Room-temperature stabilization of nanoscale superionic Ag$_2$Se

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Abstract

Superionic materials are multi-component solids in which one sub-lattice exhibits high ionic conductivity within a fixed crystalline structure. This is typically associated with a structural phase transition occurring significantly above room temperature. Here, through combined temperature-resolved x-ray diffraction and differential scanning calorimetry, we map out the nanoscale size-dependence of the Ag$_2$Se tetragonal to superionic phase transition temperature and determine the threshold size for room-temperature stabilization of superionic Ag$_2$Se. For the first time, clear experimental evidence for such stabilization of the highly ionic conducting phase at room temperature is obtained in $\sim2$ nm diameter spheres, which corresponds to a $>100$ °C suppression of the bulk phase transition temperature. This may enable technological applications of Ag$_2$Se in devices where high ionic conductivity at room temperature is required.

Keywords: phase transitions, quantum dots, silver selenide, size stabilization, superionic conductors

(Some figures may appear in colour only in the online journal)

1. Introduction

Superionic conductors have attracted renewed interest in recent years for potential applications in all-solid-state batteries [1, 2], memory devices [3, 4], thermoelectrics [5], sensors [6], and displays [7]. Although liquid phase electrolytes typically give higher ionic conductivity at room temperature, solid-state electrolytes exhibit many technologically important characteristics, including higher densities, improved stability, safety and compatibility with devices [8]. At the nanoscale, novel opportunities for engineering the phase diagram of these materials have emerged, enabling nanoionic switching devices and possibilities for size-stabilization of high ionic conductivity phases at room temperature [9–11]. Among the fast ionic conductors discovered to date, silver ion conductors are viewed as promising candidates for battery electrolytes because of their high ionic conductivity and high exchange rate with the electrode, enabling faster operating rates despite their higher materials cost and lower power density [12–15].

Cubic phase Ag$_2$Se ($\alpha$-Ag$_2$Se) is a well-known mixed ionic and electronic conductor at temperatures above 135 °C in the bulk, with an ionic conductivity greater than 2 s cm$^{-1}$ [16–18]. Below 135 °C, $\alpha$-Ag$_2$Se undergoes a solid-solid phase transition into a poorly ionic conducting orthorhombic phase ($\beta$-Ag$_2$Se) with a narrow bandgap (0.15 eV) and electronic resistivity on the order of $10^{-3}$ – $10^{-4}$ Ω cm [16, 18]. In contrast, the low temperature phase is usually observed to be tetragonal ($\gamma$-Ag$_2$Se) in nanoscale Ag$_2$Se, with quantum confinement leading to significantly higher bandgap and thus electronic resistivity [19–23]. However, accurate determination of the structural phase for nanoparticles of this size is non-trivial because of the overlap of the most prominent peaks of the high- and low-temperature phases, associated with the Debye–Scherrer broadened diffraction peaks of the nanoparticles, such that discerning the cubic phase from the tetragonal phase is not straightforward. Here, through combination of synchrotron-based temperature-resolved x-ray diffraction (TXRD) techniques with differential scanning calorimetry (DSC), the size-dependence of tetragonal to cubic (superionic) phase transition temperature in nanoscale Ag$_2$Se
Figure 1. (a) UV–vis absorbance spectra of 3.2 nm CdSe and transformed 4.5 nm Ag₂Se nanospheres. Inset shows a TEM image of as transformed Ag₂Se with diameter 4.5 ± 0.3 nm. (b) (top) Raw XRD pattern of the Ag₂Se nanospheres taken at room temperature, with corresponding azimuthally-integrated lineout (bottom) compared to a reference pattern (red) for tetragonal phase Ag₂Se from [23].

Figure 2. Temperature-resolved XRD patterns for 7 nm Ag₂Se nanospheres in (a) heating and (b) cooling process, together with reference patterns for tetragonal phase (bottom black lines) and for cubic phase (top blue lines) from Joint Committee on Powder Diffraction Standards (JCPDS) no. 04-003-5676. The arrows in (a) denote unique peaks to the tetragonal phase. The * denotes diffraction peaks from the heating stage. For clarity, these curves are offset. (c) Two raw XRD images taken below and above phase transition temperature respectively. (d) Plot of peak area intensity under the diffraction peak near $Q=2.15 \text{ Å}^{-1}$ versus temperature.
is measured, indicating a threshold size of $\sim 2.1 \pm 0.2$ nm for room temperature stabilization of superionic Ag$_2$Se. DSC confirms the successful phase stabilization in $\sim 2$ nm diameter spheres.

2. Experimental details

CdSe nanocrystals synthesis was carried out in Schlenck line system following previous work [24], except for the smallest size, which was adopted from reference [25] to remove trioctylphosphine oxide from the synthesis method. Ag$_2$Se nanoparticles were obtained by cation exchange reaction [21]. For size measurement, nanoparticles were first dispersed in toluene and then dropped on a carbon-coated copper grid for transmission electron microscopy (TEM) using a Tecnai G2 F20 X-TWIN microscope. DSC thermograms were measured on a TA Instruments DSC Q2000 apparatus at $5^\circ$C min$^{-1}$ ramp rate in a N$_2$ flow. TXRD was carried out at Stanford Synchrotron Radiation Lightsource (SSRL) at beamline 11-3 with x-ray energy of 12.735 keV and an area detector. For sample preparation, Ag$_2$Se nanoparticles dispersed in toluene were drop-cast on the surface of single crystalline SrTiO$_3$ substrates to minimize diffuse scattering background. Samples were placed on a heater, which was installed inside a helium chamber. The temperature ramp rate was set at 1 $^\circ$C min$^{-1}$, with a temperature resolution of 1.5 $^\circ$C. Raw images were processed using WxDiff to obtain diffraction intensity versus momentum transfer ($Q$) plots. Additional impedance measurements (see supporting information) were carried out in the frequency range 0.1 Hz–7 MHz using SP-200 from Bio-Logic Science Instruments with a built-in impedance analyzer. The Ag$_2$Se sample was die-pressed into pellet shape and sandwiched between two aluminum plates as contacting electrodes. Copper wires were attached to the outer surface of the electrodes using silver paste and 10 mV ac voltage was applied.

Figure 3. TXRD patterns for 3.6 nm Ag$_2$Se nanospheres in (a) heating and (b) cooling process. For clarity, the diffraction intensities of these curves are offset. (c) Plot of peak area intensity under diffraction peak near $Q = 2.35$ Å$^{-1}$, as denoted by the black arrows, versus temperature.
3. Results and discussion

The UV−vis absorbance spectra (figure 1(a)) confirm the complete transformation from 3.2 nm CdSe to 4.5 nm Ag2Se nanospheres associated with the complete disappearance of the CdSe exciton peak. XRD pattern (figure 1(b)) taken at SSRL confirms that the transformed 4.5 nm Ag2Se nanospheres are in the tetragonal phase. For all of the sizes studied in this paper except the smallest (2.16 nm), Ag2Se adopted the metastable tetragonal phase at room temperature.

TXRD was carried out on Ag2Se nanoparticles with different sizes (2.16 nm, 3.6 nm, 4.5 nm, and 7 nm) to probe the temperature-dependent structural changes. As shown in figures 2(a) and (b), the TXRD lineouts for 7 nm Ag2Se present clear evidence of peak changes with temperature, associated with the tetragonal/cubic (superionic) phase transition. The black arrows in figure 2(a) denote unique peaks to the tetragonal phase, and the peaks near Q = 2.15 Å⁻¹ and 2.35 Å⁻¹ are used as monitors of the phase transition, as shown in figure 2(d). Figure 3 shows corresponding measurements for 3.6 nm spheres. Additional measurements for 4.5 nm diameter nanoparticles are shown in figure S1. Phase transition temperatures of 5 nm and 6 nm Ag2Se spheres were measured using DSC to obtain additional data points with transition temperatures of ∼84 °C and ∼89 °C, respectively, as shown in figure S3.

The size-dependent behavior of the tetragonal to cubic (superionic) phase transition was obtained by plotting the phase transition temperatures of 2.16 nm, 3.6 nm, 4.5 nm, 5 nm, 6 nm and 7 nm Ag2Se nanoparticles versus their diameters, as shown in figure 4. Also shown here is the fitted curve to these data using a model considering the competition between surface and internal energies, which states that the suppression of nanoparticle phase transition temperatures compared to the bulk is inversely proportional to their sizes [26, 27]. Best fit gives an equation of the form $T_0(°C) = 125 − (210/D (nm))$, where $T_0$ is the phase transition temperature in °C and D is the diameter of the nanoparticle in nm. This corresponds to a bulk transition temperature of ∼125 °C for the tetragonal to cubic phase transition and is very close to previous estimated values (∼127 °C) [20]. For a nanoparticle size distribution ΔD, this equation corresponds to a broadening of the transition $\Delta T_0(°C) = 210 * (\Delta D/D) * (1/D (nm))$. Using the measured value for the size distribution of 0.6 nm full width at half-maximum (FWHM) for 4.5 nm Ag2Se nanoparticles, we calculate a broadening of ∼10 °C, which is consistent with what is observed by TXRD, indicating that the transition width in temperature is dominated by size broadening for certain size nanoparticles. By assuming the same density (28.13 mmol cm⁻³) for both tetragonal and cubic phase, and an enthalpy change of 9.17 kJ mol⁻¹ [28], the average surface energy difference between the two phases is calculated to be ∼33 mJ m⁻¹, which is on the same order of the value calculated for another superionic material Cu2S [11]. This equation also indicates that thermodynamic stabilization of the superionic phase should occur at room temperature for sizes smaller than ∼2.1 ± 0.2 nm, with the error shown here determined by the fitting error. This threshold size is consistent with reference [23] which argues that that 3 nm diameter Ag2Se spheres are still trapped in a metastable tetragonal phase, although the XRD pattern shows great similarity to the superionic Ag2Se reference pattern.

Both TXRD and DSC were applied to Ag2Se nanospheres with an average diameter of ∼2.16 nm as measured by TEM. As can be seen in figure 5(a), compared to the larger sizes, TXRD shows no evidence for reshaping of the diffraction patterns at all measured temperatures. Figure S5 shows the normalized temperature-dependent XRD lineouts with essentially no measurable changes apart from Debye–Scherer broadening of the peaks makes it difficult to definitively assign the structural phase in this case. The DSC thermogram measured on same batch of ∼2.16 nm particles, as shown in figure 5(b), presents clear evidence for phase transitions at temperatures of ∼36 °C on heating and ∼21 °C on cooling. Since the synthesis method adopted for this size nanoparticles does not involve polymer contents with phase transitions in this temperature range, the observed phase transition here should be attributed to the tetragonal/cubic phase transition. The observed peaks in the DSC thermogram are significantly broadened compared to the larger size nanocrystals, with FWHM ∼20–30 °C. This is consistent with the estimated broadening in $T_0$ simply from the size distribution although we cannot rule out here additional contributions associated with finite size broadening of the transition from thermal fluctuations [29, 30]. Impedance spectroscopy carried out on the size-stabilized particles after one heating/cooling cycle gives an ionic conductivity of ∼8.5 × 10⁻⁴ s cm⁻¹ (see supporting information), consistent with values observed in AgI nanoparticles [14]. We conclude that stabilization of the cubic (superionic) phase at room temperature is achieved in this size nanoparticles simply by cooling the nanoparticles from above the tetragonal to cubic phase transition.
temperature, which corresponds to more than 100 °C suppression compared to the phase transition temperature of the bulk.

4. Conclusions

The size-dependent behavior of the Ag$_2$Se tetragonal to cubic (superionic) phase transition temperature is mapped out by TXRD and DSC, which gives a threshold size of $\sim 2.1 \pm 0.2$ nm for room-temperature stabilization of the superionic phase. Consistent with these measurements, DSC thermogram confirms that $\sim 2.16$ nm Ag$_2$Se nanospheres are stabilized at room temperature after one heating/cooling cycle. This work may lead to new possibilities for silver-ion-based electrochemical devices, and for designing devices utilizing the different functionalities of the two phases, for example thermoelectric materials, solid-state-batteries, and nanoionic switches.

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References