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Metastable phase diagram of nanocrystalline ZrO_2-Sc_2O_3 solid solutions. Effect of varying average crystallite size

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Abstract – We have investigated the relevant features of the metastable phase diagrams of homogeneous ZrO_2-Sc_2O_3 solid solutions, composed of nanocrystals with varying average sizes ranging from 10 up to 100 nm. We have established that the presence of the observed phases and their composition and temperature boundaries strongly depend on the average nanocrystallite size.

Because of their high ionic conductivity, ZrO_2-Sc_2O_3 ceramics are considered as promising candidates for electrolytes of solid-oxide fuel cells. Since ion transport is closely related to the nature of the crystal structure, it is worth to investigate the relevant features of the stable and metastable phases of ZrO_2-Sc_2O_3, and the transitions between them. Depending on composition and temperature, several polymorphs with monoclinic, tetragonal, cubic or rhombohedral symmetries were previously observed in ZrO_2-Sc_2O_3 solid solutions. Since these phases were not previously reported for any other ZrO_2-based systems, the existence of rhombohedral phases, such as β, γ and δ, seems to be a particular feature of ZrO_2-Sc_2O_3 materials [1,2].

The tetragonal phase of ZrO_2-based materials may exhibit three forms, namely t, t' and t'' [1]. The stable tetragonal form is named as t-form. The t'-form has a wider solubility, but is unstable in comparison to the mixture of t-form and cubic phase. Finally, the t''-form has an axial ratio, *c/a*, of unity but with oxygen atoms displaced along the c axis from their ideal sites of the cubic (fluorite type) phase. The mentioned tetragonal forms have been reported in the literature for other compositionally homogeneous ZrO_2-based solid solutions, these phases gradually transforming to the cubic phase for increasing dopant content. However, in ZrO_2-Sc_2O_3 solid solutions, the t''-form was not detected in compositionally homogeneous materials with large average crystallite sizes. For these solid solutions, the rhombohedral β-phase is retained within the compositional range over which other ZrO_2-based solid solutions exhibit the t''-form [1]. We have recently determined the metastable phase diagram of nanocrystalline ZrO_2-Sc_2O_3 solid solutions [3]. This phase diagram appears to be very different from that previously proposed for the same solid solution composed of much larger crystallites, exhibiting the t”-form for small average crystallite sizes.

The aim of the present work is to determine the variations in the metastable phase diagram of nanostructured ZrO_2-Sc_2O_3 solid solutions with varying crystallite size. We investigate the composition and temperature range over which metastable phases are retained in ZrO_2-Sc_2O_3 nanopowders, with crystallite sizes ranging from 10 up to 100 nm, and Sc_2O_3 content ranging from 10 to 14 mol%. The structures of the detected phases were characterized by synchrotron X-ray powder diffraction (XPD).

Our results at room temperature confirm that the phases retained in ZrO_2-Sc_2O_3 solid solutions composed of relatively large nanocrystallites (50-100 nm) are analogous to those previously determined by other authors for samples with much coarser crystallites [1]. Differently, the t''-form or cubic phase is fully retained in samples composed of very small crystallites, with sizes ranging from 10 nm up to a critical size of about 35 nm. This information allowed us to build up a composition-crystallite size phase diagram of nanocrystalline ZrO_2-Sc_2O_3. For increasing average crystallite sizes, the system gradually transforms from a single phase (t'' tetragonal form or cubic phase) towards a mixture of two phases (cubic+β or γ+β). Phase content and structural parameters of each phase were determined by applying Rietveld refinements.

Phase transitions of nanocrystalline ZrO_2-Sc_2O_3 solid solutions at high temperatures (from 25 up to 900°C) were also investigated by in-situ XPD. Nanopowders with average crystallite sizes higher than 30-35 nm exhibit phase transitions from β or γ phases to t''-form or cubic phase depending on Sc_2O_3 content ranging from 10 to 14 mol%. The transition temperatures depend on both, average crystallite size and Sc_2O_3 content. These phase transitions studied on cooling and on heating exhibit a hysteretic behavior.

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