

Letter to the Editor

Reply to ‘Comments on the paper “Phase stability...”’

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P. Fedorov addresses his criticism to the study [1], that leads to conclusions in contrast with his paper [2]. Abstracts of both papers follow.

From [1]:

The phase stability of the system Gd_2O_3 – Nd_2O_3 up to 1,350 °C was studied. Mixed oxides were synthesized by coprecipitation of mixed oxalates. Depending on the thermal treatment, three possible structures of the oxides, namely the A (hexagonal, P63/mmm), B (monoclinic, C2/m), and C (cubic, Ia3) forms, were obtained. Below 1,300 °C the system Gd_2O_3 – Nd_2O_3 shows three monophasic (A, B, and C phase) and three biphasic regions (A+B, B+C and A+C phase). Below 550 °C the C phase is stable over the whole composition range. A validation procedure for the existence of the C phase in pure Nd_2O_3 was also set up.

From [2] (english translation):

The data on the phase transitions in the series of rare earth sesquioxides are considered in terms of the thermodynamic theory of morphotropism. It is shown that the scheme of polymorphism and morphotropism suggested by V.V. Glushkova is the most adequate. The derivatographic dehydration of lanthanum and neodymium oxide hydrates is performed. The transition of the cubic C modification into the hexagonal A modification of neodymium oxide is accompanied by the removal of volatile impurities and, thus, is not a polymorphic transition proper.

The ‘Comment’ refers to two main points in study [1].

1. The picture where thermal decomposition results are presented in T-x coordinates and the caption hereafter

reported: “Fig. 1 - Pseudobinary phase diagram of the system Gd_2O_3 – Nd_2O_3 . Lines are a guide for the eyes.” The meaning of this caption (i.e., to present the existing phases after synthesis and equilibration procedure) is well clarified in the paper, whose purpose was to locate the three main monophasic regions described: the precise position of the phase boundaries, due to the granularity of the data, could not be given. Moreover, the reader was informed that “the dashed line in the Nd rich part at low temperature is referred to a not yet well defined region where many phase boundaries may be present.”

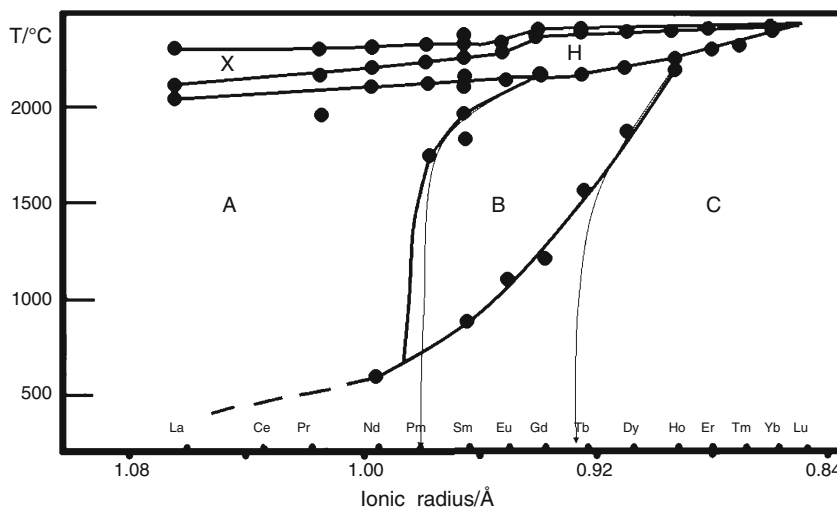
This region, (from 95 to 100% Nd) and the assessment of the whole phase diagram was left to a further study currently in progress. For this reason, no “*eutectoid invariant isothermal three-phase co-node has been lost in paper*”.

Just a little above P. Fedorov outlined that “Unfortunately, the results of [1] do not correspond to the thermodynamics of heterogeneous equilibria”. I would like to underline here that the picture reports experimental results and that these results are the real things. I am grateful to P. Fedorov for the sketch of his own phase diagram, even if it is only a pretext to introduce his second point.

2. The existence of a stable C phase in the Gd_2O_3 – Nd_2O_3 . This is the focal point of the issue. Before discussing this point, it should be observed that the C form (space group Ia3) is the most stable for lanthanides from Tb to Lu, while the A form (space group P63/mmm) is typical for lanthanides from La to Nd; the intermediate rare earth oxides exist both in the B- and C-type polymorphs, the B form (space group C2/m) being stable above 875, 1,000, and 1,250 °C for Sm_2O_3 , Eu_2O_3 , and Gd_2O_3 , respectively; [3] however, these oxides can also be found in the

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Fig. 1 Questioning about the stability fields for the rare earth sesquioxides. The data redrawn from L. Eyring [5] are superimposed to the changes proposed by [2]



B structure at room temperature. The sesquioxides of the largest ions from La_2O_3 to Nd_2O_3 are usually reported to crystallize in the A-type structure [4].

The question whether the sesquioxides from Nd to Gd can exist in the C form, if the synthesis conditions are suitable [5], is still open in literature [3, 6–9], and is “*the subject of many-year discussion*,” as also P. Fedorov states, so that no general agreement exists to date. On the contrary, this question has stimulated theoretical study of ab initio studies on structure and phase stability of rare earth sesquioxides as a function of temperature and pressure [10, 11].

The general situation is well depicted in the famous drawing [5] by L. Eyring roughly reproduced above (Fig. 1, thick lines). In the picture the changes proposed by P. Fedorov [2] are also indicated (Fig. 1, boundaries indicated by the two thin lines). A recent review by E. Schweda and Z. Kang [12] proposes essentially the same picture as in [5].

The importance of the phase investigation performed by [1] is now clear: Nd and Gd are on opposite sides of the boundary predicted by P. Fedorov. The study performed could then give indication in favor or in contrast with the theory described in [2]. As a result, no evidence of A–B phase transition was found in the low temperature region, where the C phase was always detected. Moreover, the thermal decomposition data for the B–C transformation of Gd_2O_3 (in the range 1,200–1,250 °C) and for the A–C transformation of Nd_2O_3 (at about 600 °C) are in full agreement with the data reported in [5, 12].

Now a last topic remains, about stabilization of the C phase by water impurities. I was aware of the paper of P. Fedorov [2] (cited in [1] under reference 28), and the TG-DTA thermograms for neodymium hydroxide decomposition were in substantial agreement with the data reported in [2]. P. Fedorov also detected a C cubic phase

whose stoichiometry was $\text{Nd}_2\text{O}_3 \cdot 0.3\text{H}_2\text{O}$ which upon decomposition led at 790 °C to the Nd_2O_3 A phase.

As sometimes water loss in TG-DTA may depend on the experimental conditions, as for example on flushing gas and heating rate, a prolonged (10 days total) effusion experiment was set up, as described in [1].

By this method the authors extracted all water at a relatively low temperatures of 550 °C and meanwhile tested the thermal stability of the product. As a result, a water-free sample was obtained, that resulted in a nearly pure C phase containing only traces of A.

So the authors could conclude that water is not necessary to stabilize C-TYPE Nd_2O_3 .

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