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Atomic Scale Studies of Dynamics and Structure of Technologically Significant Oxides.

Overview

Experimental data was collected to elucidate the structural development of several nanocrystalline oxides. Comprehensive data sets combining multinuclear magnetic resonance and X-ray absorption edge (mainly EXAFS) were collected for sol-gel produced MgO and ZrO_2, and in addition EXAFS data was also collected for strontium-doped La_2O_3 and doped SnO_2. The combination of probe techniques is of key importance to being able to accurately and more unambiguously understand the complex structural changes that occur in these poorly crystalline materials. A high temperature NMR probe for ^{17}O observation was constructed and this allowed *in situ* observation of structural alteration (e.g. dehydroxylation) and collection of NMR relaxation times to help understand oxygen ion motion. The NMR technique was developed to provide better characterisation of the defect structure of these materials. ^{17}O NMR provided crucial information emphasising the increasing role this technique is playing in understanding the solid-state chemistry of oxide materials.

Experimental Developments.

- A novel optically heated NMR probe was developed that operates up to 1100^{o}C. The probe is easy to construct and use with for example good high temperature stability.

- The optimum conditions for observing hydroxyl species with ^{17}O solid state NMR in sol-gel produced materials were elucidated. A surprisingly wide range of NMR parameters were found such as C_Q between ~0 and 7 MHz and T_1 as short as 0.1 ms.

- A new two-dimensional separated local field NMR experiment was developed for characterising the local structure which determines the quadrupolar and dipolar tensors, and their relative orientation at the oxygen site which is sensitive to changes in alignment of the tensors as small as ~ 5^o.

- ^{17}O NMR spectra revealed bulk, surface, defect and hydroxyl sites in the same sample, providing information about medium-range order.

Materials Information.

- For MgO nanocrystals EXAFS and ^{17}O NMR showed the nanocrystals to be quite well ordered but with defects (associated with residual organic species) that are gradually removed with extended heat treatment.

- As an amorphous ZrO_2 gel is heated the ^{17}O NMR and EXAFS both indicate that the structure remains monoclinic-like right up to crystallisation. Crystallisation is associated with the removal of the final organic fragments and that well beyond crystallisation significant hydroxyl-content remains (e.g. at 500^{o}C $ZrO_{1.76}(OH)_{0.48}$ is a more accurate description of the sample studied here).

- Dopants in ZrO_2 and SnO_2 had little effect on the initial crystallisation temperature and crystallite size but slowed subsequent crystallite growth.

- Nanocrystalline SnO_2 with up to 10 mol% Fe^{3+} or Cu^{2+} has dopants residing on the Sn^{4+} site with heating caused migration of the dopants to the surface.

- For strontium-doped La_2O_3 there is a random distribution of dopant ions at low concentrations but they cluster at higher concentrations.