Mat. Res. Bull., Vol. 25, pp. 1161-1168, 1990. Printed in the USA. 0025-5408/90 \$3.00 + .00 Copyright (c) 1990 Pergamon Press plc.

ON THE SOLUBILITY OF Fe,Cr AND ND IN ZrO<sub>2</sub> AND ITS EFFECT ON THERMAL DILATATION AND POLYMORPHIC TRANSITION

H.P.Beck and C.Kaliba Institute for Inorganic and Analytical Chemistry and Radiochemistry, Universität des Saarlandes, Im Stadtwald, D6600 Saarbrücken, West Germany

(Received June 12, 1990; Communicated by E.F. Bertaut)

### ABSTRACT

The solubility of Fe,Cr and Nb in  $ZrO_2$  by thermal treatment of the corresponding oxides at  $1300^{\circ}C$  is reported. Doping zirconia with these elements has considerable effect on thermal expansion, on the temperature of the monoclinic - tetragonal transition and on the volumechange accompanying it. It is shown that such impurities strongly influence properties which are important for the use of  $ZrO_2$  as a ceramic material.

MATERIALS INDEX: zirconium, oxides, mixed crystals

### Introduction

The low thermal conductivity and the high melting point on one hand and the high ionic mobility in one of its polymorphs on the other make ZrO<sub>2</sub> an interesting material for the application in ceramics, which excell in strength, toughness and chemical resistance. However, the large volume change during the monoclinic tetragonal transition turns out to be a considerable drawback for its use at varying temperatures, and at lower temperatures the high ionic conduction is present only when the tetragonal or cubic phase is stabilized by large amounts of an appropriate dopant. In contrast to the efforts of most investigators in this field it is the aim of our investigations to expand the field of existence of the monoclinic phase to higher temperatures and/or decrease the volume change during the transition mentioned above.

### Determination of the solubility of Fe, Cr and Nb in ZrO2

### Preparation of materials and x-ray investigations

 $ZrO_2$  was prepared by thermal decomposition of  $ZrOCl_2 \cdot 8H_2O$  (p.a. grade MERCK) at 450°C and subsequent firing for 2d at 1100°C. For the doping experiments  $Cr_2O_3$  was prepared from  $CrO_3$  (p.a.grade MERCK) by thermal decomposition on increasing the temperature slowly to 1100°C. Fe<sub>2</sub>O<sub>3</sub> (p.a.grade MERCK) and Nb<sub>2</sub>O<sub>5</sub> (purissimum,>99%, ROTH) were commercially available. Mixtures containing from 0.5 to 10 atomic% of the dopant as oxide were co-milled in a mechanical agate mortar for 1d, they were then pressed to pellets and fired in air at 1500°C for 1d (or additionally at 1300°C for 4d in the case of  $ZrO_2/Nb_2O_5$ ) and subsequently quenched to room temperature.

To complete this study of solubilities we have also prepared mixed crystals  $H_{f_X}Zr_{1-x}O_2$  by coprecipitation of appropriate mixtures from an aqueous solution of the oxichlorides with NH<sub>3</sub>, thermal dehydration of the products up to 1000°C and annealing at 1300°C for 2d. (Starting materials were furnished by TELEDYNE /WAH CHANG, Albany.)

X-ray investigations in transmission geometry on powdered specimens contained in a glass capillary were made with a Seifert MZ4 Goniometer equipped with a curved position sensitive detector (PSD) (M.BRAUN) filled with Kr/CH<sub>4</sub> and using MoK<sub>Q1</sub>-radiation. The solubilities were evaluated by close comparison of an appropriate 20 region of the diffractogramms of fired and untreated mixtures containing the strongest and/or clearly separated lines of the unreacted dopant phases. Fig.1 shows a comparison of a section in 20 from measurements on an untreated (1a) and on a fired mixture (1b) containing 2 atomic% Fe (Zr<sub>0.98</sub>Fe<sub>0.02</sub>O<sub>1.99</sub>). In this analytical procedure the strongest reflection of Fe<sub>2</sub>O<sub>3</sub> or Cr<sub>2</sub>O<sub>3</sub> can clearly be detected in untreated mixtures down to a content of less than 0.5 atomic% (x=0.005 in xMO<sub>1.5</sub> (1-x)ZrO<sub>2</sub>). In the case of ZrO<sub>2</sub>/Nb<sub>2</sub>O<sub>5</sub>-mixtures the appearance of the strongest line of the 8:1 phase Nb<sub>2</sub>Zr<sub>8</sub>O<sub>21</sub> -stable up to 1640°C according to the phase diagramm given by ROTH et al. - was taken as an indication that the solubility limit was surpassed. This foreign phase is no longer detected after annealing a mixture containing 0.5 atomic% at 1300°C for 1d.

### <u>Results</u>

### **Solubilities**

Mixed crystals containing up to about 2 atomic% of Fe or Cr as foreign cation can be prepared by annealing co-milled mixtures of the oxides at 1300°C or 1500°C. The solubility of Nb is only about 0.5 atomic% when firing the mixtures at 1300°C. However, when firing at 1500°C, the foreign phase  $Nb_2Zr_8O_{21}$  does not form up to a content of above 2 atomic% Nb, and this indicates that the solubility depends strongly on the temperature. We have therefore inve-

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stigated the stability of this mixed crystal system at lower temperatures by equilibrating specimens, which have taken up the maximum content of the dopant at higher temperatures, again at 800°C for several days. However, a segregation of the dopants into a foreign phase could not be detected.



Comparison of untreated (a) and fired (b)  $ZrO_2/Fe_2O_3$  mixtures containing 2 at% Fe

## Crystallographic properties

The accurate determination of the lattice parameters (using all clearly separated lines up to  $\theta=32^{\circ}$  on Guinier photographs taken with  $CuK_{\alpha 1}$ -radiation) showed identical values within the standard deviations for all doped phases and for the pure material prepared according to the procedure given above:

a = 511.8(4) pm, b = 521.3(3) pm, c = 531.2(4) pm and  $B = 99.21(7)^{\circ}$ .

It is known that there is complete solubility in the system  $ZrO_2/HfO_2$ . Our determination of the lattice constants of  $Hf_XZr(1-x)O_2$ , O<x<1, shows a linear Végard type dependance on the composition giving finally

a=511.8(4) pm, b=517.7(3) pm, c=528.9(4) pm and  $\beta=99.26(6)^{\circ}$ 

for pure  $HfO_2$ .

Since crystallite sizes play an important role in the kinetics of polymorphic transitions, we have determined this parameter D for the different specimens of doped and undoped  $ZrO_2$  using the halfwidth of appropriate reflections in a modified Scherrer formula D = (lambda/(B·cos0-b\_0), where b<sub>0</sub> is the broadening of the reflection due to instrumental effects as it was determined by using standard samples. Table I shows such D values for differently

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treated samples of pure and doped  $ZrO_2$ .  $ZrO_2-1$  is a precipitate from an aqueous solution of  $ZrOCl_2$  using NH<sub>3</sub>, which was dried and heated at 1100°C for 3h.  $ZrO_2-3$  is a sample of  $ZrO_2-1$  which was additionally annealed at 1300°C for 2d. Another sample was prepared by thermal decomposition of  $ZrOCl_2.8H_2O$  according to the procedure given above (2d/1100°C), and a fraction containing particle sizes between 60 and 90  $\mu$ m was then separated by sieves giving the sample named  $ZrO_2-2$ . ZrFe-2, ZrCr-2 and ZrNb-0.5 are mixed crystal samples containing the specified element in the atomic percentage given as numbers. Values derived from different reflections differ by up to 10% but within the estimated standard deviations. Prolonged heat treatment and the increase of annealing temperature is clearly reflected in the increase of annealing temperature is clearly reflected in the increase of the specimens of pure  $ZrO_2$ . The samples of doped  $ZrO_2$  have undergone a treatment comparable to that of  $ZrO_2-3$ . They show crystallite sizes of about 200 nm as compared with 300 nm for the undoped phase. The difference, which is significantly outside the standard deviation, may well be due to the fact that in this method of determining crystallite characteristics the influence of the crystallite size on the form of reflections is not separated from the effects of strain and distortion. (A separate analysis of these factors could only be done by evaluating the development of the half-widths in the higher orders of the reflections.) We assume therefore that the smaller crystallite sizes "seen" here are in fact an indication of stronger lattice distortions in the doped phases as compared with the less defect structure of undoped  $ZrO_2$ .

### TABLE I

Evaluation of mean crystalite sizes in different  $ZrO_2$ -specimens [D<sub>1</sub> from (11-1); D<sub>2</sub> from (111)]

Specimen Z	$r0_{2}-1$	2r0-2	ZrO2-3	ZrCr-2	ZrFe-2	ZrNb-0.5
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<b>D</b> -	(നന)	26(1)	126(10)	285(54)	187(23)	226(34)	195(25)
רע	(IIIII)	20(1)		203(34)	TO / ( 2 7 )	~~~~~~~	

D<sub>2</sub> (nm) 26(1) 127(11) 311(64) 167(18) 189(23) 218(31)

# Thermal dilatation and polymorphic transformation of undoped and

### <u>doped ZrO<sub>2</sub> in comparison</u>

### Experimental procedure

In the temperature range of 20 to  $1100^{\circ}$ C the thermal expansion of pure and doped  $ZrO_2$  was investigated by x-ray diffraction using a SIMON-type high temperature GUINIER camera (1) (CuK<sub> $\alpha$ 1</sub>-radiation)

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where the specimens are kept in a silica capillary of 0.2 mm diameter in a stream of heated air. The heating controller was calibrated by a series of measurements on standards with well known transition points using the camera in the mode where the film moves continuously with a slit-width of 4 mm. The temperature was measured in the gas stream using a NiCr/Ni thermocouple at a distance of 3-5 mm from the capillary tip. The first appearance of diffractions lines of a high temperature phase on the film could be correlated to the temperature with an accuracy of  $\pm 5^{\circ}$ C or  $\pm 20^{\circ}$ C at 200°C or 1100°C respectively, the uncertainty being due to a temperature gradient around the sample which increases with temperature. For a more accurate determination of the lattice constants of the ZrO<sub>2</sub> samples the film was moved in steps with temperature intervalls of 100°C and calibrated externally by a second continuous run at room temperature using Si as a standard. The lattice parameters were refined by a least squares procedure with the programm GIVER (2) using all resolved lines up to 65° in 20.

High temperature measurements in the range from 800°C to 1500°C were made with  $CuK_{\alpha 1}$  radiation using a SIEMENS D 500 goniometer equipped with a PSD (s.above) and a PAAR heating chamber. In this goniometer the specimen is irradiated as a flat sample spread on a Pt-foil which is resistance heater and sample holder at the same time. The foil is stretched by a spring mechanism to ensure alignment at different temperatures. The temperature was monitored by a Pt/PtRh10 thermocouple welded to the back of the sample holder. Diffractogramms were taken at intervalls of 50°C, and the lattice constants were refined from peak positions up to 60°C in 20 using the least squares program SAMPLE (3) which allows the refinement of the primary beam position (20=0°) as well, a possibility which was especially useful in the case of these measurements.

### <u>Results</u>

### Thermal expansion in the monoclinic phase

CAMPBELL et al.(4) have reported thermal expansion coefficients of pure monoclinic  $ZrO_2$  at intervalls of about 250°C in the range from 27 to 1110°C. Starting from room temperature their values decrease to a minimum at about 750°C and then increase again. However, we find a strictly linear temperature dependance of the lattice parameters in the whole temperature range. The increase of a,b and c is accompanied by a very slight decrease in B (from 99.2° to 98.8°). Table II contains axial ( $\alpha$ ) and volume ( $\tau$ ) expansion coefficients based on the definition

 $\alpha(T_2,T_1) = (x(T_2)-x(T_1))/x(T_1) \cdot (T_2-T_1)$ . (where  $T_1=23$ °C)

The values of CAMPBELL et al. for undoped  $\text{ZrO}_2$  are averaged and given for comparison.

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TABLE II Axial( $\alpha$ ) and volume( $\tau$ ) expansion coefficients for different specimens of monoclinic  $2rO_2$ 

Specimen	αa	$\alpha_{\mathbf{b}}$	α <sub>C</sub>	τ	τ/3	τ'
ZrO2	7.3(2)	3.6(3)	10.3(5)	22.1(9)	7.4(3)	21.2(6)
ZrFe-2	7.5(4)	3.1(6)	10.7(6)	22.6(11)	7.5(4)	21.3(9)
ZrCr-2	7.0(4)	1.1(4)	10.7(5)	20.1(10)	6.7(3)	18.8(8)
ZrNb-0.5	7.7(2)	1.8(3)	11.1(4)	21.7(6)	7.2(2)	20.6(4)
(4)	7.8	1.7	13.1			22.6

The sum of the axial coefficients  $\tau'$  corresponds well with the volume coefficient  $\tau$ , i.e. this monoclinic structure has the expansion characteristics very like those of an orthorhombic lattice. The expansion coefficient of the a axis is comparable to a mean 'isotropic' expansion derived as  $\tau/3$ . The expansion in b direction is only half as large, and it is greatest in c direction.

The effect of doping is seen quite clearly. It is especially pronounced in the case of the Cr-doped phase, where the volume expansion is reduced by about 10%. In view of the fact that the content of dopant is especially small the effect of Nb is surprising. Though the volume expansion is comparable with that of pure  $ZrO_2$ the anisotropy of the thermal dilatation is markedly increased. The expansion in the [010] direction - the smallest anyway - is additionally reduced in the Cr- and Nb-doped phase.

#### Thermal expansion in the tetragonal phase

The axial and volume expansion coefficients (calculation given above,  $T_1=1150$ °C) for the tetragonal high temperature phases in the temperature region between 1200°C and 1500°C are given in Table III together with data from the literature. Again we find a strictly linear increase with temperature. Though the standard deviations are considerably larger the precision of the values is high enough to justifiy a comparative discussion. As with the monoclinic modifications the Cr-doped phase has the smallest thermal expansion, the Nb-doped phase behaves like pure  $ZrO_2$ , doping with Fe reduces the thermal dilatation only little. In all cases the linear extrapolation of the lattice constants with the expansion coefficients given in this table does not lead to identical values for a  $\sqrt{2}$  and c - i.e. cubic metrics of the enlarged cell - until

well beyond the known melting point of ZrO<sub>2</sub>. Therefore the transformation into the cubic high temperature phase will probably always be accompanied by a discontinuous change of the lattice parameters.

When comparing the cell volumes of the tetragonal modification of doped and undoped  $ZrO_2$  it becomes evident that that of the Fedoped phase is the smallest. Our preliminary ESCA studies indicate that Cr and Fe are incorporated in the trivalent state into the  $ZrO_2$  structure - at least in the surface region accessible to this method of investigation -, and this leads to oxygen vacancies. However, it can be conjectured that Fe, substituting Zr in the tetragonal high temperature phase, changes its oxidation state to  $Fe^{2+}$  to a considerable extent as it does at high temperatures in

TABLE III Axial( $\alpha$ ) and volume( $\tau$ ) expansion coefficients for different samples of tetragonal ZrO<sub>2</sub>

Specimen	αa	αC	τ	т/З	τ'
ZrO2	15.8(15)	17.4(12)	48.4(43)	16.1(14)	49.0(41)
ZrCr-2	12.1(10)	14.0(36)	38.1(60)	12.7(20)	38.2(56)
ZrFe-2	13.5(9)	16.2(12)	43.4(27)	14.5(9)	43.1(30)
ZrNb-0.5	15.1(12)	18.3(15)	49.0(38)	16.3(13)	48.6(38)
(5)	12.4	14.4			
(6)	11.6	16.1	38.4		

iron oxide itself, and this would lead to many additional vacancies and consequently to a structure with lower density and smaller lattice parameters. In this case the volume difference between the monoclinic and the tetragonal phase is increased, and this explains that sintered pellets of such doped materials show heavy cracking and finally crumble when they have passed through the transition temperature several times. We will report on dilatometry experiments on these phases in a subsequent paper.

### <u>Conclusions</u>

The solubility limit of Fe and Cr in  $2rO_2$  is about 2 atomic% at 1300°C, and it is not enhanced by increasing the temperature to 1500°C. The solubility of Nb is small in comparison (0.5 atomic% at 1300°C), but it depends more on temperature (2 atomic% at 1500°C). Though all dopants are taken up while the material crystallizes in the tetragonal modification, there is no segregation of dopant oxide after transformation to the monoclinic low temperature modification even after prolonged equilibration at 800°C. Surprisingly, the same is true also for specimens which have been "supersaturated" with Nb at 1500°C.

We have investigated the thermal dilatation of these materials by the refinement of lattice parameters from x-ray data taken at temperatures up to  $1450^{\circ}$ C. The results presented here show that doping affects the overall thermal dilatation and also its anisotropy. Looking for  $ZrO_2$  based materials, which show a better mechanical stability during many temperature cycles, we have found a first interesting candidate in the case of ZrCr-2. This material shows the smallest volume expansion in the monoclinic as well as in the tetragonal modification and - what is most important - the smallest volume change during the transition. The opposite is true for ZrFe-2. The effect of impurities in  $ZrO_2$  on the mechanical stability of such materials is clearly seen in these investigations. The mechanical properties may be impaired or improved depending on the doping elements.

Acknowledgement: We thank Dr.Zorn for the high temperature x-ray measurements and Siemens A.G. for financial help.

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