

sixth isozyme in human sperm (10). The synthesis of this sixth isozyme must either involve an additional gene or represent a specialized modification of one of the other isozymes.

Previous efforts to reassemble functional LDH molecules after dissociation in urea, guanidine, or at acid pH were of doubtful success (11). These dissociation procedures rupture hydrogen bonds and also destroy the tertiary and secondary (helical) structure of the monomers. Such denatured monomers apparently do not recombine into tetramers nor do they exhibit enzymatic activity. Since the monomers that were dissociated by NaCl behave differently, they must have retained much of their original structure.

Enzyme activity was not greatly reduced by treatment with NaCl, and this result suggests that the monomers may retain enzyme activity. If so, the overall conformation of the monomers must have remained essentially intact. Lactate dehydrogenase with a molecular weight of 72,000 has previously been reported as enzymatically active (12) which indicates that the dimer is functional. Measurements of the degree of polymerization and concomitant enzyme activity under identical conditions should soon allow us to describe with confidence the minimal functional unit of the LDH molecule.

The formation of enzymatically active tetramers by random association of monomers demonstrates that the conformational requirements for the quaternary structure of LDH are readily available in the structure of the monomers. However, after the disruption of the secondary and tertiary structure of the monomers (as with urea) they apparently lose their ability to become

functional LDH molecules again even though the primary structure (linear sequence of amino acids) remains intact. We may conclude therefore that the simple arrangement of the primary structure of the monomers is translated with difficulty, if at all, into protein structures of greater complexity. Apparently the physical-chemical environment in the cell at the site of protein synthesis, at least in the case of LDH, is of decisive importance in determining the higher states of molecular configuration (13).

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1. The following abbreviations are used: LDH, lactate dehydrogenase; NAD, nicotinamide adenine dinucleotide; DEAE, diethylaminoethyl-cellulose.
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## Phase Transformation at High Temperatures in Hafnia and Zirconia

**Abstract.** Phase transformation curves for  $HfO_2$  and  $ZrO_2$  have been made. Transformation hysteresis is discussed. The transformation of monoclinic to tetragonal as temperature increases occurs over the range 1000° to 1200°C in  $ZrO_2$ , and 1500° to 1600°C in  $HfO_2$ . With decreasing temperature the transition back to monoclinic occurs from 970° to 750°C in  $ZrO_2$  and 1550° to 1450°C in  $HfO_2$ . These transformations have been visually observed in  $ZrO_2$ , but not in  $HfO_2$ .

In spite of the wide differences in their atomic weights and densities, the elements zirconium and hafnium have very similar chemical properties. Therefore, the oxides  $ZrO_2$  and  $HfO_2$  should also have quite similar properties such

as molecular volume, melting temperature, and crystal form. Both are monoclinic at room temperature and transform to tetragonal at high temperatures. In this work, phase transformations in  $ZrO_2$  and  $HfO_2$  were studied with a

high-temperature x-ray diffractometer assembly (1).

Figure 1 illustrates the phase transformation characteristics of spectrographically pure (2)  $ZrO_2$ . With increasing temperature, the stable monoclinic form begins to transform to the tetragonal structure at 1000°C and the transformation is complete at 1190° to 1200°C. The tetragonal form is now stable to lower temperatures when the temperature is decreased and remains tetragonal to about 970°C; it is completely transformed to monoclinic by about 750°C. The temperature is plotted against a ratio of the intensity of the strongest line (111) of the tetragonal phase and the strongest line of the monoclinic phase (111). Since these curves resemble somewhat an electrical hysteresis curve, they will be referred to as the phase transformation hysteresis curve. Impurities or additions influence the range of transition especially with decreasing temperature where the transformation temperature may extend as low as 450°C in very impure samples.

In the high-temperature diffractometer specimen mount used in this work, the sample may be viewed visually through the port where optical pyrometer measurements are made. During heating and cooling through phase-transformation points, the sample can actually be seen to change phase as a result of individual particle movement caused probably by sharp discontinuities in the thermal expansion. The transformation with decreasing temperature is easily observed, while the transformation from monoclinic to tetragonal with increasing temperature is more difficult to observe. The temperature at which greatest sample movement is noted is the point on the transformation curve where the rate of change from one phase to the other is large. These points are noted on the curves in Fig. 1.

The monoclinic phase in  $HfO_2$  is stable to a much higher temperature than this phase in  $ZrO_2$  as seen in the transformation curves shown in Fig. 2. The transformation occurs over a narrower range of about 100°C and the temperature difference across the hysteresis loop is only about 50°C. Visual evidence of the  $HfO_2$  phase change has not been observed.

Phase-change temperatures shown in Fig. 2 are considerably lower and the range is narrower than previously reported (3). The range reported here is for fresh samples which have not

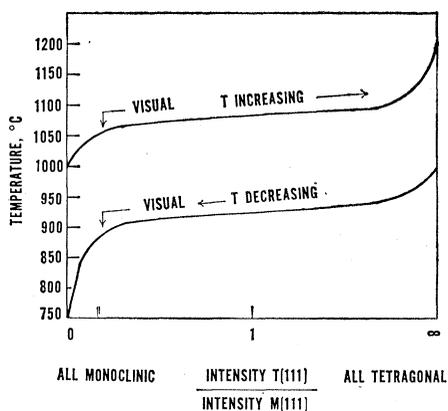


Fig. 1. Phase transformation in  $ZrO_2$  of spectrographic purity.

been previously sintered in an oxygen-deficient atmosphere. When samples are sintered at about  $1900^\circ C$ , and the temperature is lowered into the monoclinic range, and then the temperature is raised, the transformation range for monoclinic to tetragonal is about  $1650^\circ C$  to  $1900^\circ C$ , which is in good agreement with the results of Curtis *et al.* The data reported by Curtis were probably for oxygen-deficient  $HfO_2$ . X-ray patterns taken at from  $1600^\circ C$  to  $1900^\circ C$  agree well with data shown by Curtis, except that lines indexed as (102) and (103) are not observed. These lines ( $2.35\text{\AA}$ ,  $1.67\text{\AA}$ ) correspond to the two strongest lines of tantalum at high temperatures and probably resulted from contamination from the heater in the high-temperature camera. Such a contamination was induced in the present work by heating  $HfO_2$  on tantalum for 2 hours at  $1850^\circ C$ .

Whether tetragonal  $HfO_2$  is isomorphous with tetragonal  $ZrO_2$  is not yet known. Recently data were presented (4) showing that tetragonal  $ZrO_2$  powder patterns are correctly indexed on the basis of a primitive tetragonal lattice rather than a slightly distorted  $CaF_2$  lattice as reported by Ruff and Ebert (5). This new work depends

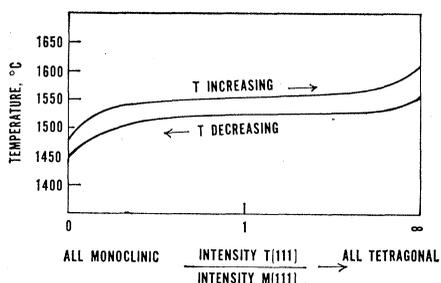


Fig. 2. Phase transformation in  $HfO_2$  of spectrographic purity.

on the appearance of very weak lines which will not index for the distorted  $CaF_2$  lattice. In this present work on  $HfO_2$ , no extra lines were observed other than those expected from a distorted  $CaF_2$  structure. No extra lines (other than those thought to be Ta impurity) were observed by Curtis *et al.* Therefore, it must be assumed that the structures of the tetragonal phases of  $ZrO_2$  and  $HfO_2$  are not the same, although it may be that the reflections missing in the  $HfO_2$  pattern are so weak that they are not detected in the diffractometer.

When one looks at the curves in Figs. 1 and 2, an obvious question is whether the size of the hysteresis loops is due in large part to a kinetic phenomenon. Results of x-ray diffraction indicate that the size of the hysteresis loops is not merely a nonequilibrium situation. Heating and cooling rates have little effect on the size of the hysteresis curves and only a few minutes are necessary to obtain a constant ratio of (111) lines for both phases at a given temperature. Electrical-resistance curves for fused

$ZrO_2$  show a similar hysteresis with increasing and decreasing temperature (6). However, very recent data (7) on electrical conductivity of  $ZrO_2$  indicate a sharp transition at  $1200^\circ$  to  $1205^\circ C$  with increasing temperature. With decreasing temperature the transition appears more sluggish, occurring between  $1050^\circ C$  and  $1000^\circ C$ . No electrical data at the transition temperature have been found for  $HfO_2$  (8).

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## Statistically Defined Displays and Pattern Detection of Cerebral Palsied Children

Abstract. *Visual displays consisting of arrays of dots are proposed as a possible method for quantifying the parameters of the hidden-figures tests. Detection of form in such displays is difficult for cerebral palsied children as a group. Oculomotor control may be one of the determining factors in successful performance of the perceptual task.*

Hidden-figure tests are visual tasks requiring identification of geometric figures and line drawings embedded in masking backgrounds. The ability to detect such camouflaged figures has been reported to vary with age, intelligence, sex, and damage to the central nervous system (1). The relatively poor performance of brain-injured subjects—which Teuber considers a nonspecific, nonlocalizable consequence of brain-injury—has been attributed to distractibility, inability to organize individual stimuli into wholes, and “pathology” in the figure-background orientation of the visual field (2).

Analysis of the nature of the perceptual deficit is limited by the *ad hoc* nature of the traditional displays. They have not been ordered in difficulty on the basis of defined structural characteristics. They are complex displays in which a given form is to be isolated from interfering, “noisy” fields; inter-

ference is organized into competing forms.

A means for identifying the parameters of the visual problem in hidden figures seems to be provided by the work of Green *et al.*, who studied perception of form in visual displays in which noise was defined in statistical terms (3). In a square matrix, alternate bars of differing density were produced by assigning to the bars different probabilities for the appearance of a black dot. As the differences in the probabilities assigned to adjacent bars decline, the alternating bars become progressively more difficult to discern. Green *et al.* found that for normal adult observers detection of horizontal or vertical arrays was a function of the statistical properties of the displays.

We adapted the Green displays in order to test the perceptual performance of brain-injured children. Our displays consisted of square matrices of