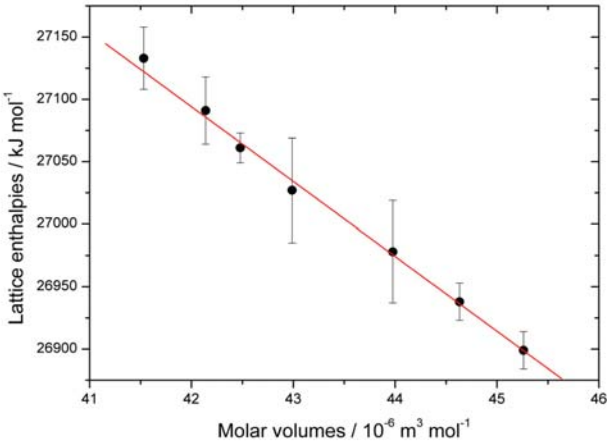

Figure 1. Variation of the lattice enthalpies vs. molar volumes of $LnPO_4$ with monazite structure (Ln = Ce to Tb in $LnPO_4$ follow consecutively from right to left)

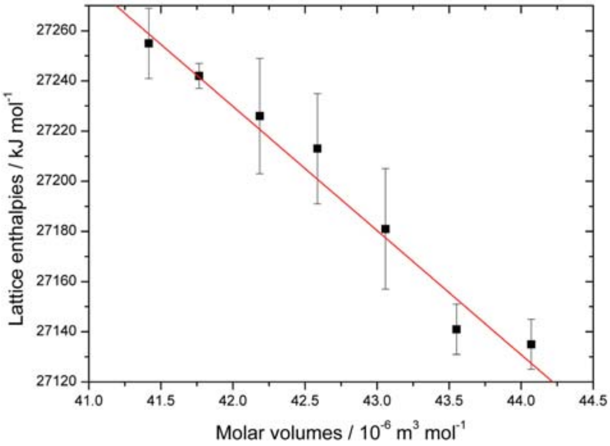

Figure 2. Variation of the lattice enthalpies vs. molar volumes of $LnPO_4$ with xenotime structure (Ln = Tb to Lu in $LnPO_4$ follow consecutively from right to left)

The novelty of the present study is based on the thermodynamic evaluation of lattice energies, on one side, and on the physical meaning and dimension obtained from the slope $(\partial\Delta_L H^\theta/\partial V_m)$, on the other. Only this slope preserves a correct shear- modulus dimension: [J m^{-3}] = [Pa]. Any other linear plot, e.g. $\Delta_L H^\theta = f\,(v_m^{1/3})$ would result in dimension [N mol^{-1}] and unclear physical meaning. Therefore, a possible improvement of the regression coefficient R^2 from a plot other than $\Delta_L H^\theta = f\,(V_m)$ would be incorrect.

The slope $(\partial\Delta_L H^\theta/\partial V_m)$ and shear moduli have the same dimension [Pa]. The meaning of the slope is of a lower limit of energy per volume of formula unit that, after being absorbed, would result in lattice deformation.

Measurements of the shear moduli of monazite $LnPO_4$ have yielded the following values of G in GPa: 64 ± 1 ($PrPO_4$), 63 ± 0.5 ($NdPO_4$), and 79 ± 7 ($EuPO_4$).[20] These results are close to the value of $G \approx 61$ GPa for the monazites found in the present work. It should be also noted that the brittle behavior of the monazites affects the accuracy of micro-indentation experiments.[20] The thermodynamic relations between the internal energy and the moduli of a solid are known at least for crystals of simple structure and small molar volumes.[10]

3. 2. Molar Polarizations

The relative dielectric permittivities, molar volumes and molar polarizations of $LnPO_4$ are presented in Table 5. Microwave dielectric properties of $LnPO_4$ as sintered ceramics have been measured at frequency of 8–12 GHz.[17] The electric field at such frequencies is considered static and uniform. The molecular volume is a portion of that of the unit cell $v_m = (1/4)V_{uc}$. The values of the molar polarizations differ for the monazite- and xenotime-type structures due to the different molar volumes and different dielectric permittivities, i.e. P_m do not change consecutively within the lanthanide series. It has been suggested that the values of ε_r below 10 for the xenotime $LnPO_4$ are due to decreased P – O bond length and stronger covalent bonding in the PO_4 tetrahedra compared with the monazite group.[18,19]

Table 5. Molar polarizations P_m of lanthanide orthophosphates

$LnPO_4$	ε_r [17]	V_m /10^{-6} m^3 mol^{-1}	P_m/10^{-3} m^3 mol^{-1}
$CePO_4$(m)	11.6	45.260	3.53
$NdPO_4$(m)	10.3	43.977	3.32
$SmPO_4$(m)	11.1	42.988	3.31
$TbPO_4$(x)	8.5	44.070	3.15
$DyPO_4$(x)	9.1	43.551	3.18
$YbPO_4$(x)	8.7	41.765	3.00

4. Conclusions

The lattice enthalpies $\Delta_L H^\theta$ of $LnPO_4$ increase slightly with increasing the atomic number in the lanthanide series and remain close to those determined by an empirically derived equation. The dependence between $\Delta_L H^\theta$ and molar volumes V_m is linear with different negative slopes for monazite and xenotime structure types. Both correspond to lattice enthalpy per molar volume and can be considered as a lower limit of the shear moduli for the series of $LnPO_4$(m) and $LnPO_4$(x), respectively. The results indicate that the change from monazite- to xenotime structure type distinctly affects the values of the shear moduli. The difference in the molar volumes has been also reflected in the molar polarizations of certain members of both groups of lanthanide orthophosphates.

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Povzetek

Z uporabo Born-Haberjevega ciklusa smo določili mrežne entalpije, $\Delta_L H^\theta$, lantanidnihorto fosfatov, $LnPO_4$ (Ln=Ce-Lu, razen Pm) ter dobljene vrednosti primerjali s tistimi, izračunanimi z drugimi metodami, predvsem z empirično zvezo, ki sta jo predlagala Glasser in Jenkins. Ugotovili smo, da (i) dimenzija in velikost parcialnega odvoda mrežne entalpije na molski volumen ustreza strižnemu modulu teh kristalov; (ii) ti moduli se razlikujejo za monazitnein ksenotimske tipe struktur $LnPO_4$. Izračunali smo molske polarizabilnosti treh $LnPO_4$ z monazitno strulturo, Ln=Ce, Nd, Sm, in za tri $LnPO_4$ sksenotimsko strukturo, Ln=Tb, Dy, Yb.