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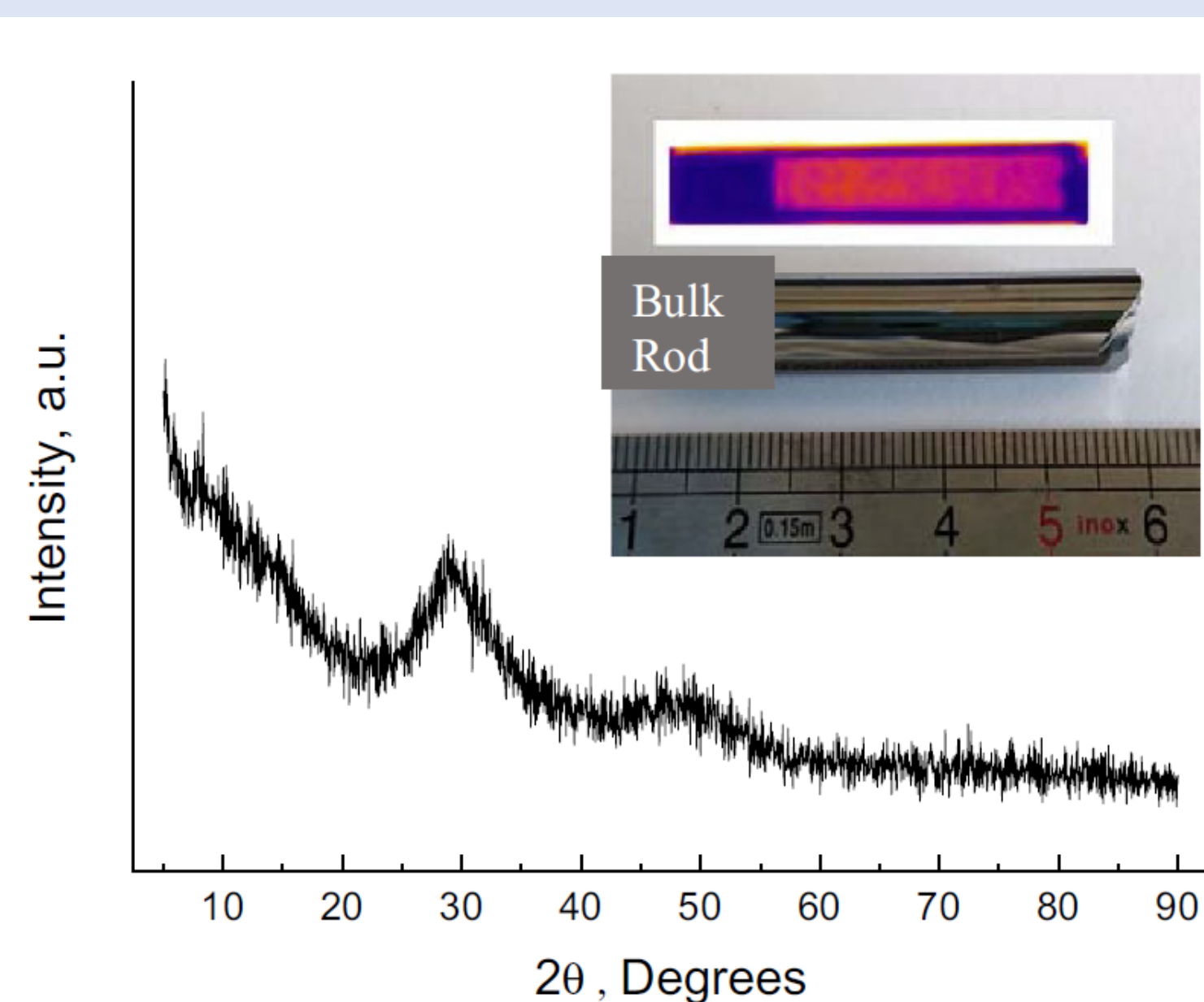
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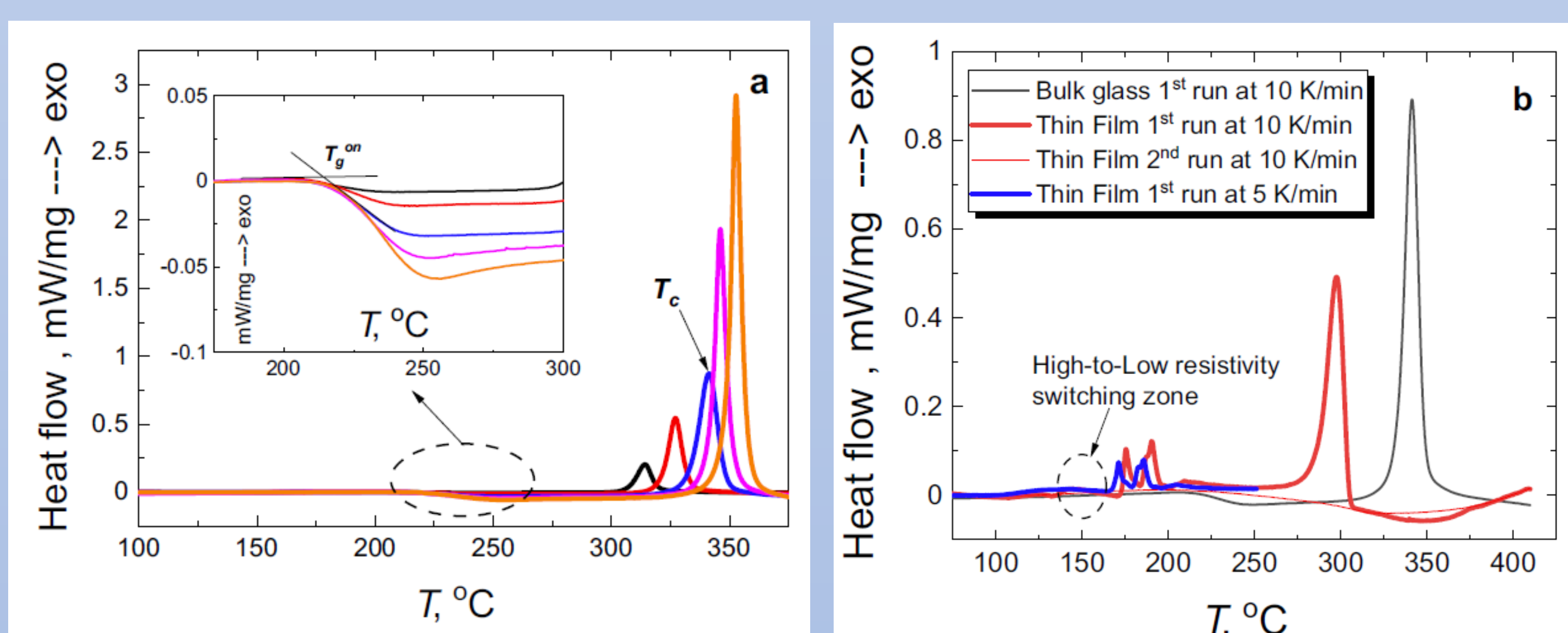
**Phase-change materials (PCMs)** are known for their unique behavior during switching between the amorphous and crystalline states. Rapid and reversible transitions between highly resistive and conductive states occurring at moderately elevated temperatures is especially intriguing for new-generation devices. Thus, we introduce a new class of PCMs based on equichalcogenides [1].

Bulk equichalcogenide  $\text{Ge}_{15}\text{Sb}_{40}\text{S}_{15}\text{Se}_{15}\text{Te}_{15}$  glasses were prepared by conventional melt quenching method using 5N-purity elements. The as-prepared glass was vitreous in nature, showing no significant reflexes in X-ray diffraction (XRD) patterns (Fig. 1) and uniform IR image (Fig. 1).



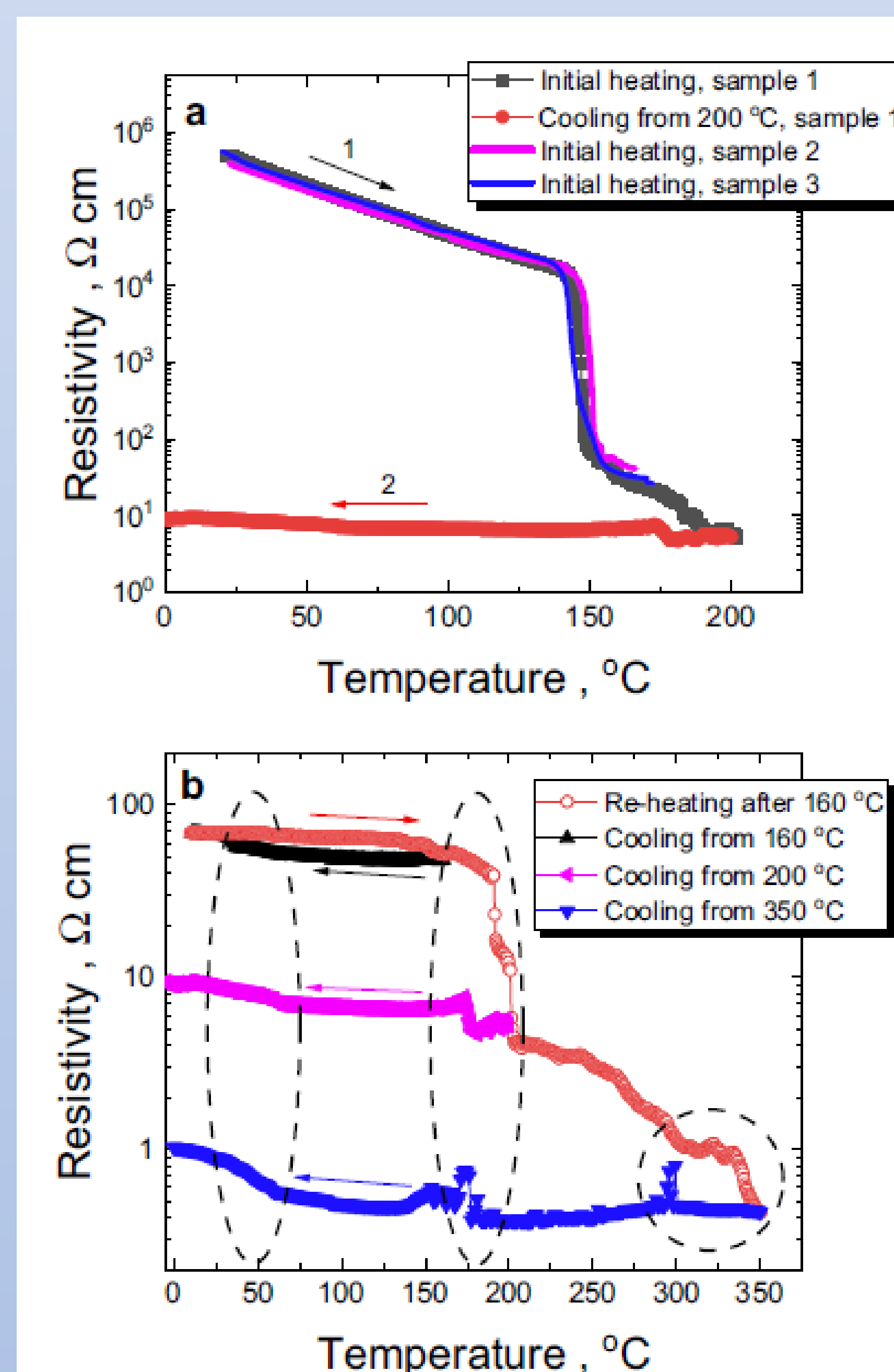
**Figure 1** - As-prepared  $\text{Ge}_{15}\text{Sb}_{40}\text{S}_{15}\text{Se}_{15}\text{Te}_{15}$  bulk glass. Main figure shows featureless XRD pattern verifying vitreous nature of the obtained bulk material. The insert shows an ingot as removed from the ampoule and its IR image, testifying good homogeneity of the prepared bulk glass.

Advantage of equichalcogenide glass is the possibility to tune the optical gap in wider than pure GST ( $\text{Ge-Sb-Te}$ ) ranges by changing S and Se concentration [2]. Together with the quite high thermal stability of  $\sim 126$  K (so-called Dietzel criterion), determined from DSC (Fig. 2) as a difference between crystallization temperature ( $T_c=341.3^\circ\text{C}$ ) and glass transition temperature ( $T_g^{\text{on}}=214.9^\circ\text{C}$ ), this material looks quite attractive for molding and fiber-drawing applications. The obtained value of Dietzel criterion is  $\sim 70$ K higher than for  $\text{Ge-Te}$  and  $\sim 100$ K higher than for GST systems. This enables certain applications (in meta-optics or waveguides), which are not possible for the conventional GST-based PCMs due to high crystallization affinity above  $T_g$ . The activation energy of crystallization ( $E_a$ ) are calculated using Ozawa method or Kissinger equation [3,4]. Respective  $E_a=182\text{kJ/mol}$  (1.9eV) and  $E_a=172\text{kJ/mol}$  (1.8 eV) values are  $\sim 0.5\text{eV}$  smaller than in pure GST-225 (which can be barely obtained in a bulk form, though).

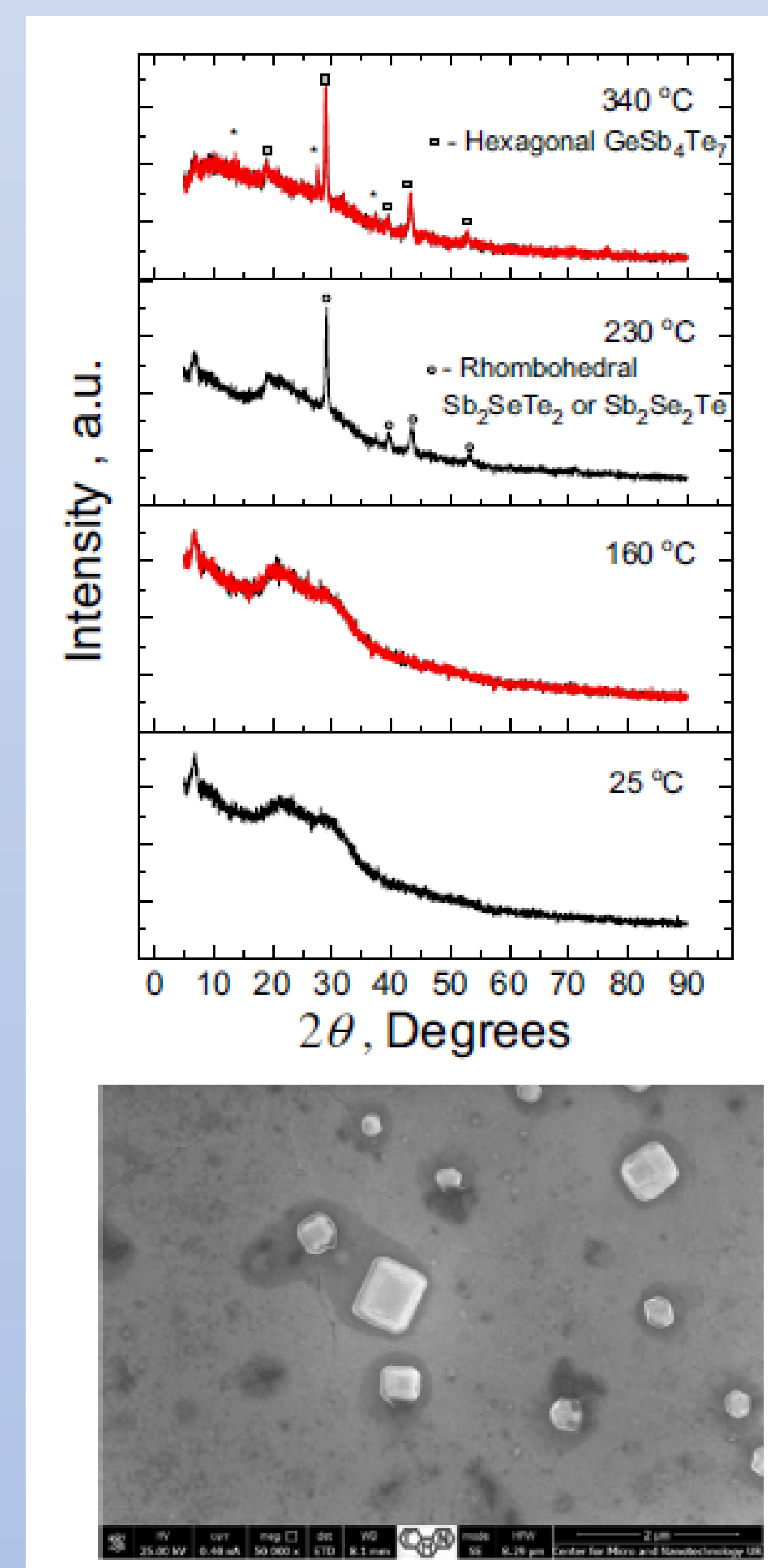


**Figure 2** - DSC curves of as-prepared bulk  $\text{Ge}_{15}\text{Sb}_{40}\text{S}_{15}\text{Se}_{15}\text{Te}_{15}$  glass and thin film. (a) DSC signals for the bulk samples were recorded with 2 (black), 5 (red), 10 (blue), 15 (magenta) and 20 (orange) K/min heating rates. They show glass transition range (insert) and exothermal crystallization peaks above  $300^\circ\text{C}$ . (b) DSC curves of thin films scraped out of glass substrate show low-temperature shift of main crystallization peak and additional crystallization peaks within  $\sim 160\text{--}200^\circ\text{C}$  range.

Resistivity measurements of the  $\text{Ge}_{15}\text{Sb}_{40}\text{S}_{15}\text{Se}_{15}\text{Te}_{15}$  film are presented in Fig. 3. The resistivity of the film shows exponential temperature behaviour typical of semiconducting material until  $\sim 140^\circ\text{C}$  (Fig. 3a). After this threshold temperature, which is much lower than  $T_g \sim 215^\circ\text{C}$  of bulk samples (Fig. 2), the resistivity suddenly drops by several orders in magnitude. In-situ XRD patterns recorded for  $\text{Ge}_{15}\text{Sb}_{40}\text{S}_{15}\text{Se}_{15}\text{Te}_{15}$  thin film at different temperatures show the absence of a significant crystalline phase at  $160^\circ\text{C}$  temperature (Fig. 4) as there are no visible crystalline reflexes in XRD signal even after 1 h at  $160^\circ\text{C}$ , the patterns being very similar to the XRD of the initial amorphous film recorded at  $25^\circ\text{C}$ . According to the obtained XRD temperature-dependent data (Fig. 4), noticeable crystalline reflexes in the investigated thin films are observed above  $\sim 200^\circ\text{C}$ , which is consistent with the observation of crystallization peaks in DSC scans of thin films (Fig. 2b). So, we can conclude that the observed abrupt changes in resistivity at  $140\text{--}160^\circ\text{C}$  are caused by changes in the structural arrangement at nanoscale towards the nuclei/small crystallites formation, which size/ordering is not enough to give a strong reflex in XRD pattern or significant heat flow signal in the DSC experiments. This effect can be also explained by “amorphous-amorphous” transition, using Peierls distortion mechanism proposed for PCMs as interplay between the short and long bonds, which ratio determines the electronic gap.



**Figure 3** - (a) Temperature dependence of resistivity measured in heating (step 1) and cooling (step 2) modes with 5 K/min rate for a fresh  $\text{Ge}_{15}\text{Sb}_{40}\text{S}_{15}\text{Se}_{15}\text{Te}_{15}$  thin film, shows rapid switching between High- and Low-resistivity states at  $\sim 145^\circ\text{C}$ . (b) If the previously heated to  $160^\circ\text{C}$  sample is cooled (black) and re-heated again (red) up to  $350^\circ\text{C}$ , a number of features can be observed on resistivity vs temperature dependences upon heating and cooling (circled).



**Figure 4** - In situ XRD studies. The patterns of  $\text{Ge}_{15}\text{Sb}_{40}\text{S}_{15}\text{Se}_{15}\text{Te}_{15}$  thin film, recorded at different target temperatures, are featureless until  $\sim 175^\circ\text{C}$ . Bottom panel shows SEM image of crystallites formed on the surface of the film after annealing at  $340^\circ\text{C}$ .

### CONCLUSION

$\text{Ge}_{15}\text{Sb}_{40}\text{S}_{15}\text{Se}_{15}\text{Te}_{15}$  equichalcogenides shows thermal stability and optical properties promising for various applications in photonics and meta-optics. The resistivity of thin film shows exponential temperature behaviour typical of semiconducting material until  $\sim 140^\circ\text{C}$  and drops several orders in magnitude above this threshold temperature, demonstrating phase-change memory effect. The formed Low-resistivity state remains stable upon cooling from  $160^\circ\text{C}$  or higher temperatures. The extended crystallites are not observed with conventional XRD at  $160^\circ\text{C}$  temperature or lower, suggesting local nanoscale mechanisms responsible for the High-to-Low resistivity switching in these materials at  $\sim 140\text{--}150^\circ\text{C}$ . Temperature-dependent Raman and XPS studies at or below  $175^\circ\text{C}$  suggest distortion of corner-shared  $\text{Ge}(\text{Te},\text{Se},\text{S})_4$  tetrahedra and  $\text{Sb}(\text{Te},\text{Se},\text{S})_3$  pyramids (including those modified by  $\text{Sb}/\text{Ge-Ge}/\text{Sb}$  bonds) with further their rearrangements into  $\text{Ge}(\text{Te},\text{Se},\text{S})_6$  octahedra and hexagonal  $\text{Sb}_2\text{Te}_3$ -like environment. Substitution of Te in the nearest environment of Ge atoms with S or Se and, possibly, formation of  $\text{Sb-Sb}/\text{Ge}$  bonds are conceivable on the basis of XPS results upon further heating above  $150^\circ\text{C}$ . According to DSC scans, the heating of the as-deposited thin films above  $175^\circ\text{C}$  leads to the crystallization of several phases at  $\sim 200^\circ\text{C}$  and  $\sim 300^\circ\text{C}$ . The observed phase-change memory effect can be explored in the all-chalcogenide