CONFINEMENT-INDUCED STRUCTURAL CHANGES OF LITHIUM AND SODIUM IN NANO-POROUS SILICA GLASS

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At ambient conditions, all alkali metals have body-centered cubic structure. At low temperatures, lithium and sodium undergo martensitic transitions to closed-packed phases at 78 K and 35 K, respectively. Their structures are highly faulted but predominantly 9R for Li while in Na also a substantial fraction of HCP develops. At high pressure, Li and Na exhibit structural transitions to FCC at 6.9 GPa and at 65 GPa, respectively [1, 2].

Nanoporous systems increasingly serve as confining matrices to study the behaviour of constrained gases and liquids, since new physical phenomena arise due to the strong interaction at the interface and as a consequence of geometrical constraints. Concerning metals, only few low-melting elements in nanoporous environments were studied so far and, generally, a moderate decrease of the melting point (< 10 K) was observed in these systems.

Zero temperature calculations of the energies of Li and Na show that the differences between the BCC and close-packed structures are very small, *i.e.* of the order of 10^{-4} eV [3]. This strongly suggests that significant structural changes due to slight variations in the energy may occur. The possibility to introduce such changes by the way of geometrical confinement provides a motivation to investigate whether such changes may indeed be observed. In the present investigation, the structures of geometrically confined metallic Li and Na have been studied as a function of temperature.

Nanoporous silica glasses (Vycor and Gelsil) with an average pore size of 9.2 nm, 7.5 nm, 5.0 nm and 2.6 nm were charged with Na and Li by vaporization and melting techniques. The filling fractions in different samples varied depending on sample dimensions and experimental conditions.

Synchrotron radiation of 12 keV was used for powder diffraction measurements at the beamline KMC-2 at BESSY (Berlin). The sample surface was adjusted at the fixed angle of ~10° to the incident X-ray beam which had a cross section of 100 µm×500 µm. The measurements were done in a furnace with Be-windows evacuated to 10^{-6} mbar and covered a temperature range from ambient temperature up to 700°C.

Contrary to the bulk behaviour, at room temperature, both lithium and sodium were found to crystallize in close-packed structures (FCC, HCP, dHCP and 9R) inside the nanopores while the bulk BCC phase is completely absent. These results indicate an upward shift of the martensitic phase transition temperatures (see above) by more than 200 K due to geometrical confinement.

Very surprisingly, on heating, no melting was observed near the bulk melting temperatures (~98°C for Na, ~180°C for Li). Instead, well defined powder diffraction patterns indicating a fully crystalline structure was observed up to the highest temperatures investigated. It should be noted that no chemical reaction between the metals and the silica glass took place. The results provide strong evidence that the reduction of the geometrical dimensions in metallic systems may indeed have profound implications for the thermodynamic equilibrium structure.

The diffraction patterns mostly reveal the simultaneous presence of several close-packed structures. A strong diffuse background indicates the presence of a large concentration of stacking faults which is also reflected in variations of peak intensities and distorted peak shapes as compared to the bulk. Figure 1 shows a spectrum of Li at ambient temperature as an example.

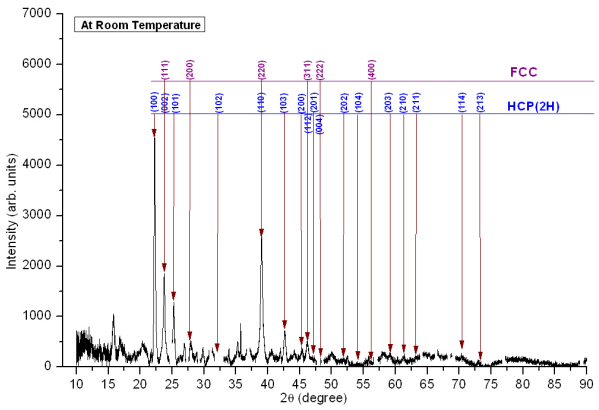

Figure 1. Powder diffraction pattern of Li in Vycor glass pores with an average size of 9.2 nm. The diffuse background has been subtracted and the Be peaks due to the furnace removed. The pattern is indexed with HCP and FCC peaks.

References

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