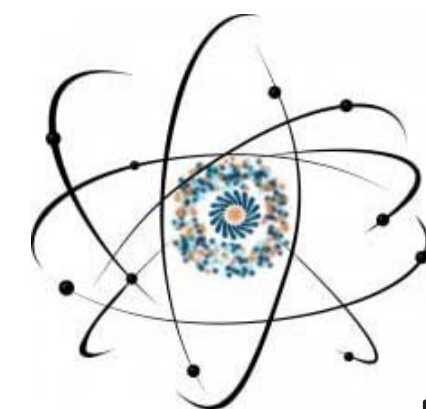


Raman Spectroscopy of Ag–In–S Polycrystals, Films, and Nanoparticles



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INTRODUCTION

Ternary compounds of Ag–In–S system, in particular AgInS₂ and AgIn₅S₈, are known semiconductor materials used for optoelectronic and photovoltaic device applications. Therefore, AgInS₂ films prepared by various techniques attract broad scientific interest [1,2]. Thermal evaporation technique enables Ag–In–S films with different element content to be prepared. Ag–In–S nanoparticles (quantum dots) of various chemical composition with intense broadband photoluminescence can be obtained by colloidal synthesis at relatively mild conditions from non-toxic reagents and are promising for application in light-emitting diodes and photocatalysis [3,4].

Raman spectroscopy is a versatile tool to study the structure of solids. It enables one to distinguish between crystalline and amorphous materials, provides important information about the type of the structure, chemical composition, and strain. Here we present a comparative Raman study of Ag–In–S polycrystals, thermally evaporated films, and nanoparticles of similar chemical composition prepared by colloidal synthesis.

MATERIALS AND METHODS

Fabrication of Ag–In–S polycrystals and thin films

Polycrystalline AgInS₂ samples as well as non-stoichiometric AgIn₄S₅ and AgIn₇S₁₀ compositions were synthesised in quartz ampoules evacuated down to 10^{−4} Torr at 1200–1420 K. Ag–In–S films of different chemical compositions were prepared by thermal evaporation from Knudsen cells.

Fabrication of Ag–In–S nanoparticles

Ag–In–S nanoparticles were obtained following the technique by Raevskaya et al. [3] with some modifications.

aqueous solutions at intense stirring AgNO₃ + glutathione + NH₄OH + InCl₃ + Na₂S (in desired proportions)

↓ aging for 30 min at 90–95 °C ↓

brightly luminescent glutathione-capped Ag–In–S nanoparticles

Size-selective fractioning: precipitation with isopropanol by centrifugation (4000 rpm, 5 min)

The presence of the nanoparticles in the colloidal solutions was confirmed by size-dependent shift of the optical absorption edge and broadband photoluminescence.

Measurements

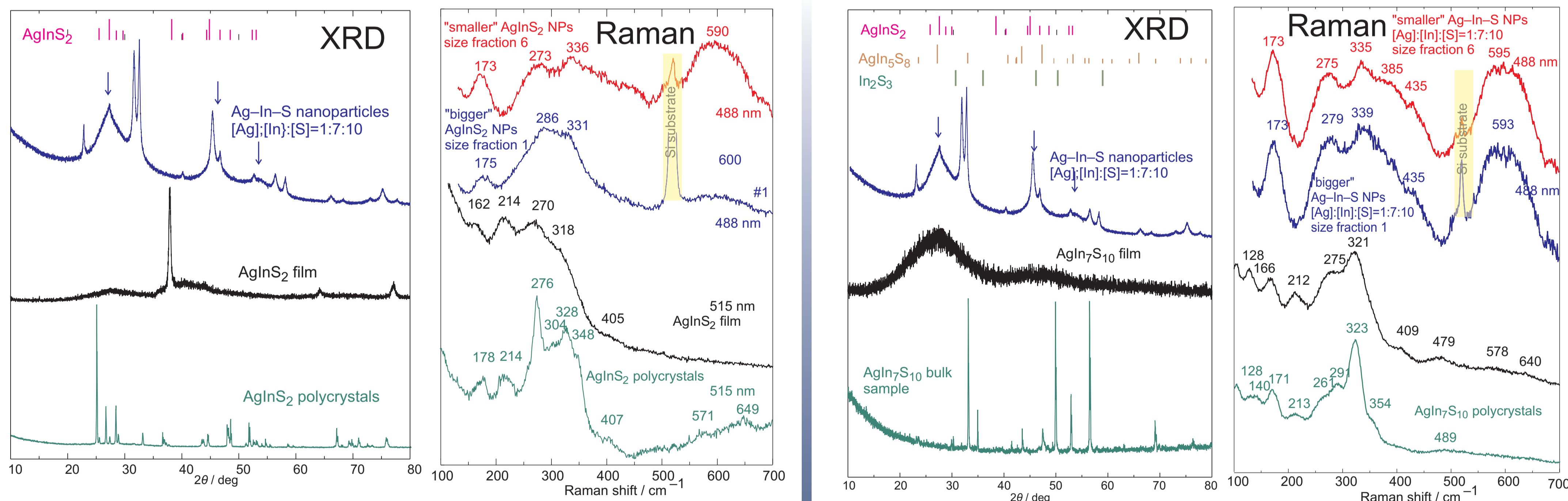
Raman spectroscopy: Horiba LabRAM with a cooled CCD camera, excitation: 488, 515, and 633 nm lasers

XRD: Rigaku Smartlab X-Ray diffractometer with Cu K_α radiation



Luminescent size-fractionated Ag–In–S QDs, [Ag]:[In]:[S]=1:4:5

RESULTS



It is seen from XRD that AgInS₂ thin films and NPs retain crystalline structure, although the broader peaks indicate noticeable lattice distortion, especially for NPs. Likewise, Raman spectra show strong broadening and merging of peaks at 300–350 cm^{−1} in the row polycrystals → films → NPs as well as vanishing of the peak at 214 cm^{−1} and increase of the 2nd-order Raman scattering for AgInS₂ NPs.

It is seen from XRD that Ag-deficient polycrystalline AgIn₇S₁₀ sample is multiphase (AgIn₅S₈ and In₂S₃) while the AgIn₇S₁₀ thin film is amorphous. However, peaks in the Raman spectrum of the film are only slightly broadened. For NPs the peak at 214 cm^{−1} vanishes and the second-order Raman scattering increases.

For NPs, the Raman spectra are almost independent of the [Ag]:[In]:[S] ratio. Since the NP size is very small and the NP surface is terminated by sulphur atoms which simultaneously also belong to the capping ligands (GSH). The lattice distortion on the NP surface determines the predominant role of surface phonons in the Raman peak broadening.

CONCLUSIONS

- 1 in the row AgInS₂ polycrystals → films → NPs the Raman spectra show strong broadening and merging of peaks at 300–350 cm^{−1}. For Ag-deficient non-stoichiometric Ag–In–S QDs the difference even between the crystalline and amorphous phase spectra is less pronounced possibly due to the initial multiphase character of the crystalline sample.
- 2 The Raman spectra of small-size NPs are practically independent of the [Ag]:[In]:[S] ratio due to the small size and the NP surface of the NPs is terminated by sulphur atoms which simultaneously belong to the GSH capping ligands.
- 3 The Raman peak broadening in the NPs is predominantly determined by the surface phonons.

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