Thermal Analysis and Thermodynamic Calculations in Rare-Earth Oxide Based Systems

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Sesquioxides RE_2O_3 (or Me_2O_3, respectively) of the rare-earth elements from lanthanum to lutetium, plus scandium, yttrium, aluminum, and gallium, are forming alone or among each other a wide variety of solid phases. For the simple oxides of one metal, the thermodynamically stable phases include A, B, C, H, X phases of the RE_2O_3 including Y_2O_3 and Sc_2O_3 [1], corundum (α-Al_2O_3), and β-Ga_2O_3 [2], see also the Figure below. Among the pseudobinary phases of 2 metals especially some garnets $Me_3Me'_5O_{12}$ and perovskites (P phases) $MeMe'O_3$ are technically relevant, e.g., as laser hosts ($Y_3Al_5O_{12}$ = "YAG") or substrates for "strain engineering" of ferroelectrics ($REScO_3$, [4]).

Liquidus temperatures in the relevant systems are often high, typically beyond 2300 K and more. This makes thermodynamic measurements, e.g. by DTA, a challenge. Fortunately, a reliable compilation of thermodynamic date for the RE_2O_3 (including Sc_2O_3 and Y_2O_3) is available [1]. Data for many pseudobinary solids and for melts in the RE_2O_3–Al_2O_3 systems, which are based on the paper by Wu & Pelton [5], are already included in the FactSage databases.

The talk reports some investigations on garnets that complement the paper [5], and on other RE_2O_3 based systems. It turns out that at very high temperatures some simple thermodynamic rules give often a satisfactory description for phases.

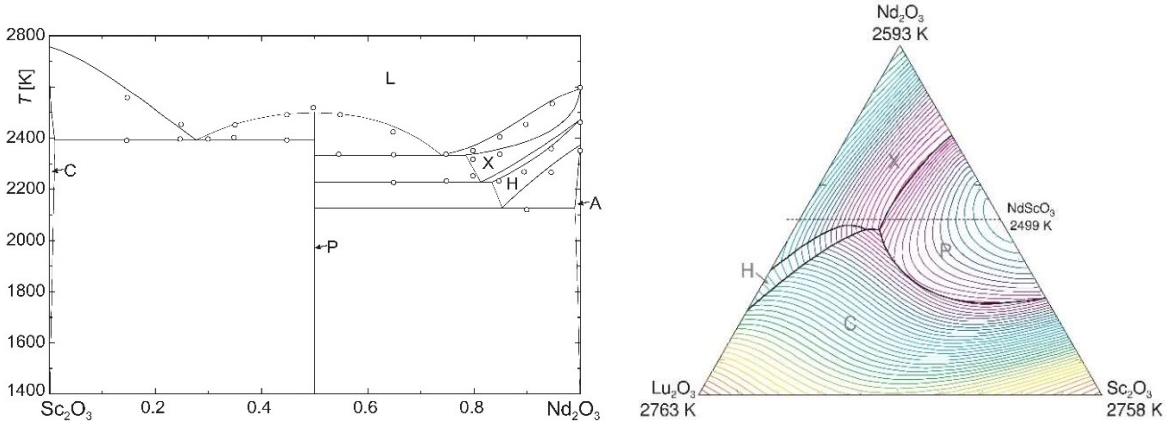

Figure left: Experimental [4] data points for the Nd_2O_3–Sc_2O_3 system together with a FactSage 7.1 thermodynamic assessment. Right: Liquidus surface in the Nd_2O_3–Lu_2O_3–Sc_2O_3 system with 10 K isotherms and labels for congruent melting points. Reprinted with permission from [6].

Literature:

[1] M. Zinkevich, Thermodynamics of Rare Earth Sesquioxides, Prog. Mater. Sci. 52 (2007) 597–647.
[2] S. Geller, Crystal structure of β-Ga_2O_3, J. Chem. Phys. 33 (1966) 676–684.
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[4] J.-M. Badie, Phases et transitions de phases à haute température dans les systèmes Sc_2O_3–Ln_2O_3 (Ln = lanthanide et yttrium), Rev. Int. Hautes Temp. Réfractaires 15 (1978) 183–199 (in French).
[5] P. Wu, A.D. Pelton, Coupled Thermodynamic-Phase Diagram Assessment of the Rare Earth Oxide-Aluminium Oxide Binary Systems, J. Alloy. Comp. 179 (1992) 259–287.
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