Most of the materials expand upon heating. There are a few families of materials which exhibit negative thermal expansion (NTE). ZrW₂O₈ is an example which gained a lot of interest in international literature recently. This cubic material has an exceptionally large and isotropic negative thermal expansion over its entire stability range (0.5 to 1050 K). At 430 K a phase transition occurs from α-ZrW₂O₈ (α = -9.1 × 10⁻⁶ K⁻¹) to β-ZrW₂O₈ (β = -5.4 × 10⁻⁶ K⁻¹). At high pressures an orthorhombic phase is formed, γ-ZrW₂O₈, which possesses a small negative expansion coefficient. A broad range of applications have been suggested for these NTE materials. In composites, their thermal expansion coefficient can be tailor-made by combining a NTE material with a positive expansion material. Adjusting the volume fraction of the different phases results in a positive, negative or even zero thermal expansion. The ZrW₂O₈ - ZrO₂ - composites studied in this paper were prepared in two ways. The first synthesis method applied, started from off-stoichiometry mixtures of the pure oxide powders of ZrO₂ and WO₃. This novel in situ process included a heating step up to 1450 K which combines the formation and sintering of ZrW₂O₈. In the conventional synthesis the starting materials were ZrO₂ and ZrW₂O₈. ZrW₂O₈ was first obtained using an optimised spray drying technique. Obviously, our "in situ" method does not require such an additional step. The crystal structure, morphology, thermal expansion behaviour and mechanical properties of these composites were tested and compared.

INTRODUCTION

The thermal expansion of a material in general is due to the specific temperature dependence of the geometrical parameters under specified conditions. Although this leads to a positive thermal expansion resulting from an increase in the population of higher energy vibration levels, in some cases negative thermal expansion is also possible. In the last decennium, several families of materials which exhibit negative thermal expansion, arising from a geometrical effect in so-called framework structures, have also been discovered. Usually, this negative thermal expansion is small, anisotropic and appears in a very small temperature interval. ZrW₂O₈ is an exception because of its large and isotropic negative thermal expansion (NTE) in a temperature range from 0.5 K to 1050 K. A cubic symmetry is found over the entire stability range with a phase transition from α-ZrW₂O₈ to -ZrW₂O₈ near 430 K [1-3]. This phase transition has an influence on the thermal expansion which changes from -8.7 × 10⁻⁶ K⁻¹ for the alpha phase to -4.9 × 10⁻⁶ K⁻¹ for the beta phase (figure 1). The negative thermal expansion behaviour of ZrW₂O₈ is caused by the presence of Rigid Unit Modes. ZrW₂O₈ consists of a network of corner-shared polyhedra with twofold coordinated oxygen atoms. These stiff polyhedra have strong M-O bonds and short O-O distances. When coupled rotations occur of these polyhedra while the intra-polyhedra bond distances and the intra-polyhedra angles remain relatively constant, the material exhibits a decrease in volume. Broad range of applications have been suggested for these NTE materials. In composites, their thermal expansion coefficient can be tailor-made by combining a NTE material with a positive expansion material. Adjusting the volume fraction of the different phases results in a positive, negative or even zero thermal expansion. The ZrW₂O₈ - ZrO₂ - composites studied in this paper were prepared in two ways. The first synthesis method applied, started from off-stoichiometry mixtures of the pure oxide powders of ZrO₂ and WO₃. This novel in situ process included a heating step up to 1450 K which combines the formation and sintering of ZrW₂O₈. In the conventional synthesis the starting materials were ZrO₂ and ZrW₂O₈. ZrW₂O₈ was first obtained using an optimised spray drying technique. Obviously, our "in situ" method does not require such an additional step. The crystal structure, morphology, thermal expansion behaviour and mechanical properties of these composites were tested and compared.
The first synthesis is a process in which an in situ formation of ZrW₂O₈ takes place. This method is based on off-stoichiometry mixtures of the pure oxide powders of ZrO₂ and WO₃. In the second synthesis, a more conventional route based on a mixture of ZrO₂ and ZrW₂O₈ was taken. The ZrW₂O₈ necessary for this route was obtained using an optimised spray drying technique [10].

EXPERIMENTAL

Chemicals

ZrO₂ was purchased from Aldrich (Germany). Polyethylene glycol (MW 20000) was bought from Fluka (Germany). WO₃ was obtained from Acros Organics (Belgium).

Instrumentation

Particle size and particle size distribution of the different powders dispersed in deionised water were determined by laser diffraction (Malvern Particle Sizer Series 2600c). The microstructures of the fracture and polished surfaces were observed by optical microscopy (Leitz labolux 12 pol S) and scanning electron microscopy (FEI 200F). Identification of the different phases present in the samples was performed by X-ray diffractometer Siemens D5000. The coefficients of thermal expansion were measured with a vertical push rod thermo mechanical analyser (TA instruments 2940), using a heating rate of 2 K per minute from room temperature to 573 K under a constant force of 0.5 N. The mechanical properties of the samples were examined with a 3-point bending test using an Instron Series 4500 coupled with a Series IX Automated Materials Testing System with a speed of 1 mm/min.

Synthesis of the composites

The spray drying technique was used in the preparation of pure ZrW₂O₈ [10]. For the preparation of the composites, two different methods were used as can be seen in figure 2a and b. In the in situ method (figure 2a), the commercially obtained oxide powders are first milled in an agate ball mill during 24 h to reduce the particle size and thus improve the homogeneity of the mixture and the sintering ability. Hereby an average particle size of 0.62 µm for WO₃ and 1.12 µm for ZrO₂ was obtained. The particle size and particle size distribution of these powders are given in table 1. For further manipulation of the mixed powders, they have to be pressed into bars but the bars were of poor quality. Therefore, aqueous slurry was prepared containing polyethylene glycol as dispersants. This additive possesses the additional benefit of reducing the friction during pressing of the bars. Using a polymer means that this organic material must be removed before sintering. An additional heating stage of 60 min at 773 K ensures that all organic material will be expelled. During this evaporation, pores are formed in the composites as can be seen in figure 3. This will have its effect on the mechanical properties of the composites. The amounts of oxides used in the preparation of the different composites are mentioned in table 2. Therefore the desired mixture of ball-milled oxides was suspended in 250 ml

Table 1. Powder particle size.

<table>
<thead>
<tr>
<th>Material</th>
<th>Particle size $d_{50}$ (µm)</th>
<th>Particle size $d_{90}$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrW₂O₈ (Spray dried)</td>
<td>12.77</td>
<td>32.46</td>
</tr>
<tr>
<td>ZrO₂ (Aldrich)</td>
<td>5.27</td>
<td>8.72</td>
</tr>
<tr>
<td>ZrO₂ (milled 24h)</td>
<td>0.74</td>
<td>0.94</td>
</tr>
<tr>
<td>WO₃ (Aldrich)</td>
<td>66.56</td>
<td>130.39</td>
</tr>
<tr>
<td>WO₃ (milled 24h)</td>
<td>0.62</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Table 2. Composition of the in-situ composites before heat treatment.

<table>
<thead>
<tr>
<th>Desired ZrW₂O₈ in the composites (wt.%)</th>
<th>Mass WO₃ (g)</th>
<th>Mass ZrO₂ (g)</th>
<th>Mass PEG (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>6.32</td>
<td>1.68</td>
<td>0.24</td>
</tr>
<tr>
<td>99</td>
<td>4.69</td>
<td>1.31</td>
<td>0.18</td>
</tr>
<tr>
<td>80</td>
<td>6.32</td>
<td>3.68</td>
<td>0.30</td>
</tr>
<tr>
<td>33</td>
<td>5.27</td>
<td>4.73</td>
<td>0.30</td>
</tr>
</tbody>
</table>
deionised water together with 3 wt.% polyethylene glycol, calculated on the mass of the oxides. The mixture was stirred for 2 h followed by an ultrasonic treatment of 1 h to break the agglomerates down. The resulting slurry was spray dried using a Büchi mini spray dryer with a 0.5 mm nozzle and a feeding rate of 5 ml per minute (Inlet temperature: 430 K; Outlet temperature: 370 K; gas flow: 800 Nl/h). Afterwards, the powder was uni-axially, cold pressed to bars (dimensions: $2 \times 2 \times 13$ mm) at a pressure of 750 MPa. The bars were thermally treated under air in a covered Pt crucible in a high temperature furnace following the temperature program described in figure 2a. After heat treatment, the bars were quenched in liquid nitrogen to avoid decomposition of ZrW$_2$O$_8$.

In the conventional method, the ZrW$_2$O$_8$ pellets synthesized using the spray drying process, are ground in an agate mortar and are manually mixed with different amounts of ZrO$_2$. Again, bars were pressed and thermally treated under air in a covered Pt crucible in a preheated furnace at 1450 K for 2 h followed by quenching in liquid nitrogen. Using this conventional route, a single composite with 80 wt.% ZrW$_2$O$_8$ was made by manually mixing with 20 wt.% ZrO$_2$ and pressing these powders into bars, followed by a thermal treatment of 2 hours at 1450 K.

**RESULTS AND DISCUSSION**

Analysis of the ZrO$_2$ - ZrW$_2$O$_8$ composite

Most of the bars prepared by the in situ method remained stable and showed no cracks after thermal treatment. Nevertheless the bars containing less than 40 wt.% ZrW$_2$O$_8$ showed some cracks after quenching, due to the high sintering temperature of ZrO$_2$ (more than
In comparison to the synthesis temperature of 1450 K [11]. Examination of the mechanical properties of these samples was therefore not possible. X-ray diffraction shows that only 2 phases are found in the composite which can be identified as α-ZrW₂O₈ and monoclinic ZrO₂ as illustrated in figure 4 for a in situ - 40 wt.% ZrW₂O₈ sample.

The microstructure of the fracture surfaces of composites with identical composition is strongly dependent on the synthetic route chosen. Figure 5a shows a SEM view obtained from a 80 wt.% composite prepared by the conventional method, whereas figure 5b reflects the same wt.% composite but as the result of an in situ process. The difference is clear. In the conventional obtained composite, ZrO₂ remains as loose powder between the larger ZrW₂O₈ grains, which is caused by the high sinter temperature of ZrO₂, which lies above the melting temperature of ZrW₂O₈. The reason why the micro-structure of the in-situ composite is different can be explained by the small dimensions of the starting powder which results in a much more homogeneous mixture. Furthermore, because ZrW₂O₈ is formed in situ, the ZrO₂ grains are more dispersed in the composite instead of the large agglomerates encountered in the conventional method.

Mechanical analysis of the in-situ composites

For composite materials, the thermal expansion can be theoretically predicted at a certain temperature by using the rule of mixtures \( \alpha_c = \sum \alpha_i V_i \). \( \alpha_i \) is the thermal expansion of the individual component at that temperature and \( V_i \) is the volume fraction present of that component. For a series of in-situ composites the experimental results obtained at 500 K are compared with those calculated by the rule of mixtures (figure 6).

![Figure 4](image4.png)  
Figure 4. X-ray diffraction pattern from the (a) pure α-ZrW₂O₈ and (b) In situ composite of 40 wt.% ZrO₂. (*) indicates the most characteristic diffraction lines for monoclinic ZrO₂.

![Figure 5](image5.png)  
Figure 5. SEM micrograph of a) 80 wt.% ZrW₂O₈ bar prepared by conventional method and b) 80 wt.% ZrW₂O₈ bar by in situ.

![Figure 6](image6.png)  
Figure 6. Thermal expansion coefficients, calculated and experimen-ental, at 498 K.
A discrepancy is found which is most pronounced in the middle area of the graph. Such a deviation can be expected taking into account that the rule of mixtures requires a sample without voids, no thermal stress and that the combined phases should have the same elastic modulus [12-13]. Our composites do certainly not fulfill these characteristics. In the middle of the region, the differences in thermal expansion coefficient and elastic modulus are the most pronounced, resulting in the highest stress and the largest deviation of the rule of mixtures. Our results can also help us to predict the composition required to obtain the desired zero thermal expansion: 64 % ZrW$_2$O$_8$ accompanied by 36 % ZrO$_2$. In literature [9], a composite prepared by the conventional method and consisting of 66 wt.% ZrO$_2$ and 33 wt.% ZrW$_2$O$_8$ was suggested to result in zero expansion. This composition was tested for the in situ measurements. The change in linear dimensions as a function of temperature is given in figure 7. From 450 K onwards, a slight thermal expansion is noted. This is coincident with the occurrence of the $\alpha$ to $\beta$ transition and can be explained as follows. The $\alpha$-phase possesses a lower negative thermal expansion coefficient ($-4.9 \times 10^{-6}$ K$^{-1}$) than the $\beta$-phase ($-8.7 \times 10^{-6}$ K$^{-1}$) and this obviously changes the compensatory effect of the ZrO$_2$ which exhibits a strongly positive expansion coefficient ($9.6 \times 10^{-6}$ K$^{-1}$) which remains constant in the entire temperature region.

Handling the bars is not simple because of the brittle nature of these ceramics. The mechanical properties were measured by a three points bending test [15]. In figure 8, the flexural strengths were plotted for the ZrW$_2$O$_8$ pure phase and 2 composites with the same composition (80 wt.% ZrW$_2$O$_8$) but with a different preparation.

$$\sigma = \frac{3LF}{2bh^3}$$  (1)

The flexural strength $\sigma$ calculated by formula 1 where $L$ is the distance between the support points, $F$ the load at rapture, $b$ the cross section of the sample and $h$ is defined as the thickness. As can be seen in figure 8, these flexural strength is similar for the pure phase and the in situ composite where as the composite prepared by the conventional method shows much lower flexural strength which was expected from the morphological analysis.

Figure 8. Flexural strength for a) pure ZrW$_2$O$_8$, b) 80 wt.% in situ and c) 80 wt.% conventional.

CONCLUSIONS

A first attempt to modify the thermal expansion of ZrW$_2$O$_8$ by the formation of composites with ZrO$_2$ has been demonstrated, using two preparation methods. In a conventional synthetic approach, the variation of the thermal expansion coefficient is shadowed by poor mechanical properties. However by using an in situ method, there is no loss in flexural strength. The use of polyethylene glycol as pressing aid largely improves the mechanical characteristics of the composite materials. Nevertheless, the formation of pores was observed due to the evaporation of organic material during thermal treatment. Further research will be performed to minimize the pore formation and improve the mechanical strength.
Acknowledgement

The authors would like to thank the Department of Solid State Physics at Ghent University for performing X-ray diffraction measurements and scanning electron microscopy. Special thanks to the laboratory for Mechanical construction and production at Ghent University for the mechanical testing. Christy De Meyer is grateful for a PhD Grant by the fund of Scientific Research - Flanders (Belgium) (F.W.O.-Vlaanderen).

References


Department of Inorganic and Physical Chemistry, Ghent University