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MELTING TEMPERATURES OF REFRACTORY OXIDES: PART II LANTHANOID SESQUIOXIDES

Prepared for publication by

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Melting temperatures of refractory oxides—Part II: Lanthanoid sesquioxides

Abstract - Experimental measurements of the melting points of the lanthanoid sesquioxides are critically reviewed and best values, with associated uncertainties, are recommended. Reasons for the quite large discrepancies, even in modern determinations, are discussed and studies to resolve the more important discrepancies are suggested.

INTRODUCTION

This is the second report from the Collaborative Study Group set up by the Commission on High Temperatures and Refractory Materials of the I.U.P.A.C. (now the Commission on High Temperature and Solid State Chemistry). The aim of the Study Group is to make a critical assessment of the published data on melting temperatures for various refractory oxides and to suggest recommended values with estimated uncertainties wide enough that further determination will probably fall within these limits. The first part (Hlavac, ref. 1) dealt with the oxides Al_2O_3 , MgO , Sc_2O_3 , SiO_2 , TiO_2 , Y_2O_3 and ZrO_2 .

The family of lanthanoid oxides is of special interest because the chemical and physical properties tend to vary smoothly with atomic number. The monotony is relieved, however, by an overlay of marked individualistic behaviour. This circumstance provides subtle variations in properties which may be used to test many hypotheses or theories of chemistry, including those pertaining to the solid state.

In oxide systems where a change of valency of the metal can occur, the atmosphere in which the samples were melted, and the nature of the containers used, are important variables. Unfortunately this information is not always available in the earlier measurements of the lanthanoid oxides.

In any oxide system of course, the solid phases need not melt congruently, although phases with very narrow ranges of homogeneity frequently do. Congruent melting of the sesquioxide phases has been assumed by all the authors of the studies quoted. This assumption is probably justified for most of the lanthanoid sesquioxides, although it must be remembered that the range of homogeneity of several (and probably all) of these oxides can extend to quite low values of O/M when in contact with the corresponding metal - see summary by Ackermann and Rauh (ref. 2); for example the lower phase boundary of $\text{Ce}_2\text{O}_{3-x}$ is as low as $\text{CeO}_{1.34}$ at a temperature of 1711°C , and Coutures (ref. 3) has reported that Gd_2O_3 heated in hydrogen can be reduced to $\text{GdO}_{1.47}$.

The data (Tables 1 to 12) are presented in the same format as that previously used by Schneider (ref. 4).

In assessing the measurements, special attention has been paid to two experimental features:

- possible changes in composition of the sample (which would alter the melting point), resulting from the atmosphere used, inappropriate furnace materials (e.g. Ta for many oxides) or reaction between the sample and its container.
- the temperature measurement, including details of any secondary standards, emissivity and wavelength data for pyrometric determinations. However, as will be clear from Tables 1-12, such information, particularly that relating to secondary standards, is often lacking from earlier papers.

The temperature scale used in reporting the measurement, if not stated, was assumed to be the appropriate IPTS (1927-1948-1968) according to the date of publication. Wherever possible, the melting point has been corrected to IPTS-68. In making this correction, the melting points of the secondary standards have also been corrected to currently accepted

values, namely

Al_2O_3	2054°C (ref. 5)
Pt	1772°C IPTS Secondary reference point (ref. 6)
Rh	1963°C " " " " (ref. 6)

These two corrections cause appreciable changes (15–20°C) in some reported melting points, since the melting point of Al_2O_3 was assumed to be 2040°C by Wisnyi and Pijanowski (ref. 7) and 2042°C by Foex (ref. 8). In the extensive series of measurements by Coutures *et al.* (ref. 9), the melting point of the secondary standard Y_2O_3 was assumed to be 2440°C. The small difference between this and the value recommended by Foex (ref. 10) (2439°C) has been neglected, since the melting temperatures reported by Coutures *et al.* have usually been rounded to the nearest 5°C.

Having regard to these experimental features, many of the published papers are difficult to evaluate, in that some experimental details are lacking, particularly regarding the secondary standard used, or the value used for its melting point. The relatively complete studies by Foex (ref. 8) and by Coutures *et al.* (ref. 9) seem to have given the necessary attention to the experimental conditions: measurement method, calibration using Al_2O_3 and Y_2O_3 as secondary standards and blackbody conditions with emissivity estimates at 0.65 μm . In particular Coutures *et al.* (ref. 9) have given special attention to the melting atmosphere in order to maintain stoichiometric oxides. For this purpose praseodymium and terbium oxides were melted under slightly reducing conditions (argon with 10% H_2) to prevent the formation of Pr^{4+} and Tb^{4+} ; Eu_2O_3 was melted under pure oxygen to minimize the reduction of Eu^{3+} to Eu^{2+} .

Moreover, a great advantage of the radiation-concentration devices, such as the solar furnace, is the ability to use a "self-crucible" technique, rather than crucibles or tungsten or molybdenum. This avoids interactions between the liquid oxides and the crucible, and possible oxygen potential limitations. For example tungsten is known to be dissolved by liquid yttrium sesquioxide (ref. 11). Ackermann and Rauh (ref. 12) have clearly shown the influence of the crucible in the case of lanthanum sesquioxide. At 2427 K for example the congruently vaporizing composition is $\text{La}_2\text{O}_{2.980}$ in a tungsten crucible and $\text{La}_2\text{O}_{2.998}$ with a rhenium crucible, showing considerably less reduction of this sesquioxide by rhenium. No data are available for molybdenum. The data of Ackermann and Rauh could explain the fact that the melting point values obtained by Foex (ref. 8) and Coutures *et al.* (ref. 9) are all slightly higher than the values obtained with metallic sample holders.

In the most recent study by Mizuno *et al.* (ref. 13) samples were melted by solar radiation in a controlled atmosphere, and they report values ($\pm 20^\circ\text{C}$) of the freezing points measured in vacuum, argon and air. In general, the values in air and argon were similar, somewhat lower values being obtained in *vacuo*. However, the same trends are seen in their reported measurements of the freezing points of Al_2O_3 and Y_2O_3 , suggesting perhaps a systematic error

Reported Freezing Points of Al_2O_3 and Y_2O_3 (ref. 13) ($^\circ\text{C}$ IPTS 68)

	Air	Ar	Vacuum	Recommended (refs. 5 and 10)
Al_2O_3	2071	2066	2037	2054
Y_2O_3	2449	2449	2427	2439

in their measurement system. We have therefore corrected their measured freezing points of lanthanoid oxides by making the following assumptions

- the melting points of Al_2O_3 and Y_2O_3 are the same in the three indicated atmospheres (the reviews in ref. 3 and 8 suggest this to be true, within experimental error).
- the correction to be applied at a given measured temperature is a linear interpolation between the corrections at the measured freezing points of Al_2O_3 and Y_2O_3 in the same atmosphere.

These corrections markedly decrease the differences in the freezing points as function of atmosphere.

However as noted in the discussion on Gd_2O_3 (see Section 1.8), there is a considerable difference between the freezing point of Gd_2O_3 given by Mizuno *et al.* (ref. 13) (corrected temperatures 2366 to 2383°C, both $\pm 20^\circ\text{C}$) and that obtained recently from the same team (ref. 14) (19 experiments, giving 2414 $\pm 25^\circ\text{C}$), although the ranges do overlap. This most recent measurement may indicate that the freezing points of the other lanthanoid oxides given by Mizuno *et al.* (ref. 13) may also be too low, rather than too high. This point has been taken into account in selecting the recommended values.

The studies by Foex (ref. 8) and by Coutures *et al.* (ref. 9) could be criticized because the thermal analysis method used is not an equilibrium method. The experimental procedure was checked by measuring the melting point of the $\text{ZrO}_2\text{-La}_2\text{Zr}_2\text{O}_7$ eutectic. The temperature of melting measured by Cabannes *et al.* (ref. 15) using a modified Riley method (equilibrium method) with an accurate emissivity measurement was 2223°C . This agrees very well with the result obtained by the same authors using the method by Foex or Coutures *et al.* in dynamic conditions: 2225°C .

SELECTED VALUES

The selected values have been divided into three classes:

Recommended values, where the set of experimental determinations is reasonably consistent and precise.

Probable values, where the consensus of experimental values is less convincing.

Estimated values, where experimental data are lacking or are very uncertain.

In each case, the uncertainties given are rather subjective estimates that future, more precise, measurements will have c. 95% probability of lying within the uncertainty band.

La_2O_3

Ten values (Table 1) of the melting point of La_2O_3 are given in the literature, mostly reasonably consistent. Runs were performed either in neutral atmosphere (He, Ar) air or vacuum; the temperature was usually measured with optical pyrometers except in two cases where they were measured with tungsten-rhenium thermocouples. Measurements under air are preferable, because La_2O_3 when melted under argon could have appreciable nonstoichiometry (Ackermann and Rauh (ref. 12)):

The selected value is $(2305 \pm 15^\circ\text{C})$, the weighted average of the eight measurements carried out in air, which are reasonably consistent. Two of the three measurements made under conditions where reduction could well have occurred (Lambertson and Gunzel, ref. 16 and Mordovin *et al.*, ref. 17), give much lower melting temperatures, but that by Tresviatskii *et al.* (ref. 18) in Ar agrees well with the selected value. However, unambiguous corrections could not be made to this measured value, since the calibration temperature is not clearly given.

RECOMMENDED VALUE : $2305 \pm 15^\circ\text{C}$.

Ce_2O_3

The melting temperature of Ce_2O_3 is not well known. The early (1925) measurement of 1692°C by Friederich and Sittig (ref. 19) is presumably far too low (Ackermann and Rauh (ref. 20) and Benezech and Foex (ref. 21) have made vaporization measurements up to 2180°C without any signs of melting). There are three more recent measurements of samples close to Ce_2O_3 due to Sata and Yoshimura (ref. 22), Tresviatskii *et al.* (ref. 18) and Mordovin *et al.* (ref. 13). Sata and Yoshimura (ref. 22) gave a value of $2210 \pm 10^\circ\text{C}$, measured in H_2 , while Mordovin *et al.* gave $2142 \pm 30^\circ\text{C}$ (corrected to 2145°C) for a sample prepared from CeO_2 annealed in hydrogen at 2000-2200K for 10 min; the fused material was unstable in air, so no analysis for composition was possible. However a comparison of our selected values for the other lanthanoid oxides shows that the values reported by Mordovin *et al.* are usually lower by about 100K, indicating a melting temperature of $\sim 2240^\circ\text{C}$. The measurement by Tresviatskii *et al.* (ref. 18), $2240 \pm 20^\circ\text{C}$ was carried out in Ar in a molybdenum container; no final analysis was reported. In view of the ease of oxidation and, at high temperatures, reduction of Ce_2O_3 , there can be no guarantee that these measurements refer to the stoichiometric oxide, but for the present, we suggest the

PROBABLE VALUE : $2230 \pm 50^\circ\text{C}$

Watson (ref. 23) in a study of the oxygen potentials of solid and liquid cerium oxides, measured the melting behaviour of CeO_{2-x} for a given CO/CO_2 ratio. Under these conditions, if the condensed phase remains in equilibrium with the gas, the oxide melts at a single temperature, the O/Ce of the condensed phase changing as the melting proceeds. He reports liquidus points of 1850, 1930 and 1970°C for O/Ce (liq) = 1.60, 1.64 and 1.66 respectively, and infers solidus points with O/Ce greater by ~ 0.05 . Since $\text{CeO}_{2-x}(\text{s})$ is probably single-phase in this region of the phase diagram, this would imply, if Ce_2O_3 melts congruently at $\sim 2230^\circ\text{C}$, solidus and liquidus lines which decreases sharply from the congruently melting Ce_2O_3 at 2230°C to a congruently melting minimum with O/Ce < 1.6 at $T < 1850^\circ\text{C}$. This seems unlikely, and further study of the melting behaviour of oxides between Ce_2O_3 and CeO_2 is clearly required.

Pr₂O₃

Only five values of the melting point have been published (Table 2). The measurement of Foex (ref. 8) in air, may relate to a hyperstoichiometric oxide, but agrees excellently with that of Coutures *et al.* (ref. 9), carried out in a reducing atmosphere, $2312 \pm 10^\circ\text{C}$. The two measurements by Tresviatskii *et al.* (ref. 18) and Mordovin *et al.* (ref. 17) which are lower by 50 and 200°C are difficult to assess because the calibration method for the temperature measurements is not given. The recent measurements of Mizuno *et al.* (ref. 13) (circa $2250 \pm 20^\circ\text{C}$ in reducing atmospheres) are substantially lower than those of refs. 8 and 9. The reason for this is not clear, since the lower measurements have been corrected using melting points of Al_2O_3 and Y_2O_3 . They do however represent freezing points, rather than melting points, although there is no reason to expect substantial super-cooling in these systems.

PROBABLE VALUE : $2300 \pm 25^\circ\text{C}$.

Nd₂O₃

Seven measurements are found in the literature (Table 3). Runs were performed either under neutral, reducing or oxidizing conditions and except for one, the temperatures were measured pyrometrically. These give:

- the unweighted average of five values (excluding that of Mordovin *et al.* (ref. 17), which appears too low): 2291°C
- the recommended value is weighted towards the more precise and well-defined measurements of Coutures *et al.* (ref. 9): $2320 \pm 20^\circ\text{C}$ - this value is identical with that obtained by Tresviatskii *et al.* (ref. 18), although the basis of their temperature calibration is not clearly stated.

RECOMMENDED VALUE : $2320 \pm 20^\circ\text{C}$.

Pm₂O₃

The melting point of Pm_2O_3 has been measured by Chikalla *et al.* (ref. 24) : $2320 \pm 25^\circ\text{C}$, somewhat lower than that estimated in ref. 9, 2375°C . The mean of the selected values for Nd_2O_3 and Sm_2O_3 , the immediate neighbours, is 2327°C .

PROBABLE VALUE : $2320 \pm 40^\circ\text{C}$.

Sm₂O₃

Eight values are reported in the literature (Table 4). The average of the four preferred values (3 and 6-8) is 2330°C . We have excluded values 1 and 2 because of the high uncertainty given by the authors, and values 4 to 6 because of the absence of calibration details. As before, the value of Mizuno *et al.* (ref. 13) is distinctly lower than those of Foex (ref. 8) and Coutures *et al.* (ref. 9). Bearing in mind the possibility of super-cooling, and the smaller uncertainty in the higher values, we suggest the

RECOMMENDED VALUE : $2335 \pm 15^\circ\text{C}$.

Eu₂O₃

The discrepancies for this oxide are quite large (Table 5). Wisnyi and Pijanowski (ref. 7) have found a melting point of $2067 \pm 30^\circ\text{C}$, Mordovin *et al.* (ref. 17) 2006°C and Coutures *et al.* (ref. 9) $2360 \pm 10^\circ\text{C}$. The reason for these large differences in temperatures could be:

- emissivity is over estimated (a value of approximately 0.9 to 0.95 was used in ref. 7);
- reaction of the liquid with the crucible (tungsten is known to diffuse into liquid rare earth oxides and could also react);
- non-stoichiometry : reduction under vacuum, helium, argon or hydrogen is probable, plus reduction by the tungsten sample holder.

Because of the above reasons we have considered only the results from self-container experiments under oxidizing conditions (values 3, 5, 6 and 7 in Table 5); rather more weight is given to the more precise measurements of Coutures *et al.* (ref. 9) in pure oxygen, to give a

PROBABLE VALUE : $2350 \pm 20^\circ\text{C}$.

Gd₂O₃

The measurements for Gd₂O₃ (Table 6) almost fall into two groups: those from the (often poorly defined) measurements (values 1, 2, 4, 5), averaging around $2340 \pm 30^\circ\text{C}$ and the notably higher values from the (better defined) experiments (values 3 and 7) averaging at $2425 \pm 25^\circ\text{C}$, with only one value, due to Tresviatskii *et al.* (ref. 18) lying between these.

Preliminary values from some new measurements organized within the IUPAC commission have recently become available (refs. 14,16,25).

These are summarized below:

<u>Furnace</u>	<u>Sample Holder</u>	<u>Environment</u>	<u>Melting Point</u>	
Solar	Self-crucible	air	$2440 \pm 15^\circ\text{C}$	
Xe arc	Self-crucible	air	$2439 \pm 15^\circ\text{C}$	Photo-electric pyrometer
			$2412 \pm 20^\circ\text{C}$	Two-colour pyrometer
Solar	Self-crucible	air	$2414 \pm 25^\circ\text{C}$	(ref. 14)
Ta tube	Tungsten	vacuum	$2400 \pm 15^\circ\text{C}$	
Xe arc	Self-crucible	air	$2400 \pm 5^\circ\text{C}$	(ref. 25)

The published value of Yoshimura *et al.* (ref. 25) (2393°C) has been corrected to allow for their measured value of the melting point of Y₂O₃, $2433 \pm 4^\circ\text{C}$. Although these new measurements have not resolved completely the discrepancy of the experimental determinations in air, they do suggest the lower values (below 2380°C) reported earlier (see Table 6) are not correct. However an appreciable uncertainty must remain on the

RECOMMENDED VALUE : $2420 \pm 20^\circ\text{C}$.

Tb₂O₃

Five values have been published (Table 7). The measurement of Foex (ref. 8) in air, may relate to a hyperstoichiometric oxide, but agrees well with those of Coutures *et al.* (ref. 9), carried out in a reducing atmosphere, which may indicate a relatively flat liquidus near the sesquioxide composition. Because of the lack of details concerning the calibration method, we have considered only the data of Foex and Coutures *et al.*, taking for the

PROBABLE VALUE : $2410 \pm 15^\circ\text{C}$.

Dy₂O₃, Ho₂O₃, Er₂O₃, Yb₂O₃, Lu₂O₃ - (Tables 8, 9, 10, 11, 12).

Because of the high melting point of the above oxides ($> 2400^\circ\text{C}$) rather few determinations have been carried out: for example only four values have been published for Lu₂O₃. Moreover except for the work of Foex (ref. 8) and Coutures *et al.* (ref. 9) and Mizuno *et al.* (ref. 13) the method used for the calibration of the temperature measurements are not given. The measurements of Mizuno *et al.* (ref. 13), indicate that there are only small differences in melting point (a range of only 20°C (within the experimental uncertainty)) for a given oxide when melted in air, argon and vacuum. At this stage recommended values cannot be given. We propose only probable valued weighted towards the more precise results of Foex and Coutures *et al.*

Dy ₂ O ₃	PROBABLE VALUE	$2408 \pm 15^\circ\text{C}$
Ho ₂ O ₃	PROBABLE VALUE	$2415 \pm 15^\circ\text{C}$
Er ₂ O ₃	PROBABLE VALUE	$2418 \pm 15^\circ\text{C}$
Yb ₂ O ₃	PROBABLE VALUE	$2435 \pm 15^\circ\text{C}$
Lu ₂ O ₃	PROBABLE VALUE	$2490 \pm 15^\circ\text{C}$

For Tm₂O₃ only one value have been found (2380°C after Tresviatskii *et al.* (ref. 18)); this is lower than an estimate from the results of the Coutures *et al.* (ref. 9) which would be $2425 \pm 20^\circ\text{C}$.

TABLE 1. Melting point of La_2O_3 (IPTS 68) °C

Authors (Year)	Ref.	Purity %	Method*	Furnace	Sample Holder	Environment	Temp. Meas.*	Calibration (t °C)	Reported mp °C	Corrected Melting Point °C (IPTS 68)
1) WARTENBERG & REUSCH (1932)	27	100(?)	O.D.H.	Flame	Self container	Air	O.P.	Pt (1773)	2315	2309
2) LAMBERTSON & GUNZEL (1952)	16	99	E.A.H.	W heating element	W	He	O.P.	Pt (1769)	2210 ± 20	2217 ± 20
3) SATA & KIYOURA (1963)	28	99.9	D.T.A.	W heating element	W	Ar + ε H ₂	W-Re T.C.	Pt (1769) Rh (1960)	2304 ± 2	2311 ± 2
4) FOEX (1966)	8	99.9	O.D.C.	Solar furnace	Self container	Air	O.P.	Al ₂ O ₃ (2042)	2300	2315
5) MORDOVIN & et al. (1967)	17	99.6	O.D.H.	W heating element	W	H ₂	O.P.	Not clearly stated Al ₂ O ₃ & Cr ₂ O ₃ mp	2220 ± 30	2224 ± 30
6) NOGUCHI & MIZUNO (1967)	29	99.9	O.D.C.	Solar furnace	Self container	Air	O.P.	(Standard W lamp)	2257 ± 20	2260 ± 20
7) TRESVIATSKII et al. (1971)	18	99.9	D.T.A.	W heating element	Mo	Ar	20% W-Re T.C.	Not clearly stated	2310 ± 20	2310 ± 20
8) COUTURES et al. (1975)	9	99.9	O.D.C.	Solar furnace	Self container	Air	O.P.	Y ₂ O ₃ (2440)	2320 ± 10	2320 ± 10
9) MIZUNO et al. (1981)	13	99.9	O.D.C.	Solar furnace	Self container	Air Ar Vacuum	O.P.	Al ₂ O ₃ and Y ₂ O ₃ (see text)	2296 ± 30 2283 ± 20 2254 ± 20	2283 ± 20 2272 ± 20 2268 ± 20
10) YOSHIMURA, SOMIYA, YAMADA (1985)	25	>99.9	O.D.C.	Arc imaging furnace	Self container	Air	D.P.	Std. W-Lamp & Al ₂ O ₃ (2054) Y ₂ O ₃ (2433)	2300 ± 3	2304 ± 5

* For meaning of abbreviations see Table 12.

TABLE 2. Melting point of Pr_2O_3 (IPTS 68)°C

Authors (Year)	Ref.	Purity %	Method	Furnace	Sample Holder	Environment	Temp. Meas.	Calibration ($\pm$ °C)	Reported mp °C	Corrected Melting Point °C (IPTS 68)
1) FOEX (1966)	8	99.9	O.D.C.	Solar furnace	Self container	Air	O.P.	Al_2O_3 (2042)	2295	2310
2) MORDOVIN et al. (1967)	17	99.5	O.D.H.	W heating element	W	H_2	O.P.	Not clearly stated	2117 ± 30	2121 ± 30
3) TRESVIATSKII et al. (1971)	18	99.9	D.T.A.	W heating element	Mo	H_2	20% W-Re T.C.	Not clearly stated	2260 ± 20	2260 ± 20
4) COUTURES et al. (1975)	9	99.99	O.D.C.	Solar furnace	Self container	90% A 10% H_2	O.P.	Y_2O_3 (2440)	2312 ± 10	2312 ± 10
5) MIZUNO et al. (1981)	13	99.9	O.D.C.	Solar furnace	Self container	Air Ar Vacuum	O.P.	Al_2O_3 and Y_2O_3 (see text)	2276 ± 20 2264 ± 20 2228 ± 20	2263 ± 20 2253 ± 20 2243 ± 20

TABLE 3. Melting point of Nd_2O_3 (IPTS 68) °C

Authors (Year)	Ref.	Purity %	Method	Furnace	Sample Holder	Environment	Temp. Meas.	Calibration ($\pm$ °C)	Reported mp °C	Corrected Melting Point °C (IPTS 68)
1) LAMBERTSON & GUNZEL (1952)	16	99	E.A.H.	W heating element	W	He	O.P.	Pt (19769)	2272 $\pm$ 20	2279 $\pm$ 20
2) FOEX (1966)	8	99.9	O.D.C.	Solar furnace	Self container	Air	O.P.	Al_2O_3 (2042)	2310	2326
3) MORDOVIN et al. (1967)	17	99.0	O.D.H.	W heating element	W	H_2	O.P.	Not clearly stated	2213 $\pm$ 30	2217 $\pm$ 30
4) NOGUCHI & MIZUNO (1967)	29	99.9	O.D.C.	Solar furnace	Self container	Air	O.P.	(Standard W lamp)	2233 $\pm$ 20	2237 $\pm$ 20
5) TRESVIATSKII et al. (1971)	18	99.9	D.T.A.	W heating element	Mo	Ar	20% W-Re T.C.	Not clearly stated	2320 $\pm$ 20	2320 $\pm$ 20
6) COUTURES et al. (1975)	9	99.99	O.D.C.	Solar furnace	Self container	Air	O.P.	Y_2O_3 (2440)	2325 $\pm$ 10	2325 $\pm$ 10
7) MIZUNO et al. (1981)	13	99.9	O.D.C.	Solar furnace	Self container	Air Ar Vacuum	O.P.	Al_2O_3 and Y_2O_3 (see text)	2290 2270 $\pm$ 20 2240	2277 2259 $\pm$ 20 2254

TABLE 4. Melting point of Sm_2O_3 (IPTS 68) °C

Authors (Year)	Ref.	Purity %	Method	Furnace	Sample Holder	Environment	Temp. Meas.	Calibration (t °C)	Reported mp °C	Corrected Melting Point °C (IPTS 68)
1) WISNYI & PLJANOWSKI (1957)	7	Not stated	O.D.H.	W heating element	W	He H ₂ Vacuum	O.P.	Al_2O_3 (2040)	2300 ± 50	2318 ± 50
2) CURTIS & JOHNSON (1957)	30	~99	O.D.H.	Not stated	Not given	Air	O.P.	Not given	2350 ± 50	2354 ± 50
3) FOEX (1966)	8	99.9	O.D.C.	Solar furnace	Self container	Air	O.P.	Al_2O_3 (2042)	2320	2335
4) MORDOVIN et al. (1967)	17	99.55	O.D.H.	W heating element	W	Ar	O.P.	Not clearly stated	2263 ± 30	2267 ± 30
5) NOGUCHI & MIZUNO (1967)	29	99.9	O.D.C.	Solar furnace	Self container	Air	O.P.	(Standard W lamp)	2233 ± 20	2237 ± 20
6) TRESVIATSKII et al. (1971)	18	99.9	D.T.A.	W heating element	Mo	Ar	T.C.	Not clearly stated	2340 ± 20	2340 ± 20
7) COUTURES et al. (1975)	9	99.99	O.D.C.	Solar furnace	Self container	O ₂	O.P.	Y_2O_3 (2440)	2325 ± 10	2345 ± 10
8) MIZUNO et al. (1981)	13	99.9	O.D.C.	Solar furnace	Self container	Air Ar Vacuum	O.P.	Al_2O_3 and Y_2O_3 (see text)	2310 2308 2284	2297 2297 2298

TABLE 5. Melting point of Eu_2O_3 (IPTS 68) °C

Authors (Year)	Ref.	Purity %	Method	Furnace	Sample Holder	Environment	Temp. Meas.	Calibration (t °C)	Reported mp °C	Corrected Melting Point °C (IPTS 68)
1) WISNYI & PIJANOWSKI (1957)	7	Not stated	O.D.H.	W heating element	W	He H ₂ Vacuum	O.P.	Al_2O_3 (2040)	2050 ± 30	2067 ± 30
2) SCHNEIDER (1961)	31	>99.9	E.A.H.	Induction	Ir	Air	O.P.	Au (1063) Pt (1769) Rh (1960)	2240 ± 10	2247 ± 10
3) FOEX (1966)	8	99.0	O.D.C.	Solar furnace	Self container	Air	O.P.	Al_2O_3 (2042)	2330	2345
4) MORDOVIN et al. (1967)	17	99.9	O.D.H.	W heating element	W	Ar	O.P.	Not clearly stated	2003 ± 30	2006 ± 30
5) NOGUCHI & MIZUNO (1967)	29	99.9	O.D.C.	Solar furnace	Self container	Air	O.P.	(Standard W lamp)	2291 ± 20	2295 ± 20
6) COUTURES et al. (1975)	9	99.9	O.D.C.	Solar furnace	Self container	O ₂	O.P.	Y_2O_3 (2440)	2360 ± 10	2360 ± 10
7) MIZUNO et al. (1981)	13	99.9	O.D.C.	Solar furnace	Self container	Air Ar Vacuum	O.P.	Al_2O_3 and Y_2O_3 (see text)	2345 2335 2288 ± 20	2333 2324 2302 ± 20

TABLE 6. Melting point of Gd_2O_3 (IPTS 68)°C

Authors (Year)	Ref.	Purity %	Method	Furnace	Sample Holder	Environment	Temp. Meas.	Calibration (t °C)	Reported mp °C	Corrected Melting Point °C (IPTS 68)
1) WISNYI & PIJANOWSKI (1957)	7	Not stated	O.D.H.	W heating element	W	He H ₂ Vacuum	O.P.	Al ₂ O ₃ (2040)	2330 ± 20	2348 ± 20
2) CURTIS & JOHNSON (1957)	30	~99	O.D.H.	Not stated	Not stated	Air	O.P.	Not stated	2350 ± 50	2354 ± 50
3) FOEX (1966)	8	99.9	O.D.C.	Solar furnace	Self container	Air	O.P.	Al ₂ O ₃ (2042)	2395	2411
4) MORDOVIN et al. (1967)	17	99.79	O.D.H.	W heating element	W	Ar	O.P.	Not clearly stated	2324 ± 30	2327 ± 30
5) NOGUCHI & MIZUNO (1967)	29	99.9	O.D.C.	Solar furnace	Self container	Air	O.P.	(Standard W lamp)	2330 ± 20	2334 ± 20
6) TRESVIATSKII et al. (1971)	18	99.9	D.T.A.	W heating furnace	Mo	Ar	20% W-Re T.C.	Not clearly stated	2380 ± 20	2380 ± 20
7) COUTURES et al. (1975)	9	99.99	O.D.C.	Solar furnace	Self container	Air	O.P.	Y ₂ O ₃ (2440)	2440 ± 10	2440 ± 10
8) MIZUNO et al. (1981)	13	99.9	O.D.C.	Solar furnace	Self container	Air Ar Vacuum	O.P.	Al ₂ O ₃ and Y ₂ O ₃ (see text)	2394 2380 2353	2383 2370 2366

TABLE 7. Melting point of Tb_2O_3 (IPTS 68)°C

Authors (Year)	Ref.	Purity %	Method	Furnace	Sample Holder	Environment	Temp. Meas.	Calibration ($\pm$ °C)	Reported mp °C	Corrected Melting Point °C (IPTS 68)
1) FOEX (1966)	8	99.9	O.D.C.	Solar furnace	Self container	Air	O.P.	Al_2O_3 (2042)	2390	2406
2) MORDOVIN et al. (1967)	17	99.7	O.D.H.	W heating element	W	H ₂	O.P.	Not clearly stated	2293 $\pm$ 30	2297 $\pm$ 30
3) NOGUCHI & MIZUNO (1967)	29	99.9	O.D.C.	Solar furnace	Self container	Air	O.P.	(Standard W lamp)	2304 $\pm$ 20	2308 $\pm$ 20
4) TRESVIATSKII et al. (1971)	18	99.9	D.T.A.	W heating element	Mo	Ar	20% W-Re T.C.	Not clearly stated	2370 $\pm$ 20	2370 $\pm$ 20
5) COUTURES et al. (1975)	9	99.9	O.D.C.	Solar furnace	Self container	Ar - 10% H ₂	O.P.	Y_2O_3 (2440)	2410 $\pm$ 10	2410 $\pm$ 10

TABLE 8. Melting point of Dy_2O_3 (IPTS 68)°C

Authors (Year)	Ref.	Purity %	Method	Furnace	Sample Holder	Environment	Temp. Meas.	Calibration (t °C)	Reported mp °C	Corrected Melting Point °C (IPTS 68)
1) WISNYI & PIJANOWSKI (1957)	7	Not stated	O.D.H.	W heating element	W	He H ₂ Vacuum	O.P.	Al ₂ O ₃ (2040)	2340 ± 10	2357 ± 10
2) FOEX (1966)	8	99.9	O.D.C.	Solar furnace	Self container	Air	O.P.	Al ₂ O ₃ (2042)	2390	2406
3) MORDOVIN et al. (1967)	17	99.7	O.D.H.	W heating element	W	H ₂	O.P.	Not clearly stated	2293 ± 30	2297 ± 30
4) NOGUCHI & MIZUNO (1967)	29	99.9	O.D.C.	Solar furnace	Self container	Air	O.P.	(Standard W lamp)	2228 ± 20	2232 ± 20
5) TRESVIATSKII et al. (1971)	18	99.9	D.T.A.	W heating element	Mo	Ar	20% W-Re T.C.	Not clearly stated	2360 ± 20	2360 ± 20
6) COUTURES et al. (1975)	9	99.9	O.D.C.	Solar furnace	Self container	Air	O.P.	Y ₂ O ₃ (2440)	2410 ± 10	2410 ± 10
7) MIZUNO et al. (1981)	13	99.9	O.D.C.	Solar furnace	Self container	Air Ar Vacuum	O.P.	Al ₂ O ₃ and Y ₂ O ₃ (see text)	2355 2345 2337	2343 2334 ± 20 2350

TABLE 9. Melting point of Ho_2O_3 (IPTS 68) °C

Authors (Year)	Ref.	Purity %	Method	Furnace	Sample Holder	Environment	Temp. Meas.	Calibration (t °C)	Reported mp °C	Corrected Melting Point °C (IPTS 68)
1) FOEX (1966)	8	99.9	O.D.C.	Solar furnace	Self container	Air	O.P.	Al_2O_3 (2042)	2395	2411
2) MORDOVIN et al. (1967)	17	99.73	O.D.H.	W heating element	W	Ar	O.P.	Not clearly stated	2353 ± 30	2357 ± 30
3) NOGUCHI & MIZUNO (1967)	29	99.9	O.D.C.	Solar furnace	Self container	Air	O.P.	(Standard W lamp)	2330 ± 20	2334 ± 20
4) TRESVIATSKII et al. (1971)	18	99.9	D.T.A.	W heating element	Mo	Ar	20% W-Re T.C.	Not clearly stated	2370 ± 20	2370 ± 20
5) COUTURES et al. (1975)	9	99.99	O.D.C.	Solar furnace	Self container	Air	O.P.	Y_2O_3 (2440)	2420 ± 10	2420 ± 10
6) MIZUNO et al. (1981)	13	99.9	O.D.C.	Solar furnace	Self container	Air Ar Vacuum	O.P.	Al_2O_3 and Y_2O_3 (see text)	2365 2355 ± 20 2338	2353 2345 ± 20 2351

TABLE 10. Melting point of Er_2O_3 (IPTS 68) °C

Authors (Year)	Ref.	Purity %	Method	Furnace	Sample Holder	Environment	Temp. Meas.	Calibration ($\pm$ °C)	Reported mp °C	Corrected Melting Point °C (IPTS 68)
1) FOEX (1966)	8	99.9	O.D.C.	Solar furnace	Self container	Air	O.P.	Al_2O_3 (2042)	2400	2416
2) MORDOVIN et al. (1967)	17	99.93	O.D.H.	W heating element	W	Ar	O.P.	Not clearly stated	2388 ± 30	2392 ± 30
3) NOGUCHI & MIZUNO (1967)	29	99.9	O.D.C.	Solar furnace	Self container	Air	O.P.	(Standard W lamp)	2345 ± 20	2349 ± 20
4) TRESVIATSKII et al. (1971)	18	99.9	D.T.A.	W heating element	Mo	Ar	20% W-Re T.C.	Not clearly stated	2390 ± 20	2390 ± 20
5) COUTURES et al. (1975)	9	99.99	O.D.C.	Solar furnace	Self container	Air	O.P.	Y_2O_3 (2440)	2420 ± 10	2420 ± 10
6) MIZUNO et al. (1981)	13	99.9	O.D.C.	Solar furnace	Self container	Air Ar Vacuum	O.P.	Al_2O_3 and Y_2O_3 (see text)	2375 2360 ± 20 2357	2364 2350 ± 20 2370

TABLE 11. Melting point of Yb_2O_3 (IPTS 68)°C

Authors (Year)	Ref.	Purity %	Method	Furnace	Sample Holder	Environment	Temp. Meas.	Calibration (t °C)	Reported mp °C	Corrected Melting Point °C (IPTS 68)
1) FOEX (1966)	8	99.9	O.D.C.	Solar furnace	Self container	Air	O.P.	Al_2O_3 (2042)	2420	2436
2) MORDOVIN et al. (1967)	17	99.8	O.D.H.	W heating element	W	Ar	O.P.	Not clearly stated	2373 ± 30	2377 ± 30
3) NOGUCHI & MIZUNO (1967)	29	99.9	O.D.C.	Solar furnace	Self container	Air	O.P.	(Standard W lamp)	2355 ± 20	2359 ± 20
4) TRESVIATSKII et al. (1971)	18	99.9	D.T.A.	W heating element	Mo	Ar	20% W-Re T.C.	Not clearly stated	2400 ± 20	2400 ± 20
5) COUTURES et al. (1975)	9	99.99	O.D.C.	Solar furnace	Self container	Air	O.P.	Y_2O_3 (2440)	2435 ± 10	2435 ± 10
6) MIZUNO et al. (1981)	13	99.9	O.D.C.	Solar furnace	Self container	Air Ar Vacuum	O.P.	Al_2O_3 and Y_2O_3 (see text)	2387 2376 ± 20 2372	2376 2366 ± 20 2385

TABLE 12. Melting point of Lu_2O_3 (IPTS 68) °C

Authors (Year)	Ref.	Purity %	Method	Furnace	Sample Holder	Environment	Temp. Meas.	Calibration (t °C)	Reported mp °C	Corrected Melting Point °C (IPTS 68)
1) MORDOVIN et al. (1967)	17	99.88	O.D.H.	W heating element	W	Ar	O.P.	Not clearly stated	2468 ± 30	2472 ± 30
2) NOGUCHI & MIZUNO (1967)	29	99.9	O.D.C.	Solar furnace	Self container	Air	O.P.	(Standard W lamp)	2428 ± 10	2432 ± 10
3) COUTURES et al. (1975)	9	99.9	O.D.C.	Solar furnace	Self container	Air	O.P.	Y_2O_3 (2440)	2490 ± 10	2490 ± 10
4) MIZUNO et al. (1981)	13	99.9	O.D.C.	Solar furnace	Self container	Air Ar Vacuum	O.P.	Al_2O_3 and Y_2O_3 (see text)	2460 2456 ± 20 2448	2450 2446 ± 20 2460

Abbreviations: D.P. Digital pyrometer;
D.T.A. Differential thermal analysis;
E.A.H. Observation after heating;
O.D.C. Observation during cooling;
O.D.H. Observation during heating;
O.P. Optical pyrometer;
T.C. Thermocouple.

DISCUSSIONS AND RECOMMENDATIONS

Not surprisingly, there is a fairly consistent pattern for measurements of the melting points of the lanthanoid oxides by various authors. In general the values increase in the order

Mordovin *et al.* < Noguchi and Mizuno < Tresviatskii *et al.* < Foex $\approx$ Coutures *et al.*

Some possible reasons for this are discussed in the text, but the discrepancies still remain larger than expected.

The recommended, probable and estimated values for the melting points of the entire lanthanoid sesquioxide family are shown in Table 13 and plotted in the Figure. The most notable irregularity is the peak in the curve at Gd_2O_3 . However this seems to be clearly established, since all four studies (refs. 8,9,13 and 18) of the whole series find that Gd_2O_3 has a higher melting point than the neighbouring oxides, (irrespective of the actual values). This is presumably related to the filling of all the seven f orbitals with one electron at this element, this symmetry giving an additional stability to the Gd-O bond in the solid, as discussed by Coutures *et al.* (ref. 9). The dip in the melting point curve at Ce_2O_3 is less well established, although the three measurements would have to be substantially in error. However, as discussed in the text, these measured values could be lower than the melting point of stoichiometric Ce_2O_3 .

This assessment gives the "state of the art" concerning the melting points of the lanthanoid sesquioxides. For many of them the data are close to those of Coutures *et al.* (ref. 9). The main reasons for this are:

- the measurements were carried out in good blackbody conditions with an emissivity between 0.97 and 0.98;
- no contamination by the sample holder;
- the experiments were made under the most appropriate oxygen potential to retain the composition of the melted oxide at Ln_2O_3 .

The importance of the atmosphere and the sample holder are very well illustrated by comparing particular results obtained for example by Mordovin *et al.* (ref. 17) and Coutures *et al.* (ref. 9). For the most reducible oxide (Eu_2O_3) the difference is 360°C, whereas for the less reducible (Lu_2O_3) the difference is only 20°C. Data on the nonstoichiometry of heavy rare earth sesquioxides in the liquid state under hydrogen are given by Coutures *et al.* (ref. 26) and shown in Table 14. The nonstoichiometry expressed as the O/Ln ratio is obtained by reoxidation with a micro-thermobarometer of sample heated for 10 min under hydrogen.

The following new measurements are recommended to elucidate the trend of results noted above:

- (1) Measurements of the melting points of Gd_2O_3 and Nd_2O_3 (which are available in high purity) at a range of oxygen potentials ($p(O_2) = 10^{+5}$ to 10^{-3} Pa), with a variety of different sample holders (molybdenum, tungsten, rhenium, self-crucible). The change in composition of the sample and contamination by the crucible material after the measurements should be determined.
- (2) If the effect of change of oxygen potential and thus, stoichiometry, for whatever reason, is appreciable, further experiments with Eu_2O_3 and Pr_2O_3 as well as Gd_2O_3 over much wider ranges of oxygen potential would be invaluable to elucidate effect of non-stoichiometry on the melting and solidification points extending if possible down to the lower phase boundary of the sesquioxides.
- (3) A very interesting (but difficult) study would be the determination of the solidus-liquidus curves for the CeO_{2-x} system, where the solid/solution phase probably extends from $1.3 < O/Ce < 2$ near the liquidus. As noted in the text, the technique of heating the oxides slowly in a gas of fixed CO/CO₂ ratio could provide considerable useful information.

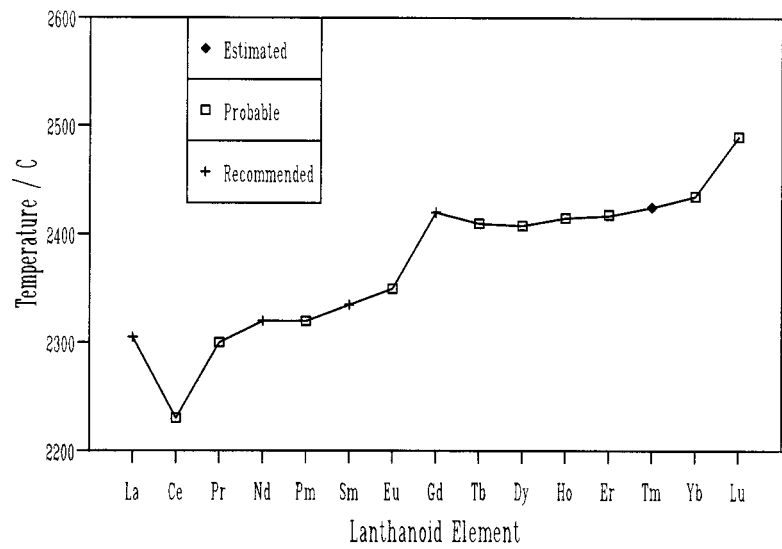
As noted earlier, it is always assumed that the highest melting point (congruent melting) occurs at a mole ratio of O/Ln = 1.5, and although this is probably true, there is no experimental evidence for this assumption.

TABLE 13. Recommended, probable or estimated melting point of lanthanoid sesquioxides, °C (IPTS 68)

Ln_2O_3	Recommended Melting Point	Probable Melting Point	Estimated Melting Point
La_2O_3	2305 ± 15		
Ce_2O_3		2230 ± 50	
Pr_2O_3		2300 ± 25	
Nd_2O_3	2320 ± 20		
Pm_2O_3		2320 ± 40	
Sm_2O_3	2335 ± 15		
Eu_2O_3		2350 ± 20	
Gd_2O_3	2420 ± 20		
Tb_2O_3		2410 ± 15	
Dy_2O_3		2408 ± 15	
Ho_2O_3		2415 ± 15	
Er_2O_3		2418 ± 15	
Tm_2O_3			2425 ± 20
Yb_2O_3		2435 ± 15	
Lu_2O_3		2490 ± 15	

TABLE 14. Non-stoichiometry of some rare earth sesquioxides after melting under hydrogen for 10 min at $T \sim T_{\text{fus}} + 200^\circ\text{C}$

Ln_2O_3	O/Ln
Gd_2O_3	1.469
Dy_2O_3	1.482
Ho_2O_3	1.487
Er_2O_3	1.488



Melting Points of Lanthanoid Oxides

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