

# 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.

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## 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  $M_{14}X_{26}$ ;  $M = \text{metal}$ ,  $X = \text{O/N}$ ) 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  $\beta$ -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 thermogravimetical 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  $\theta/\theta$  diffractometer and recorded with a position-sensitive detector (Braun OED 50M) with an aperture of  $6^\circ$ . The radiation used was Cu  $K\alpha$ . The detector was moved with a step size of  $0.015^\circ$  in  $\theta$  and a step time of 10 s. Diffractograms were typically recorded in an angular range between  $10$  and  $60^\circ$  in  $2\theta$ . The resulting time for a single diffractogram was then about 22 min and for the whole pattern 7 h. Figs. 2

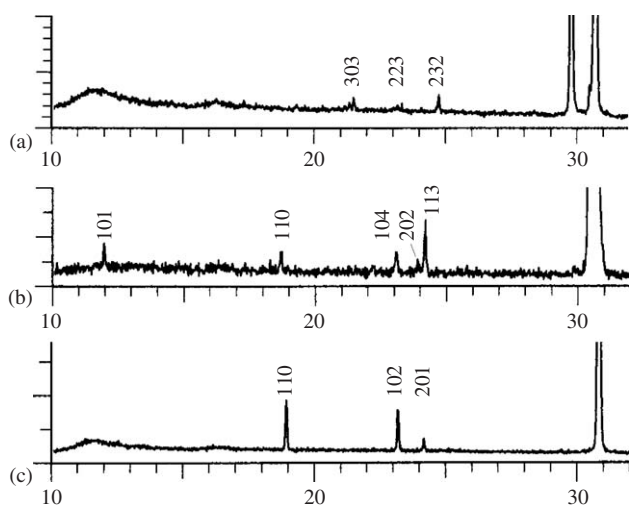


Fig. 1. X-ray diffractograms showing the superstructure reflections to fluorite in the angular range  $2\theta = 10\text{--}32^\circ$  for (a)  $\text{Zr}_{50}\text{Sc}_{12}\text{O}_{118}$ , (b)  $\text{Zr}_{10}\text{Sc}_4\text{O}_{26}$  and (c)  $\text{Zr}_3\text{Sc}_4\text{O}_{12}$ . Indexing is given just for the strongest superstructure reflections. The strong reflection around  $30.4^\circ$  corresponds to fluorite (111).

and 3 show the parts of the diffractograms between  $10$  and  $31.5^\circ$  in  $2\theta$ . DTA and TG measurements were performed on a Netsch STA 409.

## 3. Results and discussion

### 3.1. The reaction of the $\beta$ -phase with $\text{NH}_3$

Pure  $\text{Zr}_{50}\text{Sc}_{12}\text{O}_{118}$  was used for the reaction with ammonia up to  $780^\circ\text{C}$ . The diffractogram shown in Fig. 2 reveals at  $500^\circ\text{C}$  the formation of the fluorite (111) reflection at  $2\theta = 30.4^\circ$  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  $780^\circ\text{C}$  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  $24.13^\circ$  appearing in addition to the (111)<sub>F</sub> reflection. The diffraction pattern for this phase,  $\text{Zr}_{50}\text{Sc}_{12}\text{O}_{109}\text{N}_6$ , is similar to the one of  $\text{Zr}_{10}\text{Sc}_4\text{O}_{26}$  (compare Fig. 1 or [4]). Quenching from  $780$  to  $25^\circ\text{C}$  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  $\beta$ -phase.

If the same experiment is performed up to  $1000^\circ\text{C}$  one will observe the same behaviour and then at  $800^\circ\text{C}$  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  $2\theta = 11.256^\circ$  is only present as a very weak hump for two consecutive diffractograms at approximately  $780^\circ\text{C}$ .

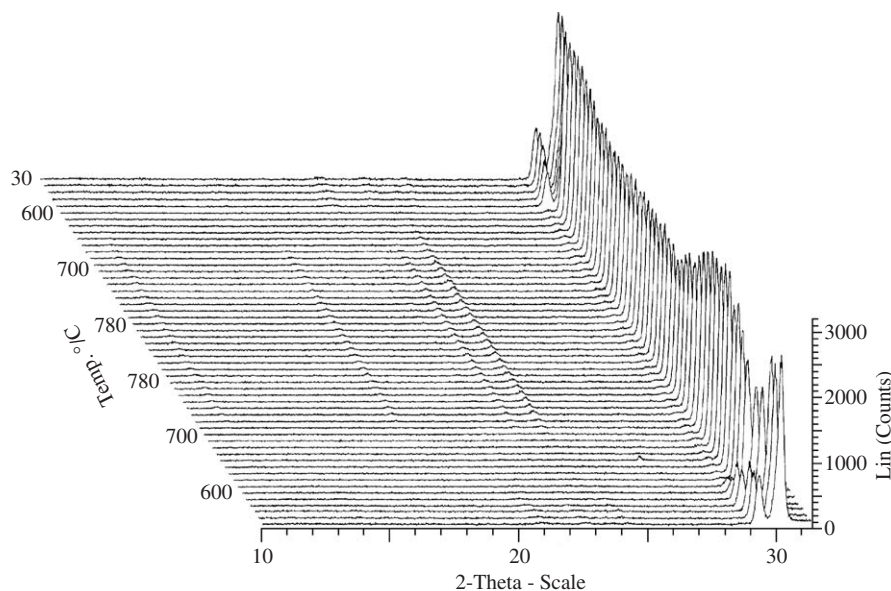


Fig. 2. Time- and temperature-controlled X-ray diffractogram (angular range  $2\theta = 10\text{--}31.5^\circ$ ) for the reaction of  $\text{Zr}_{50}\text{Sc}_{12}\text{O}_{118}$  with ammonia up to  $780^\circ\text{C}$  showing the formation of  $\text{Zr}_{50}\text{Sc}_{12}\text{O}_{109}\text{N}_6$ .

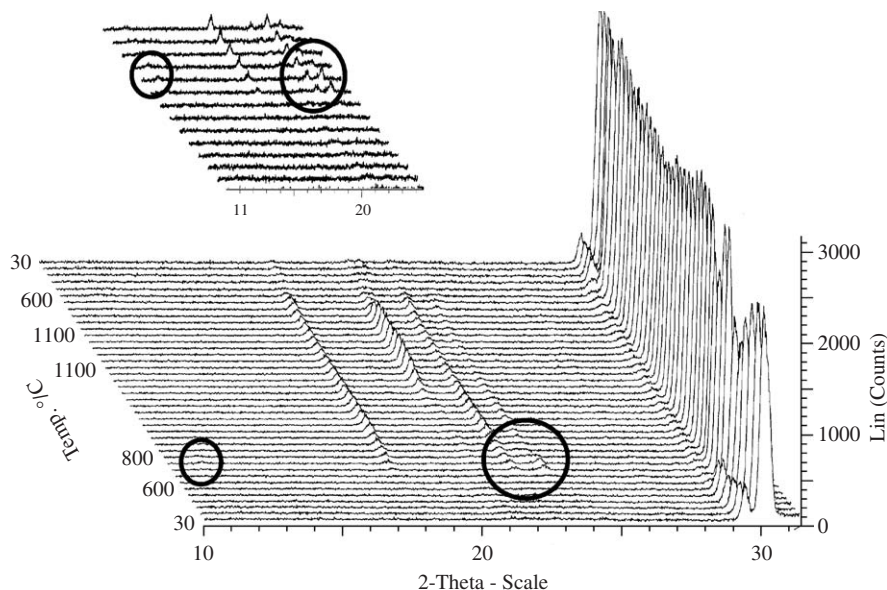
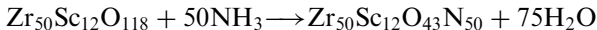
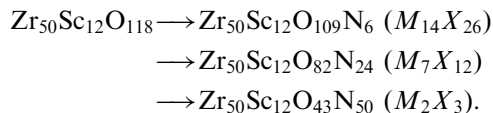


Fig. 3. Time- and temperature-controlled X-ray diffractogram (angular range  $2\theta = 10\text{--}31.5^\circ$ ) for the reaction of  $\text{Zr}_{50}\text{Sc}_{12}\text{O}_{118}$  with ammonia up to  $1000^\circ\text{C}$  forming finally  $\text{Zr}_{50}\text{Sc}_{12}\text{O}_{43}\text{N}_{50}$ . Circles indicate the 2 regions where the superstructure reflections of a nitrated  $M_{14}X_{26}$ -phase can be seen.

Finally, at  $900^\circ\text{C}$  a  $M_2X_3$  bixbyite-type structure is formed. The reaction of  $\text{Zr}_{50}\text{Sc}_{12}\text{O}_{118}$  with ammonia is eliminating water according to



and yields an oxide-nitride with bixbyite structure ( $Ia\bar{3}$ ). The lattice constant determined from a quenched sample at  $25^\circ\text{C}$  was  $a = 1009.254(3)$  pm. This structure type might be explained with a cell 8-times the one of fluorite and  $\frac{1}{4}$  of the anions missing in an ordered way (along one of the 4 body diagonals of the primitive anion cube). The time- and temperature-resolved diffractograms indicate that until the  $M_2X_3$  composition is reached two more phases with a vacancy ordering in the fluorite structure are found.

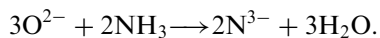


The above formulas are based on

- a fixed ratio of Zr/Sc (4.1667) during the reaction,
- that no reduction of  $\text{Zr}^{4+}$  to  $\text{Zr}^{3+}$  occurs,
- the assumption that the loss of  $3\text{O}^{2-}$  is compensated by incorporation of  $2\text{N}^{3-}$  and one vacancy into the lattice,
- that the superstructures to the fluorite structure are generated strictly by the well-known vacancy ordering for compositions  $\text{MX}_{1.71}$  and  $\text{MX}_{1.86}$ .

Essentially, this is the same vacancy ordering like in pure zirconium oxide nitrides or in pure zirconium scandium oxides. Since none of the metals are reduced under these conditions the lost negative charge due to the loss of

oxygen and the generation of vacancies has to be compensated by an uptake of  $\text{N}^{3-}$ .



We have also performed experiments nitriding  $\text{Zr}_3\text{Sc}_4\text{O}_{12}$  with ammonia. This reaction yields at ( $1000^\circ\text{C}$ ) also a compound with bixbyite structure. The composition found can be formulated as  $\text{Zr}_6\text{Sc}_8\text{O}_{15}\text{N}_6$ . X-ray diffraction revealed a lattice constant  $a = 1000.663(3)$  pm which is smaller than the  $1009.254$  pm for the nitrogen-richer product  $\text{Zr}_{50}\text{Sc}_{12}\text{O}_{43}\text{N}_{50}$ . In general, from a  $\text{Zr}_n\text{Sc}_m\text{O}_{2n+\frac{3}{2}m}$  with an anion-deficient fluorite structure a bixbyite structure will be formed with a composition of  $\text{Zr}_n\text{Sc}_m\text{O}_{\frac{n}{2}+\frac{3}{2}m}\text{N}_n$ .

Since the Zr/Sc ratio of the reactants can be determined best in the three ordered phases the third oxide-nitride phase with a defined O/N ratio and  $M_2X_3$  composition will be produced from  $\text{Zr}_{10}\text{Sc}_4\text{O}_{26}$  and has a composition  $\text{Zr}_{10}\text{Sc}_4\text{O}_{11}\text{N}_{10}$ . Rietveld refinements of the powder patterns prove that like in the pure zirconium scandium oxides a statistical distribution on the cation sites between  $\text{Zr}^{4+}$  and  $\text{Sc}^{3+}$  exists. A neutron diffraction study of  $\text{Zr}_{50}\text{Sc}_{12}\text{O}_{43}\text{N}_{50}$  (in progress) will better show the details for cation and anion statistics on the different sites within the structure.

### 3.2. Thermal decomposition of oxide-nitrides under air

Fig. 4 shows the mass gain from  $\text{Zr}_{50}\text{Sc}_{12}\text{O}_{43}\text{N}_{50}$  to  $\text{Zr}_{50}\text{Sc}_{12}\text{O}_{118}$  upon oxidation in a temperature range from  $25$  to  $1200^\circ\text{C}$ . Between  $400$  and  $600^\circ\text{C}$  the sample increases in weight due to the uptake of oxygen. The differential thermal analysis (DTA) shows three exothermic peaks at

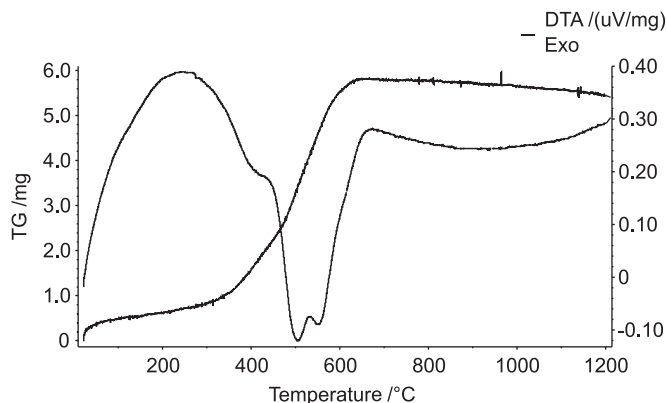


Fig. 4. TG and DTA for the reoxidation of  $Zr_{50}Sc_{12}O_{43}N_{50}$  to  $Zr_{50}Sc_{12}O_{118}$  on air at a heating rate of 2 K.

420, 500 and 550 °C assigned to three partial reactions and the formation of three ordered intermediate structures (between  $MX_{1.5}$  and  $MX_{1.9}$ ). The first at 420 °C is assigned to  $MX_{1.5} \rightarrow MX_{1.71}$  the second to  $MX_{1.71} \rightarrow MX_{1.86}$  and the third to  $MX_{1.86} \rightarrow MX_{1.90}$ . If the sample is heated up to 1200 °C  $MX_{1.9}$  is formed. It is observed that the reoxidation rate (see thermogravimetric curve) for the first process namely the formation of the fluorite structure from bixbyite is smaller than the one for the two following reactions where only different vacancy ordering within the fluorite structure takes place. The sample mass for the experiment was 60 mg and the increase of 4.8 mg corresponds to 8% related to  $Zr_{50}Sc_{12}O_{43}N_{50}$  (theory 7.7%). The slightly higher than expected mass gain might be an indication for additional nitrogen-containing species trapped in the structure. A behaviour as observed for  $ZrTiO_{1.06}N_{1.90}$  [7] or for the oxidation of ZrN [8] in which the uptake of oxygen was faster than the release of trapped dinitrogen species was not observed from the TG curves in this study.

#### 4. Conclusion and outlook

The nitridation of Zr/Sc-oxides with ammonia yields new Zr/Sc-oxide-nitrides. The observation of the reaction path for  $Zr_{50}Sc_{12}O_{118}$  under  $NH_3$  using time- and temperature-controlled X-ray diffraction revealed that at temperatures above 500 °C vacancy ordering is present. Depending on temperature the ordered fluorite superstructures for  $M_{14}X_{26}$ ,  $M_7X_{12}$  occur and finally products with the bixbyite structure are formed. Under an oxidizing atmosphere like in air the decomposition of the Zr/Sc-oxide-nitrides with bixbyite structure starts at 400 °C and the exchange of  $N^{3-}$  with  $O^{2-}$  is complete at 600 °C to yield  $Zr_{50}Sc_{12}O_{118}$ . Under nitrogen there is no exchange but at higher temperatures (1200 °C)  $Zr_{50}Sc_{12}O_{43}N_{50}$  decomposes to ZrN and a Zr/Sc-oxide-nitride component.

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#### References

- [1] S.J. Clarke, C.W. Michie, J. Rosseinsky, J. Solid State Chem. 146 (1999) 399–405.
- [2] G. Van Tendeloo, G. Thomas, in: Advances in Ceramics, vol. 12, American Ceramic Society, Ohio, 1983, pp. 164–183.
- [3] R. Sharma, D. Nädle, E. Schweda, Chem. Mater. 13 (2001) 4014–4018.
- [4] M.R. Thornber, D.J.M. Bevan, J. Graham, Acta Crystallogr. B 24 (1968).
- [5] K. Wurst, E. Schweda, D.J.M. Bevan, J. Mohyla, K.S. Wallwork, M. Hofmann, Solid State Sci. 5 (2003) 1491–1497.
- [6] G. Brunauer, H. Boysen, F. Frey, H. Ehrenberg, J. Phys.: Condens. Matter 14 (2002) 135–144.
- [7] S.J. Clarke, C.W. Michie, J. Rosseinsky, Chem. Mater. 12 (2000) 863–865.
- [8] H. Wiame, M.-A. Centeno, S. Picard, P. Bastians, P. Grange, J. Eur. Ceram. Soc. 18 (1998) 1293–1299.