

IN SITU STRUCTURAL STUDY OF CERAMIC MATERIALS BY HIGH-TEMPERATURE NEUTRON AND HIGH-RESOLUTION SYNCHROTRON X-RAY POWDER DIFFRACTION TECHNIQUES

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We have developed high-temperature techniques to measure *in situ* neutron powder diffraction and synchrotron x-ray powder diffraction. The new furnace for high-temperature neutron diffraction study does not yield any extra peaks due to heaters and refractory, thus we are able to easily measure very small neutron peaks from the sample. Quality neutron-diffraction data at high temperatures up to 1600°C were analyzed by Rietveld method for various materials as calcium titanate, yttrium tantalate and silicon nitride. The tilting of Ti-O octahedra was found to be the key to understand the phase transitions in the calcium titanate. The high-resolution synchrotron X-ray diffraction enabled to determine exactly the unit-cell parameters around a phase transition point and the phase transition temperatures of perovskite-related materials as A-site deficient lanthanum titanate and barium titanate. The axial ratio b/a of orthorhombic lanthanum titanate continuously decreased with an increase of temperature.

Keywords: HIGH TEMPERATURE NEUTRON DIFFRACTION HIGH TEMPERATURE SYNCHROTRON X-RAY DIFFRACTION PHASE TRANSITION

NEW GAS HYDRATE STRUCTURES

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The clathrate hydrates are model systems for the study of repulsive hydrophobic interactions between their host water molecules and the guest gas atoms or molecules. High-pressure studies provide a means to vary the guest-host distances and are thus a powerful tool to explore such interactions. In addition, gas hydrates are commonly found in nature and their high-pressure properties are directly relevant to modeling of the Earth and other planets and satellites. Until recently, very little information was available on the high-pressure structures of gas hydrates.

Using both neutron and synchrotron x-ray techniques, we have now explored the high-pressure structures of a number of gas clathrate hydrates. Work on methane hydrate has revealed that rather than decomposing into ice and methane as had been predicted, methane clathrate hydrate forms a new hexagonal hydrate with a 3.5(5):1 water methane ratio at 0.8 GPa. This hydrate undergoes further transformation to a dihydrate at 1.9 GPa, which remains stable up to at least 10 GPa. The existence of these transitions has important consequences for modeling of Saturn's moon Titan and the origins of its atmospheric methane. And methane dihydrate, which has a water network related to that of ice Ih, provides a simple system to explore water methane interactions in a new density regime. Recent studies of nitrogen and argon hydrates reveal similar behavior but with different structural systematics, which will be discussed.

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HIGH TEMPERATURE POLYMORPHISM OF Pr METAL: POSSIBLE DISORDERED POLYTYPE STRUCTURE

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The crystal structures of trivalent rare earth (RE) metals show several stacking variants (hcp, dhcp, fcc, 9R), which have been reported to vary either with atomic number or with pressure. Although further investigations completed the classification at room temperature and high pressure, only few observations have been made at high temperature where structure changes exist for most of RE metals. The clear tendency towards polytypism in RE metals has led to the formulation of a reordering mechanism for dhcp-fcc phase transition [1], and the phenomenological consideration predicts the existence of a disordered phase in Pr on the temperature axis of the phase diagram [2]. It was shown also, in the framework of statistical-mechanical theory that the constrained form of disordered stacking could be a ground state of a polytype [3]. The high-temperature region neighboring the dhcp-fcc hysteresis domain on phase diagram of Pr metal is unexplored in detail, and no structural data are available on this transition at ambient pressure. In this paper, we report results of a high-resolution synchrotron diffraction study of Pr metal in the temperature range from room temperature to melting point. Depending on experimental conditions, onset of different stable polytypes was observed in the intermediate region of temperatures between the dhcp and fcc domains.

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PHASE TRANSITIONS IN Al-44at%Zn AND Al-48at%Zn ALLOYS

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The equilibrium Al-Zn alloys are two-phase systems: A (Al-rich fcc) and B (Zn-rich hcp). Precipitation and dissolution phenomena and phase transitions in alloys, having variable Zn content and subjected to different thermal treatments, were studied by XRD (S.Popovic, B.Grzeta, Croat.Chem.Acta 72(1999)621-643). The title alloys were: (i) quenched from the solid solution temperature, T_{ss}, in water at RT (samples WQ); (ii) slowly cooled from T_{ss} to RT (samples SC). SC was closer to equilibrium than WQ, the latter having residual strains, quenched-in vacancies and a non-uniform distribution of B grains. Microstructure of SC depended on temperature in a different way than that of WQ, during slow heating from RT to T_{ss}. B exhibited an anisotropy in thermal expansion and a change in the grain shape. Above 500 K a partial dissolution of B in A and above 560 K a partial transition of B and A into the A1 (fcc) phase took place. The solid solution, Ass, was formed above 700 K for SC and above 880 K for WQ. During slow cooling to RT, SC and WQ behaved in a similar way and a delay of phase transitions was observed. Instead of transitions according to the phase diagram, A (M/B) + B - A1 + A (M/A1) - Ass, this sequence was found: A (M/B) + B - A1 + B + A (M/A1,B) - Ass. A similar behavior was observed for alloys, having 54 and 62 at% Zn.

Keywords: PHASE TRANSITIONS AL-ZN ALLOYS POWDER DIFFRACTION