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Letter to the Editor

Comment on the paper "Phase stability study of the pseudobinary system Gd_2O_3–Nd_2O_3 ($T \leq 1350$ °C)" by G. A. Costa, C. Artini, A. Ubaldini, M. M. Carnasciali, P. Mele, and R. Masini

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In the paper [1] the interaction between Gd_2O_3 and Nd_2O_3 has been studied. In order to investigate a low-temperature region, precipitation with thermal decomposition of the precursor was used therein. Phase fields were presented in T-x co-ordinates. Low-temperature continuous solid solution of cubic C-forms of rare earth oxides and limited solid solutions on the base of high-temperature hexagonal A-Nd_2O_3 and monoclinic B-Gd_2O_3 are shown. The resulting picture was called "the Gd_2O_3–Nd_2O_3 phase diagram".

Unfortunately, the results of [1] do not correspond to the thermodynamics of heterogeneous equilibria. Figure 2 form [1] violates the phase rule. Figure 1 shows the correct scheme of phase equilibria, corresponding to the positions of single-phase fields as revealed in [1]. The eutectoid invariant isothermal three-phase co-node has been lost in paper [1].

This mistake may arise from incorrect experiments or incorrect interpretation of results. It seems that both take place.

The polymorphism and morphotropic of rare-earth sesquioxides are the subject of many-year discussion (see, for example, review of Zinkevich [2] and paper [3]). The stability of cubic C-forms for the cerium subgroup is a point of disaccord. Numerous researches (see for example [3]) established that this form of R_2O_3 is stabilized for La–Gd by water impurity. The thermodynamic theory of morphotropy [4] indicated that the cubic form cannot be stable for R = La–Gd. The stable low-temperature C-polymorphs appear starting with Tb.

The experiments carried out in [1] fail to prove the stability of the cubic oxide at low temperatures. But they clearly demonstrate that dehydration of cubic Nd_2O_3 at 550 °C induces the onset of its transformation, as lines of the A-phase appear in the X-ray diffraction pattern. It is this A-phase that is stable at low temperatures.

The matter is not whether cubic rare-earth oxides of cerium subgroup can exist at low temperatures. The matter is whether they are stable. The experiments made in [1] imply their instability. Accordingly, the results given in [1] do not refer to a phase diagram, which would have suggested that equilibrium is acquired. Figure 2 in [1] is not a phase diagram either in its pattern or contents.

It must be noted that, for practice, non-equilibrium cubic forms, including cubic solid solutions, are of considerable interest. They should be distinguished by high reactivity, developed internal surface, and high ionic conductivity, thus being of interest for applications.

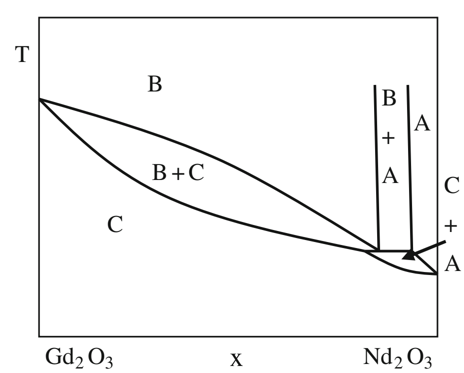

Fig. 1 The correct scheme of phase equilibria, corresponding to date of work [1]

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