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Thermodynamic consistencies and anomalies among end-member lanthanoid garnets

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ABSTRACT

Lanthanoid (or lanthanide) garnets are ionic solids of technological importance in their use in electronic materials. They are also of interest in respect of their systematic relationships and as geochemical tracers. As a consequence, there is considerable published thermodynamic information for these garnets.

Based principally on the computational results of Moretti and Ottonello (1998) [8], we here examine the thermodynamic information for consistencies and anomalies among the ferri-, alumino-, and gallo-garnets using relations between thermodynamic properties that we have established over recent years. The principal properties of interest are formula volume, heat capacity, entropy, and formation enthalpy (from which the Gibbs free energy may be obtained), and isothermal compressibility. We also establish additive single-ion values for trivalent lanthanide cations which may be applied in estimating properties for related materials.

Since the results of the work of Moretti and Ottonello are based upon consistent computational analyses, we should expect generally smooth relations. These are, indeed, found for various of the properties (except for the europium garnets), with some uncertainty in the absolute entropies, and anomalies in the formation enthalpies of europium and ytterbium/lutetium garnets. The results of some more recent experimental work are included in our analyses. Values for the (unknown) promethium garnets are estimated by averaging the properties of the neighbouring neodymium and samarium garnets.

1. Introduction

Over the past two decades and more, colleagues and this author have established a number of useful relations among the thermophysical properties of ionic solids, principally based on the fact that the energetics of ionic solids are essentially controlled by the long-range charge (coulombic) interactions opposed by the short-range repulsions, with only small contributions from other interactions [1]. Furthermore, the standard thermodynamic quantities (such as heat capacity, entropy, and enthalpy) of these materials are integrals over their frequency distributions so that the values generated are insensitive to details of the phonon spectrum [2] and thus largely independent of crystal structural details [3]. These considerations result in reliable correlations among the thermophysical properties, the charges involved, and the formula volumes of the materials, corresponding to a "Volume-Based Thermodynamics" (VBT) [4,5].

Although the lanthanides are not much involved in basic research (and often thus regarded as rare-earth elements), they quite abundant in nature and may play an increasing role in technological applications. Garnets containing lanthanide cations (with general chemical formula $Ln_3M_5O_{12}$) receive considerable thermodynamic attention because of their importance for the electronics industry (consider the ubiquity of Nd:YAG lasers – that is, lasers based on Nd-doped yttrium aluminium garnet material, $Y_3Al_5O_{12}$). They are also of interest in respect of their systematic relationships [6] and as geochemical tracers [7]. However, the behaviour of these lanthanides is not always straightforward: for example, while most exist only as trivalent ions, Ln^{3+}, Eu also can take on divalency while Ce can be quadrivalent, leading to their enrichment or depletion in minerals relative to the other rare-earths – these are the so-called europium and cerium anomalies [7]. The current paper examines the thermodynamics of a large number of lanthanoid (often loosely termed lanthanide) garnets by means of VBT and other relations.

The lanthanoid garnets form in the crystal-structure space group $\boldsymbol{Ia\bar{3}d}$, with the *f*-block Ln^{3+} cations eight-coordinated to oxygen in distorted cubes, and with M^{3+} both octahedrally six-coordinated to oxygen and tetrahedrally four-coordinated to oxygen. The cations all lie in symmetry-controlled positions, with only oxygen having variable fractional coordinates.

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2. Thermodynamic properties

The physico-chemical properties of lanthanoid garnets have received considerable attention, with their advantage of providing a closely-homologous group among which relationships may be examined in detail. Their spectroscopic [6] and thermodynamic [8] properties have been thoroughly examined and reported, and we here use the important thermodynamic data together with other data in considering correlations among these properties.

The principal properties of interest are formula volume, heat capacity, entropy, and formation enthalpy (from which the Gibbs free energy may be obtained), and isothermal compressibility. Table 1 contains corresponding data for the lanthanoid ferri-, alumino-, and gallo-garnets. A noticeable feature in the table is the closeness of the ratio C_p/S to unity, *i.e.*, ambient heat capacities and entropies are closely equal [3]. Since most of our results are derived from the consistent computational analyses of Moretti and Ottonello [8], we should expect generally smooth relations with some discrepancies based upon particular properties of the constituent lanthanide ion.

We initiate examination of the data by considering systematic relations. As a preliminary example, shown in figure 1 are plots for the formula volumes of the alumino-, ferro- and gallo-lanthanoid garnets. The expected systematic variation associated with the decreasing volumes of the later lanthanide ions is clear, together with the smaller volume of the Y^{3+} ion.

Supplementary figures S1a to S1f represent data for formula volume, isochoric heat capacity, absolute entropy, formation enthalpy, lattice energy, and isothermal compressibility, respectively, while Supplementary figures S2a to S2f represent additive single-ion values for the same properties. (Figure S1a duplicates figure 1 for ease of comparison within the Supplementary figures.)

TABLE 1
Formation enthalpy, absolute entropy, formula volume, heat capacity, isothermal compressibility, lattice energy of lanthanoid garnets [8], and ratio of heat capacity to entropy. Italicised values for the unknown promethium garnets are linear interpolations.

Lanthanoid Garnets	$\Delta_f H$/ kJ · mol^{-1}	S/ J · K^{-1} · mol^{-1}	S^b/ J · K^{-1} · mol^{-1}	V_m/ nm^3	C_p/ J · K^{-1} · mol^{-1}	$C_p{}^b$/ J · K^{-1} · mol^{-1}	$10^3\beta$/ GPa^{-1}	U_{POT}/ kJ · mol^{-1}	U_{POT}(limiting)^c/ kJ · mol^{-1}	C_p/S
$Y_3Fe_5O_{12}$	−5085.9	394.0		0.237	411.0		6.20	−56,358	−58,529	1.04
$La_3Fe_5O_{12}$[a]	−4704.8	424.4		0.258	417.8		6.75	−55,124	−56,906	0.98
$Ce_3Fe_5O_{12}$[a]	−4701.3	421.6		0.255	415.7		6.68	−55,247	−57,082	0.99
$Pr_3Fe_5O_{12}$	−4754.2	418.3		0.253	414.2		6.64	−55,398	−57,256	0.99
$Nd_3Fe_5O_{12}$	−4828.9	414.8		0.250	413.7		6.54	−55,577	−57,470	1.00
$Pm_3Fe_5O_{12}$	*−4913*	*412*		*0.248*	*413*		*6.49*	*−55,689*	*−57,615*	*1.00*
$Sm_3Fe_5O_{12}$	−4997.3	408.8	435.1	0.246	412.1	450.8	6.44	−55,801	−57,761	1.01
$Eu_3Fe_5O_{12}$	−4720.1	408.0	432.2	0.245	412.8	467.6	6.42	−55,879	−57,864	1.01
$Gd_3Fe_5O_{12}$	−4994.3	405.9	450.8	0.242	410.7	433.0	6.33	−56,031	−58,083	1.01
$Tb_3Fe_5O_{12}$	−5030.2	419.3	446.9	0.241	411.7	432.2	6.32	−56,099	−58,197	0.98
$Dy_3Fe_5O_{12}$	−5012.1	416.7	427.3	0.239	410.3	426.2	6.26	−56,230	−58,391	0.98
$Ho_3Fe_5O_{12}$	−5038.3	414.7	473.1	0.237	409.1	445.7	6.20	−56,302	−58,509	0.99
$Er_3Fe_5O_{12}$	−5044.9	412.8	483.9	0.235	407.9	428.0	6.15	−56,339	−58,657	0.99
$Tm_3Fe_5O_{12}$	−5016.3	411.3		0.234	409.2		6.11	−56,456	−58,773	0.99
$Yb_3Fe_5O_{12}$	−4879.1	393.2		0.233	407.2		6.08	−56,517	−58,879	1.04
$Lu_3Fe_5O_{12}$	−4967.7	391.1		0.231	407.1		6.05	−56,580	−58,994	1.04
$Y_3Al_5O_{12}$	−7159.0	305.2		0.216	356.6		5.59	−57,200	−59,879	1.17
$La_3Al_5O_{12}$[a]	−6564.2	314.3		0.235	369.2		6.03	−55,752	−58,229	1.17
$Ce_3Al_5O_{12}$[a]	−6589.2	323.2		0.233	367.4		6.00	−55,898	−58,405	1.14
$Pr_3Al_5O_{12}$	−6660.1	324.2		0.231	366.0		5.95	−56,073	−58,581	1.13
$Nd_3Al_5O_{12}$	−6765.6	323.0		0.228	364.2		5.88	−56,282	−58,802	1.13
$Pm_3Al_5O_{12}$	*−6869*	*320*		*0.226*	*363*		*5.83*	*−56,414*	*−58,948*	*1.13*
$Sm_3Al_5O_{12}$	−6972.9	317.7		0.225	362.0		5.79	−56,546	−59,096	1.14
$Eu_3Al_5O_{12}$	−6708.4	306.2		0.224	361.2		5.77	−56,636	−59,198	1.18
$Gd_3Al_5O_{12}$	−7010.7	316.9		0.221	359.4		5.70	−56,816	−59,424	1.13
$Tb_3Al_5O_{12}$	−7059.1	319.0		0.220	358.6		5.68	−56,897	−59,538	1.12
$Dy_3Al_5O_{12}$	−7064.4	318.9		0.218	357.2		5.64	−57,051	−59,735	1.12
$Ho_3Al_5O_{12}$	−7104.5	319.3		0.216	356.6		5.60	−57,137	−59,854	1.12
$Er_3Al_5O_{12}$	−7129.5	315.6		0.215	354.6		5.56	−57,242	−60,005	1.12
$Tm_3Al_5O_{12}$	−7112.4	314.6		0.213	354.3		5.53	−57,320	−60,125	1.13
$Yb_3Al_5O_{12}$	−6987.9	312.3		0.212	354.0		5.52	−57,395	−60,231	1.13
$Lu_3Al_5O_{12}$	−7089.0	298.3		0.211	352.8		5.48	−57,470	−60,353	1.18
$Y_3Ga_5O_{12}$	−5718.8	360.2		0.231	387.4		6.03	−57,457	−58,529	1.08
$La_3Ga_5O_{12}$[a]	−5246.4	371.4		0.252	397.8		6.57	−56,132	−56,906	1.07
$Ce_3Ga_5O_{12}$[a]	−5258.7	380.0		0.249	396.3		6.51	−56,265	−57,082	1.04
$Pr_3Ga_5O_{12}$	−5314.9	380.7		0.247	395.2		6.44	−56,425	−57,256	1.04
$Nd_3Ga_5O_{12}$	−5403.9	379.0		0.244	393.5		6.37	−56,618	−57,470	1.04
$Pm_3Ga_5O_{12}$	*−5496*	*376*		*0.242*	*392*		*6.32*	*−56,739*	*−57,615*	*1.04*
$Sm_3Ga_5O_{12}$	−5588.4	373.5		0.241	391.4		6.26	−56,859	−57,761	1.05
$Eu_3Ga_5O_{12}$	−5316.1	361.1		0.239	390.6		6.24	−56,941	−57,864	1.08
$Gd_3Ga_5O_{12}$	−5602.6	371.2		0.237	389.1		6.17	−57,106	−58,083	1.05
$Tb_3Ga_5O_{12}$	−5644.2	373.5		0.235	388.4		6.13	−57,180	−58,197	1.04
$Dy_3Ga_5O_{12}$	−5637.2	372.1		0.233	387.0		6.07	−57,321	−58,391	1.04
$Ho_3Ga_5O_{12}$	−5669.6	374.1		0.232	387.3		6.02	−57,400	−58,509	1.04
$Er_3Ga_5O_{12}$	−5685.3	370.3		0.230	385.5		5.97	−57,496	−58,657	1.04
$Tm_3Ga_5O_{12}$	−5661.1	367.1		0.228	384.0		5.95	−57,567	−58,773	1.05
$Yb_3Ga_5O_{12}$	−5530.9	366.7		0.227	384.5		5.91	−57,636	−58,879	1.05
$Lu_3Ga_5O_{12}$	−5623.8	350.7		0.226	382.8		5.88	−57,703	−58,994	1.09

[a] La and Ce garnets are not stable under ambient conditions. Promethium is not known in nature.
[b] Reference [9].
[c] U_{POT}(limiting) values for the gallogarnets from $Nd_3Ga_5O_{12}$ to $Lu_3Ga_5O_{12}$ have earlier been reported by Petrov, in a corrected version [10]. There are slight differences between those published and the values listed here on account of small differences in the reference values used.