

Vacancy Ordering in the ZrO₂ Rich Part of the Systems Ca–Zr–O–N, Mg–Zr–O–N, and Y–Zr–O–N

M. Lerch, J. Wrba, and J. Lerch

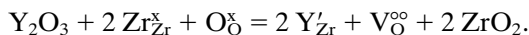
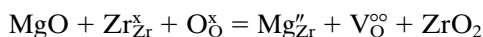
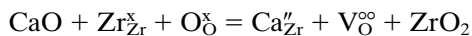
Lehrstuhl für Silicatchemie, Universität Würzburg, Röntgenring 10-11, 97070 Würzburg, Germany

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CaO, MgO, and Y₂O₃ doped zirconia samples were nitrated at temperatures between 1400 and 2000°C in a graphite heated resistance furnace in a nitrogen atmosphere. Depending on the content of nitrogen and aliovalent oxides, different types of ordered (β type) and disordered (tetragonal, cubic) phases were observed. Nitridation of pure ZrO₂ results in the formation of the β'' phase. With increasing content of the aliovalent oxides, other β type phases (β' , β) are detectable. The stability fields of the individual β type phases are determined by the ratio of V_N/V_{total} and by the kind of dopant oxide. In the system Y–Zr–O–N, the transition tetragonal–cubic was observed for higher Y₂O₃ concentrations. In this case, the “effective” total concentration of vacancies is the dominant factor which controls the transition. © 1996 Academic Press, Inc.

INTRODUCTION

The possibility to stabilize the high temperature polymorphs of zirconia (tetragonal, cubic) at ambient temperature by doping ZrO₂ with aliovalent oxides like CaO, MgO, or Y₂O₃ is well known. To maintain charge neutrality, anion vacancies form. This process can be described by the following equations:

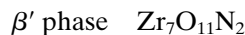


These anion vacancies which are distributed randomly in the lattice are the main reason for the outstanding electrical properties (ionic conductivity) of zirconia ceramics.

Incorporation of nitrogen into the zirconia lattice is another possible way to form anion vacancies. Direct nitridation of ZrO₂ in a nitrogen atmosphere was reported first by Cheng and Thompson (1). The following equation describes the vacancy formation process.



The results of our recent studies (2–5) in the system Zr–O–N are given below and include all zirconium oxynitride phases synthesized by direct nitridation of ZrO₂, belonging to the system ZrO₂–Zr₃N₄.



The β type phases are structurally derived from the fluorite-type structure of cubic zirconia. Anion vacancies are ordered in the lattice which leads to a trigonal distortion of the fluorite structure. Details of the crystal structures are given in (5–7). It should be remarked that phases with ordered anion vacancies are also known from the systems Ca–Zr–O, Mg–Zr–O, and Y–Zr–O. This was recently reviewed by Stubican (8). Zr₃Y₄O₁₂, Mg₂Zr₅O₁₂, and MgZr₆O₁₃ are examples of phases with ordered vacancies corresponding structurally to the β and β' phase in the system Zr–O–N (A_7X_{12} and A_7X_{13} type). Long annealing times are necessary for the synthesis of ordered oxide samples, whereas the vacancies in nitrogen doped samples show an ordered arrangement, even if the samples are quenched from high temperatures.

For the system Y–Zr–O–N, Shaw *et al.* (9) reported a transition from the β'' phase with ordered vacancies to a tetragonal structure (randomly distributed vacancies) with increasing yttria content. Further details of the systems Ca–Zr–O–N, Mg–Zr–O–N, and Y–Zr–O–N (high temperature XRD investigations, etc.) are given elsewhere (10). Vacancy distribution is an important factor for the mobility of vacancies which determines the ionic conductivity.

EXPERIMENTAL

All samples in the systems Ca–Zr–O–N, Mg–Zr–O–N, and Y–Zr–O–N were prepared by direct nitridation of the corresponding oxides in a nitrogen atmosphere. For the

preparation of the Ca–Zr–O, Mg–Zr–O, and Y–Zr–O starting materials, zirconia powder was mixed with magnesia, calcia, or yttria in 2-propanol, dried, and pressed into pellets isostatically (all powders: Alfa, Karlsruhe, Germany). The pellets were heated in air at 1750°C for 3 days. After grinding, XRD measurements were carried out for phase analysis. The prepared samples contain 0.05–15 mol% of the aliovalent dopant oxide. Again, these powders were pressed isostatically into pellets and nitrided in the graphite furnace. The following conditions were used to prepare samples within a wide range of incorporated nitrogen: temperature, 1400–2000°C; nitridation time, 2–4 h; nitrogen pressure, 1–4 bar; graphite heated resistance furnace (KCE, Roedental, Germany). The nitrogen content of the samples was up to 11 mol%.

All XRD investigations were carried out with a STOE STADIP powder diffractometer (CuK α_1 radiation, $\lambda = 154.06$ pm, position sensitive detector). Quantitative phase analysis was done using the polymorph method described by Garvie and Nicholson (11). For N/O analysis, the method of hot gas extraction was used (Leco, Munich, Germany).

RESULTS AND DISCUSSION

As known from our recent work (5–7), direct nitridation of zirconia leads to the formation of β type phases. From a structural point of view, they can be described by an ordered arrangement of Bevan clusters (Zr₇O₈N₄) and Zr₇O₁₄ units stacked along the [001] axis of the trigonally distorted fluorite lattice (5). The individual β type phases differ in the stacking sequence along the c direction. Synthesis conditions like cooling time are the determining factor for the formation of the individual β type phases. During cooling, the diffusion of nitrogen and oxygen ions is the main factor that controls the formation of ordered phases from the tetragonal or cubic high temperature phases with randomly distributed vacancies, which exist at temperatures above 1000°C (3).

Nitriding pure ZrO₂ leads to the formation of a mixture of β'' phase and monoclinic ZrO₂ using the described parameters of synthesis. With increasing concentration of the aliovalent oxides or nitrogen in the zirconia samples the amount of monoclinic ZrO₂ decreases. The nitrogen incorporation into zirconia can be controlled by parameters like nitridation temperature or nitrogen pressure. For an analysis of the superlattice reflections of the β type phases, a reasonable amount of stabilized phase is necessary. The intensities of these superlattice reflections are about 1/1000 of the strongest reflection. Figure 1 illustrates the problem. It presents an X-ray powder diagram of β' phase (system Mg–Zr–O–N) measured with the usual parameters of data collection (1 h, position sensitive detector). Only the reflections which are very similar to those of cubic

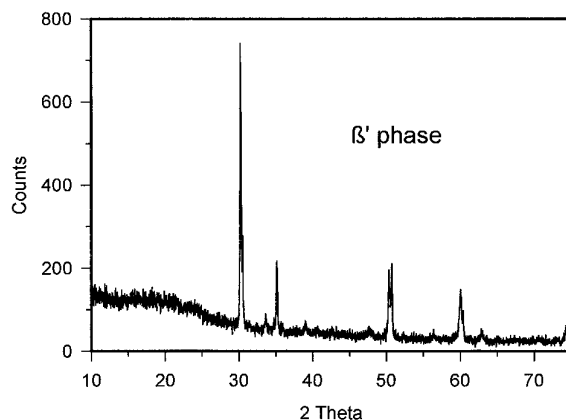


FIG. 1. X-ray powder diagram of Zr_{0.878}Mg_{0.122}O_{1.61}N_{0.177} (measuring time, 1 h).

zirconia (fluorite structure) can be observed. The 2 theta range between 10° and 26°, which is very important for the determination of the individual β type phases, has to be investigated very carefully by XRD. Measuring times of 20 h and the use of a position sensitive detector were necessary for a good analysis. The presence of a large amount of monoclinic ZrO₂ (>30%) also leads to difficulties in identifying the individual β type phases undoubtedly. Monoclinic ZrO₂ can be suppressed by large contents of dopant oxide or nitrogen, though higher concentrations of the oxides lead to samples with randomly distributed vacancies. The nitridation process at high temperatures (graphite heated furnace, $T > 1900^\circ\text{C}$), which is necessary for the dissolution of large amounts of nitrogen, results in the formation of significant amounts of rock salt type Zr(N,O,C) phases (12). However, a careful N/O analysis of the β type phases is not possible in the presence of such phases with varying composition, because hot gas extraction is a method to determine the total nitrogen/oxygen content of a sample. Thus, the range of samples which can be investigated is limited.

System Ca–Zr–O–N

More than 50 different Ca–Zr–O samples were nitrided under the conditions described above. An XRD phase analysis was carried out for all samples. For the following detailed studies, only samples with insignificant amounts of the rock salt type Zr(N,O,C) phases and monoclinic ZrO₂ were considered. Figure 2 presents the results for some Ca–Zr–O–N samples. β'' , β' , β , and phases with randomly distributed vacancies can be observed in this system. The diagrams of the β type phases are very similar, because the crystal structures differ only in the stacking sequence of Bevan clusters and Zr₇O₁₄ units. An N/O analysis (accuracy: $\sim 1\%$ of the present N/O) was done with all samples. For the calculation of the nitrogen content

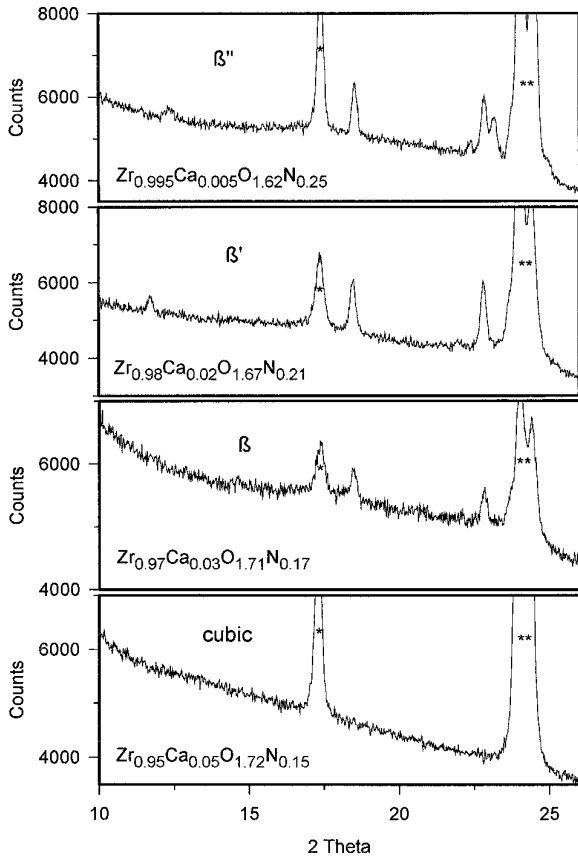


FIG. 2. X-ray powder diagrams of some typical Zr–Ca–O–N samples in the instructive 2 theta range between 10° and 26°. Reflections of monoclinic ZrO₂ are marked (measuring time, 20 h).

of the individual phases, the results of the quantitative phase analysis (polymorph method (11)) were used. As shown by electron energy loss spectroscopy (EELS) measurements, no nitrogen can be detected in the monoclinic phase of nitrated ZrO₂ samples (2). The results for the system Ca–Zr–O–N are shown in Table 1.

In order to find a systematic dependence of the individual vacancy order type as a function of compositional variables, parameters like the concentration of vacancies caused by the incorporation of nitrogen (V_N) and the aliovalent oxide (V_{Ca}) or the total concentration of vacancies ($V_{total} = V_N + V_{Ca}$) were checked. The terms V_N and V_{Ca} are defined in the following way:

$$V_{N,Ca} = 100 [V_{O}^{\circ\circ}]_{N,Ca} = 100 \frac{V_{O(N,Ca)}^{\circ\circ}}{O_x^x + N'_O + V_{O(Ca)}^{\circ\circ} + V_{O(N)}^{\circ\circ}}.$$

No satisfying correlation between these parameters and the phases obtained was found. However, looking at the term V_N/V_{total} , a significant correlation is observed. As known from the system Zr–O–N ($V_N/V_{total} = 1$), the nitr-

ation leads to the formation of β'' phase. From V_N/V_{total} values of 1 to ~ 0.93 the β'' phase is stable. The β' phase was detected in the range between ~ 0.93 and ~ 0.8 , the β phase between ~ 0.8 and ~ 0.65 . For samples with lower V_N/V_{total} values, the vacancies are distributed randomly. This is shown clearly in Fig. 3. Generally, the amount of incorporated nitrogen decreases with increasing content of calcia.

System Mg–Zr–O–N

Similar investigations were carried out in the system Mg–Zr–O–N. The results are presented in Fig. 4. Again, V_N/V_{total} is the most important term for the formation of the individual β type phases. Only the β'' and β' phases are observed in the system Mg–Zr–O–N. In the V_N/V_{total} range between 1 and ~ 0.96 the β'' phase is stable. For all lower values (the investigations were carried out down to ~ 0.4) the β' phase exists. No phases with randomly distributed vacancies (tetragonal, cubic) or other β type phases were detected.

System Y–Zr–O–N

The investigations in the system Y–Zr–O–N lead to the results presented in Fig. 5. β'' , β' , tetragonal, and cubic phases are observed. In contrast to the Mg–Zr–O–N system, the stability range of the β' phase is very small. Down to a V_N/V_{total} value of ~ 0.93 the β'' phase exists. The β' phase is stable in the range between ~ 0.93 and ~ 0.87 . Below this level tetragonal and cubic phases are observed.

Nitrogen containing zirconia shows a tendency to ordered vacancies; the arrangement in cation stabilized samples is usually randomly distributed for the investigated range of dopant oxide concentration. As described in the Introduction, some compounds with ordered vacancies exist in the systems Ca–Zr–O, Mg–Zr–O, and Y–Zr–O. As an example, Scott (13) reported an ordered arrangement of the cations in Y₃Zr₄O₁₂ which corresponds to the β phase (Zr₇O₈N₄) in the Zr–O–N system. If an ordered arrangement of cations or anions is necessary for ordered vacancies, the observed long annealing times for the preparation of, e.g., Y₃Zr₄O₁₂ are evident. Diffusion processes of cations are much slower than those of anions in fluorite structures with an anion deficiency. No experimental data about N/O ordering in β type phases are available. A systematic study of N/O ordering in oxynitride ceramics was presented recently by Thompson (14). From his studies, N/O ordering in Zr–O–N β type phases is very probable. The high mobility of anions in zirconia is the main reason for the fast formation of the ordered structures which are favored at low temperatures from an energetical point of view.

At very low concentrations of the aliovalent oxides, the vacancy ordering in the systems (Ca,Mg,Y)–Zr–O–N is

TABLE 1
Correlation between Some Chemical Parameters (V_N , V_{Ca} , V_{total} , V_N/V_{total}) and the Type of Vacancy Ordering in the System Ca–Zr–O–N

Composition	Crystal structure	V_N (%)	V_{Ca} (%)	V_{total} (%)	V_N/V_{total}
Zr _{0.9995} Ca _{0.0005} O _{1.60} N _{0.266}	β''	6.65	0.025	6.68	0.996
Zr _{0.9990} Ca _{0.0010} O _{1.58} N _{0.278}	β''	6.95	0.050	7.00	0.993
Zr _{0.9975} Ca _{0.0025} O _{1.60} N _{0.262}	β''	6.55	0.125	6.68	0.981
Zr _{0.9950} Ca _{0.0050} O _{1.62} N _{0.249}	β''	6.23	0.250	6.48	0.961
Zr _{0.9925} Ca _{0.0075} O _{1.67} N _{0.213}	β''	5.33	0.375	5.70	0.934
Zr _{0.9900} Ca _{0.0100} O _{1.57} N _{0.283}	β'	7.08	0.500	7.58	0.934
Zr _{0.9800} Ca _{0.0200} O _{1.67} N _{0.208}	β'	5.20	1.000	6.20	0.839
Zr _{0.9800} Ca _{0.0200} O _{1.66} N _{0.211}	β'	5.27	1.000	6.27	0.840
Zr _{0.9700} Ca _{0.0300} O _{1.70} N _{0.183}	β	4.57	1.500	6.07	0.753
Zr _{0.9700} Ca _{0.0300} O _{1.71} N _{0.172}	β	4.30	1.500	5.80	0.741
Zr _{0.9600} Ca _{0.0400} O _{1.73} N _{0.152}	$\beta + c/t$	3.79	2.000	5.79	0.655
Zr _{0.9600} Ca _{0.0400} O _{1.72} N _{0.158}	$\beta + c/t$	3.94	2.000	5.94	0.663
Zr _{0.9500} Ca _{0.0500} O _{1.74} N _{0.142}	c/t	3.54	2.500	6.04	0.586
Zr _{0.9500} Ca _{0.0500} O _{1.72} N _{0.153}	c/t	3.83	2.500	6.33	0.605
Zr _{0.9250} Ca _{0.0750} O _{1.74} N _{0.126}	c/t	3.14	3.750	6.89	0.456
Zr _{0.9250} Ca _{0.0750} O _{1.74} N _{0.124}	c/t	3.09	3.750	6.84	0.452
Zr _{0.9000} Ca _{0.1000} O _{1.72} N _{0.123}	c/t	3.08	5.000	8.08	0.381
Zr _{0.9000} Ca _{0.1000} O _{1.70} N _{0.132}	c/t	3.31	5.000	8.31	0.398
Zr _{0.8750} Ca _{0.1250} O _{1.73} N _{0.100}	c/t	2.51	6.250	8.76	0.286
Zr _{0.8750} Ca _{0.1250} O _{1.72} N _{0.101}	c/t	2.52	6.250	8.77	0.288
Zr _{0.8500} Ca _{0.1500} O _{1.69} N _{0.108}	c/t	2.69	7.500	10.19	0.264
Zr _{0.8500} Ca _{0.1500} O _{1.71} N _{0.096}	c/t	2.39	7.500	9.89	0.242

dominated by the influence of nitrogen. No phase exists in the systems Ca–Zr–O, Mg–Zr–O, or Y–Zr–O which corresponds structurally to the β'' phase in the Zr–O–N system, in contrast to the β and β' phases. With a decrease-

ing value of V_N/V_{total} the influence of the aliovalent oxides rises. The effect of the individual oxides is significantly different. However, a transition from β'' to β' phase is observed for all investigated systems. It may be possible

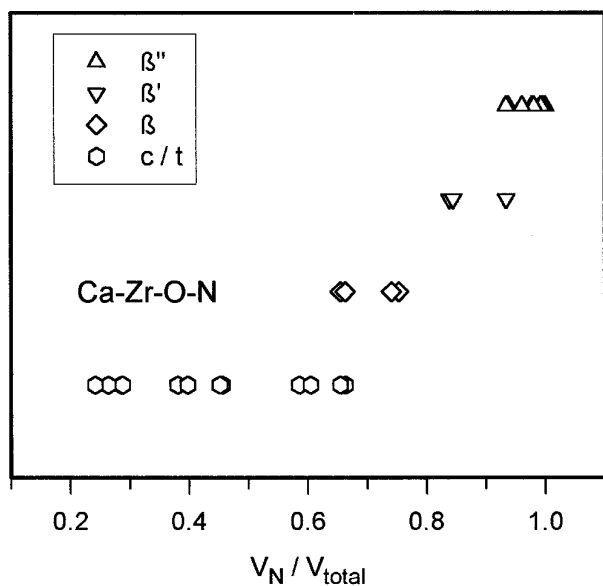


FIG. 3. β type phases and phases with randomly distributed vacancies in the system Ca–Zr–O–N as a function of V_N/V_{total} . To present the data in a clear way, the symbols are placed on four different levels of the meaningless ordinate.

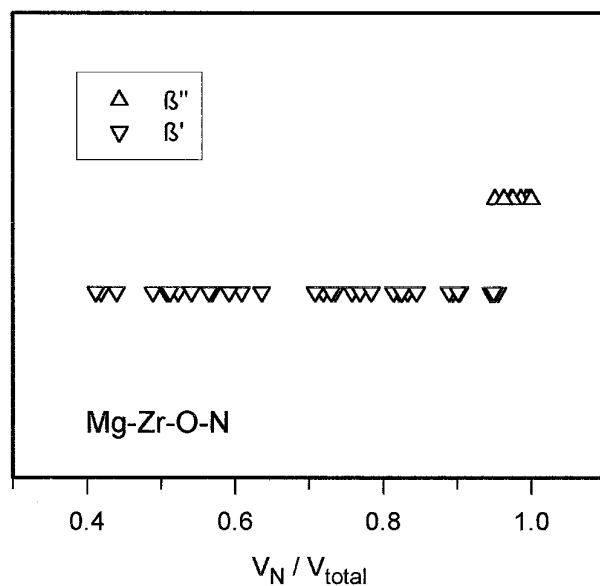


FIG. 4. β type phases in the system Mg–Zr–O–N as a function of V_N/V_{total} . To present the data in a clear way, the symbols are placed on two different levels of the meaningless ordinate.

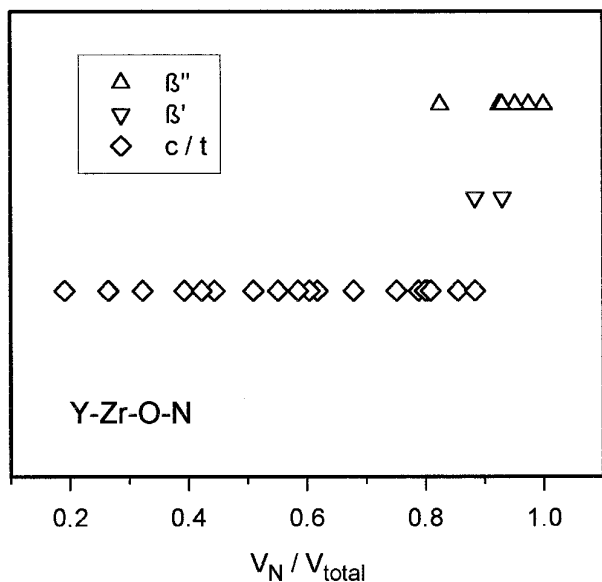


FIG. 5. β type phases and c/t phases in the system Y-Zr-O-N as a function of V_N/V_{total} . To present the data in a clear way, the symbols are placed on three different levels of the meaningless ordinate.

that a phase with an extremely narrow stability range was not detected in our investigations, e.g., a Y-Zr-O-N phase crystallizing in the β structure. The effect of incorporated nitrogen and aliovalent oxide on vacancy ordering seems to be very complex in this range of composition. The fast ordering kinetics are due to the incorporated nitrogen, the individual type of ordered structure seems to be influenced strongly by the type of the dopant oxide.

In the system Y-Zr-O-N, tetragonal and cubic phases with randomly distributed vacancies are observed. As reported by Cheng and Thompson (15), the stabilization effects of nitrogen and yttria are additive. Thus, the dominating factor for the transition tetragonal-cubic seems to be the sum of all anion vacancies V_{total} . However, such calculations do not lead to really satisfying results. This is very significant in the case of samples which are dominated extremely by yttria or nitrogen. There is no definite V_{total} value for the transition tetragonal-cubic. The stabilization effect of vacancies due to the incorporation of yttria or nitrogen is not identical. Looking at the phase diagrams $\text{ZrO}_2\text{-CaO}$ (8), $\text{ZrO}_2\text{-MgO}$ (8), $\text{ZrO}_2\text{-Y}_2\text{O}_3$ (8), and $\text{ZrO}_2\text{-Zr}_3\text{N}_4$ (3), the concentration of dopant ions which is necessary for a full stabilization of the cubic phase at a given temperature is not identical for the individual systems. At a temperature of 1350°C, the lowest possible temperature for comparison of all systems, the following vacancy concentrations ($V_{\text{Ca,Mg,Y,N}}$) are necessary for fully stabilized zirconia: $\text{ZrO}_2\text{-CaO}$, ~6.5%; $\text{ZrO}_2\text{-MgO}$, ~7.0%; $\text{ZrO}_2\text{-Y}_2\text{O}_3$, ~3.5%; $\text{ZrO}_2\text{-Zr}_3\text{N}_4$, ~6.7%. These data can be calculated easily from the phase diagrams. All these values are very similar, only that of the yttria system

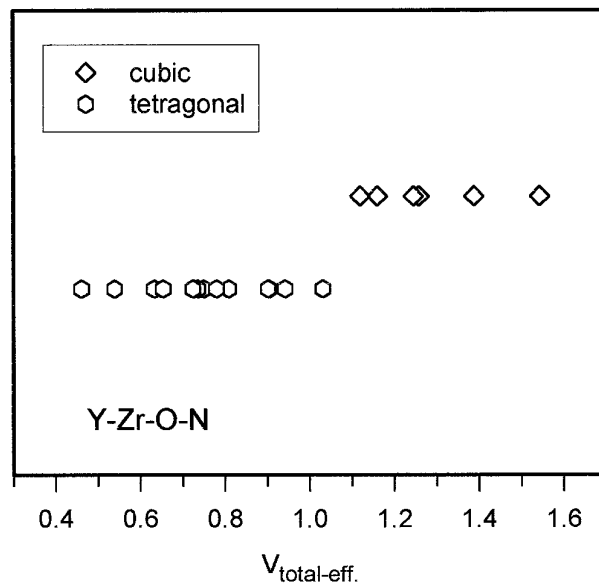


FIG. 6. Cubic and tetragonal phases in the system Y-Zr-O-N as a function of $V_{\text{total-eff}}$. To present the data in a clear way, the symbols are placed on two different levels of the meaningless ordinate.

is significantly smaller. Hence, for the calculations in the Y-Zr-O-N system this behavior has to be considered. An "effective" vacancy concentration ($V_{\text{total-eff}}$) was used which is defined in the following way: $V_{\text{total-eff}} = V_N/6.7 + V_Y/3.5$. Figure 6 presents the results. Pure cubic phase is observed for all $V_{\text{total-eff}}$ values above 1.1. The stabilization effects of yttria and nitrogen are additive if the individual effective concentrations are considered. The model of the effective vacancy concentration was also tested in the case of the ordering processes in the Y-Zr-O-N system, but no significantly better result could be obtained. Such a simple model cannot explain the complex behavior of the ordering process.

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