Revision 1

Enthalpies of formation of rare earth niobates, RE_3NbO_7

Aleksandra Mielewczyk-Gryn[1,2], Alexandra Navrotsky[1]*

[1] Peter A. Rock Thermochemistry Laboratory and NEAT ORU (Nanomaterials in the Environment, Agriculture, and Technology Organized Research Unit), University of California, Davis, One Shields Avenue, CA 95616, USA

[2]Department of Solid State Physics, Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland

*corresponding author: anavrotsky@ucdavis.edu

Abstract

High-temperature oxide melt solution calorimetry was used to investigate energetics of a series of rare earth niobates RE_3NbO_7. All of investigated compounds were found to be stable in enthalpy in respect to their oxides. The enthalpy of formation from oxides becomes more exothermic as the size of the RE cation increases, a trend seen previously in other RE compounds including pyrochlores, perovskites, and phosphates. For smaller RE cations the enthalpy of exchange of RE between niobates and titanates is close to zero, whereas larger RE are energetically favored in the titanate pyrochlores. Implications of the results from the geochemical and material engineering points of view are discussed.

Keywords

Niobates, oxide melt solution calorimetry, heat of formation; pyrochlore, defect fluorite, rare earth minerals

Introduction

The rare earth elements (RE) include lanthanides, yttrium and scandium. Geochemically classified as incompatible elements, they do not readily substitute into major rock- forming minerals but partition into minor phases and are important petrologic indicators of processes involving melting (McLennan 1998; Pertermann et al. 2004; Wood and Blundy 1997). Their isotope systematics play major roles in geologic dating (DePaolo and Wasserburg 1976). Rare earths are critical elements for technology, with widespread uses in lighting, computers, cell phones, magnets, and biomedical applications (Sastri et al. 2003).

Despite the name 'rare earth', these elements are not particularly scarce in their total crustal abundance, which surpasses that of such commonly used elements as copper or lead (Golev et al. 2014). However, rare earths are not usually found in unique minerals or rich ores. Rather they are often present together in minor to trace concentrations in other minerals. This leads to the necessity of extracting and separating them from different kinds of ores. Despite the mostly low abundances of RE in crustal and mantle rocks, minerals that contain these elements as significant components make up approximately 12 % of the total number of mineral species known to date, although only a small fraction have been used for the extraction of rare elements (Linnen et al. 2014). The bulk of global LRE (light rare earths, La – Eu) manufacture (70 – 80 %) comes from bastnasite-(Ce); monazite-(Ce) is another important LRE mineral, while xenotime-(Y) and ion-adsorbed clays are the major sources of HRE (heavy rare earths, Gd–Lu) (Linnen et al. 2014). Pyrochlore and zircon account for over 90 % of the Nb and Zr production and also contain relatively high concentrations of REE (Linnen et al. 2014).

The coexistence of rare earths and niobium in ores is relatively common; for example in the large rare earth deposit Bayan Obo in Inner Mongolia the ore comprises more than 100 intergrown minerals containing iron, rare earths, fluorine and niobium (Ding et al. 2013). The Mount Weld carbonatite in Australia contains world class rare earth oxide and niobium/tantalum deposits. (Gupta and Krishnamurthy 2005). Other examples of niobium and rare earth containing deposits are St-Honoré and Aley, Canada; Mrima, Kenya; Ondurakorume, Namibia; Araxá, Brazil (Cordeiro et al. 2011). Some of these deposits are still not actively mined and are potential future sources of rare earths.

Sustainability of rare earth supply, use, and recycling is very important and must take many factors into consideration. Sustainability impacts of RE can be analyzed from techno-scientific, environmental, social and economic points of view (McLellan et al. 2013). The present work focuses on the first topic - science and technology. The analysis of thermodynamic properties of rare earth containing compounds can help in understanding processes forming the rare earth containing minerals and improving methods of their extraction from ores. Extracting rare earths from ores is also a part of environmental, social and economic sustainability assessments.

In addition to being possible sources of rare earth elements and of niobium, rare earth niobates have interesting properties for technical applications. Within this family, Y_3NbO_7 has been found to be an oxygen ion conductor in a wide range of oxygen partial pressure (J. H. Lee et al. 1998) while La_3NbO_7 is a proton conductor (Shimura et al. 2002).

The problem of finding proper materials for electrochemical devices is well known. Materials exhibiting high conductivity are usually not very chemically stable e.g. $BaZrO_3$ proton conductor (Gonçalves and Muccillo 2014). Thus finding new stable materials exhibiting high conductivity seems crucial, especially if the materials are ion conductors in the undoped state. Rare-earth niobates, since they are inherently defective materials (López-Conesa et al. 2013), are good candidates. From another point of view, Doi et al. (Doi et al. 2009) found that, depending on the lanthanide, the materials show different magnetic behavior. The same group reported that the lanthanide element also influences the symmetry of the compound (Doi et al. 2009). Further structural studies were done by high resolution transmission microscopy (HRTEM) and selected area electron diffraction (SAED) (López-Conesa et al. 2013). They showed that, although niobates containing small rare earth cations exhibit the fluorite *Fm*-3*m* structure, microdomains of pyrochlore phase (*Fd*-3*m*) can be found, suggesting considerable ordering at the nanoscale.

Despite studies of structure and magnetic and electrical properties,, there is no analysis of thermodynamic properties of these materials. In the present study we determined the enthalpies of formation of rare earth niobates, RE_3NbO_7, by high temperature oxide melt solution calorimetry. These compounds also represent end-members for the charge-coupled substitution of rare earths and niobium into minerals, see below. The thermodynamic stability of RE minerals and differences in thermodynamic properties for different rare earths are important to their petrogenesis, mining, and chemical separation of different rare earths and of RE from niobium while processing the ore.

Experimental Methods

Polycrystalline samples of RE_3NbO_7 were synthesized by solid-state reaction. The nominal amounts of RE_2O_3 oxides and Nb_2O_5 were mixed in an agate mortar under ethanol. The hygroscopic RE sesquioxides were preheated overnight at 900 °C prior to the synthesis. The powders were pressed into pellets and calcined two times at 1400 °C, with intermediate grinding and re-pelletizing.. The phase purity of the samples was checked by powder X-ray diffraction (XRD) using a Bruker diffractometer (Cu Kα radiation, 1.540596 Å) operated at 45 kV and 40 mA. JADE 6.1 software was used to analyze the data and a whole pattern fitting refinement was applied to determine the unit cell parameters.

The enthalpies of formation from binary oxides of the investigated compounds were measured by high temperature oxide melt solution calorimetry in a recently commercialized version of a Tian-Calvet twin calorimeter, (Navrotsky 1977; 1997), namely the the Setaram AlexSYS. Pressed pellets of the initially powdered samples were dropped from room temperature (25 ^oC) into a molten sodium molybdate ($3Na_2O$-$4MoO_3$) solvent held in a platinum crucible in the calorimeter at 800 ^oC. Oxygen was bubbled through the solvent at 5 ml/min and flushed over it at 60 ml/min. The calorimeter was calibrated using the heat content of corundum. The calorimetric methodology is the same as used previously for lanthanum orthoniobate (Mielewczyk-Gryn et al. 2014). The samples were generally pressed into pellets and weighed in air. In the case of terbium oxide, because its possible tendency to oxidize, the samples were pelletized in a glove box filled with nitrogen and transported to the calorimeter in glass vials, limiting contact with laboratory air to a few seconds.

Results

The X-ray diffraction patterns of the ground powders confirmed that pure phase material has been prepared. Figure 1 presents diffractograms of samples belonging to three different space groups (*Pnma*, $C222_1$, *Fm*-3*m*). Figure 2 presents the relation between lattice parameters and ionic radii of the rare earth elements. Gradual linear increase of unit cell parameter values for bigger lanthanides can be seen; which is consistent with the trend found by Doi et al. (Doi et al. 2009). Cell parameters of specific compounds match values reported earlier (Cai and Nino 2007; 2010; Doi et al. 2009; Klimenko et al. 1992; Kovyazina et al. 2003).

The enthalpies of drop solution for niobates, rare-earth (III) oxides and niobium (V) oxide at 1178 K in sodium molybdate and the calculated enthalpies of formation from oxides of the niobates are summarized in Table 1. The thermochemical cycles used in the calculations are presented in Table 2. All studied rare earths dissolve as trivalent ions (Helean and Navrotsky 2002). The enthalpies of formation from oxides versus the rare earth atom radii are depicted in Figure 3. The accuracy of calorimetric measurements varies from ± 1 % to ± 4 % depending on the sample and the accuracy of formation enthalpies is between ± 2.6 and ± 5.5 kJ/mol calculated by error propagation.

Discussion

Figure 3 shows the trend between enthalpy of formation from oxides and ionic radius of the RE. The lower stability for niobates of smaller RE is consistent with findings that this group belongs to the intrinsically disordered defect fluorite structure, while for bigger RE cations the structure is ordered pyrochlore (Doi et al. 2009; Kovyazina et al. 2003). Partial disorder via the mechanism of cation anti-site defect formation probably results in a decrease of energetic stability, i.e. in less exothermic formation enthalpies. In the pyrochlore and fluorite compounds containing a large A cation and a smaller B cation, the larger value of r_A/r_B brings about increased distortion from the cubic structure and decreased symmetry (van Berkel and Ijdo 1986; Yokogawa et al. 1988). Indeed, following such a trend, one finds that for ruthenates RE_3RuO_7, stable phases exist only for Nd, Sm, and Eu, reflecting the small radius of Ru^{5+} (van Berkel and Ijdo 1986). In RE niobates the situation is complex since, depending on the size of the RE ion, three different space groups occur. Although there is no distinct break in the enthalpy of formation at each change in space group, there is clearly a difference in slope of the trend within each group (see Fig. 3 or Fig. 4). In particular, the slope for samples with orthorhombic structure is much smaller than for the others. Doi et al. observed only a small change of cation - oxygen bond length with lanthanide radius increase from Nd to La, while for other RE niobates the change is larger (Doi et al. 2009).

The lower stability of the phases containing smaller lanthanides is also consistent with the observations on natural pyrochlores containing Nb and RE; they contain mostly lighter and larger RE (La through Sm). Commonly their content of RE heavier than Gd is below detection limits (Lumpkin and Ewing 1995).

The enthalpies of formation of the niobates with defect fluorite structure can be compared to those of compounds with pyrochlore structure. The pyrochlore structure can be viewed as an ordered derivative of the fluorite structure, where the A and B cations are ordered along the <110> direction. The anion vacancy occurs in the tetrahedral interstice between adjacent B-site cations. Natural pyrochlores conform to the general formula $A_{2-m}B_2X_{6-w}Y_{l-n}*pH_2O$ where A = Na, Mg, K, Ca, Mn, Fe^{2+}, Sr, Sb, Cs, Ba, RE, Pb, Bi, Th, and U in

8-fold coordination, B = Nb, Ta, Ti, Zr, Sn, W, Fe^{3+}, and Al in 6-fold coordination, X = O, and Y = O, OH, or F (Lumpkin and Mariano 1995). Simplified RE pyrochlore compositions include $RE_2Ti_2O_7$, $RE_2Zr_2O_7$ and $RE_2Sn_2O_7$. These model compounds have been studied extensively to characterize the order-disorder transition between pyrochlore and fluorite, which can be induced by changes in chemical composition, by quenching from high temperature, by grinding, and by radiation damage (Meilicke and Haile 1995; Wang et al. 2000; Zhang et al. 2013). Enthalpies of formation from oxides of rare earth titanates, zirconates and niobates are shown in Figure 4. For smaller rare earths (Y to Ho) the enthalpies of formation of titanates and niobates overlap. For larger RE cations, the stabilities of niobates and titanates differ. For all cases, the enthalpy of formation of niobates and titanates from oxides is more exothermic than values for zirconates and stannates. These results reflect the difference in acidity between niobium, zirconium and tin oxides. From another point of view, the similarity of the values for titanates and niobates reflects both similar acidity of niobia and titania and the existence of the pyrochlore phase microdomains found by SAED, and Raman spectroscopy, suggesting some pyrochlore – like local ordering in the niobates (Kovyazina et al. 2003; López-Conesa et al. 2013).

The energetics of rare earth exchange between titanates and niobates is very interesting from the geochemical point of view. Many high temperature thorium and rare earth deposits contain niobates, tantalo- and titano-niobates of rare earths (Titayeva 1994). The minerals containing both RE and Nb often also contain Ti. This is especially true for natural pyrochlore minerals (Cordeiro et al. 2011; Crockett and Sutphin 1993; Torró et al. 2012). The exchange reaction between rare earth niobates and titanates can be written as:

$$RE_2Ti_2O_7 + 1/2RE_2O_3 + 1/2Nb_2O_5 = RE_3NbO_7 + 2TiO_2 \quad (1)$$

The coupled substitution $Nb^{5+} + RE^{3+} = 2Ti^{4+}$ is charge balanced. Table 3 lists the enthalpies of exchange (reaction (1)). For RE with smaller ionic radii the enthalpy of this reaction is close to zero. For lighter lanthanides the enthalpy is more endothermic.

Lau et al. (Lau et al. 2008; Lau et al. 2006) have shown that in RE pyrochlores, additional stuffing of RE^{3+} into Ti^{4+} sites is possible. The maximum of 'stuffing' substitution was stoichiometry $Ln_2(Ti_{1.33}RE_{0.67})O_{6.67}$ for RE = Ho - Lu, with compounds showing the distorted fluorite structure, in which excess RE^{3+} cations occupy *A* and *B* sites randomly. The structure of such compounds is similar to that of cubic fluorite found for RE_3NbO_7 (for smaller RE). For slightly bigger RE (Tb and Dy) the structure is partially disordered even at maximum stuffing and RE^{3+} cations mix mainly on the Ti^{4+} site with little disorder on the RE site. Generally these results show that the stuffing process is more difficult for larger RE (Lau et al. 2008; Lau et al. 2006). Our study has shown that the energetics of RE titanates and niobates is similar for smaller RE, which is consistent with the fact that substitution leading to distortion to fluorite structure is more favorable for these compounds since the exchange reaction enthalpy is near zero.

The exchange reaction between niobates and zirconates can be written analogously to reaction (1), as:

$$RE_2Zr_2O_7 + 1/2RE_2O_3 + 1/2Nb_2O_5 = RE_3NbO_7 + 2ZrO_2 \quad (2)$$

The enthalpy of this reaction is much more endothermic than for titanates (see Table 3). This can explain why in nature pyrochlores containing Nb and Zr are relatively rare in comparison to those containing Nb and Ti. This also suggests that the traces of ZrO_2 found in ores containing pyrochlore are indeed the effect of formation of separate phases, rather than an effect of exchange reactions between niobates and zirconates (Caprilli et al. 2006; Yaroshevskii and Bagdasarov 2008).

The calorimetric data obtained here refer to the stability at room temperature of the indicated structures produced by cooling samples from high temperature. It is possible that there is a greater extent of disorder *in situ* at high temperature, perhaps extending the stability field of the most disordered structure, namely the defect fluorite. It is also possible that there are additional phase transitions at high temperature. The present work provides no information on such processes.

The entropies of formation from binary oxides are expected to be small except possibly for disordered phases (defect fluorite) with some configurational entropy. Thus the enthalpy term is expected to be dominant in the free energy and the stability trends seen in the enthalpies should apply over a wide temperature range. In particular, the trends in stability of niobates, titanates and zirconates are expected to hold at high temperature, i.e. in igneous environments, as well as near room temperature.

The similar energetics of niobates and titanates also is interesting from a materials engineering point of view. The stability of compounds is one of the crucial factors when it comes to utilizing them in working electrochemical devices like fuel cells or gas pumps. Obviously more stable materials are better for technical applications. RE titanates were successfully utilized in as a solid electrolyte in solid oxide fuel cells (SOFC) (Shlyakhtina and Shcherbakova 2012). Interest has turned to materials with defect fluorite structure since their conductivity is usually intrinsic and does not require additional elements as dopants. The doping, which often involves oxides of Sr and Ba, can cause technological problems in humid atmospheres and also can influence the stability of compounds (Goncalves et al. 2014). Thus finding relatively stable material with intrinsic conductivity would be beneficial. The electrical properties of the niobates investigated here will be a topic for further research.

Moreover, since RE titanates and niobates have similar energetics for heavier lanthanides and the exchange reaction enthalpy is close to zero, it is probably possible to synthesize intermediate phases between stuffed RE titanates and RE niobates. Such materials can potentially have interesting magnetic and electrical properties.

It should be emphasized that for all previously investigated RE fluorites and pyrochlores, the same trend is visible: the bigger the ionic radius of RE, the more stable the compound relative to binary oxides. Such behavior is intrinsic to changes in the rare earth bonding character and is well documented in the thermodynamics of other group of materials; especially rare-earth perovskites (Cheng and Navrotsky 2003; Cheng et al. 2005; Kanke and Navrotsky 1998; Lamberti et al. 1997) and phosphates (Ushakov 2001; Ushakov et al. 2004).

Implications

The energetics of rare earth niobates, RE_3NbO_7, occurring in three different space groups have been determined by high temperature oxide melt solution calorimetry. Enthalpies of formation from the oxides become more exothermic with increasing RE ionic radius, which also leads to more ordered structures (pyrochlore rather than defect fluorite). The RE niobates are end-members for the charge coupled substitution of RE + Nb for Ti or Zr in natural pyrochlores. This exchange reaction is generally more favorable for smaller RE ions and for Ti compared to Zr. Further work could examine more complex pyrochlore compositions, including those containing F and OH substitution. Also the stability of the niobates containing two different lanthanides (e.g. $RE_2(RE'_{0.5}Nb_{0.5})_2O_7$) could be investigated to establish the maximum possible stable substitutions in these compounds. The new thermochemical data in this paper represent a start toward a more quantitative determination of the energetics of RE partitioning among mineral phases important to petrology, rare earth mining, and materials science and technology.

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Figure captions:

Figure 1 Powder X-ray diffraction patterns for lanthanum, gadolinium and yttrium niobates.

Figure 2. Variation of unit cell parameters for rare-earth niobates. Ionic radii for eight-fold coordination after Shannon (Shannon 1976).

Figure 3. The enthalpy of formation from binary oxides of rare-earth niobates belonging to different space groups. Ionic radii for eight-fold coordination after Shannon (Shannon 1976). Lines drawn to guide the eye.

Figure 4 Comparison of the enthalpies of formation from binary oxides of rare-earth niobates, titanates (Helean and Navrotsky 2002), stannates (Lian 2006) and zirconates (Lamb 1973) with fluorite related structures. Ionic radii for eight-fold coordination after Shannon (Shannon 1976).

Tables:

Table 1 Enthalpies of drop solution in sodium molybdate ($3Na_2O$-$4MoO_3$) at 800 °C of binary oxides and enthalpies of formation from these oxides of rare earth niobates at 25 ^oC. The number in parentheses gives the number of measurements done. The errors for measured values are two standard deviation of the mean.

Binary oxide	ΔH_{ds} (kJ/mol)	Rare-earth Niobate	$\Delta H_{f,ox}$(kJ/mol)
La_2O_3	-221.81±2.25 (7)$^+$	La_3NbO_7	-160.76±3.39
Nd_2O_3	-156.95±1.05 (8)*	Nd_3NbO_7	-154.68±3.32
Eu_2O_3	-122.46±1.80 (8)*	Eu_3NbO_7	-143.57±3.52
Gd_2O_3	-134.48±1.70 (8)*	Gd_3NbO_7	-131.64±3.11
Tb_2O_3	-114.15±1.33 (8)*	Tb_3NbO_7	-118.63±2.75
Ho_2O_3	-109.51±1.84 (8)*	Ho_3NbO_7	-90.85±3.37
Er_2O_3	-107.20±1.75 (6)$^\#$	Er_3NbO_7	-84.49±3.95
Yb_2O_3	-82.65±1.30 (6)$^\#$	Yb_3NbO_7	-65.54±2.61
Y_2O_3	-116.34±1.21 (8)*	Y_3NbO_7	-84.60±2.65
Nb_2O_3	127.48±0.80 (11)$^+$		

*this work, $^+$(Mielewczyk-Gryn et al. 2014), $^\#$ (Qi et al. in preparation)

Table 2 Thermodynamic cycles used to determine the enthalpies of formation from oxides.

La_3NbO_7 (s, 298 K)= $\frac{3}{2}\,RE_2O_3$ (dis, 1073 K) + $\frac{1}{2}$ Nb_2O_5 (dis, 1073 K)	ΔH_{ds}
RE_2O_3 (s, 298 K) = RE_2O_3 (dis, 1073 K)	ΔH_1
Nb_2O_5 (s, 298 K) = Nb_2O_5 (dis, 1073 K)	ΔH_2
$\frac{3}{2}\,RE_2O_3$ (s, 298 K) + $\frac{1}{2}$ Nb_2O_5 (s, 298 K) = RE_3NbO_7 (dis, 298 K)	$\Delta H_{f,ox}$

$$\Delta H_{f,ox} = -\ \Delta H_{ds} + \frac{3}{2}\Delta H_1 + \frac{1}{2}\,\Delta H_2$$

Table 3 The enthalpies of exchange (reaction (1) and (2) for RE titanates and zirconates, Ionic radii for eight-fold coordination after Shannon (Shannon, 1976).

RE	RE ionic radius (Å)	ΔH_R Ti-Nb(1) (kJ/mol)	ΔH_R Zr-Nb (2) (kJ/mol)
Yb	0.985	-4.96±6.51	-
Er	1.004	4.89±7.85	-
Ho	1.015	3.35±7.98	-
Y	1.019	-1.60±4.15	-
Tb	1.04	13.13±5.95	-
Gd	1.053	18.24±5.81	74.64±6.81
Eu	1.066	39.68±7.76	-

Nd	1.109	-	83.08±6.62
La	1.16	-10.84±6.20	61.26±7.70

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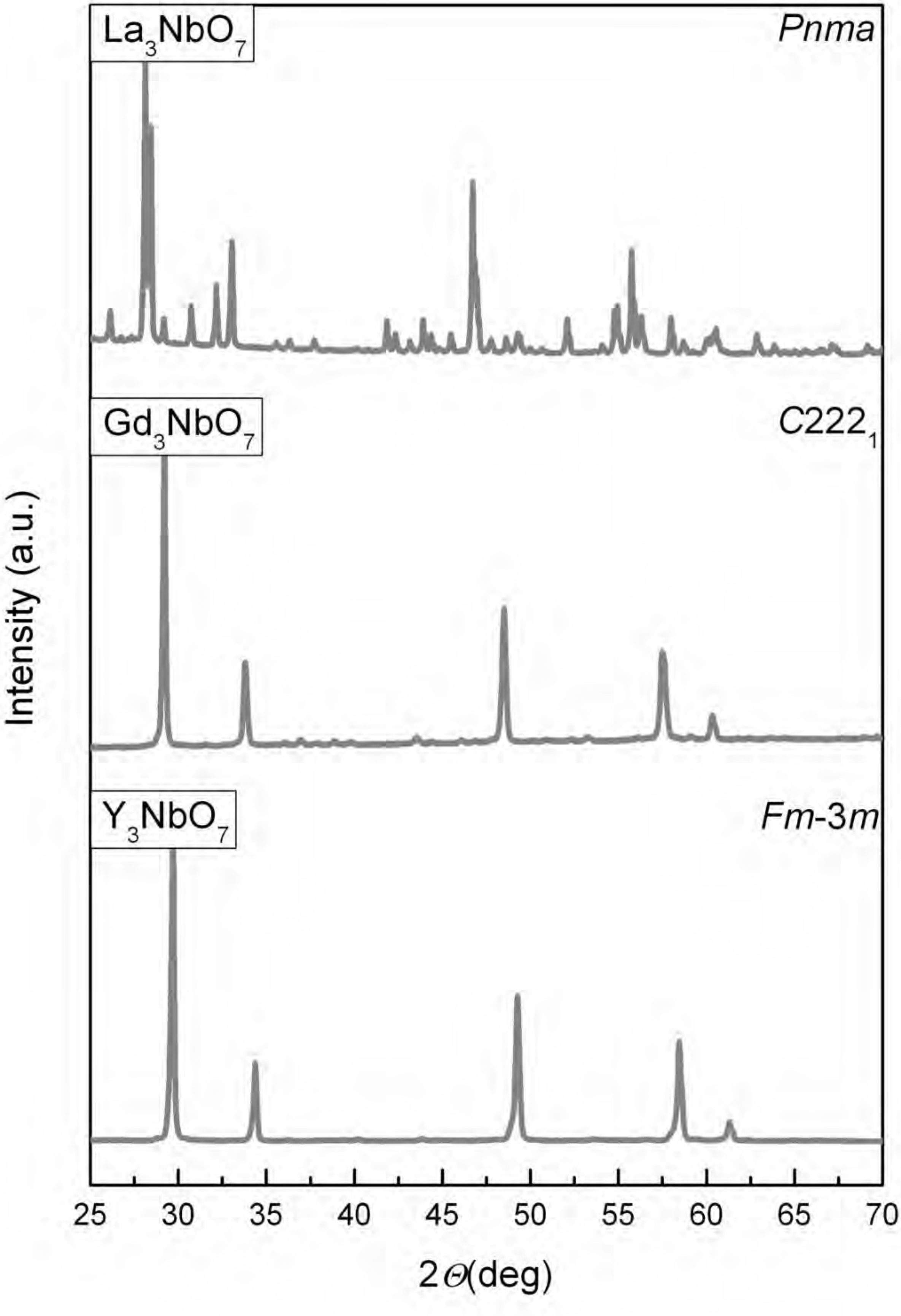
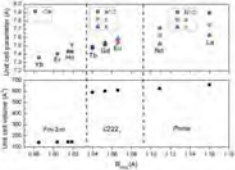
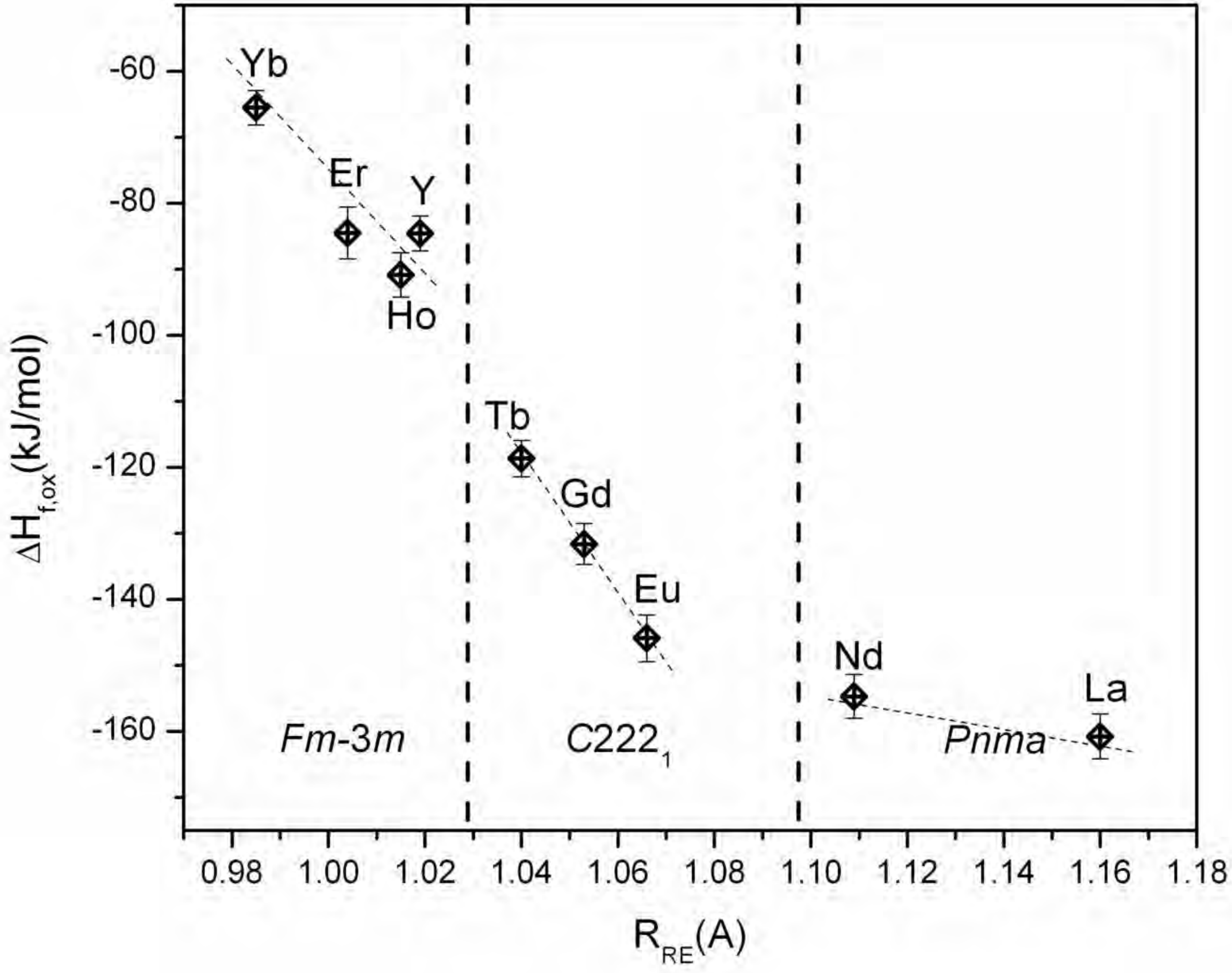
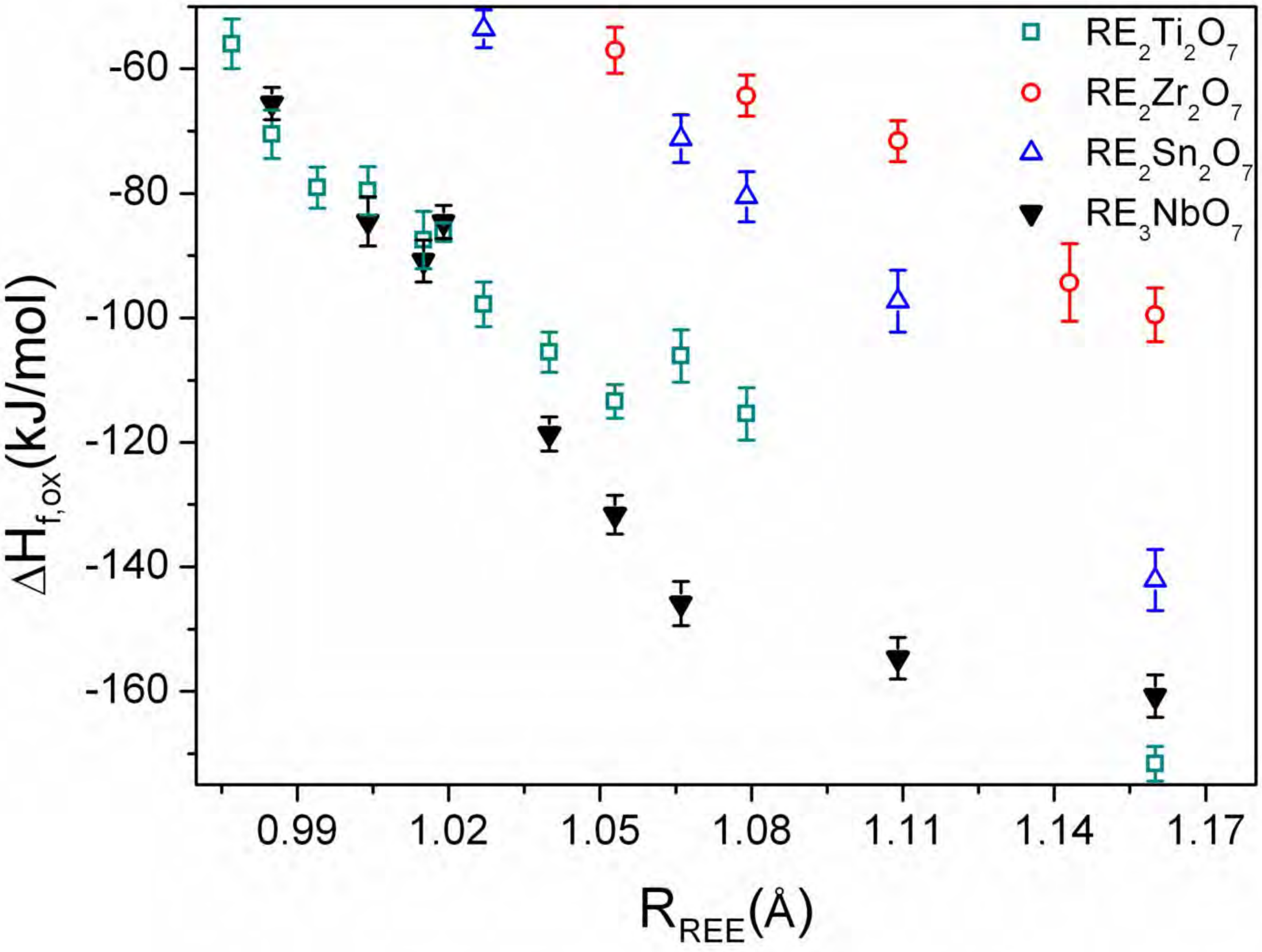

La3NbO7
Pnma
Gd3NbO7
C2221
Y3NbO7
Fm-3m
Intensity (a.u.)
25
30
35
40
45
50
55
60
65
70
2Θ(deg)


Unit cell parameter (Å)
a/√2
b
c
b/√2
a
c
Yb
Er
Ho
Y
Tb
Gd
Eu
Nd
La
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
Unit cell volume (Å³)
700
600
500
400
300
200
100
Fm-3m
C222₁
Pnma
0.98
1.00
1.02
1.04
1.06
1.08
1.10
1.12
1.14
1.16
1.18
R(Å)


Yb
Er
Y
Ho
Tb
Gd
Eu
Nd
La
Fm-3m
C222$_1$
Pnma
-60
-80
-100
-120
-140
-160
0.98
1.00
1.02
1.04
1.06
1.08
1.10
1.12
1.14
1.16
1.18
$\Delta H_{f,ox}$(kJ/mol)
R_{RE}(A)



$\Delta H_{f,ox}$(kJ/mol)
-60
-80
-100
-120
-140
-160
0.99
1.02
1.05
1.08
1.11
1.14
1.17
R_{REE}(Å)
$RE_2Ti_2O_7$
$RE_2Zr_2O_7$
$RE_2Sn_2O_7$
RE_3NbO_7