Electronic Supplementary Material (ESI) for CrystEngComm

SUPPLEMENTARY INFORMATION

Ordered Coalescence of Nano-Crystals during Rapid Solidification of Ceramic Melts

Daniel Grüner[a] and Zhijian Shen*[a]

[a] *Department of Materials and Environmental Chemistry, Arrhenius Laboratory, Stockholm University, 10691 Stockholm, Sweden. Fax: +46 8 152187; Tel: +46 8 162388; E-mail: shen@mmk.su.se*

EXPERIMENTAL METHODS

1. Materials

Dense aluminosilicate-zirconia beads of approximately 125 μm diameter and overall chemical composition of 60-70% ZrO_2, 28-33% SiO_2 and less than 10% Al_2O_3 were used as precursors. The ceramic beads were prepared by a gas atomization process in which the ceramic melt was gas atomized through a nozzle forming melt droplets that were further rapidly solidified in a water bath.

2. Laser sintering

An Yb-fiber laser with 1060-1100 nm wave length and a focused beam diameter of approximately 100 μm was applied. The laser has a maximum power of 200 W, but it turned out that it is sufficient to apply 50 W at an exposure speed of ≤ 7000 mm/s to melt the targeted aluminosilicate-zirconia beads. From the melting features we estimate that the peak temperature exceeds the melting point of zirconia (2715°C).

3. Microstructure characterization

Fracture surfaces and natural surfaces of the laser-sintered bodies were studied using a JSM-7000F (JEOL, Tokyo, Japan) field emission scanning electron microscope. For more detailed studies of the microstructure, thin foils for transmission electron microscopy (TEM) were prepared. Approximately 0.5 mm × 2.5 mm wide and 0.3 mm thick pieces were cut from the bulk material using a low-speed saw equipped with a diamond wafering blade (Buehler, Lake Bluff, IL, USA), ground to 0.1 mm thickness using diamond abrasives fixed on polymer sheets, and ion-milled to electron transparency using a JEOL IS-09100 ion slicer operated at 5 kV. TEM images were obtained using a JEOL JEM-3010 TEM operated at 300 kV and recorded using a KeenView CCD camera (Olympus Soft Imaging Systems, Münster, Germany). A JEOL JEM-2100 TEM was used to record EDX spectra at 200 kV accelerating voltage.

SUPPORTING DATA

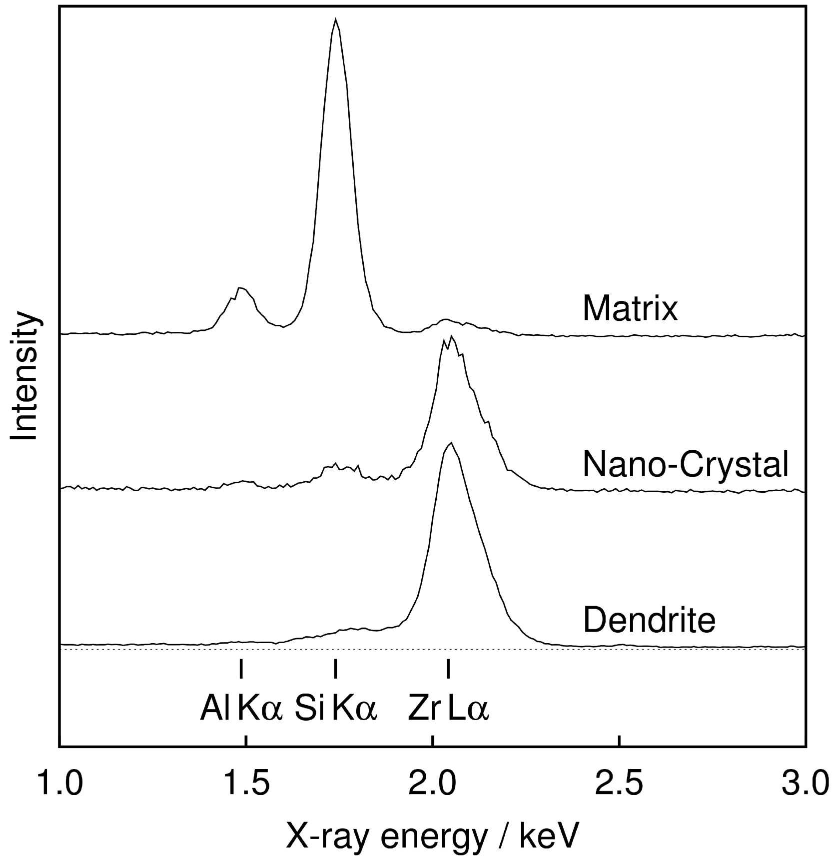

Figure S1. EDS spectra of regions of the TEM foil containing a dendritic crystal, an isolated nano-crystal and the glass matrix. While dendritic crystals and nano-crystals are composed of almost pure ZrO_2, the matrix is essentially free from zirconia and comprises mainly silica and a minor amount of alumina.

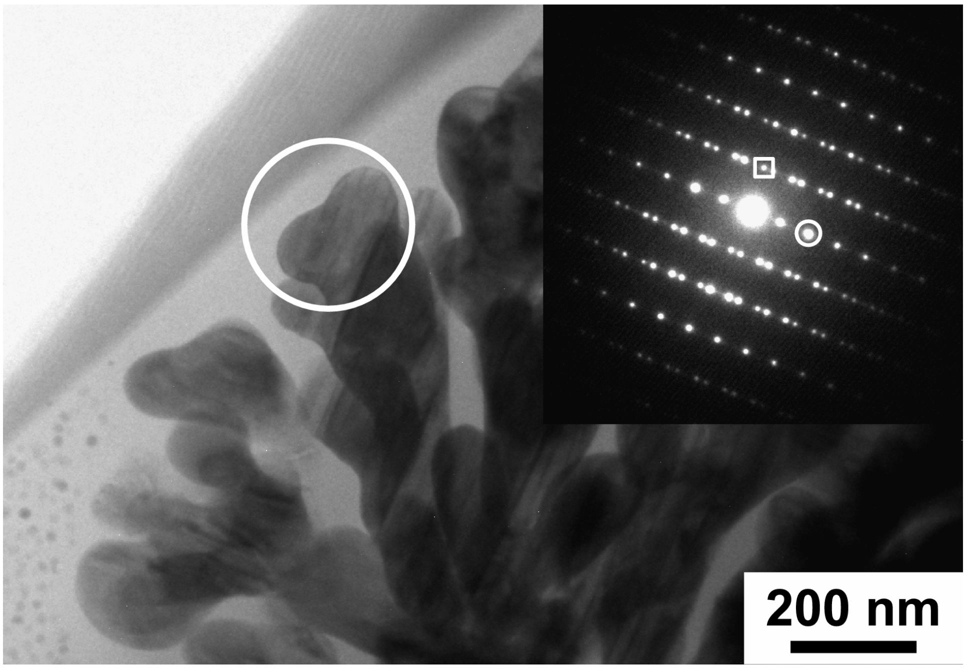

Figure S2. Dendritic zirconia crystals frequently show a banded contrast in bright field TEM images due to polysynthetic twinning on the (100) plane, which is confirmed by inspecting the selected area electron diffraction pattern (inset) taken along [011] from the region inside the circle. The reflections marked with a circle and a square are indexed 200 and 01-1 (twin component 1), respectively.

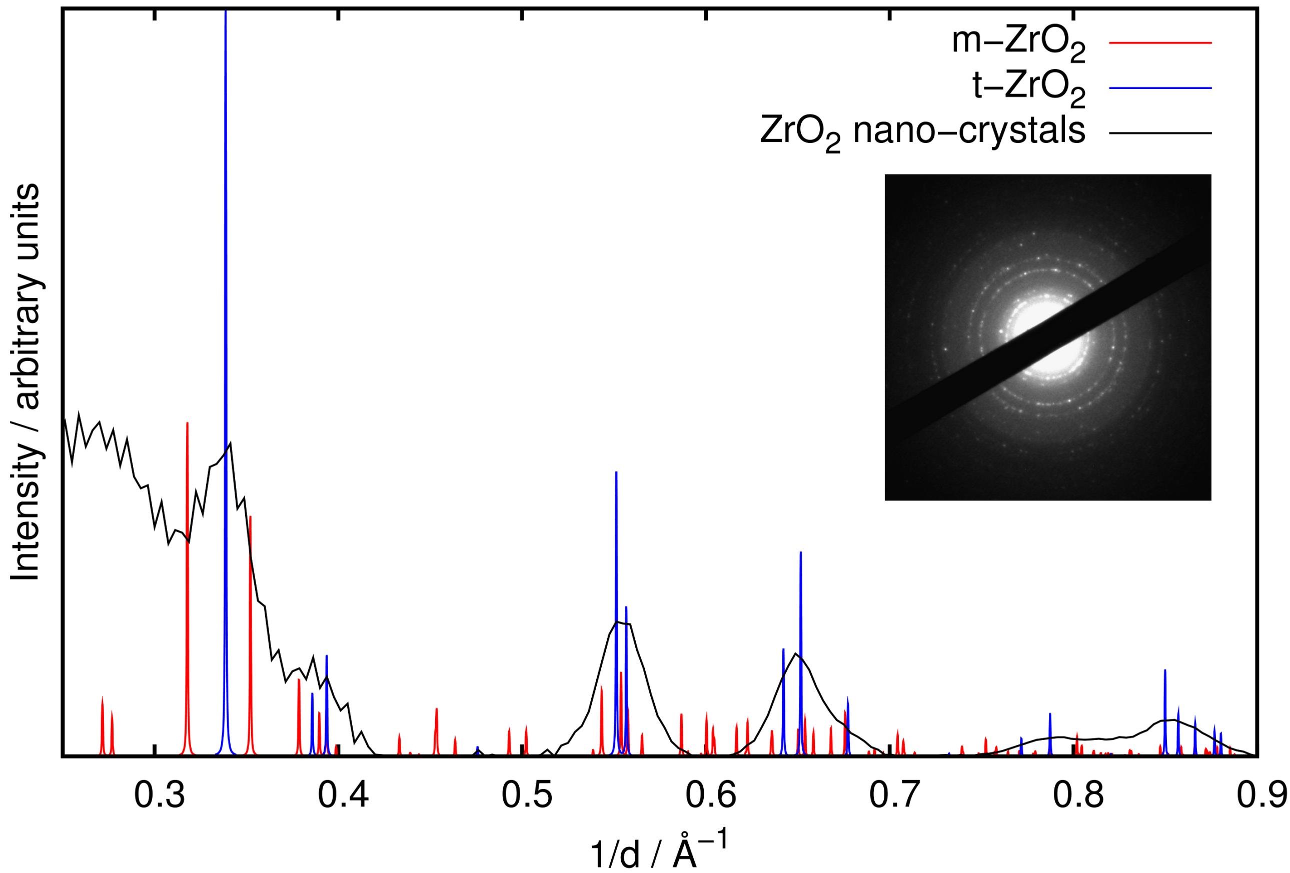

Figure S3. The inset shows a selected area electron diffraction pattern of a region of the laser sintered aluminosilicate-zirconia composite body containing zirconia nano-crystals embedded in an amorphous aluminosilicate matrix. The diffraction pattern shows rings of intensity from the randomly oriented nano-crystals. The intensity in the rings has been integrated using the program ELD (Zou, X. D.; Y. Sukharev, Y.; Hovmöller, S. *Ultramicroscopy* 1993, **49**, 147-158) and plotted as a function of 1/*d*. The observed peak positions match the calculated ones for tetragonal zirconia (blue), but not for monoclinic zirconia (red).