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Structural and optical study of undoped and Ag-doped Sb_2S_3 polycrystals and thin films

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INTRODUCTION

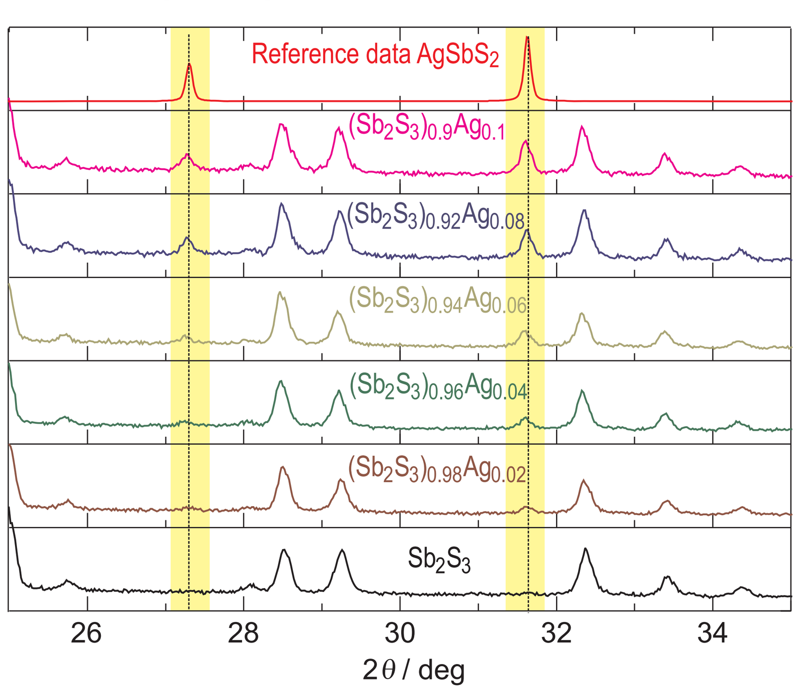
Sb_2S_3 is a phase-change material characterised by extraordinary variation of optical parameters (band gap, refractive index) under reversible phase transitions between the crystalline and amorphous states. Its important advantage is very low optical absorption ($k < 10^{-5}$) in the near-infrared and visible spectral range both in the amorphous and crystalline states. This enables its application as a medium for building up neural networks. Thermal transport in Sb_2S_3 is dominated by the contribution of phonons rather than electronic thermal conductivity. This makes it promising for thermoelectric devices. Sb_2S_3 has a noticeable potential for applications in solar energy conversion. Doping Sb_2S_3 with silver, in particular, increases its refractive index, thereby making it attractive for applications in photonics as well as reduces its intrinsic high electric resistivity what is essential for its use as buffer layer in photovoltaics. Here we present an X-ray diffraction (XRD) and Raman spectroscopic study of polycrystalline Sb_2S_3 and Sb_2S_3:Ag ingots as well as thermally evaporated films of similar compositions.

EXPERIMENTAL

- Sb_2S_3 was synthesised from high-purity elemental Sb (99.999%) and S (99.9995%) by two-temperature synthesis with the "hot" (Sb-containing) zone temperature of 650 ^{o}C and subsequent cooling down to room temperature at a rate 50 K/h. $(Sb_2S_3)_{1-x}Ag_x$ alloys were synthesised from $Sb_2S_3$and colloidal Ag in evacuated quartz ampoules at 650 ^{o}C.
- 2.1–2.5 μm thick $(Sb_2S_3)_{1-x}Ag_x$ films were prepared by flash evaporation at 1200 ^{o}C on cold silicon and silicate glass substrates without any post-preparation annealing of the films.
- X-ray diffraction (XRD) studies were performed using an AXRD Benchtop diffractometer with Cu K_α radiation and a Ni filter.
- Micro-Raman spectra were measured at room temperature using a Horiba XPloRa Plus spectrometer (532 nm laser, CCD camera, instrumental resolution better than 2.5 cm^{-1}).

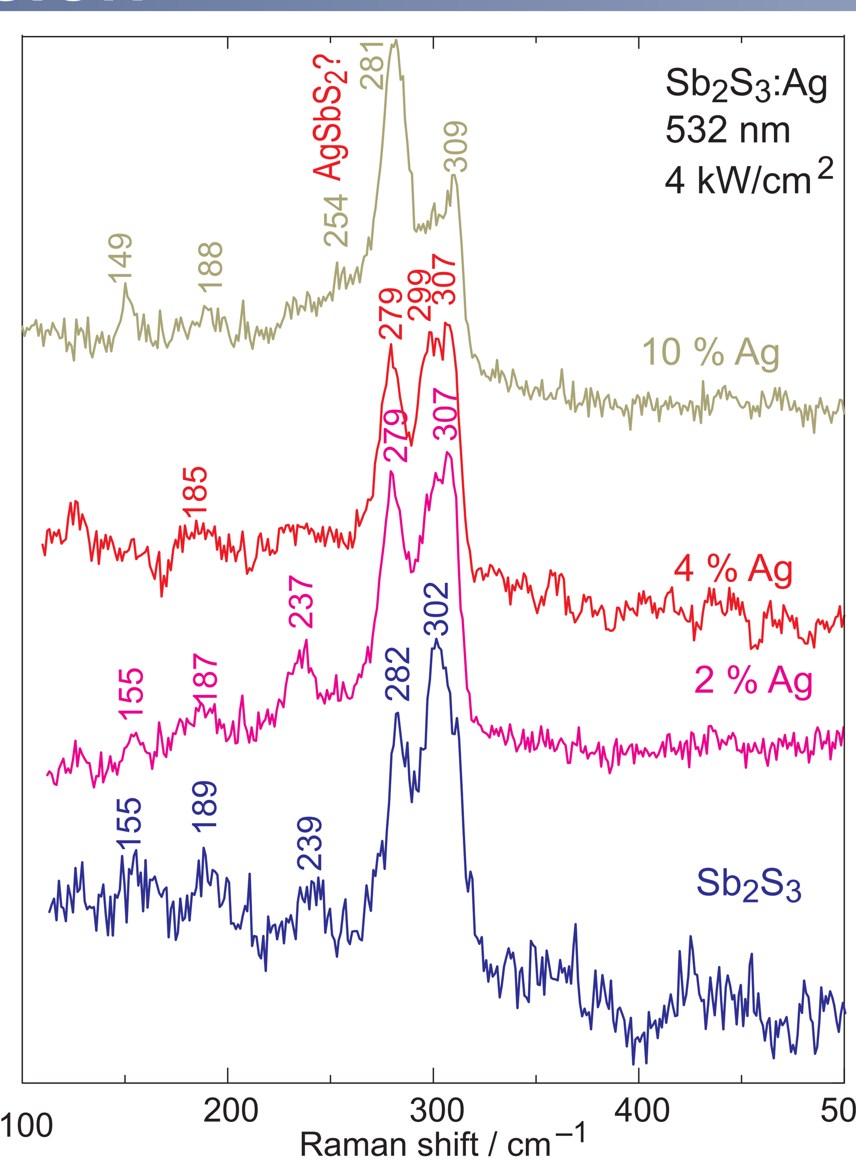
RESULTS AND DISCUSSION

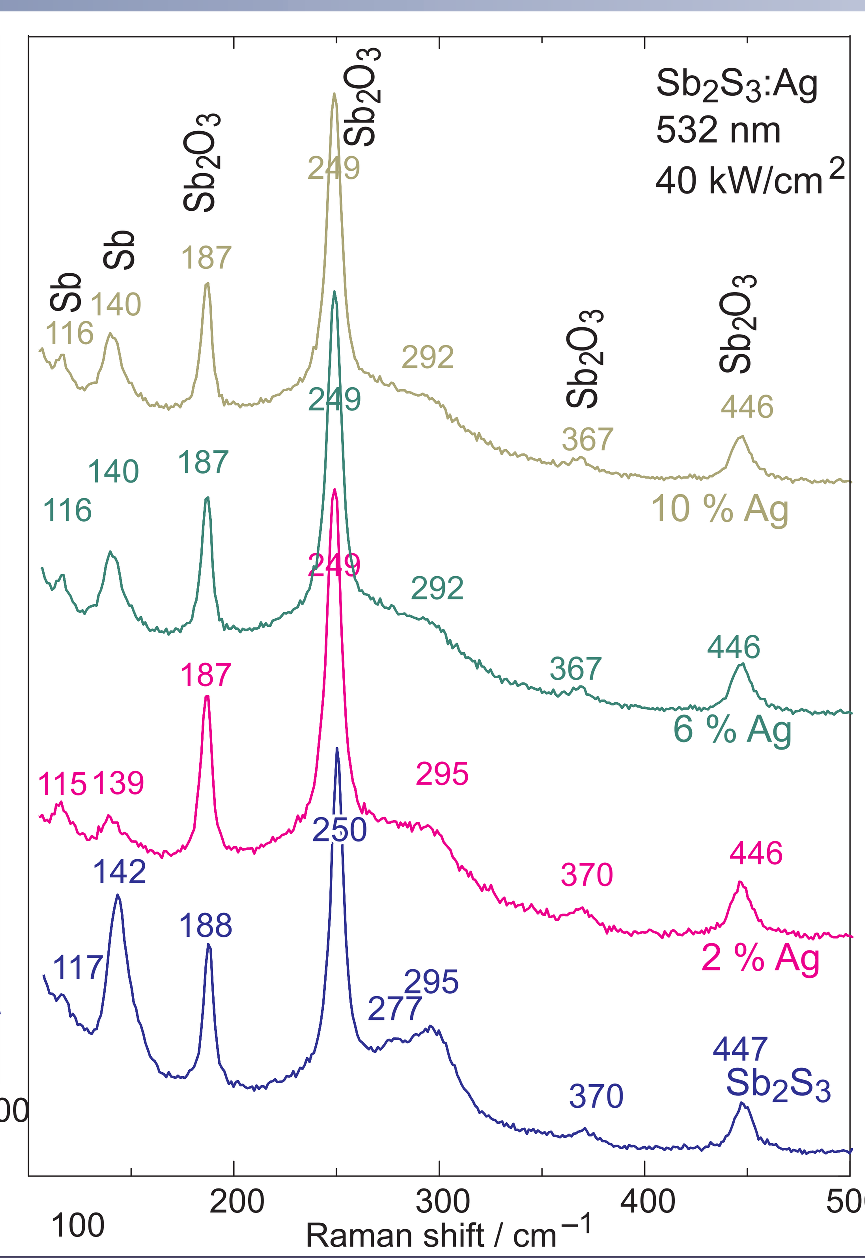
Polycrystals



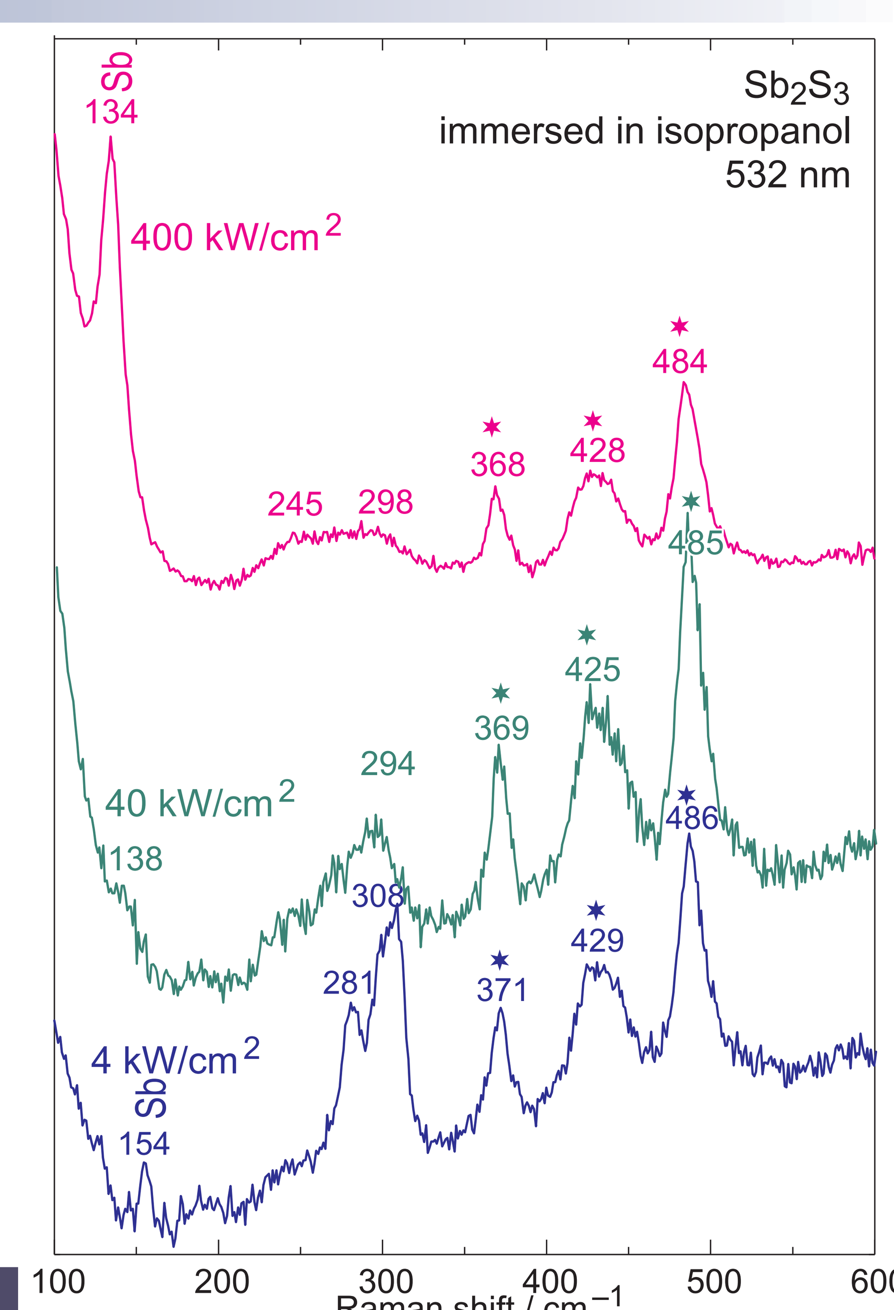
XRD: For the Ag-containing samples crystalline $AgSbS_2$ phase is present additionally to crystalline Sb_2S_3.

Raman: a feature at 254 cm-1 in the spectrum of the x=0.10 sample can be due to the crystalline $AgSbS_2$, but it is questionable



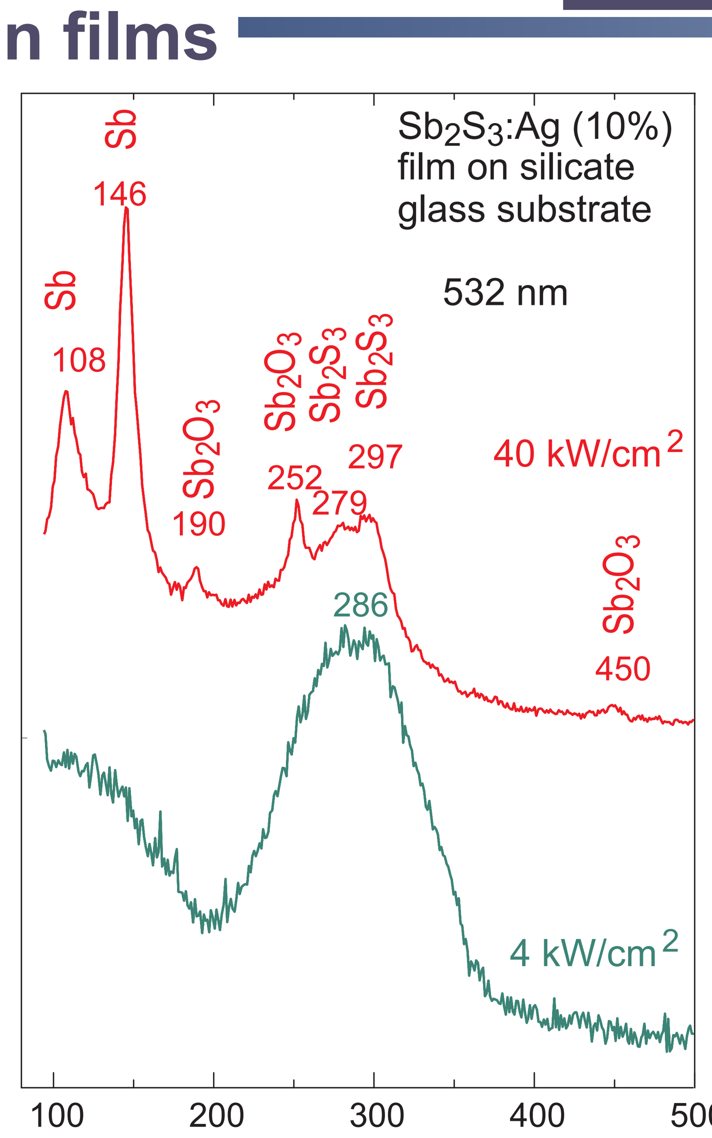


Raman spectra of polycrystalline $(Sb_2S_3)_{1-x}Ag_x$ show the formation of elemental Sb and Sb_2O_3 at elevated P_{exc} due to the heating of the sample surface by the tightly focused laser light and oxidation by the ambient air.

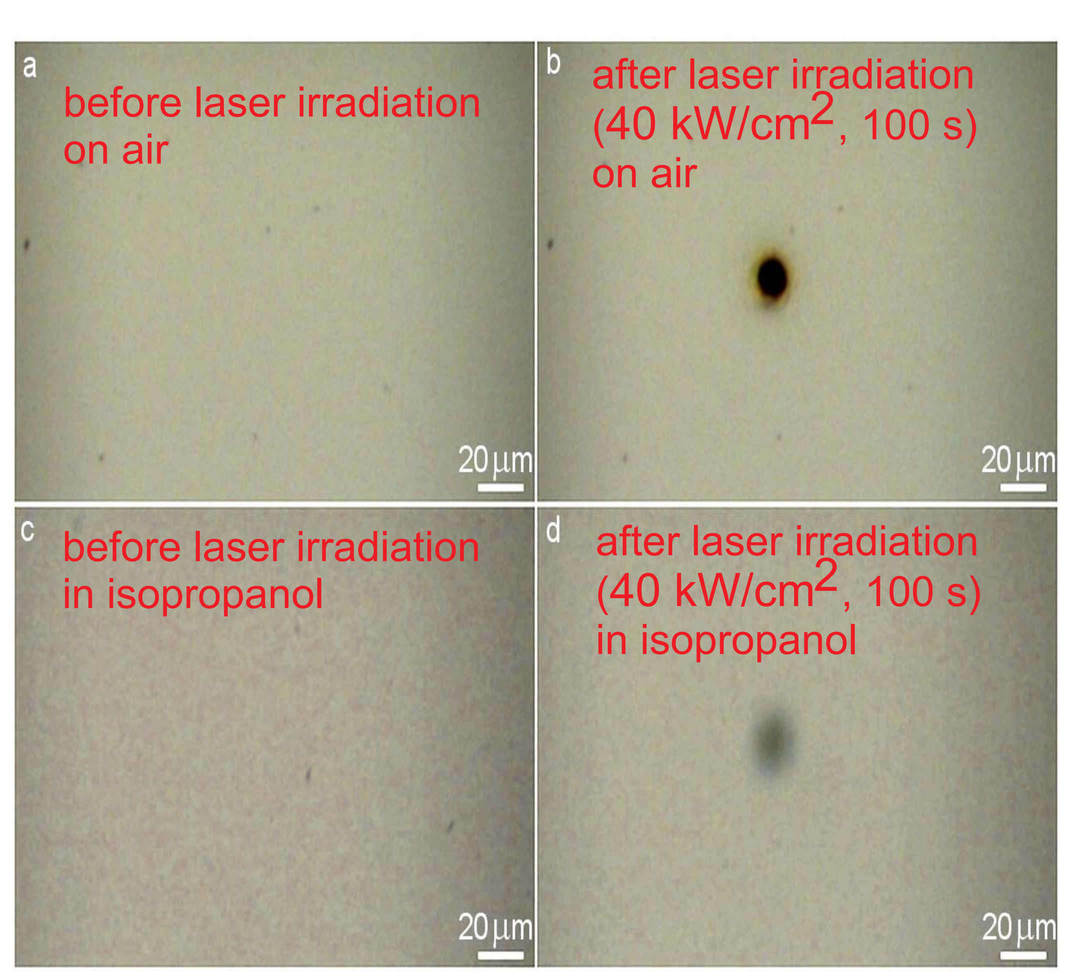


Raman measurements in liquid isopropanol: elemental Sb features appear at elevated P_{exc} due to the heating-induced reaction while the Sb_2O_3 features do not appear at all due to blocking the access of the ambient air.

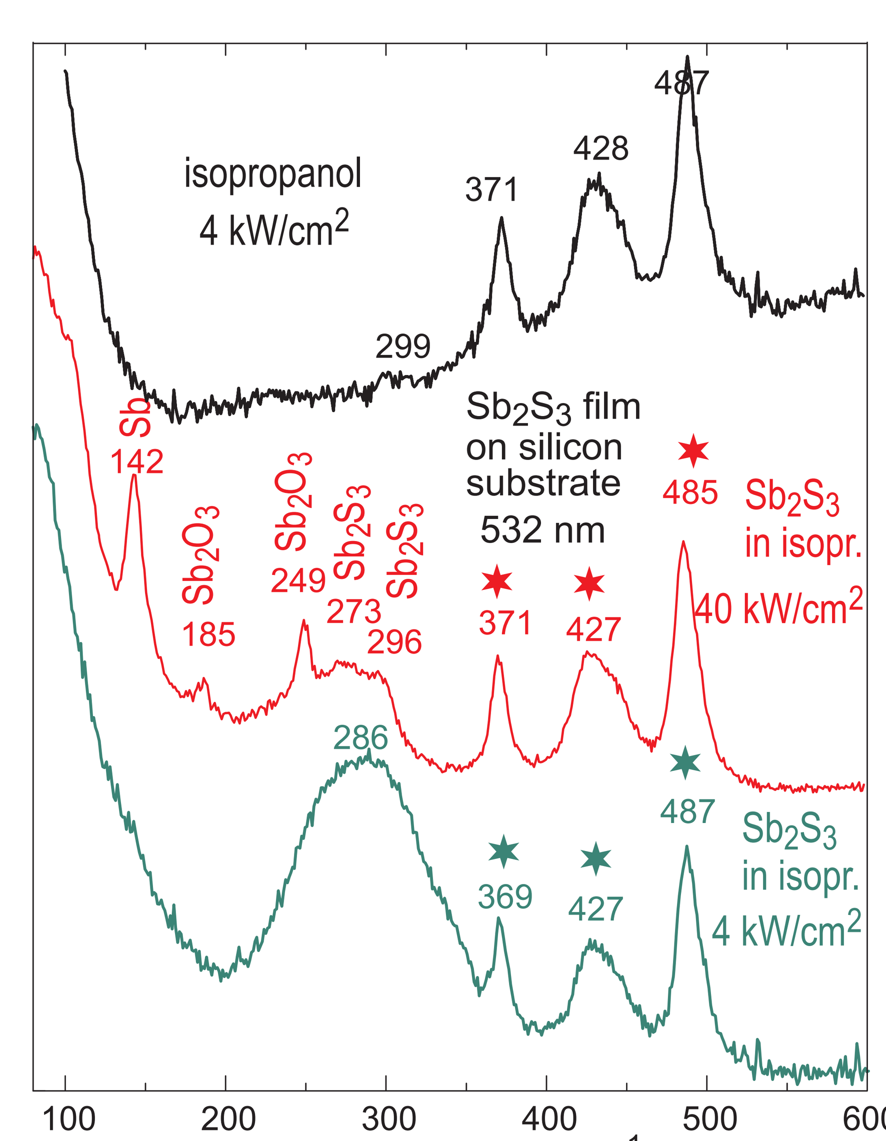
Thin films



Raman spectra of Sb_2S_3:Ag thin films at a low P_{exc}=4 kW/cm^2 show their **amorphous** structure. At P_{exc}=40 kW/cm^2 one can observe the features of elemental Sb and Sb_2O_3 formed due to the laser heating of the sample surface and oxidation by the ambient air.



Sb_2S_3 is a photoplastic material readily experiencing surface deformation under illumination. The nonthermal nature of this effect is clearly confirmed by optical microscopy where the formation of a pit in the laser spot during the Raman measurement is equally visible for the samples illuminated on air and in isopropanol, meaning that the photodeformation does not depend of heat dissipation provided by the liquid.



Raman measurements in liquid isopropanol: at elevated P_{exc} both elemental Sb and Sb_2O_3 features appear since oxygen comes from voids in the film where it was stored since the film condensation after the evaporation.

Acknowledgement

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CONCLUSIONS

❶ Sb_2S_3:Ag polycrystals and thin films (Ag content up to 10 %) were obtained by high-temperature synthesis and thermal evaporation, respectively. XRD data confirmed the orthorhombic (stibnite) structure of the synthesised polycrystalline Sb_2S_3:Ag ingots, the Ag-containing samples show the presence of the $AgSbS_2$ phase as well..

❷ Raman measurements performed at a low laser power density P_{exc}=4 kW/cm^2 assume the possible presence of the $AgSbS_2$ phase, but cannot provide unambiguous evidence for its existence.

❸ Raman measurements at increased P_{exc}=40 kW/cm^2 revealed photostructural and photochemical transformations, namely the formation of elemental Sb and Sb_2O_3 phases due to the heating of the sample surface by the tightly focused laser light and oxidation by the ambient air.

❹This thermal effect is accompanied by a nonthermal effect of photoinduced material transport from the laser spot(well known for amorphous chalcogenides. Formation of the pit on the sample surface at Raman measurements performed in liquid isopropanol confirms the nonthermal nature of the photoinduced material transport.

❺ In the Raman spectra of Sb_2S_3:Ag polycrystals immersed in liquid isopropanol measured at elevated P_{exc} elemental Sb features appear due to the chemical reaction on the surface induced by laser heating while the Sb_2O_3 -related features do not appear at all due to blocking the access of the ambient air by isopropanol.

❻ Raman spectra of Sb_2S_3:Ag thin films measured at a low P_{exc}=4 kW/cm^2 clearly reveal their amorphous structure.

❼ In the Raman spectra of Sb_2S_3:Ag thin films in isopropanol measured at elevated P_{exc} the Sb_2O_3 -related features appear since oxygen comes from voids in the film where it was stored since the film condensation after the evaporation.