

Energetics and structure of the B-type solid solution in the Nd₂O₃-Y₂O₃ system

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Abstract

The system Nd₂O₃-Y₂O₃ contains solid solution phases with several different structures. Single phase B-type (Nd_{1-x}Y_x)₂O₃ solid solutions in the range $0.2 \leq x \leq 0.5$ were formed at 1873 K and retained on cooling to ambient temperature. They showed a linear composition dependence of lattice parameters, enabling extrapolation to $x = 0$ and $x = 1$ for comparison with the structures of the stable endmembers. A positive enthalpy of formation from A-type Nd₂O₃ and C-type Y₂O₃ determined using oxide melt solution calorimetry indicated entropic stabilization of the B-type phase. A positive interaction parameter for mixing in the B-type solid solution, $\Omega = 47.46 \pm 4.04$ kJ/mol, was obtained by fitting the data using a regular solution model. This value is significantly more positive than that obtained by previous phase diagram analysis using the CalPhaD approach. Exsolution into two B-type phases is predicted to occur below 1427 K, making it unimportant for the equilibrium phase relations which will be dominated by other structures at low temperature.

Introduction

Rare earth (RE) oxides are high melting refractory materials. Mixed metal rare earth sesquioxides $(A_{1-x}B_x)_2O_3$ form a complex series of compounds and solid solutions. The possibility of precisely tuning their properties through composition and structure makes them attractive to applications like lasers, high dielectric constant gates, and thermal barrier coatings.¹⁻³ Recent research on alloying and doping with RE elements demonstrates their importance as advanced multicomponent systems, sometimes called high entropy materials. Understanding the phase relations in RE oxides thus becomes very important to improve and optimize the performance of advanced multicomponent systems.⁴⁻⁶

Pure and mixed RE sesquioxides exist in different polymorphic forms whose stability is mainly governed by cation radii, temperature, and pressure. A-type ($P\bar{3}m1$), B-type ($C2/m$), and C-type ($Ia\bar{3}$) structures are favored below about 2300 K (Figure 1).⁷ Above this temperature, more symmetric structures like H-type ($P6_3/mmc$) and X-type ($Ia\bar{3}m$) are formed.⁸ B-type $(Nd_{1-x}Y_x)_2O_3$, the solid solution studied in this work, forms in a wide composition range ($0.1 \leq x \leq 0.5$) below about 2300 K. The occurrence of stable polymorphs is usually predictable through its correlation with atomic parameters like atomic radii and bond valence factors.⁹⁻¹¹ Various authors studied their polymorphic phase transitions,^{7, 12, 13} investigated the structure relations between different polymorphs,^{1, 8, 14, 15} and proposed links between their stability and atomic radii.^{2, 8} Foex and Traverse⁸ reported the existence of a C-type structure for all the RE sesquioxides at ambient conditions. At ambient pressure and high temperature, depending on the radius of the RE ion, the C-type structure is either retained or it transforms to A/B-type. High temperature phases such as H-type and X-type are usually hard or impossible to quench at ambient temperature. Usually,

phases with larger cation radii (La-Nd), intermediate cation radii (Sm-Gd), and smaller cation radii (Tb-Lu) crystallize in A-type, B-type, and C-type polymorphs, respectively.⁸ Commonly observed trends indicate that $C \rightarrow B \rightarrow A$ transformations involve reduction in unit cell volume as the cation coordination changes from six to seven oxygen atoms.¹⁶ For most Ln-sesquioxides, $C \rightarrow B \rightarrow A$ transformations occur with increasing temperature and pressure, consistent with entropy increase and volume decrease.^{8, 17, 18}

At ambient pressure, the B-type polymorph is reported for Sm-Ho sesquioxides between 900-2300 K.⁸ Hoekstra and Gingerich¹⁸ reported that the B-type structure is possible for all the end members of Ln-sesquioxides beyond Sm under pressures of 2 to 4 GPa between 1178 and 1293 K. Endmembers Nd_2O_3 and Y_2O_3 of the B-type solid solution studied here usually crystallize in A-type and C-type structures, respectively, at ambient pressure.^{17, 19, 20} Nd_2O_3 forms a B-type phase only at intermediate temperatures and pressures.¹² Boulesteix et al.¹⁴ observed B-type Nd_2O_3 at room temperature for a brief period of only 10 minutes by oxidizing a thin layer of metallic neodymium under an electron beam. Reports on binary and ternary systems confirm that the B-type polymorph occurs more frequently in multicomponent materials.¹³ For instance, Nd_2O_3 forms the B-type structure when an oxide with a slightly smaller cation radius than Nd, such as Sc_2O_3 , is added.^{2, 21}

Chavan et al.²² reported three different cation sites (two 7-coordinated and one 6-coordinated) in $(\text{Nd}_{1-x}\text{Y}_x)_2\text{O}_3$ B-type solid solutions produced after several heat treatment cycles and final slow cooling. Coutures et al.¹⁷ were the first to report the homogeneity range of $(\text{Nd}_{1-x}\text{Y}_x)_2\text{O}_3$ B-type solid solution using X-ray diffraction and thermal analysis on samples after melting followed by annealing at 1673 K and quenching. Adylov et al.¹⁹ studied the phase relations using X-ray fluorescence and thermal analysis. There were some discrepancies in the B+C

homogeneity range reported by the two authors. More recently, Huang et al.²⁰ and Fabrichnaya et al.²³ reassessed the experimental thermodynamic data for the $\text{Nd}_2\text{O}_3\text{-Y}_2\text{O}_3$ system using a substitutional solution model and provided an optimized dataset for thermodynamic modeling. However, they used the previously reported experimental phase diagrams for the optimization of missing thermodynamic parameters. Zinkevich²⁴ recalculated the phase diagram and reported optimized parameters using a regular solution model. Figure 2 displays the $\text{Nd}_2\text{O}_3\text{-Y}_2\text{O}_3$ phase diagram reported by Huang et al.²⁰ showing a comparison between his work and previously reported experimental phase diagrams. The reported thermodynamics data on $(\text{Nd}_{1-x}\text{Y}_x)_2\text{O}_3$ solid solutions lack direct experimental measurements, which are essential to validate the optimized and calculated thermodynamic parameters.

In this work, we report directly measured enthalpies of formation of the B-type monoclinic solid solution phase in the $\text{Nd}_2\text{O}_3\text{-Y}_2\text{O}_3$ system and obtain the interaction parameter for the mixing enthalpy. We also report variation in structural parameters with composition of $(\text{Nd}_{1-x}\text{Y}_x)_2\text{O}_3$ B-type solid solution synthesized via solid-state reaction at 1873 K.

Experimental methods

Nd_2O_3 and Y_2O_3 (Alfa Aesar $\geq 99.99\%$ pure metals Nd and Y) were used to prepare the solid solutions. Before the synthesis, the oxides were dried at 1100 K for about 8 hours. Powder mixtures of six different compositions ($x = 0.2, 0.3, 0.35, 0.4, 0.45$, and 0.5) were ground in a mortar and pestle under ethanol, dried and hand-pressed into pellets using an arbor press and pellet die. The pellets were placed into platinum crucibles for sintering in air at 1873 K for about 20 to 40 hours, followed by rapid cooling.

Backscattered electron imaging and compositional measurements were carried out using a Cameca SX-100 electron microprobe to confirm the homogeneity of all the samples. Synthetic RE orthophosphate crystals were used as standards for Nd and Y.

Powder X-ray diffraction scans were collected for all the samples at room temperature using Bruker D2 Advance diffractometer. The diffractometer was operated with Cu-K α radiation and a rotating sample holder. Measurements were done at 30 kV and 30 mA with 0.01° step size and 1 s/step dwell time. Lattice parameters were obtained by Rietveld refinement^{25, 26} using the GSAS-2²⁷ software package. Instrument-related parameters were corrected by peak fitting of the LaB₆ 660a²⁸ standard. Si-640c²⁹ was used as an internal standard to refine the sample displacement. Structural parameters of the Sm₂O₃ B-type phase reported by Kennedy and Avdeev³⁰ were used to refine the sample containing the highest Y₂O₃ content ((Nd_{0.5}Y_{0.5})₂O₃) after replacing each Sm site with Nd and Y. Subsequent refinements were carried out in the order of decreasing Y₂O₃ concentration such that the last obtained structure was used for successive refinements. The Nd/Y fractions on each cation site were constrained based on the nominal concentration and assumed random distribution of cations at each site. The position coordinates of Nd and Y at each cation site were constrained to be the same. Lattice parameters, position coordinates, Nd/Y site fractions, crystallite size, microstrain, preferred orientation model parameters were sequentially refined.

Prior to calorimetry, all samples were first annealed at 1100 K for about 8 hours. They were then checked using X-ray diffraction to confirm phase purity. The dried samples were crushed, ground into a fine powder, and hand-pressed into 3-5 mg pellets using a tungsten carbide pellet die with pressure just enough to prevent the pellet from breaking while weighing and dropping. High temperature drop solution calorimetry was performed using an AlexSYS isoperibol

Tian-Calvet twin calorimeter. The pellets were dropped from room temperature to the sodium molybdate ($3\text{Na}_2\text{O}-4\text{MoO}_3$) solvent equilibrated at 1073 K with oxygen flushing over it at 60 ml/min and bubbling through it at 5 ml/min. The calorimeter was calibrated against the heat content of 5 mg $\alpha\text{-Al}_2\text{O}_3$ (Sigma-Aldrich, high purity Al_2O_3 annealed and checked for phase purity before calibration) pellets. The mean of six drop solution enthalpies and two standard deviation of the mean are reported. The methodology has been described in detail previously.³¹

Results

X-ray diffraction analysis of all the samples confirmed the presence of a single B-type $(\text{Nd}_{1-x}\text{Y}_x)_2\text{O}_3$ solid solution (Figure 3 and Figure 4). As shown in Figure 5 for $(\text{Nd}_{0.6}\text{Y}_{0.4})_2\text{O}_3$ B-type solid solution, wavelength dispersive electron microprobe measurements confirmed all the measured compositions close to the nominal compositions.

Figure 4 displays a typical profile fitting from Rietveld refinement. The weighed profile R-factor (R_w) variation can be seen at the bottom of Figure 4. Rietveld refinements resulted in $R_w < 10$ and goodness of fit (GOF) < 2 , indicating a satisfactory fit for all samples. Table 1 lists the obtained lattice parameters with the uncertainty in their last digits. The low uncertainty values indicate a good fit. Figure 6 shows a linear reduction in unit cell parameters with increasing Y_2O_3 concentration in the B-type solid solution.

The calorimetric data are listed in Table 3. Negative drop solution enthalpies of all B-type solid solution samples imply exothermic dissolution in sodium molybdate solvent at 1073 K. The variation in ΔH_{ds} of B-type $(\text{Nd}_{1-x}\text{Y}_x)_2\text{O}_3$ solid solution with Y_2O_3 concentration and inverse of mean cation radii (r_m^{-1}) can be seen in Figure 7. The ΔH_{ds} of endmember oxides, Nd_2O_3 and Y_2O_3 , from our earlier work³² are also shown. The important observation is that the enthalpies of drop

solution deviate exothermically from linearity with composition, implying an endothermic (destabilizing) heat of mixing in the solid solutions. The enthalpy of formation from oxides at 298 K was calculated for each composition using the thermodynamic cycle in Table 2.

Discussion

Crystallography

A linear decrease in lattice parameters with increasing concentration of smaller cation is in accord with Vegard's law.³³ It suggests that there are no specific strong interactions (ordering or clustering) that would affect the lattice parameters. Least-squares fitting of the data was performed by weighting each data point corresponding to their ranges obtained from Rietveld refinement (Figure 8). With the resulting coefficient of determination (R^2) = 0.997, we estimated the endmember volumes by extrapolation, $V_m^{B-Nd_2O_3} = 46.91 \pm 0.06 \text{ cm}^3/\text{mol}$ and $V_m^{B-Y_2O_3} = 41.39 \pm 0.17 \text{ cm}^3/\text{mol}$. For both endmember B-type oxides, our extrapolated V_m^B lies close to the molar volume reported in the literature at room temperature, $V_m^{B-Nd_2O_3} = 46.8 \text{ cm}^3/\text{mol}$ estimated by extrapolation of linear dependence of V_m on rare earth cation radii²⁴ and measured $V_m^{B-Y_2O_3} = 41.13 \text{ cm}^3/\text{mol}$ for a phase quenched from high pressure $\sim 2 \text{ GPa}$ and temperature above 723 K³⁴. Using $V_m^{C-Y_2O_3} = 44.88 \text{ cm}^3/\text{mol}$ at 300 K determined by X-ray diffraction³⁵ and mean $V_m^{B-Y_2O_3}$ estimated in this study, we report a volume change on C $\rightarrow$ B phase transition $V^{C \rightarrow B, Y_2O_3} = -3.49 \text{ cm}^3/\text{mol}$ and a relative volume change $\sim -7.8 \%$, lying near the reported values of $V^{C \rightarrow B, Y_2O_3} = -3.67 \text{ cm}^3/\text{mol}$ and relative volume change $\sim -8.2 \%$.²⁴ Similarly, $V^{B \rightarrow A, Nd_2O_3}$ was calculated using $V_m^{A-Nd_2O_3} = 46.25 \text{ cm}^3/\text{mol}$ determined via X-ray diffraction by Douglas³⁶ and $V_m^{B-Nd_2O_3}$ estimated in this work. The calculated volume change on B $\rightarrow$ A phase

transition $V^{B \rightarrow A, \text{Nd}_2\text{O}_3} = -0.66 \text{ cm}^3/\text{mol}$ and a relative volume change $\sim -1.4 \%$ was found to be in close agreement with the reported volume change of $-0.9 \text{ cm}^3/\text{mol}$ and relative volume change $\sim -1.9 \%$.²⁴

Negative volume change during $C \rightarrow B \rightarrow A$ polymorphic phase transformation implies that the structural change is favored under compression. A negative dP/dT slope has been reported by previous authors.^{16, 34} Since increasing temperature increases the system's entropy, a decrease in volume can be expected based on the Clapeyron equation.³⁷ However, the increase in coordination number during $C \rightarrow B \rightarrow A$ polymorphic phase transformations implies local volume expansion within the first coordination shell of the cation. Thus, the decrease in molar volume could be attributed to more close packed stacking of the polyhedra, which may be achieved by increase in edge sharing and decrease in corner sharing between the polyhedra during $C \rightarrow B \rightarrow A$ phase transformations.^{15, 30, 36, 38}

Thermochemistry

The endothermic enthalpies of formation from binary oxides in their usual room temperature structures (A-type for Nd_2O_3 and C-type for Y_2O_3) show that the B-type solid solutions are energetically unstable with respect to a mixture of stable endmember structures. This implies that the B-type $(\text{Nd}_{1-x}\text{Y}_x)_2\text{O}_3$ solid solutions are entropy stabilized and can exist stably only at high temperatures.

To obtain physically realistic equations for the enthalpy of formation within the B-type solid solution from A-type Nd_2O_3 and C-type Y_2O_3 , one needs to consider three factors: the enthalpy of mixing within the B-type solid solution and the enthalpies of $A \rightarrow B$ transformation of Nd_2O_3 and $C \rightarrow B$ transformation of Y_2O_3 . Because the range of the B-type solid solution is

limited ($0.2 \leq x \leq 0.5$), constraining the endmember energetics ($x = 0$ and $x = 1$) in the B phase is critical. The simplest equation incorporating these factors can be written as:

$$\Delta H_{f,B}^{ox,298K} = \Delta H_{tr}^{A \rightarrow B, Nd_2O_3} (1 - x) + \Delta H_{tr}^{C \rightarrow B, Y_2O_3} x + \Delta H_{mix}^B \quad (1)$$

Within the regular solution approximation, the enthalpy of mixing in the B-type solid solution is

$$\Delta H_{mix}^B = \Omega x (1 - x) \quad (2)$$

where the interaction parameter, Ω , is a constant. Rather than attempting to obtain all three parameters (two transition enthalpies and one interaction parameter from the heats of formation over a limited composition range), we chose to constrain the two transformation parameters from independent data in the literature.

Table 4 lists reported values of $\Delta H_{tr}^{A \rightarrow B, Nd_2O_3}$ and $\Delta H_{tr}^{C \rightarrow B, Y_2O_3}$ with some details of the method used for their calculation or measurement. An average of the similar values reported by Zinkevich²⁴ and Hoekstra³⁴, $\Delta H_{tr, Y_2O_3}^{C \rightarrow B} = 12.96$ kJ/mol was used in this study. The negative value of $\Delta H_{tr, Nd_2O_3}^{A \rightarrow B}$ reported by Zinkevich²⁴ was not considered since Nd_2O_3 is stable in the A-type structure at ambient conditions^{13, 14, 16}. Instead, considering the reversibility of B to A polymorphic phase transition in Nd_2O_3 ^{7, 13}, a positive value of $\Delta H_{tr, Nd_2O_3}^{A \rightarrow B} = 0.55$ kJ/mol reported by Wu et al.¹⁶ was used. We believe that this approach, using transition enthalpies that are constrained by independent experiments and phase equilibria, is the most reasonable one to obtain physically realistic thermochemical parameters.

The composition dependence of $\Delta H_{f,B}^{ox,298K}$ fitted to a quadratic equation (eq. 3) resulted in $R^2 = 0.971$, as shown in Figure 9.

$$\Delta H_{f,B}^{ox,298K} = (-47.46 \pm 4.04) x^2 + (57.78 \pm 4.48) x + (1.34 \pm 1.04) \quad (3)$$

Eq. 3 can be written in the form of eq. 1 as follows

$$\Delta H_{f,B}^{ox,298K} = (1.34 \pm 1.04) (1 - x) + (11.66 \pm 1.63) x + (47.46 \pm 4.04) x (1 - x) \quad (4)$$

The above approach (eq. 1, 2 and 4) yields an interaction parameter of $\Omega = 47.46 \pm 4.04$ kJ/mol for two moles of ions being mixed ($(Nd_{1-x}Y_x)_2O_3$) or an interaction parameter of $\Omega' = 23.73 \pm 2.02$ kJ/mol for one mole ($Nd_{1-x}Y_xO_{1.5}$). Within the regular solution approximation, a critical exsolution temperature to form two B-type phases in a solvus symmetrical about $x = 0.5$ would be given by $\Omega'/2R = 1427$ K.

Our results support the existence of two varieties of B-type structures suggested by Schneider and Roth's ² study on various rare earth oxide systems. Our calculated critical exsolution temperature is likely below that of decomposition of the B-type solid solutions to other structures. Thus, such exsolution need not be considered in constructing an equilibrium phase diagram.

Various authors reassessed the experimental phase diagrams based on thermal analysis and X-ray diffraction/fluorescence studies^{17, 19} after critically assessing experimental thermodynamic data and assuming random mixing of cations.^{24, 39} The existence of homogeneous B-type $(Nd_{1-x}Y_x)_2O_3$ in the range $0.2 \leq x \leq 0.5$ agrees well with previously reported experimental and reassessed phase diagrams.^{7, 21, 23, 41} So far, there are no reports on the experimentally measured thermodynamic properties of other ternary phases or solid solutions in the Nd_2O_3 - Y_2O_3 system. The reported optimized interaction parameter for regular solution model assumption for B-type $(Nd_{1-x}Y_x)_2O_3$, $\Omega = 10.8$ kJ/mol,²⁴ is significantly less endothermic than the one obtained directly by calorimetry in this study. It is essential to point out that there have been discrepancies in previously reported homogeneity ranges of low temperature polymorphs^{17, 19, 20, 24} and Gibbs free energy equation for regular solution model²⁴. Since the parameters optimized from phase

equilibria are not independent of each other and the phase diagrams themselves contain uncertainties, comparing the interaction parameter obtained experimentally in this study with those optimized from the differences between calculated and experimental phase diagrams may not be fruitful. We recommend direct enthalpy measurements of the neighboring phases, especially those that form significant solid solutions, before more complete comparisons can be made.

Moreover, the regular solution model assumes the random mixing of cations in the solid solution. Chavan et al.²² suggested non-random mixing indicated by the preferred occupancies at cation sites obtained from Rietveld refinements. However, their results do not provide a convincing argument on preferred site occupancies since they refined site occupancies along with preferred orientation parameters, both of which affect the 2 θ -peak intensities. The refined occupancies may not be reliable without prior investigation of any preferred orientation in the powder samples that show specific high-intensity peaks. We conclude that the B-type (Nd_{1-x}Y_x)₂O₃ structure needs further investigation to reveal structural details. Employing techniques like transmission electron microscopy and pair-distribution function analysis to unravel the structural details, bonding characteristics, and coordination environment could help gain a better insight into the mixing characteristics of sesquioxide structures.

Conclusion

B-type (Nd_{1-x}Y_x)₂O₃ solid solution forms as a single phase in the range $0.2 \leq x \leq 0.5$ and shows linear composition dependence of lattice parameters. Directly measured enthalpy of formation data confirms that the B-type solid solution is energetically metastable and presumably entropy stabilized and will not be thermodynamically stable at lower temperatures. Due to significant differences between the experimental (this study) and optimized values (previous

study) of interaction parameters and previously reported discrepancies in the experimental phase diagrams and solution models, more experimental thermodynamic studies and re-evaluation of the phase diagram are needed.

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Figures

Figure 1. Crystal structures of rare earth sesquioxide (R_2O_3) polymorphs stable below about 2300 K. Polyhedra show the coordination environment of rare earth ions in (a) A-type ($P\bar{3}m1$) with 7-fold coordination³⁸, (b) B-type ($C2/m$) with both 6-fold and 7-fold coordination³⁰, and (c) C-type ($Ia\bar{3}$) with 6-fold coordination³⁹.

Figure 2. Calculated phase diagram of Nd_2O_3 - Y_2O_3 reported by Huang et al.²⁰ showing the comparison between his work and experimental studies by Coutures et al.¹⁷ and Adylov et al.¹⁹.

Figure 3. XRD scans using $Cu-K\alpha$ radiation ($\lambda=0.154$ nm) confirming the presence of a single B-type structure in all the $(Nd_{1-x}Y_x)_2O_3$ compositions in $0.2 \leq x \leq 0.5$ range after sintering at 1873 K.

Figure 4. XRD pattern after Rietveld refinement showing the observed (red) and calculated (black) profiles for $(Nd_{0.6}Y_{0.4})_2O_3$ B-type solid solution with added internal standard (Si-640c)²⁹ ($R_w = 6.59$, $GOF = 1.67$). The zoomed-in part shows the fitting of the highest intensity peaks.

Figure 5. WDS measurements done over the scanned backscattered electron image of $Nd_{0.6}Y_{0.4}O_{1.5}$ shown on left with measured mean Y cation at. % = 41.016 and two standard deviation of 0.494.

Figure 6. Variation in lattice parameters (in nm) of $(\text{Nd}_{1-x}\text{Y}_x)_2\text{O}_3$ B-type solid solution ($0.2 \leq x \leq 0.5$) with increasing Y_2O_3 concentration. Least-squares fitting of all the lattice parameters shows a linear trend with increasing Y_2O_3 concentration.

Figure 7. Enthalpy of drop solution (ΔH_{ds}) of B-type $(\text{Nd}_{1-x}\text{Y}_x)_2\text{O}_3$ solid solution with composition (bottom x-axis) and inverse of mean cation radius (r_m^{-1}) (top x-axis). Quadratic fit of the data (dashed curve): $\Delta H_{\text{ds}} = (104.14 \pm 9.49) x^2 + (-48.73 \pm 6.7) x + (-154.98 \pm 1.12)$, $R^2 = 0.994$.

Figure 8. Molar volume of the B-type $(\text{Nd}_{1-x}\text{Y}_x)_2\text{O}_3$ solid solution (V_m^B in cm^3/mol) extrapolated to the endmember compositions using least-squared fitting. Figure also shows the comparison of V_m^B estimated in this work with V_m^B and $V_m^{A/C}$ (stable endmembers) reported in literature. Extrapolated values in this work (empty squares) $V_m^{B-\text{Nd}_2\text{O}_3} = 46.91 \pm 0.06 \text{ cm}^3/\text{mol}$ at $x = 0$ and $V_m^{B-\text{Y}_2\text{O}_3} = 41.39 \pm 0.17 \text{ cm}^3/\text{mol}$ at $x = 1$. Values reported in the literature (B-type: empty circles and A/C-type: empty triangles) $V_m^{B-\text{Nd}_2\text{O}_3} = 46.8 \text{ cm}^3/\text{mol}$ ²⁴ and $V_m^{A-\text{Nd}_2\text{O}_3} = 46.25 \text{ cm}^3/\text{mol}$ ³⁶ at $x = 0$ and $V_m^{B-\text{Y}_2\text{O}_3} = 41.13 \text{ cm}^3/\text{mol}$ ³⁴ and $V_m^{C-\text{Y}_2\text{O}_3} = 44.88 \text{ cm}^3/\text{mol}$ ³⁵ at $x = 1$; Linear fit (dashed line) equation: $V_m = (-5.52 \pm 0.16) x + (46.91 \pm 0.06)$, $R^2 = 0.997$.

Figure 9. Enthalpy of formation of B-type $(\text{Nd}_{1-x}\text{Y}_x)_2\text{O}_3$ solid solution from binary oxides at 298 K with respect to Y_2O_3 mole fraction (bottom x-axis) and mean cation radius (r_m^{-1}) (top x-axis).

Quadratic fit after including the oxide endmembers^{16, 24, 34} (solid curve): $\Delta H_{f,B}^{ox,298K} = (-47.46 \pm 4.04) x^2 + (57.78 \pm 4.48) x + (1.34 \pm 1.04)$, $R^2 = 0.971$.

Tables

Table 1. Lattice parameters a, b, c, and molar volume per formula unit (V_m) with uncertainties in their last decimal place (in brackets) obtained using the Rietveld method on $(Nd_{1-x}Y_x)_2O_3$ B-type solid solutions ($0.2 \leq x \leq 0.5$) produced by sintering at 1873 K.

Sample	R_w	GOF	a (nm)	b (nm)	c (nm)	β (°)	V_m (cm ³ /mol)
$Nd_{0.8}Y_{0.2}O_{1.5}$	9.4	1.94	1.4286(1)	0.36446(2)	0.89047(4)	100.424(2)	45.773(4)
$Nd_{0.7}Y_{0.3}O_{1.5}$	5.39	1.47	1.4259(1)	0.36276(1)	0.88751(5)	100.437(2)	45.319(4)
$Nd_{0.65}Y_{0.35}O_{1.5}$	5.47	1.34	1.4239(1)	0.36126(1)	0.88526(4)	100.481(2)	44.951(4)
$Nd_{0.6}Y_{0.4}O_{1.5}$	6.59	1.67	1.4223(1)	0.36028(1)	0.88352(3)	100.498(2)	44.686(3)
$Nd_{0.55}Y_{0.45}O_{1.5}$	6	1.53	1.4203(1)	0.35928(1)	0.88169(4)	100.521(3)	44.406(3)
$Nd_{0.5}Y_{0.5}O_{1.5}$	7.11	1.58	1.4188(1)	0.35831(2)	0.87998(5)	100.529(1)	44.152(5)

Table 2. Thermodynamic cycle used to calculate the enthalpy of formation ($\Delta H_f^{ox,298K}$) of B-type $(Nd_{1-x}Y_x)_2O_3$ solid solution from binary oxides at 298 K.

	Reactions	Enthalpy
1.	$(Nd_{1-x}Y_x)_2O_{3(s,298K)} \rightarrow (1-x) Nd_2O_{3(sln,1073K)} + x Y_2O_{3(sln,1073K)}$	ΔH_1
2.	$Nd_2O_{3(s,298K)} \rightarrow Nd_2O_{3(sln,1073K)}$	$^*\Delta H_2$
3.	$Y_2O_{3(s,298K)} \rightarrow Y_2O_{3(sln,1073K)}$	$^*\Delta H_3$
	$(1-x)Nd_2O_{3(s,298K)} + x Y_2O_{3(s,298K)} \rightarrow (Nd_{1-x}Y_x)_2O_{3(s,298K)}$	$\Delta H_f^{ox,298K}$

$$\begin{aligned} * \Delta H_2 &= -156.95 \pm 1.05 \text{ kJ/mol (8)}^{32} \\ \Delta H_3 &= -116.34 \pm 1.21 \text{ kJ/mol (8)}^{32} \end{aligned}$$

$$\Delta H_f^{\text{ox}, 298\text{K}} = -\Delta H_1 + (1 - x) \Delta H_2 + x \Delta H_3$$

Table 3. Mean enthalpy of drop solution of B-type $(\text{Nd}_{1-x}\text{Y}_x)_2\text{O}_3$ in $3\text{Na}_2\text{O}-4\text{MoO}_3$ solvent at 1073 K and calculated enthalpy of formation from oxides at room temperature using thermodynamic cycle in Table 2.

Sample	ΔH_{ds} (kJ/mol)	$\Delta H_f^{\text{ox}, 298\text{K}}$ (kJ/mol)
$(\text{Nd}_{0.8}\text{Y}_{0.2})_2\text{O}_3$	$-160.48 \pm 2.56^*(6)^{**}$	11.65 ± 2.71
$(\text{Nd}_{0.7}\text{Y}_{0.3})_2\text{O}_3$	$-160.41 \pm 1.34(6)$	15.64 ± 1.57
$(\text{Nd}_{0.65}\text{Y}_{0.35})_2\text{O}_3$	$-159.39 \pm 3.24(6)$	16.65 ± 3.34
$(\text{Nd}_{0.6}\text{Y}_{0.4})_2\text{O}_3$	$-157.56 \pm 2.1(6)$	16.85 ± 2.25
$(\text{Nd}_{0.55}\text{Y}_{0.45})_2\text{O}_3$	$-155.72 \pm 2.32(6)$	17.04 ± 2.45
$(\text{Nd}_{0.5}\text{Y}_{0.5})_2\text{O}_3$	$-153.44 \pm 2.26(6)$	16.8 ± 2.4

* Two standard deviation

** Number of measurements

Table 4. Enthalpy of $\text{C} \rightarrow \text{B}$ and $\text{B} \rightarrow \text{A}$ polymorphic phase transitions of endmember oxides reported by various authors.

Transition enthalpy (kJ/mol)	Transition temperature (K) at ambient pressure	Method used	Reference
$\Delta H_{\text{tr}, \text{Nd}_2\text{O}_3}^{\text{A} \rightarrow \text{B}} = -0.4$	--	Estimated after reassessing the previously reported experimental thermodynamic data	[24]
$\Delta H_{\text{tr}, \text{Nd}_2\text{O}_3}^{\text{B} \rightarrow \text{A}} = -0.55$	none	DFT calculations used to calculate the difference in formation enthalpy of A- and B-type polymorphs at absolute zero temperature and pressure	[16]
$\Delta H_{\text{tr}, \text{Y}_2\text{O}_3}^{\text{C} \rightarrow \text{B}} = 12.83$	2756 K ⁴²	P-T dependence using Anvil apparatus and X-ray diffraction and applying Clausius-Clapeyron equation	[34]
$\Delta H_{\text{tr}, \text{Y}_2\text{O}_3}^{\text{C} \rightarrow \text{B}} = 11.09$	2756 K ⁴²	Extrapolation of P-T dependence of RE oxides to apply Clausius-Clapeyron equation	[24]

$\Delta H_{\text{tr}, \text{Y}_2\text{O}_3}^{\text{C} \rightarrow \text{B}} = 53.44$	P-T relations obtained using Anvil apparatus and X-ray diffraction	[43]
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$\Delta H_{\text{tr}, \text{Y}_2\text{O}_3}^{\text{C} \rightarrow \text{B}} = 54.28$	P-T relations obtained using Anvil apparatus and Raman spectroscopy	[44]
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$\Delta H_{\text{tr}, \text{Y}_2\text{O}_3}^{\text{C} \rightarrow \text{B}} = 50.10$	P-T relations obtained using Anvil apparatus and X-ray diffraction	[45]
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-- not reported
