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On the rhombohedral-cubic phase transition of solid solutions $ROF-CaF_2$ with R=Gd, Tb and Dy¹

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Abstract

The rhombohedral-cubic phase transition typical of stoichiometric rare earth oxide fluorides of the formula type ROF was investigated for the ROF-based solid solution systems $R_{1-x}Ca_xO_{1-x}F_{1+x}$, with R=Gd. Tb, Dy, by differential scanning calorimetry and by X-ray powder diffraction. It was found that the solubility limit of CaF_2 in these ROF is almost identical with x < 0.09 and that the transition temperatures decrease with increasing CaF_2 content. At $x \approx 0.9$ this decrease is approximately 290 K, 250 K and 240 K for R=Gd, Tb and Dy, respectively, as compared to the transition temperatures of pure ROF. The formula volumes of the rhombohedral as well as the cubic solid solutions were determined as a function of x, and the structural implications of the observed trend is discussed for the rhombohedral modification. A partial tentative phase diagram is exemplarily proposed for $Gd_{1-x}Ca_xO_{1-x}F_{1+x}$. © 1997 Elsevier Science S.A.

Keywords: Solid solution systems $R_{x_{i}}Ca_{x}O_{x_{i}}F_{x_{i}x_{i}}$ with R = Gd, Tb, Dy; Rare earth oxide fluorides; Phase transitions; Lattice parameters; Phase diagrams

1. Introduction

The stoichiometric rare earth oxide fluorides of the formula type ROF with R = La - Er and Y undergo a firstorder phase transition from a low temperature rhombohedral β -modification to a cubic, presumably fluorite-type high temperature α -modification [1,2]. While the temperatures, enthalpies and entropies of this transition have been studied successfully in detail by Petzel et al. [3], investigations on the crystal chemistry of α -ROF prove to be difficult, because it is practically impossible to preserve the high temperature modification of the stoichiometrically composed compounds by rapid quenching to room temperature. Müller and Petzel [4] have recently performed a high temperature X-ray diffraction study of the $\alpha \rightarrow \beta$ transition and were able to derive reasonably reliable room temperature lattice parameters of stoichiometric α -ROF by extrapolation. Roether [2] has shown that α -ROF can be stabilized for R = La - Dy by incorporation of small amounts of excess fluoride ions into the lattice, and the lattice parameters given by him therefore relate to slightly

non-stoichiometric, fluorine-rich oxide fluorides. Gorbulev et al. [5] studied the phase diagrams of the systems ROF-MF, with R = La, Gd, Y and M = Ca, Sr, Ba. They observed that wide, but in no case continuous regions of solid solutions based on cubic α -ROF as well as on MF₂ exist at high temperatures, especially for M = Ca and Sr. These regions narrow sharply with decreasing temperature, and the solubilities of MF₂ in ROF and of ROF in MF₂ both become insignificant at temperatures close to the $\alpha \rightarrow \beta$ transition points of stoichiometric ROF. The authors also mention that the transition temperatures of ROF are only slightly lowered if the compounds are saturated with MF₂, e.g. by 12 K and 5 K in case of the systems YOF-CaF₂ and LaOF-CaF₂, respectively. These results indicate that the formation of ROF-based mixed crystals with MF, is not an appropriate means to stabilize the high temperature modification of ROF under equilibrium conditions at room temperature. However, on studying tentatively the transitional behaviour of samples of the composition $Gd_{1-x}Ca_xO_{1-x}F_{1+x}$ with $0 \le x \le 0.15$ by differential scanning calorimetry (DSC) we noticed that the solid solution range actually extends to x = 0.1 and that the transition temperature decreases by more than 200 K within this range. We furthermore observed that for $x \ge 0.1$ and hence in the neighbouring two-phase region only the

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¹Dedicated to Professor Werner Fischer on the occasion of his 95th birthday.

 α -GdOF but not the β -GdOF based solid solution exists beside the CaF,-based solid solution at room temperature. Since these observations were in contradiction to the respective part of the phase diagram by Gorbulev et al. [5], we decided to perform a detailed investigation by DSC into the thermochemical and structural properties of the ROF-based solid solutions for R = Gd, Tb and Dy with CaF₂. These rare earth oxide fluorides were selected because the ionic radii of the respective R^{3+} -ions for CN 8 [6] and hence the formula volumes of α -ROF [4], namely 41.707 Å³ (GdOF), 41.119 Å³ (TbOF) and 40.314 Å' (DyOF), are closest to the formula volume of CaF_{2} , 40.789 Å³. Assuming $r(O^{2^{-}}) > r(F^{-})$ one could therefore expect that the formation of ROF-based solid solutions with CaF, would cause a decrease of the formula volumes in case of GdOF and TbOF and an increase for DyOF. However, considering the results of Mann and Bevan [8] and of Greis et al. [9] that in β -YOF and β -PrOF, respectively, the distances R^{3+} -F⁻ are larger than the distances $R^{3+}-O^{2-}$, one could as well predict a general increase of the formula volumes of solid solutions ROF-CaF, provided the ionic radii of R^{3+} and Ca^{2+} are very similar. This conclusion also appears quite reasonable if the positive deviations from Vegard's rule, as observed by Gorbulev et al. [5] for cubic solid solutions in the system LaOF-CaF₁, are taken into account.

2. Experimental section

2.1. Preparation and X-ray characterization of samples

Stoichiometric rare earth oxide fluorides were prepared by solid state reaction of RF_3 (prepared in this laboratory) with R₂O₃ (99.99% stated purity, Auer-Remy), as described elsewhere in detail [3]. Tb₂O₃ was obtained by reduction of Tb₄O₇ with highly purified hydrogen at 1300 K. Samples of the ROF-CaF, systems were obtained either by annealing of intimate mixtures of ROF and CaF, (99.999% stated purity, Merck suprapur) or of mixtures containing appropriate amounts of RF₃, R₂O₃ and CaF₂, in gas-tight platinum ampoules at 1400 K for 2 days. After this treatment the samples were mechanically homogenized and submitted to a second annealing in hermetically closed molybdenum containers at 1750 K prior to the DSC measurements (see below). Quenching of samples was achieved by dropping the platinum ampoules into ice water with an estimated rate of 10^3 K s⁻¹. The weight loss of the platinum ampoules and of the molybdenum crucibles was generally < 1 mg out of a total weight of approximately 900 mg after the different steps of thermal treatment, and it could hence be safely concluded that the composition of the samples had not changed during these procedures.

All samples were characterized by their X-ray powder diffraction patterns (Guinier method, $CuK\alpha_1$ -radiation, silicon reference material NBS 640 A used as internal

calibration standard). The θ -values were measured with an accuracy of $\Delta \theta = \pm 0.005$, and the lattice parameters were evaluated using the computer program LSUCRE [7].

2.2. DSC measurements

The DSC-measurements were performed in a Netzsch apparatus, type DSC 404. The samples and the reference material (corundum powder) were contained in cylindrical, vacuum-outgassed molybdenum containers with gas-tight lids. Heating and cooling were performed at a rate of 5 K min⁻¹ in an atmosphere of dry argon, containing 5% hydrogen and flowing with a rate of $3.5 \ \text{I} \text{ h}^{-1}$. The evaluation of the peak onset temperatures and the peak areas as well as the temperature and enthalpy calibration procedures were performed as described in detail in our previous work [3]. Comparison of the temperatures and enthalpies of transition of pure ROF found in this work with our previous results allowed to conclude that the accuracy of the data to be presented in the following section is ± 3 K for the temperatures and $\pm 5\%$ for the enthalpies of transition.

3. Results and discussion

The thermochemical and structural results of this study are summarized in Table 1 and presented in Figs. 1-5. One recognizes an almost identical behaviour of these solid solution systems; In all cases the temperatures and enthalpies of the transitions decrease with increasing CaF, content, and the transition effect eventually vanishes at approximately 9% CaF, (Figs. 1 and 2). The shape of the DSC signals is typical of a first-order phase transition for CaF, contents <5% and becomes more or less diffuse close to the disappearance of the otherwise perfectly reproducible phenomenon, as exemplified in Fig. 3 by the superimposed DSC curves of four heating and cooling cycles for $Gd_{1-x}Ca_xO_{1-x}F_{1+x}$ with x = 0.0, 0.024 and 0.061. The formula volumes of the rhombohedral solid solutions decrease very weakly with increasing CaF2content (Fig. 4). As exemplified for $Gd_{1-x}Ca_xO_{1-x}F_{1+x}$ in Fig. 5, the lattice parameter a_{β} increases weakly while c_{β} decreases significantly with increasing x. For the cubic solid solutions, which could only be preserved by rapid quenching for CaF₂-contents \geq 3%, a trend of the formula volumes could not be definitely recognized, because the accuracy of the lattice parameters of the quenched samples was of the same order of magnitude as the possible trend of a_{α} with x. The positive trend of V_{β} with increasing x is very small for R=Gd and is more pronounced for R=Tb and Dy despite of the fact that $r(\text{Gd}^{3+})$ and $r(\text{Tb}^{3+}) >$ $r(Ca^{2+}) > r(Dy^{3+})$. We therefore conclude that it is not the assumed size of the cations but the substitution of O^{2-} by F⁻ which predominantly determines the lattice dimensions of the rhombohedral solid solutions. Considering the Table 1

| R | x | $T_{\rm tr}/{\rm K}$ | $\Delta H^{\circ 0}_{\mathrm{T,tr}}/\mathrm{Jmol}^{-1}$ | <i>a</i> "/Å | $V_{\rm a}/{\rm \AA}^3$ | $V_{\beta}/\text{\AA}^3$ | a _β /Å ^b | $c_{\mu}/\text{Å}^{b}$ |
|----|--------|----------------------|---|--------------------|-------------------------|--------------------------|--------------------------------|------------------------|
| Gd | 0 | 889 | 7083 | 5.505° | 41.707* | 41.607 | 3.8671 | 19.276 |
| | 0.0115 | 857 | 5958 | - | - | 41.618 | 3.8683 | 19.269 |
| | 0.0243 | 822 | 3844 | - | - | 41.594 | 3.8681 | 19.260 |
| | 0.0493 | 765 | 2336 | 5.5057 | 41.723 | 41.635 | 3.8715 | 19.245 |
| | 0.0608 | 732 | 1603 | 5.5100 | 41.821 | 41.652 | 3.8736 | 19.232 |
| | 0.0745 | 690 | 1228 | 5.5075 | 41.764 | - | - | - |
| | ≥0.1 | - | - | 5.5040 | 41.685 | - | - | - |
| ТЬ | 0 | 848 | 6407 | 5.479 ^ª | 41.119* | 40.760 | 3.8418 | 19.133 |
| | 0.0195 | 795 | 4375 | - | - | 40.787 | 3.8430 | 19.134 |
| | 0.0344 | 755 | 2807 | 5.4747 | 41.022 | 40.806 | 3.8445 | 19.128 |
| | 0.0456 | 707 | 2151 | 5.4724 | 40.971 | 40.827 | 3.8469 | 19.114 |
| | 0.0574 | 676 | 679 | 5.4737 | 41.000 | - | | - |
| | 0.0698 | 634 | 546 | 5.4607 | 40.708 | 40.791 | 3.8479 | 19.087 |
| | ≥0.1 | - | - | 5.4740 | 41.007 | - | - | - |
| Dy | 0 | 841 | 6373 | 5.443° | 40.314* | 39.991 | 3.8151 | 19.036 |
| | 0.0179 | 779 | 3501 | - | - | 40.077 | 3.8195 | 19.033 |
| | 0.032 | 752 | 2955 | 5.4399 | 40.245 | 40.109 | 3.8214 | 19.029 |
| | 0.05 | 713 | 2456 | 5.4381 | 40.205 | 40.159 | 3.8250 | 19.017 |
| | 0.064 | 653 | 1408 | 5.4445 | 40.347 | 40.106 | 3.8249 | 18.993 |
| | ≥0.1 | - | - | 5.4420 | 40.292 | - | - | - |

Thermochemical and structural data of the rhombohedral-cubic phase transition of ROF-based solid solutions R_{1-}, Ca_{1-}, F_{1+} , with R = Gd. Tb. Dy

* From Ref. [4]. * Hexagonal setting.

crystal structure of β -ROF as presented by Mann and Bevan [8] for YOF and by Greis et al. [9] for PrOF, it can be assumed that on the formation of rhombohedral solid solutions $R_{1-x}Ca_xO_{1-x}F_{1+x}O^{2^-}$ is partially substituted by F^- in the O^{2^-} layers and R^{3+} by Ca^{2+} in the metal layers. While it is normally taken for granted that $r(O^{2^-})>r(F^-)$ for CN 4, it has been shown by [8] and [9] that in β -ROF the $R^{3+} - O^{2-}$ distances are noticeably smaller that the distances $R^{3+} - F^-$, a finding, which is indirectly corroborated by the results of this work, if the close similarity of the cationic radii is taken into account.

It is difficult to unambiguously construct the details of a phase diagram based on the results cutlined above. Though the $ROF-CaF_2$ solid solutions are binary systems appar-

ently undergoing a first order polymorphic phase transition, and the α and β one-phase regions must therefore be separated from each other by a two-phase area, the shapes of the DSC signals do not hint at a transition through such an area (see Fig. 3). However, it can be argued that the width of this area is too small to be detected by the thermal analytical method applied here. Based on this supposition and on the X-ray results a tentative partial phase diagram of the system $Gd_{1-x}Ca_xO_{1-x}F_{1+x}$ is presented in Fig. 6. One recognizes one-phase regions, namely α and β , and a two-phase region $\alpha + \alpha'$, in which α' designates CaF_2 saturated with GdOF. Although we could neither locate exactly the GdOF-rich border of the two-phase region $\alpha' + \alpha$ nor the slope of this border and the interval separating it from the β -region, it is obvious that the



Fig. 1. Temperatures of the rhombohedral-cubic phase transition of ROF-based solid solutions $R_{1-x}Ca_xO_{1-x}F_{1+x}$ with R = Gd, Tb, Dy.



Fig. 2. Enthalpies of the rhombohedral-cubic phase transition of ROFbased solid solutions $R_{1-1}Ca_rO_{1-1}F_{1+1}$ with R=Gd, Tb, Dy.



Fig. 3. Superimposed DSC curves of four heating-cooling cycles for the rhombohedral-cubic phase transition of $Gd_{1-1}Ca_{1}O_{1-1}F_{1+1}$.



Fig. 4. Lattice parameters of rhombohedral solid solutions $Gd_{1-x}Ga_xO_{1-x}F_{1-x}$ in hexagonal setting as a function of x.



Fig. 5. Formula volumes of the rhombohedral solid solutions $R_{+,v}Ca_vO_{+,v}F_{+,v}$ with R = Gd. Tb, Dy.



Fig. 6. Tentative partial phase diagram of the binary system GdOF-CaF,.

results of this work differ significantly from the observation of Gorbulev et al. [5] as far as this limited part of the phase diagram is concerned.

Since the thermochemical data for the systems $Tb_{1-x}Ca_xO_{1-x}F_{1+x}$ and $DyCa_xO_{1-x}F_{1+x}$ are almost identical to those of the Gd-containing system, the respective partial phase diagrams are supposedly very similar to the diagram plotted in Fig. 6 and are not presented here in detail.

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