

## Stabilization of the superionic conducting phase of silver iodide by size and pressure effects

Enhancement of the performance and safety of batteries has been recently highlighted because of the widespread use of mobile electronic devices such as laptop computers and smartphones. At present, organic liquid electrolytes are generally used for batteries, and they have safety problems such as liquid spill and ignition. Although all-solid-state batteries, which contain solid electrolytes instead of organic liquids, have been actively investigated in order to overcome these problems, the ionic conductivity of solid electrolytes is generally lower than that of liquid electrolytes. Silver iodide (Agl) is known not only as one of the most traditional solid electrolytes but also as one of the fastest ionic conductors. Above 147°C, bulk AgI exists as the  $\alpha$ -phase, which shows very high Ag<sup>+</sup> conductivity of more than 1 S/cm owing to the sublattice melting of Ag<sup>+</sup>. Below 147°C, however, the  $\alpha$ -phase undergoes a structural phase transition to the poorly conducting  $\beta/\gamma$ -phases, limiting the application of AqI as a solid electrolyte. Various methods have been attempted to stabilize the  $\alpha$ -phase down to a lower temperature. For example, in bulk AgI, the phase transition temperature is decreased by applying a moderate pressure. It was reported that the  $\alpha$ -phase exists stably down to 100°C at 0.3 GPa [1]. In our previous studies, it was revealed that the phase transition temperature from the  $\alpha$ -phase to the  $\beta/\gamma$ -phases decreased with decreasing particle

size of AgI [2,3]. Although the  $\alpha$ -phase was stabilized down to 40°C in AgI nanoparticles with a diameter of 11 nm, there are still no reports on the stabilization of the  $\alpha$ -phase at room temperature. As reported here, we investigated the phase transition behavior of AgI nanoparticles under pressure through synchrotron powder X-ray diffraction (PXRD) and observed the stabilization of the  $\alpha$ -phase down to room temperature by a combination of pressure and size effects.

The AgI nanoparticles used in this work were prepared by liquid-phase synthesis in accordance with previous research [2]. Their mean diameter and size distribution were estimated to be  $11.4 \pm 4.5$  nm through transmission electron microscopy (TEM, Figs. 1(a) and 1(b)).

First, the phase transition behavior of the AgI nanoparticles under ambient pressure was investigated through variable-temperature PXRD measurements at SPring-8 **BL02B2** with synchrotron radiation of  $\lambda = 0.581$ Å. A powdered sample was loaded into 0.3 mm borosilicate glass capillaries, and the measurement temperature was controlled using a nitrogen gas flow. At the beginning of the measurement, it was indicated that the as-synthesized AgI nanoparticles consisted of  $\beta/\gamma$ -phases at ambient temperature and pressure (Fig. 1(c)). It should also be noted that the crystal sizes of the  $\beta$ - and  $\gamma$ -phases (13.4 and 10.2 nm, respectively) calculated using the



Fig. 1. (a) TEM image and (b) size distribution of the AgI nanoparticles. Variable-temperature synchrotron PXRD patterns for the AgI nanoparticles (c) at ambient pressure and (d) at 0.18 GPa. Blue and red curves denote PXRD patterns corresponding to only  $\beta/\gamma$ -phases and the  $\alpha$ -phase, respectively. Green curves correspond to a mixture of these phases [4].

Scherrer equation were in good agreement with the mean diameter determined by TEM observation. In the heating process, the AgI nanoparticles consisted of  $\beta/\gamma$ -phases up to 130°C, and the  $\beta/\gamma$ -phases gradually changed to the  $\alpha$ -phase between 150 and 190°C. In the cooling process, on the other hand, the  $\alpha$ -phase gradually changed to the  $\beta/\gamma$ -phases below 130°C, and the phase transition was completed at 20°C while a small amount of the  $\alpha$ -phase remained at 30°C. To determine the phase transition temperatures from the PXRD results, the fraction of the  $\alpha$ -phase at each temperature was calculated by Rietveld refinement of the PXRD patterns and is plotted against temperature in Fig. 2(a). By defining the phase transition temperature as the temperature at which the fraction of the  $\alpha$ -phase reaches 50%, the phase transition temperatures in the heating and cooling processes were estimated to be 162 and 39°C, respectively. These values are consistent with the phase transition temperatures determined from the onsets of peaks in differential scanning calorimetry (DSC) as shown in Fig.2(b).

Next, the phase transition behavior of the AgI nanoparticles under pressure was investigated through variable-temperature PXRD measurements at SPring-8 BL10XU with synchrotron radiation of  $\lambda = 0.497$  Å. A powdered sample was loaded into the hole of a rhenium gasket on a diamond anvil cell with sodium chloride as the pressure transmitting medium and pressure marker. The measurement pressure was controlled using a gas membrane and was calibrated using the equation of states of sodium chloride. The measurement temperature was controlled using an electric resistance heater on the cell. As shown in Fig. 1(d), in the heating process at 0.18 GPa, the initial  $\beta/\gamma$ -phases gradually changed to the  $\alpha$ -phase between 110 and 147°C, which was a lower temperature than at ambient pressure. In the cooling process, in contrast, the diffraction patterns did not change and only the  $\alpha$ -phase was observed, even at 20°C, at 0.18 GPa. This is the first observation of the stabilization of the  $\alpha$ -phase at room temperature. As with the case of the ambientpressure data, the fraction of the  $\alpha$ -phase at each temperature was calculated by Rietveld refinement of the PXRD patterns and is plotted against temperature in Fig. 2(a). At 0.18 GPa, the transition temperature in the heating process was estimated to be 123°C, which is lower than that under ambient pressure by 39°C. According to the phase diagram of bulk AgI [1], the transition temperature decreased by 41°C at 0.18 GPa. This value is consistent with the result for our nanoparticles. Thus, it can be concluded that the stabilization of the  $\alpha$ -phase at room temperature under pressure observed in the AgI nanoparticles originates

from both size and pressure effects.

In summary, we investigated the pressure effect on the phase transition behavior of AgI nanoparticles with a diameter of  $11.4 \pm 4.5$  nm through variabletemperature synchrotron PXRD measurements under pressure. The  $\alpha$ -phase was stabilized down to 20°C by applying a moderate pressure of 0.18 GPa to the AgI nanoparticles as a result of the combination of pressure and size effects.



Fig. 2. (a) Temperature dependence of the fraction of the  $\alpha$ -phase at ambient pressure (triangles) and at 0.18 GPa (circles). Open and closed symbols represent the heating and cooling processes, respectively. Blue, green, and red colors correspond to those in Figs. 1(c) and 1(d). (b) DSC thermograms of the AgI nanoparticles at ambient pressure [4].

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