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Non-elastic Mechanical Behaviour in $SrZrO_3$ by Reorientation

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The crystal structure of different phases in (Ca–Sr)ZrO_3 and (Sr–Ba)ZrO_3 was studied with X-ray diffractometry. One orthorhombic phase, two tetragonal phases and one cubic phase were obtained. Mechanical measurements carried out in compression on polycrystalline specimens with different molecular compositions showed that specimens belonging to the orthorhombic phase and one of the tetragonal phases displayed a non-elastic behaviour that could be explained by a reorientation process. Specimens from the other tetragonal phase and the cubic phase displayed a purely elastic behaviour.

1. Introduction

Non-elastic mechanical behaviour in polycrystalline ceramic substances at room temperature is very uncommon. Funk, Nemeth and Tinklepaugh [1] found that samples of strontium zirconate exhibited non-elastic behaviour and the authors proposed that the phenomenon could be explained by crystal reorientation. This non-elasticity is thus associated with irreversible rotations about crystal axes, and not a plasticity due to the motion of dislocations.

In this paper a further investigation of the mechanical behaviour is presented and an attempt is made to find a correlation of the non-elastic deformation with differences in lattice parameters.

A preliminary investigation showed that by replacing Sr in $SrZrO_3$ by Ca or Ba, a single-phase material was obtained whose crystal structure changed at room temperature from orthorhombic via two tetragonal phases to the ideal cubic perovskite. As it was of interest to study the effect in the different non-cubic phases, this system was considered a suitable object for investigation.

2. Properties

The melting point of $SrZrO_3$ is about 2650° C and its theoretical density 5.48 g cm^{-3}. The symmetry of the phase existing at room temperature is orthorhombic [2]. On heating, the material becomes tetragonal at 700° C with the axial ratio for the sub-cell $c/a < 1$. This form exists up to 830° C where another tetragonal modification, but with $c/a > 1$, is formed. This phase is stable up to approximately 1200° C where it transforms to the cubic form [3]. At room temperature $BaZrO_3$ is cubic and $CaZrO_3$ orthorhombic.

3. Preparation of Samples

The different zirconates were prepared separately by calcination at 1300° C and wet-grinding in alcohol for 5 h, after which they were dried and the desired composition was weighed. On mixing and after another grinding in a ball-mill for 5 h, the material was dried and the powder was dry-ground for a short while. The specimens were pressed and subjected to a final sintering at 1550° C. The sintered specimens had the shape of circular discs with a diameter of approximately 25 mm and a thickness of approximately 10 mm. The plane surfaces of the discs were polished to the highest parallelism possible. The density of the samples obtained varied between 94 and 96% of the theoretical density. Test specimens were sawn and polished to final dimensions of $5 \times 5 \times 10$ mm^3.

4. Measurements

X-ray studies were conducted with a Philips high angle goniometer, and a detector system consisting of a scintillation detector combined with a pulse-height analyser. CuKα radiation was used. The lattice parameters were calculated from the line groups $N = h^2 + k^2 + l^2 = 12, 16, 22, 24$ and 26 where 12, 22 and 26 are most suitable for the calculation in the orthorhombic phase while

$N = 16$ and 24 are most suitable for the tetragonal phases.

The mechanical measurements were performed in compression with a modified testing machine provided with a compression jig specially designed for testing small, hard samples. The samples were compressed between two plane-parallel rods of tungsten carbide. The deformation was measured with an inductive transducer as the displacement between the parallel surfaces, consequently the elastic deformation of the machine itself did not affect the result. The deformation rate was constant 5×10^{-4} min^{-1}.

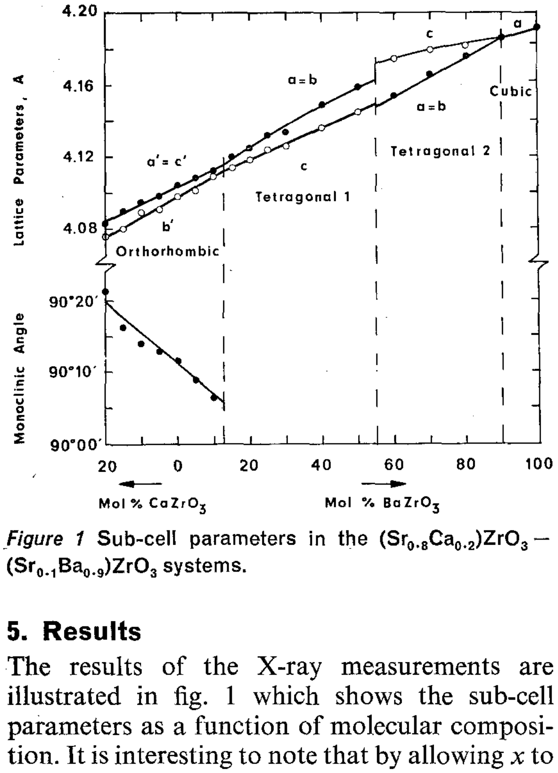

Figure 1 Sub-cell parameters in the $(Sr_{0.8}Ca_{0.2})ZrO_3$ – $(Sr_{0.1}Ba_{0.9})ZrO_3$ systems.

5. Results

The results of the X-ray measurements are illustrated in fig. 1 which shows the sub-cell parameters as a function of molecular composition. It is interesting to note that by allowing x to increase from 0 to 0.9 in the formula $(Sr_{1-x}Ba_x)ZrO_3$ the same phases are obtained as those displayed by $SrZrO_3$ on heating from room temperature to 1200° C. As in the findings of the high temperature investigation, the diffractograms of the two tetragonal phases show a few faint "extra" lines, thus proving that these phases are of multiple-cell type. One of these lines is situated at $2\theta \approx 10.5°$ corresponding to a lattice distance of about twice the edge of the sub-cell. Also the remaining extra lines may be indexed under the assumption that one or more cell parameters are doubled. From the diffractogram alone it is not possible to find which (one or several) of the cell edges are doubled. In the diffractogram of the cubic phase no extra lines could be detected, proving the structure to be cubic with no superstructure.

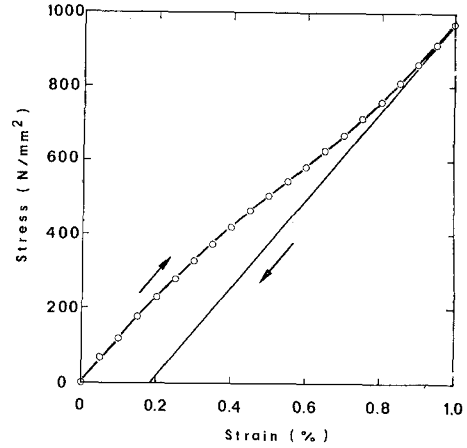

Figure 2 Stress-strain curve for a sample of the molecular composition $(Sr_{0.85}Ca_{0.15})ZrO_3$ obtained in compression.

A stress-strain curve for a sample with the composition $(Ca_{0.15}\ Sr_{0.85})\ ZrO_3$ is shown in fig. 2. At first the curve reveals a linear elastic part; then there is a non-linear part under which an unloading takes place linearly, with the same slope as the initial portion of the curve. Reloading follows the unloading curve and to develop further plastic deformation, the previous stress has to be exceeded. The yielding process is more or less completed at failure. A measure of the plastic strain is therefore obtained by inserting a straight line in the diagram as shown in fig. 2 and measuring the distance between the initial point of the curve and the point where the straight line intersects the strain axis. A more reproducible value of then-on elastic deformation can be obtained by successive unloadings and loadings and by measuring the additional non-elastic deformation for a defined load increase as a function of the load. When increasing the load, the stress-strain curve follows the line on the left of fig. 3. At a certain point, unloading the sample $\Delta\sigma$ (25 N mm^{-2}) causes an expansion following the line on the right side of fig. 3. Renewed loading takes place upwards along the same line. In this way it is possible to separate the non-elastic deformation per stress unit from the elastic deformation. By then, drawing the function $\Delta\epsilon_p/\Delta\sigma$ as a function of the load and

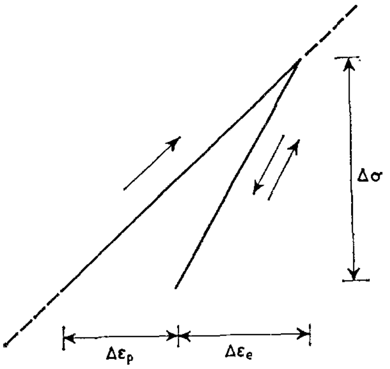

Figure 3 Part of a schematic stress-strain curve. For explanation see text.

integrating the area below this curve, a value can be obtained for the total non-elastic deformation. This function is shown in fig. 4 for a specimen with the composition $(Sr_{0.85}Ca_{0.15})ZrO_3$. Approximately 40 points were measured for each specimen to plot such a curve.

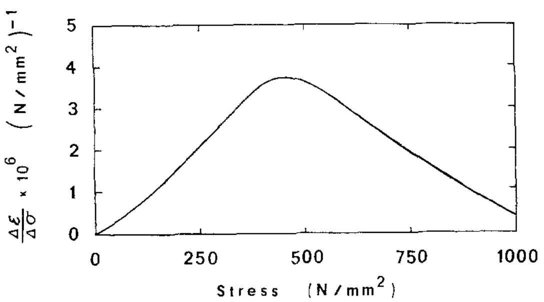

Figure 4 Plastic strain per stress unit as a function of stress. Same sample as in fig. 2.

The results of the mechanical measurements are shown in fig. 5 where the plastic deformation is given as a function of the composition. The dots correspond to measured values obtained from the stress-strain diagrams while the circles correspond to values calculated from X-ray data (see Discussion). As apparent from fig. 5 a fully measurable non-elastic strain was obtained with specimens from the orthorhombic and one of the tetragonal phases, whereas specimens from the other tetragonal and the cubic phases did not reveal any plasticity.

Furthermore there was a tendency towards a difference in breaking stress for specimens of both groups. Specimens displaying non-elastic strain could generally be loaded to above 1000 N mm^{-2} before the material started to crack, whereas samples, solely revealing elastic deformation, began to crack at lower loads (about 700 to 800 N mm^{-2}).

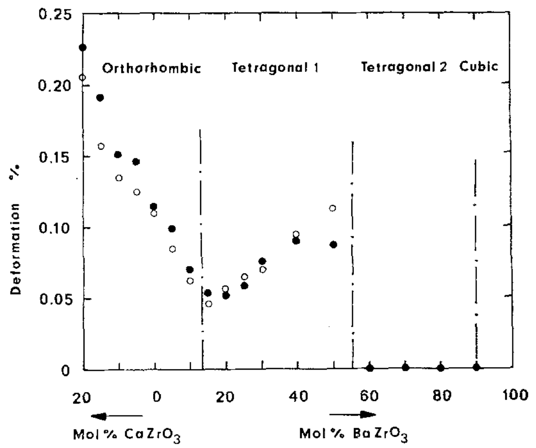

Figure 5 Plastic deformation as a function of the molecular composition. Dots correspond to mechanical measurements. Circles correspond to values calculated from X-ray data.

6. Discussion

The symmetry of perovskites is usually cubic at sufficiently high temperatures, but they may undergo one or more phase transitions on cooling. One well-known example is barium titanate that is transformed from a cubic to a tetragonal structure with $c/a > 1$ at 120° C. When a single crystal undergoes such a transition the c-axis may fall along any of the three original cube edges. A small perfect crystal, provided its surfaces are not constrained, may transform to a single tetragonal crystal. However, for a crystal whose surfaces are constrained, as in a polycrystalline sample prepared by high-temperature sintering, the neighbouring grains interlock causing twinning in such a way that the strain energy is reduced. This twinning causes the crystallite to break up into regions or domains with different crystallographic orientation. When a uniaxial mechanical load is applied to the specimen, for energetic reasons, it will be advantageous for some domains to reorientate. A domain so orientated that its c-axes are close to the direction of the load, will reorientate 90° so that the c-axes lie parallel to the direction of one of the original a-axes. If a twinned crystal is observed under polarised light in a microscope and the crystal is subjected to an external load the migration of the twin boundaries can be observed [4].

The existence of the reorientation process can also be verified by X-ray investigation [5]. This domain reorientation gives rise to a non-linear stress-strain curve but whether the reorientation gives rise to plasticity depends on whether it is permanent or not when the stress is removed. The lattice parameters in the orthorhombic phase are characterised by two axes of almost the same length, while the third is approximately $\sqrt{2}$ times longer. For pure $SrZrO_3$, the X-ray measurements gave the following values: $a_0 = 5.814$ Å; $b_0 = 8.196$ Å; $c_0 = 5.794$ Å. It may be expected that under a compressive load cells with their a_0-axis orientated close to the direction of the load can switch over 90° so that the c_0-axis falls along the original a_0-axis. The direction of the b_0-axis, however, cannot shift. The strain for a cell that can switch over will be proportional to $1 - c_0/a_0$ and the constant of proportionality specifies the number of participating cells. The value $1 - c_0/a_0$ can be shown to be roughly equal to $\triangle v$ (in radians) where $\triangle v$ is the deviation from 90° when the lattice parameters are expressed in monoclinic parameters. As apparent from fig. 1, $\triangle v$ is an approximately linear function of the molecular composition in the orthorhombic phase. Fig. 5 shows that the plastic strain also varies linearly with the molecular composition. The measuring points for the mechanical measurements are found to be in good agreement with the values calculated from the X-ray measurements according to $\epsilon_p = \text{const}\ x \triangle v$, if the constant chosen is equal to 1/3. These calculated values were inserted in fig. 5 as circles. The constant 1/3 for this process was proposed by Funk *et al* [1]. Their investigation gave, however, considerably lower strain values than those obtained here. An explanation for their lower values is that their investigation was carried out in flexure where specimens break considerably sooner than in compression and therefore the reorientation process is far from completed when the material fails.

In the first tetragonal phase two axes of the sub-cell are equal and somewhat longer than the third. By analogy with the strain in the orthorhombic phase, a strain proportional to $a - c/a$ can be expected. The measured values from the mechanical tests are found to be in good agreement with those calculated from the X-ray measurements using $\epsilon_p = \text{const}\ x(a - c(a))$. The constant of proportionality proved to be close to 1/3 for this phase also.

The mechanical measurements in the second tetragonal phase show no plasticity. A small non-linearity, however, could be observed in the first part of the stress-strain curve for samples from this phase. This non-linearity was not plastic but purely elastic so that unloading before fracture followed the loading curve. A possible explanation for the difference in mechanical behaviour between, on one hand the orthorhombic and the first tetragonal phases and on the other hand, the second tetragonal phase, is the sequence of phase transitions which the material undergoes on cooling from the sintering temperature.

Samples from the second tetragonal phase undergo only one phase transition on cooling to room temperature. The domain pattern can thus be expected to be relatively uncomplicated so that on unloading the reorientation is not permanent and the deformation is purely elastic. This would be analogous to the findings of Subbarao *et al* [5] for tetragonal $BaTiO_3$ where no permanent deformation is obtained on unloading.

For samples from the first tetragonal or orthorhombic phase the conditions can be expected to be different. On sintering these phases undergo, besides the transition from cubic to tetragonal, one or two further transitions. In particular, the transition between the two tetragonal phases can be the reason for a more complicated domain pattern. Thus the reorientation will be permanent on unloading and the resulting deformation will be non-elastic.

The specimen with the composition $(Sr_{0.1}Ba_{0.9})ZrO_3$ displays a purely elastic stress-strain curve which is in agreement with its cubic symmetry.

The tendency towards higher breaking strength observed for specimens displaying a plastic strain can be explained by the stress concentrations obtained in the samples under loading being smoothed out by the reorientation process.

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