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Zirconium scandium oxide nitrides: Formation and decomposition followed in situ by XRD and thermal analysis

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Abstract

The dark green powder of $Zr_{50}Sc_{12}O_{43}N_{50}$ was produced from $Zr_{50}Sc_{12}O_{118}$ under a constant flow of ammonia. $Zr_{50}Sc_{12}O_{43}N_{50}$ crystallizes cubic with space group $Ia\bar{3}$ and $a = 1009.254(3)$ pm in the C–M_2O_3 structure (bixbyite structure). The reaction path was followed by in situ X-ray diffraction and showed that the substitution of $3O^{2-}$ by $2N^{3-}$ generates additional vacancies on the anion sites in the fluorite basis structure. On the way to the bixbyite structure time- and temperature-controlled X-ray diffractograms revealed the known fluorite-related superstructures (i.e. the vacancy distribution) for the compositions $M_{14}X_{26}$ and M_7X_{12}. The reverse process, i.e. the oxidation of the oxide nitride was followed in DTA/TG experiments exhibiting the different vacancy orderings at 420, 500 and 520 °C.

Keywords: Nitridation; Zirconium scandium oxide nitrides; In situ study; Anion-deficient; Fluorite-related

1. Introduction

The reaction path for the nitridation of zirconia with ammonia is quite well characterized. Starting with ZrO_2, $Zr_{14}O_{22}N_4$ ($MX_{1.86}$ or $M_{14}X_{26}$; $M =$ metal, $X =$ O/N) and $Zr_7O_8N_4$ ($MX_{1.71}$ or M_7X_{12}) are formed under ammonia at temperatures below 1000 °C. Finally, at around 1100 °C Zr_2ON_2 ($MX_{1.5}$ or M_2X_3—bixbyite structure) is formed [1]. The intermediate compounds, i.e. $Zr_{14}O_{22}N_4$ and $Zr_7O_8N_4$ crystallize in anion-deficient fluorite-related structures [2,3]. These structures exhibit the same vacancy ordering on the anion sites like $Zr_{10}Sc_4O_{26}$ and $Zr_3Sc_4O_{12}$ [4]. Therefore, it was interesting to investigate the influence of the degree of nitridation on the vacancy distribution in the Zr/Sc-oxide-nitrides. The starting material for this study on the nitridation of scandium-doped zirconia was an ordered phase namely $Zr_{50}Sc_{12}O_{118}$ ($MX_{1.9}$ or $M_{62}X_{118}$) the so-called β-phase. Its structure was determined recently by Wurst et al. [5] and exhibits the most dilute ordered vacancy distribution so far known for the anion-deficient-fluorite-related phases.

2. Experimental

2.1. Synthesis of precursor materials

$Zr_{50}Sc_{12}O_{118}$ was prepared via a sol–gel method using $ZrOCl_2 \cdot 5H_2O$ dissolved at 25 °C in water. The stoichiometric amount of Sc_2O_3 in HNO_3 was added and also a mixture of ethyleneglycol and citric acid (50/50). The whole mixture was refluxed for 8 h until the formation of a gel. The gel was dried at 120 °C and then fired at 1200 °C for 72 h. X-ray diffraction indicated phase-pure $Zr_{50}Sc_{12}O_{118}$. Diffractograms for $Zr_{50}Sc_{12}O_{118}$, $Zr_{10}Sc_4O_{26}$ and $Zr_3Sc_4O_{12}$ are shown in Fig. 1. The compound was then treated at 1100 °C under a constant flow of ammonia to yield after 80 h the dark green powder with nominal composition $Zr_{50}Sc_{12}O_{43}N_{50}$. The sample needs to be quenched rapidly under ammonia. Analysis of this oxide nitride was performed using hot-gas extraction methods and by calculation from the decomposition reaction in thermogravimetrical runs and yielded for $Zr_{50}Sc_{12}O_{43}N_{50}$: N = 10.1% (calc.: 10.78%).

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2.2. Time- and temperature-resolved X-ray diffraction

Time- and temperature-resolved X-ray diffraction patterns were taken from a SIEMENS D5000 θ/θ diffractometer and recorded with a position-sensitive detector (Braun OED 50M) with an aperture of 6°. The radiation used was Cu $K\alpha$. The detector was moved with a step size of 0.015° in θ and a step time of 10 s. Diffractograms were typically recorded in an angular range between 10 and 60° in 2θ. The resulting time for a single diffractogram was then about 22 min and for the whole pattern 7 h. Figs. 2 and 3 show the parts of the diffractograms between 10 and 31.5° in 2θ. DTA and TG measurements were performed on a Netsch STA 409.

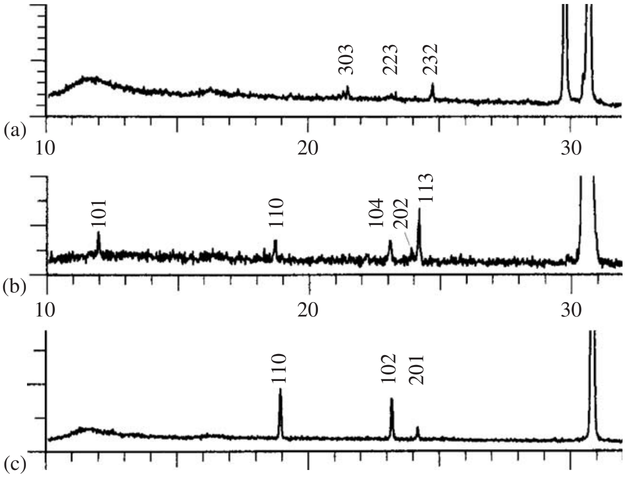

Fig. 1. X-ray diffractograms showing the superstructure reflections to fluorite in the angular range $2\theta = 10-32°$ for (a) $Zr_{50}Sc_{12}O_{118}$, (b) $Zr_{10}Sc_4O_{26}$ and (c) $Zr_3Sc_4O_{12}$. Indexing is given just for the strongest superstructure reflections. The strong reflection around 30.4° corresponds to fluorite (1 1 1).

3. Results and discussion

3.1. The reaction of the β-phase with NH_3

Pure $Zr_{50}Sc_{12}O_{118}$ was used for the reaction with ammonia up to 780 °C. The diffractogram shown in Fig. 2 reveals at 500 °C the formation of the fluorite (1 1 1) reflection at $2\theta = 30.4°$ from its rhombohedral split in the low-temperature phase. This is in agreement with the known phase transition from the rhombohedral phase with vacancy ordering to the fluorite phase with a statistical vacancy distribution [6]. At 780 °C an ordered superstructure appears which can be recognized from its very small super-structure reflections at $2\theta = 11.88$, 18.62, 22.99, 23.88 and 24.13° appearing in addition to the $(1\,1\,1)_F$ reflection. The diffraction pattern for this phase, $Zr_{50}Sc_{12}O_{109}N_6$, is similar to the one of $Zr_{10}Sc_4O_{26}$ (compare Fig. 1 or [4]). Quenching from 780 to 25 °C under ammonia atmosphere is necessary to prepare this phase. Cooling down slowly under a constant flow of ammonia shows the formation of a structure like β-phase.

If the same experiment is performed up to 1000 °C one will observe the same behaviour and then at 800 °C the formation of a phase isostructural to the M_7X_{12} fluorite superstructure type. Both the unit cells M_7X_{12} and $M_{14}X_{26}$ differ only in the c lattice constant which is simply doubled for the latter compound. This can be seen in the diffractogram Fig. 3, where the superstructure reflection at $2\theta = 11.256°$ is only present as a very weak hump for two consecutive diffractograms at approximately 780 °C.

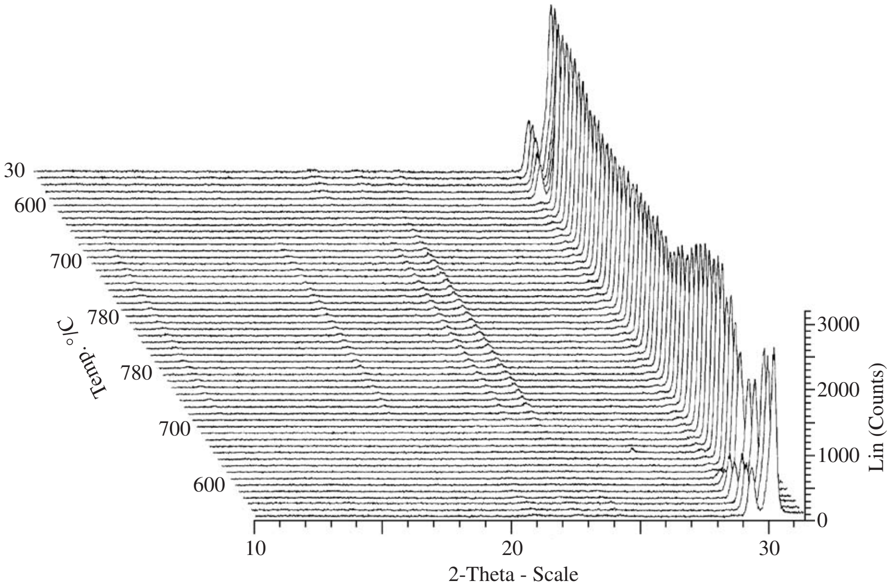

Fig. 2. Time- and temperature-controlled X-ray diffractogram (angular range $2\theta = 10-31.5°$) for the reaction of $Zr_{50}Sc_{12}O_{118}$ with ammonia up to 780 °C showing the formation of $Zr_{50}Sc_{12}O_{109}N_6$.