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Infrared transmission of sintered 3 mol% Y_2O_3–ZrO_2 gel

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Translucent ZrO_2 film was successfully prepared by gelling hydrothermally produced nano-ZrO_2 powders. The film (300 μm thick) was found to transmit light to 6.5 μm (40% transmission) when sintered at 1200 °C, but transmission was totally lost after sintering at 1300 °C for 1 h. Residual organic material such as urea, which was used for preparing the powder, dominated the transmission of the film in the region between 1.3 and 4.5 μm when sintered below 1000 °C. When sintered above 1000 °C, the microstructure controlled the transmission. Both organic residuals and the microstructure of the zirconia were found to determine the transmission in 4.5–6.5 μm region.

1. Introduction

Zirconia has been used as a refractory for decades because of its high-temperature stability and superior corrosion resistance. The development of transformation-toughened high-strength zirconia has opened an area in advanced structural application [1]. In addition to high mechanical performance, zirconia can transmit light in the infrared region up to ~6 μm with a 1–2 mm thickness [2]. The properties which zirconia possesses, e.g. infrared transmission, high strength, high erosion/corrosion resistance and refractoriness, have made it an attractive candidate for infrared applications. For example, zirconia is used in the windows of infrared sensors operated under harsh mechanical and thermal environments [3].

Zirconia infrared window material can be prepared by using single-crystal zirconia, by pressureless sintering or by hot isostatic pressing zirconia polycrystals [4]. The single-crystal zirconia has excellent optical properties. However, it is very expensive and difficult to produce a larger piece of single-crystal zirconia [3]. It is also expensive to manufacture zirconia objects by hot isostatic pressing. Pressureless sintering is the most economical way to prepare zirconia and can produce objects with the least limitation in geometry. Yet, the sintered body will not be transparent if there are defects within it, such as pores and grain boundaries, due to severe light scattering. The transmission can be improved if the object is fully dense or consists of fine pore/grain size. The small pore size is beneficial for minimizing light scattering in the infrared region because the scattering efficiency is very size dependent. Recently, research has shown that hydrothermally synthesized ZrO_2 can be sintered to nearly full density below 1400 °C with a small grain size [5].

The purpose of this study was to investigate infrared transmission of sintered zirconia gel using infrared spectroscopy. The effect of the residual starting compounds used in hydrothermal synthesis of ZrO_2 powder on the infrared transmission was studied as a function of sintering temperature during the sintering process between 700 and 1300 °C. The change in the transmission of ZrO_2 in the mid-infrared (1–6.5 μm) region was correlated to the development in microstructure.

2. Experimental procedure

The nanocrystalline powder was prepared by a hydrothermal process using a high-pressure vessel equipped with heating furnace. A 30 ml solution containing 1.0 M zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$), 0.062 M yttrium chloride ($YCl_3 \cdot 6H_2O$) and 1.5 M urea ($(NH_2)_2CO$) was thoroughly mixed in a Pyrex glass tube and covered with a glass cap. The glass tube was then sealed in the pressure vessel. The vessel was heated to 250 ± 4 °C at ~20 MPa for 3 h. After heat treatment, the vessel was quenched in cold water and opened to take the powder (with solution) out. The powder aggregates were washed with excess hot water five times to remove chloride residue. The powder aggregates were put into a methanol solution and broken with an ultrasonic probe for 5 min. The solution was cast on to a Petri dish to form a film with a thickness of ~500 μm after drying in ambient for 4 weeks. The film was then heat treated at temperatures between 150 and 1300 °C for 1 h using a high-temperature furnace (heating rate $\simeq 15\,°C\,min^{-1}$). The IR spectra of sintered zirconia were analysed by Fourier transform–infrared spectroscopy (FT–IR, Perkin–Elmer, 1760-X). An X-ray diffractometer (XRD, Sintag, XDS-2000, copper radiation) and transmission electron microscope (TEM, Philip 430, 300 keV) were used to determine the crystal structure and size of the zirconia samples. The X-ray diffraction

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instrument broadening was corrected by using ZrO_2 sintered at 1500 °C, which had a size greater than 1 μm. An atomic force microscope (AFM, Nanoscope II, Digital Instruments) was also used to determine the grain size of the ZrO_2. Imaging was performed at a constant force mode using 200 μm Si_3N_4 cantilevers with integrated tips at a scan rate of 1.93 Hz. AFM photographs were taken to determine the average grain size of sintered ZrO_2 samples. A line plot image was used to determine the grain size of gelled ZrO_2.

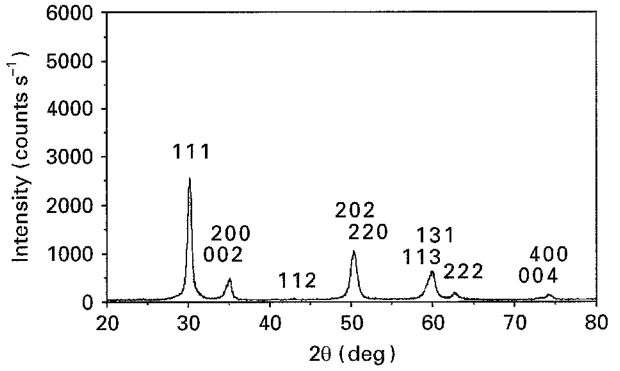

Figure 1 X-ray diffraction pattern of as-prepared ZrO_2 powders at 25 °C.

3. Results and discussion

The film was translucent after it dried. The XRD result showed that the film consisted of ZrO_2 crystallites other than the monoclinic phase. It was difficult to determine whether the ZrO_2 was tetragonal or cubic phase due to overlapping diffraction lines, such as (0 0 2) and (2 0 0), see Fig. 1. The crystal size for as-formed ZrO_2 determined by the (1 1 1) diffraction line using Scherer's and Warren's equation was ~20 nm. This was comparable to that obtained by TEM, 15–25 nm (see Fig. 2) and AFM ~25 nm, using the line plot image. The crystal size of ZrO_2 started to grow when sintered at 1100 °C and above, as revealed by the AFM shown in Fig. 2. The grain size increased from 25 nm to 50 and 90 nm when sintered at 1000 and 1200 °C for 1 h, respectively. The grain size

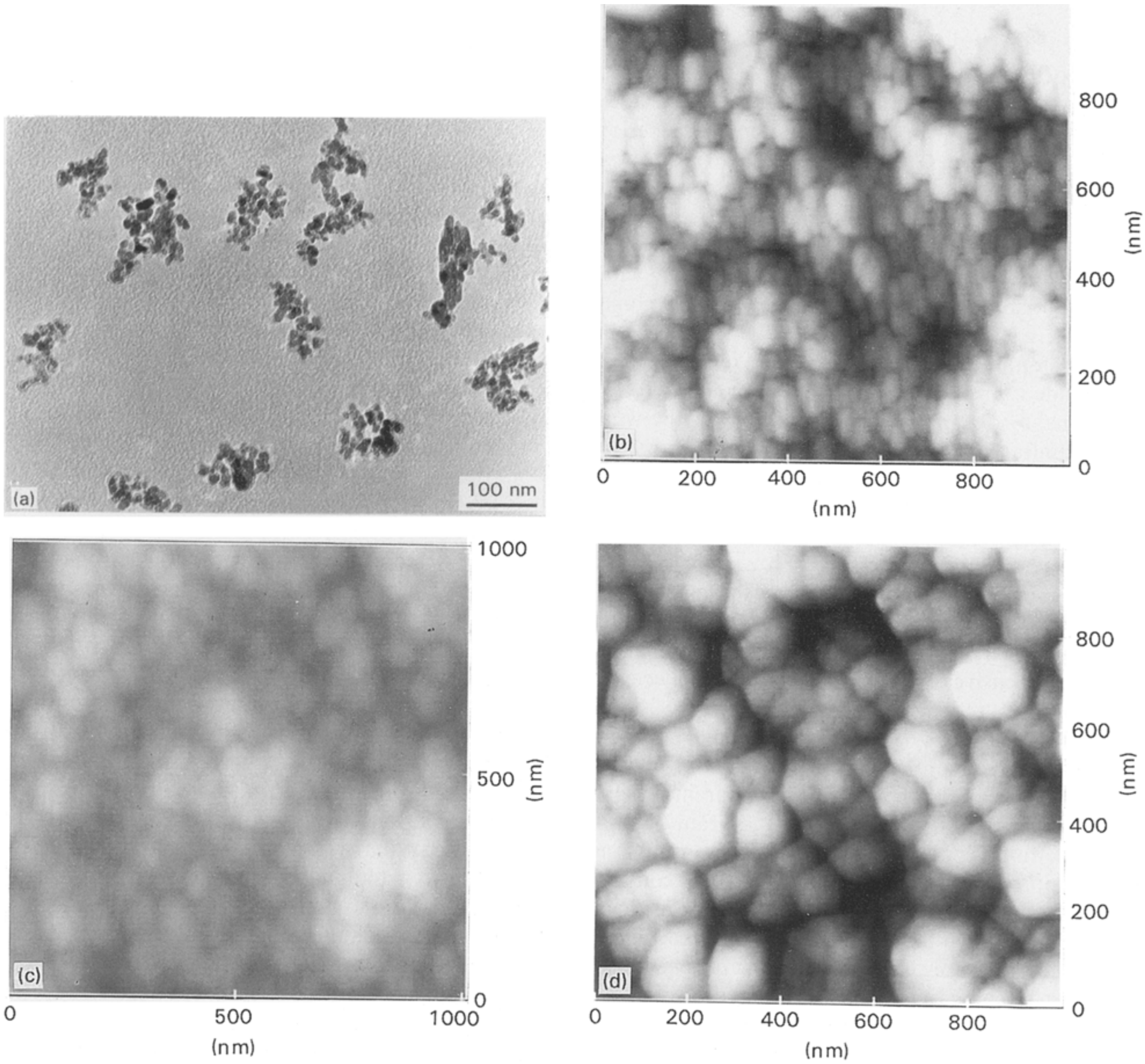

Figure 2 (a) Transmission electron micrograph of the as-prepared ZrO_2 powders, and AFM images of the film sintered at different temperatures: (b) 1000 °C, (c) 1100 °C, (d) 1200 °C and (e) 1300 °C.

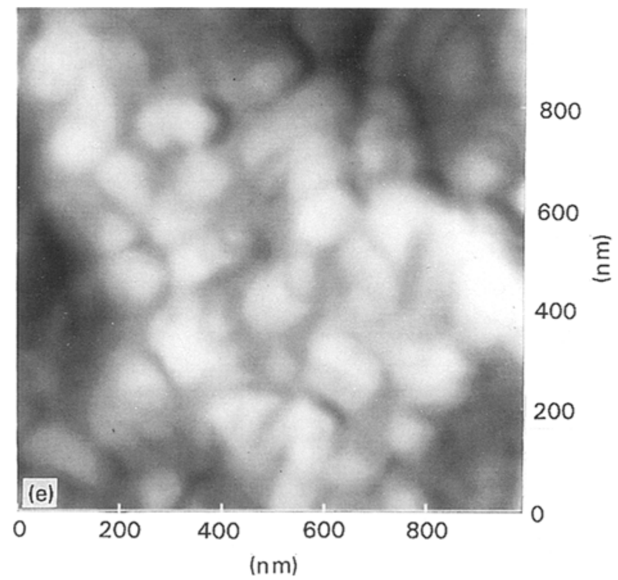

Figure 2 (continued).

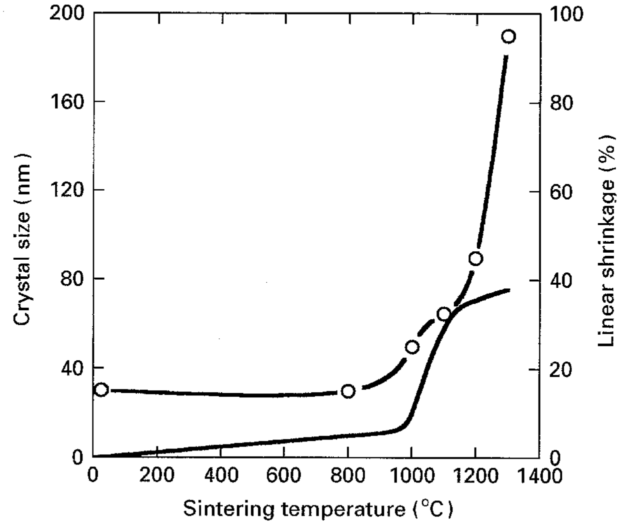

Figure 3 (○) Crystal size and (—) shrinkage of ZrO_2 film sintered at different temperatures.

increased to 190 nm after sintering at 1300 °C for 1 h. The onset of the shrinkage curve for sintering ZrO_2 began at 1000 °C which indicated the densification process started at this temperature, see Fig. 3.

Fig. 4 shows IR spectra of ZrO_2 film sintered at 700, 800, 900, 1000, 1100 and 1200 °C for 1 h. The cut-off wavelength for the ZrO_2 appeared around 7 μm. The absorption bands at 1.39, 1.88, 3.0 and 6.1 μm were due to the presence of molecular water or a hydroxyl group. The 1.39 and 1.88 μm absorption peaks were probably due to hydrogen-bonded H_2O. The peak intensity at 1.88 μm decreased after being treated at 150 °C which indicated a loss of surface water at this temperature. The peak intensity did not change until the sintering temperature was above 700 °C. Both the 1.38 and 1.88 μm peak intensities started to decrease at 800 °C which meant the tightly bonded water started to evaporate significantly and vanished at temperatures above 1000 °C, as shown in Figs 5 and 6. A sintering temperature as high as 1000 °C was required to remove the H_2O in ZrO_2 similar to the case of SiO_2 gel [6]. The strong absorption band appearing at 3 μm was mainly due to the combination of OH dimer, molecular water, intramolecular H-bond OH groups and residues of urea or its dissociation products, i.e. $H_2N–C=O$ and $H^+N–C=O$. Water, $–NH_2$ and $=N–C=O$ were also responsible for the absorption band appearing at 6.1 μm [7]. The 6.1 μm band decreased as the sintering temperature increased which was parallel to the diminishing of the 3 μm band. The 3 μm band completely disappeared

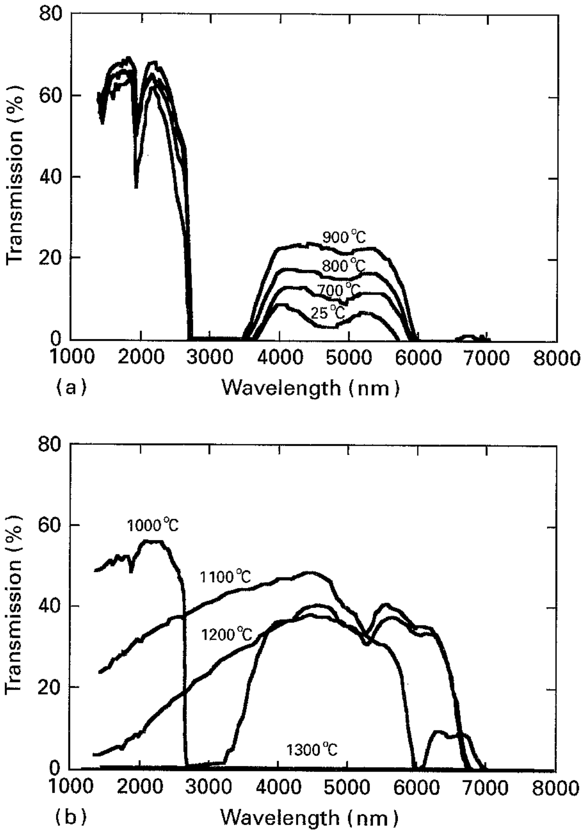

Figure 4 (a, b) Infrared spectra of as-prepared ZrO_2 film, and films sintered from 700–1300 °C.

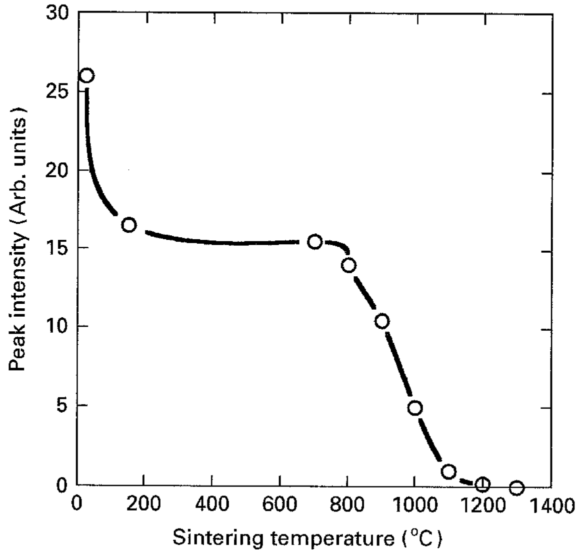

Figure 5 Effect of sintering temperature on the absorption peak intensity at 1.88 μm for ZrO_2 film.

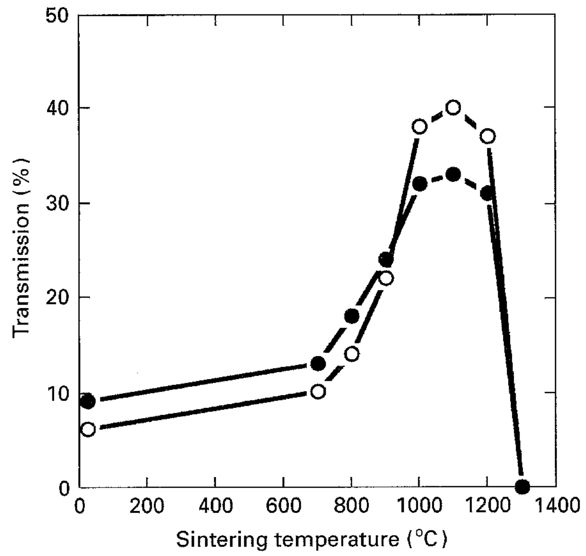

Figure 6 Effect of sintering temperature on the transmission at (○) 4.9 and (●) 5.3 µm for ZrO_2 film.

when the ZrO_2 was sintered at 1100 °C (Fig. 4). The 6.1 µm band existed until sintered at 1300 °C. The absorption band at 6.1 µm for samples sintered above 1000 °C was attributed to the urea-related species such as =N–C=O because no water absorption (3 µm band) was observed. The absorption bands at 4.9 and 5.3 µm were probably caused by the N^+–H group. These bands decreased in intensity with increasing sintering temperature and existed up to 1200 °C, see Fig. 4. There was no absorption between 1.3 and 4.5 µm after sintering between 1000 and 1300 °C. The transmission in the 1.3–4.5 µm region decreased with increasing sintering temperature above 1000 °C and vanished when the film was sintered at 1300 °C. The transmission in this region increased monotonically with wavelength when the sintering temperature was above 1000 °C. The transmission decreased with increasing wavelength when the wavelength was longer than 4.5 µm.

There are two mechanisms involved which determine the transmission of the film in this region (1–7 µm). First, the residual organic functional groups which have absorption bands in the region will decrease the transmission. The transmission will increase when the sintering temperature is high enough to decompose or evaporate the organic materials. Secondly, the microstructural features present in the ZrO_2, such as pores and grain boundaries, will scatter light and thus decrease the transmission of the film. For a ceramic system consisting of very small crystal size, e.g. nanosized, there will be a considerable amount of grain-boundary volume. In this case, the system may be considered as a composite in which pores and ZrO_2 crystals are embedded within a continuous amorphous grain-boundary matrix. These pores and crystals serve as scattering sources because they have refractive indices different from that of the grain-boundary matrix. The size effects of pores or crystals on the transmission of the light can be described in terms of a size parameter, x, i.e. $x = 2\pi R/\lambda$, where R is the equivalent radius of the pore or crystal and λ is the wavelength. The scattering efficiency is proportional to x^4 when Mie scattering is applied as shown by Equation 1 [8]

$$Q_{\mathrm{SCA}} = 8/3x^4|m^2 - 1/m^2 + 2|^2 \qquad (1)$$

where $m = n_{\mathrm{pore}}/n_{\mathrm{gb}}$ or $m = n_{\mathrm{ZrO_2}}/n_{\mathrm{gb}}$ and n is the refractive index. The transmission can be expressed as below [9]

$$I = I_o\exp(-3Q_{\mathrm{SCA}}Vx/4r) \qquad (2)$$

where V is the volume fraction of the pores or crystalline phase. The transmission at $\lambda = 1.7$ and 2.1 µm where no organic absorption occurred, does not change significantly (only less than 10%) when sintered below 1000 °C.

The transmission decreased 20% when sintered at 1100 °C, and 40% after sintering at 1200 °C. This was due to slight densification or grain growth for ZrO_2 sintered below 1000 °C and the effect of the microstructure change was minimized. The difference in transmission between samples sintered from 600–1000 °C was due to a change in organic concentration in the film after sintering. However, the transmission started to decrease when the sintering temperature was over 1000 °C where the ZrO_2 crystals started to grow and coalescence of the pores occurred, which increased pore size in the ZrO_2. Both the increase in pore size and the crystal size caused increased scattering and reduced the transmission. Another reason for the reduction of this transmission was that the volume fraction of the grain-boundary phase decreased because of increasing crystal size when sintered above 1000 °C. This is shown by Equation 2 when the increased volume of a crystalline phase decreases the transmission.

For ZrO_2 sintered at 1100 and 1200 °C, the transmission increased with increasing wavelengths between 1.3 and 4.5 µm. This was because the size parameter was inversely proportional to the wavelength. The scattering efficiency was smaller when the wavelength increased, resulting in an increased transmission (to about 4.5 µm) as described in Equation 2. The transmission of the film was again controlled by the absorption from residual organic material such as N^+–H functional groups between 4.5 and 6.5 µm, which lowered the transmission.

4. Conclusion

Translucent ZrO_2 film was successfully prepared by sintering hydrothermally produced ZrO_2 powder gel. The transmission of sintered ZrO_2 film in the infrared region (1.3–7 µm) depended on the sintering temperature and wavelength. The sintering temperature determined the amount of residue or decomposed organic starting materials which affected the transmission by their characteristic absorption bands. The variation in microstructure features such as crystal size, pore size and the volume of grain-boundary phase and pores which cause scattering, can be related to the wavelength-dependent transmission. The absorption mechanism dominated the transmission of the film when sintered below 1000 °C in all wavelengths, while microstructure features controlled the transmission in the 1.3–4.5 μm region when sintered above 1000 °C. The size parameter, which decreased with increasing wavelength, was responsible for the wavelength-dependent transmission in this region when ZrO_2 film was sintered at 1100 °C or above. Absorption from the residual organic material was responsible for the lowered transmission of the film in the region from 4.5–6.5 μm.

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