

We have determined the phase diagram of nanopowdered ZrO_2 containing 10 to 14 mol% Sc_2O_3 with average crystallite sizes ranging from 30 nm up to 100 nm by X-ray powder diffraction, using the D10B-XPD synchrotron beam line of LNLS (Campinas, Brazil). Our study shows that the boundaries of c or t' , β and γ phases strongly depend on both, Sc_2O_3 content and crystallite size. The transition temperatures related to cooling and heating processes decrease for decreasing crystallite sizes. In addition, the experimental results corresponding to a whole heating/cooling cycle indicate the presence of a clear hysteresis effect.

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Synchrotron XRD and XAS studies of nanocrystalline ZrO_2 - Y_2O_3 solid solutions

Ismael Fábregas,^a Noemi Walsøe de Reca,^a Diego Lamas,^b Aldo Craievich,^c Marcia Fantini,^c ^a*CINSO (Solid State Research Centre), CONICET.* ^b*Laboratorio de Caracterización de Materiales, Universidad Nacional del Comahue, (Argentina).* ^c*Instituto de Física, Universidade de São Paulo, (Brazil).* E-mail: Ismaelfabregas@gmail.com

Because of their excellent mechanical and electrical properties, zirconia-yttria (ZrO_2 - Y_2O_3) solid solutions are being widely investigated, in particular because it is a potential candidate to be used as electrolyte in solid state oxide fuel cells. An important analysis of these material properties is related to their dependence on nanoscopic scale and composition.

The crystallographic structure and short range order of a series of nanocrystalline ZrO_2 - Y_2O_3 solid solutions with varying Y_2O_3 content was studied by synchrotron radiation X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). Powdered samples were synthesized by a pH-controlled nitrate-glycine gel-combustion process. Our XRD results indicate the presence of the t' -form of the tetragonal phase ($c/a > 1$) in samples with up to 8 mol% Y_2O_3 , and the t'' -form ($c/a = 1$) for 10 mol% Y_2O_3 . Notice that in the t'' -form the oxygen anions are displaced from their ideal positions in the fluorite type structure of the cubic phase. For solid solutions with Y_2O_3 contents higher than 11 mol% the cubic phase is observed. The t'/t'' and t'' /cubic compositional boundaries were determined to be at (9 ± 1) and (10.5 ± 0.5) mol% Y_2O_3 , respectively. These composition limits agree well with those reported by Yashima et al [1] for materials composed of larger (micrometric) crystallites synthesized by arc melting followed by a rapid quenching. The c/a ratios of the t' -form determined for the nanostructured polycrystals studied here are slightly smaller than those determined by Yashima et al.[1] for powders composed of larger (micrometric) crystallites.

A complementary XAS study of the same ZrO_2 - Y_2O_3 solid solutions near the absorption edges of Zr and Y demonstrated that the t'' /cubic transition is related to a tetragonal-to-cubic symmetry change of the first oxygen coordination shell around Zr atoms, without any significant changes in the environment of Y atoms.

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Large anharmonicity in end members of $AgPb_mSbTe_{2+m}$

Sofie Kastbjerg, Mogens Christensen, Martin Søndergaard, Bo Brummerstedt Iversen. *Center for Materials Crystallography, Department of Chemistry and iNANO center, Aarhus University (Denmark).* E-mail: sofie@inano.dk

Thermoelectric materials are functional materials with the ability to interconvert electrical and thermal energy, which make them applicable in active cooling and power generation through exploitation of waste heat. The thermoelectric figure of merit, zT , is optimized in materials with low thermal conductivity, low electric resistivity and high thermopower. The solid solution of $AgPb_mSbTe_{2+m}$, also known as LAST (Lead-Antimony-Silver-Tellurium), has in recent years been intensively investigated due to their promising thermoelectric properties. Several of the available commercial thermoelectric modules are based on the LAST compounds. The materials are power generators used in space crafts, military applications and pacemakers. The end member compounds $AgSbTe_2$ ($m = 0$) and $PbTe$ ($m = \infty$) have been reported to have extremely low lattice thermal conductivities of 0.63 and 2.4 W/mK, respectively.[1] The value for $AgSbTe_2$ is close to the minimum possible value. To understand and explain these physical properties of the advanced crystallographic studies have been performed.

Both $AgSbTe_2$ and $PbTe$ are semiconducting ionic compounds crystallizing with the rocksalt structure in the cubic space group $Fm-3m$. Multi-temperature synchrotron powder diffraction data between 90 and 1000 K have been measured at Spring8 at a wavelength of $\lambda = 0.50007 \text{ \AA}$ and subsequently Rietveld refined. The refined unit cell axes show near linear thermal expansion and the refined atomic displacement parameters have been modeled using the Debye model. Furthermore, the Rietveld refinements indicate structural disorder in the rocksalt structure. The disorder partly explains the low thermal conductivities.

An additional effect lowering the thermal conductivities is large anharmonicity of the chemical bonds in the crystals, revealed by high Grüneisen parameters of 2.0 and 1.5 for $AgSbTe_2$ and $PbTe$, respectively.[1] It is believed that anharmonicity of the chemical bonds drives the phonon-phonon umklapp and normal processes that intrinsically limits the high temperature lattice thermal conductivity.[2] The anharmonicity have been investigated through high and low temperature high-resolution neutron single crystal diffraction data obtained at the Lujan Center, Los Alamos National Laboratory. From these data the nuclear density and anharmonicity are refined using Gram-Charlier coefficients and from the low and high temperature refinements the positional disorder and the anharmonicity of the atoms can be separated.

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