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Note

Thermal Diffusivity and Conductivity of Li_2ZrO_3 Using the Modulated Electron Beam Technique

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Thermal diffusivity and thermal conductivity of three Li_2ZrO_3 specimens with two different density values, 82.6 and 87% theoretical density, have been measured between 350 and 900°C. The modulated electron beam thermal diffusivity method was used. Heating the specimens above some 850°C but below 900°C results in a reversible increase in both the diffusivity and the conductivity. When heating to higher temperatures generally still higher increases are noticed but measurements become rapidly unstable and irreversible.

KEY WORDS: breeding material; fusion reactor; Li_2ZrO_3; thermal conductivity; thermal diffusivity.

1. INTRODUCTION

Lithium metazirconate, Li_2ZrO_3, still belongs to a family of promising ceramic candidate materials for breeding tritium in a fusion reactor, together with several other lithium compounds—see, e.g., Li_2SiO_3 [1]. Properties such as thermal diffusivity and conductivity, thermal emissivity, specific heat, and thermal expansion are of primordial importance, although literature on these subjects is still scarce.

The equipment used for the diffusivity–conductivity, and actually for the emissivity measurements is the "modulated electron beam thermal diffusivity apparatus." A comprehensive general discussion of the principle of the method has been published earlier [2], while a detailed description of the specific equipment used is in press [3].

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2. SPECIMENS

2.1. The Li_2ZrO_3 Sample Material

The Li_2ZrO_3 material has been prepared by Flipot et al. [4]. A powder mixture of lithium carbonate (Li_2CO_3) and zirconia (ZrO_2) is calcined under air at some 500 to 675°C. After cold pelletizing this powder is sintered between 950 and 1000°C, generally for more than 20 h. Densities up to 93% TD (theoretical density) are then obtained. The pellets are contamination free but do contain some (less than 1%) free ZrO_2. The material thus obtained has an essentially monoclinic lattice. The average grain size ranges from 1 to 3 μm. In the density range from 70 to 93% TD, all pores can be considered to be open (which is favorable for tritium release) and with a bimodal size distribution at some 0.04 and 0.5 μm. The melting point amounts to approximately 1530°C. No cracking is visible at 60× magnification.

2.2. Preparation of Specimens

Specimens should be plan-parallel disks with a diameter of 8 mm and a thickness of approximately 1 mm. These disks are cut from the original larger cylinders (14 mm in diameter and 20 mm in length) with the aid of a diamond saw and are finished off with 600-mesh SiC abrasive powder.

Li_2ZrO_3 reacts with the CO_2 and absorbs readily the H_2O contained in the ambient air. Therefore, the specimens are dried (800°C, 10 h) and sealed in a plastic bag under dry N_2 and preserved in a desiccator.

Since the specimens have a high electrical resistance, and since the thermal diffusivity measurements are carried out under electron bombardment, it is necessary to deposit a conducting layer on all surfaces of the specimen. A tungsten layer, 0.35 μm thick, is deposited on the specimen by the chemical vapor deposition technique. The contribution of this layer to the effective diffusivity–conductivity values was evaluated and found to be negligible.

Putting the specimens into the sample holder occurs under flowing dry N_2 in order to avoid exposure to the air again.

3. PARAMETERS REQUIRED FOR DATA REDUCTION

In order to calculate thermal diffusivity–conductivity values after data acquisition (temperature and phase difference), a number of parameters have to be taken into account. A full description of the calculation technique is given in the literature [5].

3.1. Spectral and Total Emissivities

Spectral and total emissitivities were measured for two wavelengths, 0.65 and 2.3 μm, by a method developed earlier [6] using a spectrophotometer and a mirror system. These emissivity values concern the tungsten-covered specimens. Consequently, they are not representative characteristics for the Li_2ZrO_3 material.

3.2. Thermal Expansion Correction Factor

The thermal expansion correction factor Δd was calculated from thermal expansion data provided by Brauns [7] and is represented by

$$\Delta d = 1 - 3.1835 \times 10^{-3} + 1.3540 \times 10^{-5} T - 1.1817 \times 10^{-8} T^2 + 8.0206 \times 10^{-12} T^3$$

where Δd is in % and T is in K.

3.3. Specific Heat

Specific heat was obtained from values provided by Timmermans [8] and is represented by

$$C_p = 2.4097 \times 10^{-1} + 3.0691 \times 10^{-3} T - 4.8131 \times 10^{-6} T^2 + 3.2482 \times 10^{-9} T^3 - 7.9996 \times 10^{-13} T^4$$

where C_p is in $J \cdot g^{-1} \cdot K^{-1}$ and T is in K.

3.4. Density ρ

Two different densities were obtained from measurements on three specimens (without the W layer), one specimen with 82.6% TD (3.43 $g \cdot cm^{-3}$) and two specimens, 87/A and 87/B, both with 87.0% TD (3.61 $g \cdot cm^{-3}$).

4. RESULTS AND DISCUSSION

When heating the specimens gradually by electron bombardment at the beginning of the measurements, desorption of gases from the pores (air, N_2,...) occurs. This leads to visible ionization phenomena and unstable measurements. After some 30 min, stable measurements are possible.

Figures 1 and 2 show the smoothed measured values of the thermal

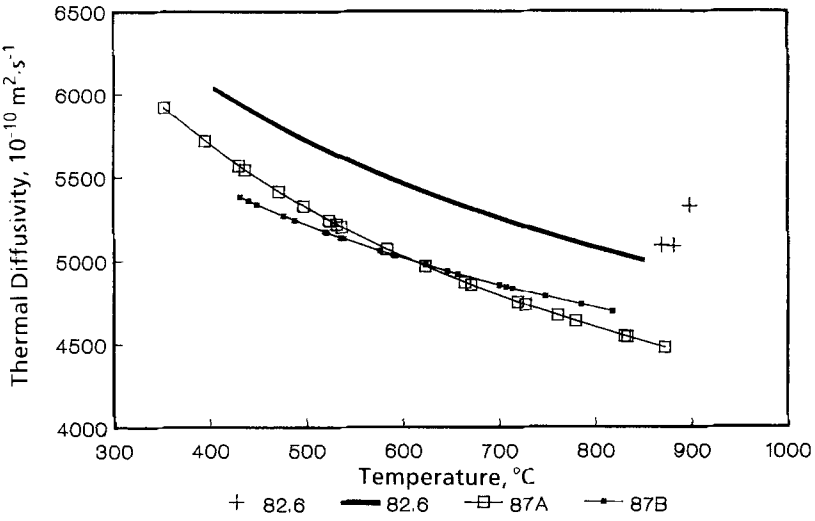

Fig. 1. Smoothed measured results of thermal diffusivity versus temperature for three specimens, one with 82.6% TD and two, 87A and 87B, with 87% TD. For the specimen with 82.6% TD the three real points measured above 850°C are also indicated as an illustration for the increase above that temperature.

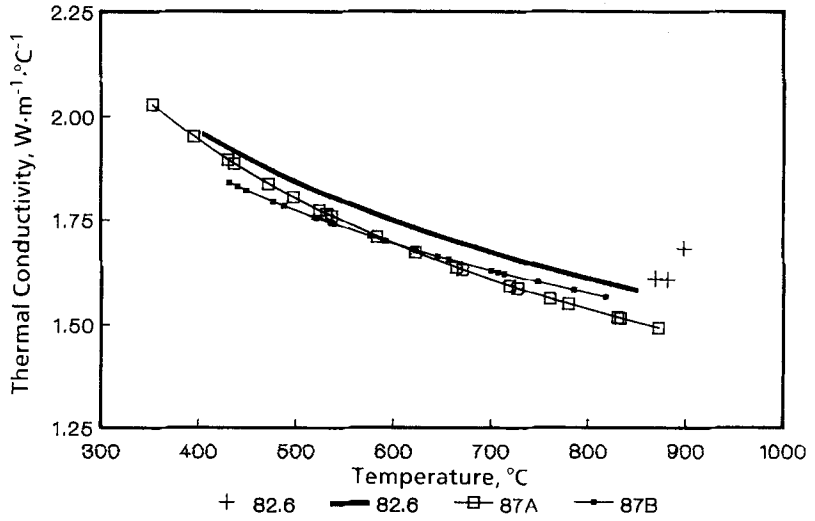

Fig. 2. Smoothed measured results of thermal conductivity versus temperature for three specimens, one with 82.6% TD and two, 87A and 87B, with 87% TD. For the specimen with 82.6% TD the three real points measured above 850°C are also indicated as an illustration for the increase above that temperature.

diffusivity and the thermal conductivity, respectively, for the three specimens. Scatter of the individual values is generally better than 5%. For specimens 87A and 87B the averaged measured points are also shown. For specimens 82.6, next to the smoothed curve three actual values measured above 850°C are also shown. Each specimen exhibits a nearly linear decrease with temperature of both the diffusivity and the conductivity up to roughly 850°C. At higher temperatures a leveling out or even a slight increase in the conductivity seems to occur, but here a certain hysteresis effect sets in. In order not to overload the figures this effect has not been shown. When the specimens are heated well above about 850°C both the diffusivity and the conductivity increase as a whole by some 10 to 20% and even more in the lower temperature range. This hysteresis effect is reversible as long as the specimens have not been heated above some 900°C. Above this temperature, generally diffusivity and conductivity still increase but the specimens are subject to an unpredictable behavior. Measurements become unfeasible due to the apparition of high instabilities. The fact that the sintering temperature is approached or possibly exceeded is most probably accountable for this. Also, it could be noticed that the tungsten layer covering the specimens disappeared for the largest part and, particularly, from the nonheated surface.

It can be remarked that the results for specimens 87A and 87B conform with each other in the temperature range considered. A relative difference of some 2.5% maximum is noticed. On the other hand, specimen 82.6 shows a value a few percent higher than that of the 87A or B specimens, although an approximately 5% lower value was to be expected in view of the lower density. This cannot be explained readily but could be due to a different microstructure.

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