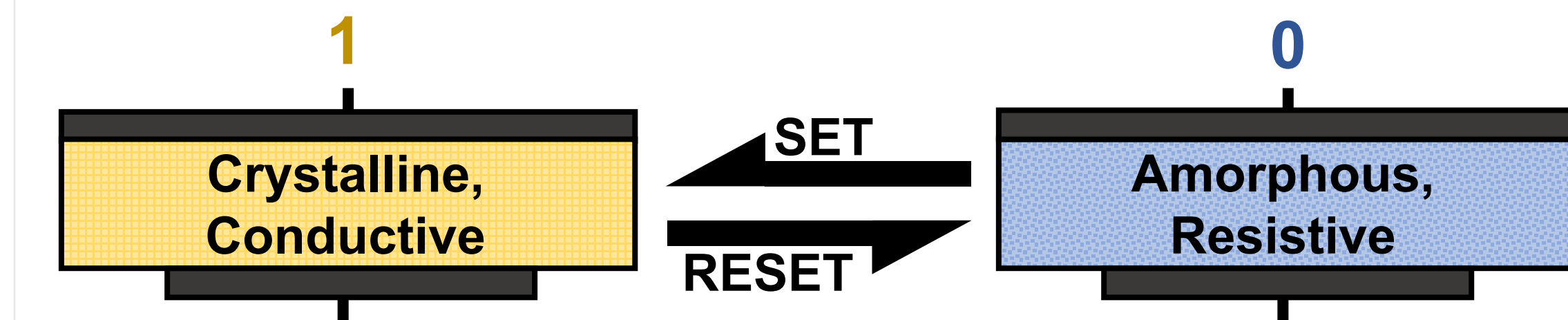


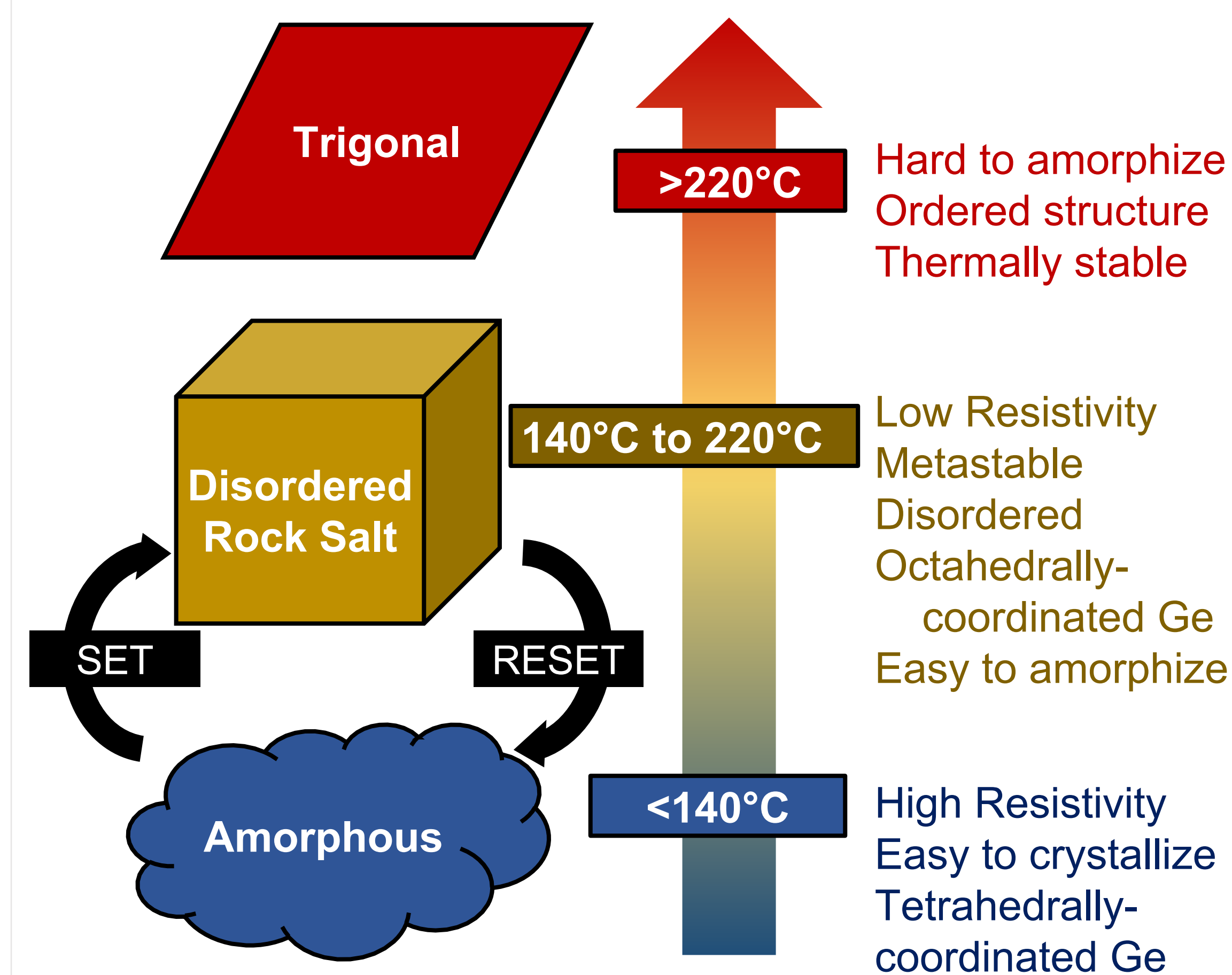
Amorphous and crystalline phases of phase change materials (PCMs) are used to write and read data

PCRAM (Phase-Change Random Access Memory) is a nonvolatile memory application that uses the resistivity difference between two distinct phases. The transformations are driven through an applied voltage that can crystallize or amorphize the materials. Accordingly, data is stored, even without an applied power source, to the device[1].

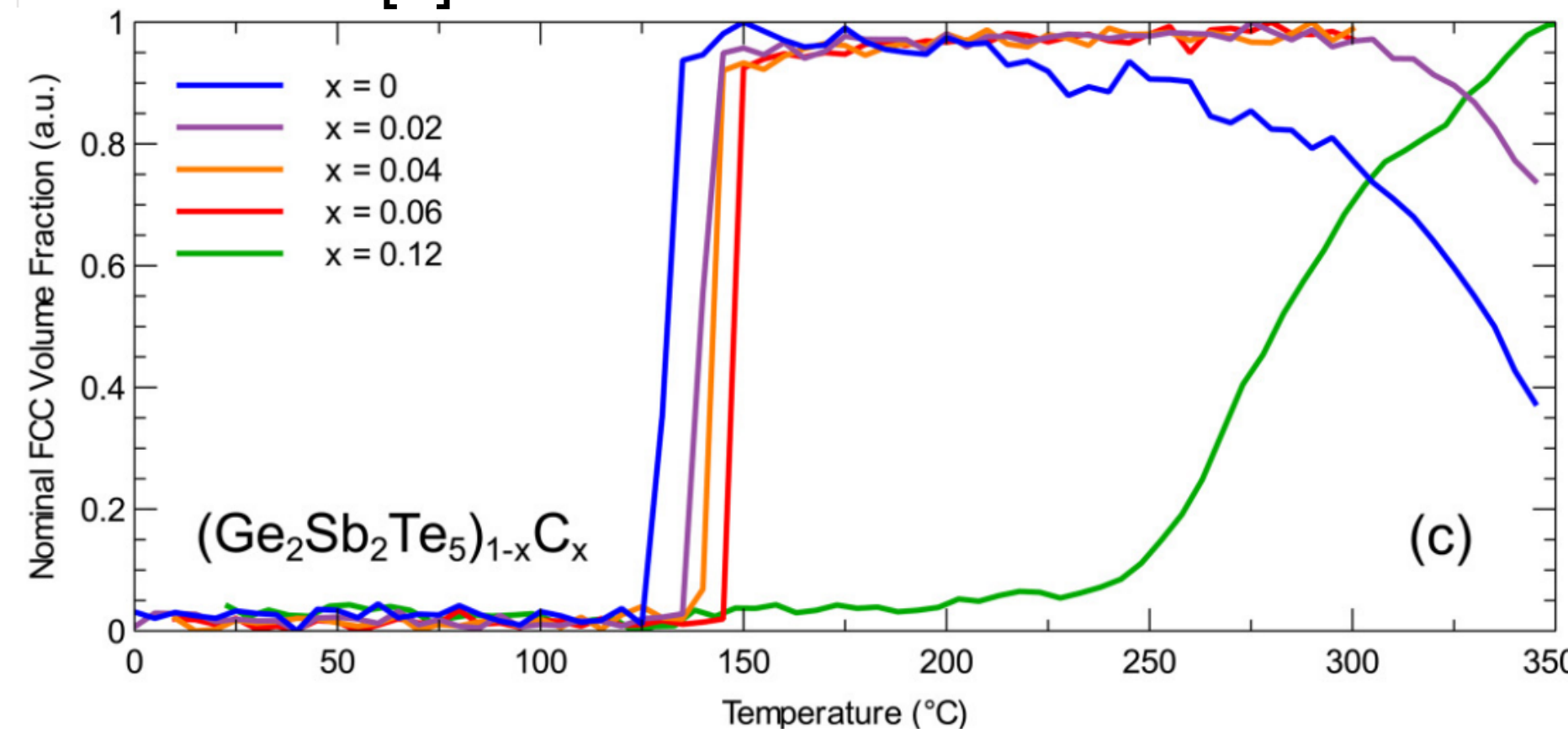


$\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) is a PCRAM candidate, with fast crystallization, but is limited by poor thermal stability

Poor thermal stability is a result of GSTs low crystallization temperature, which remains a major obstacle for its application[2].



Some dopants can increase the crystallization temperature and provide a path for improved thermal stability. However, the mechanism of change, and the affect of dopants on atomic structures and transformation kinetics remain poorly understood [2].

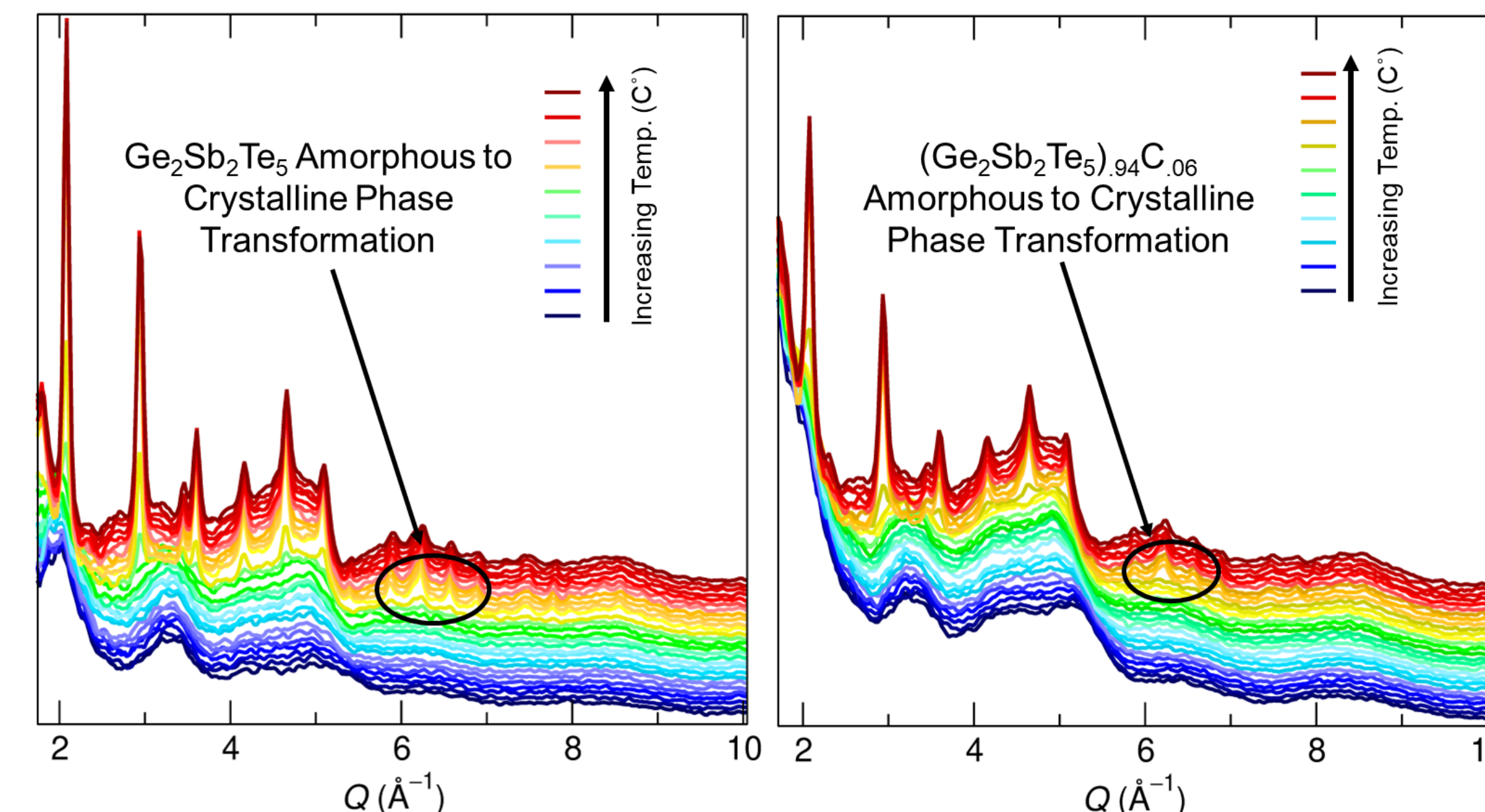


We report here on GST's transformation, and the role of carbon to modify it, using *in situ* X-ray scattering and spectroscopy.

Acknowledgements

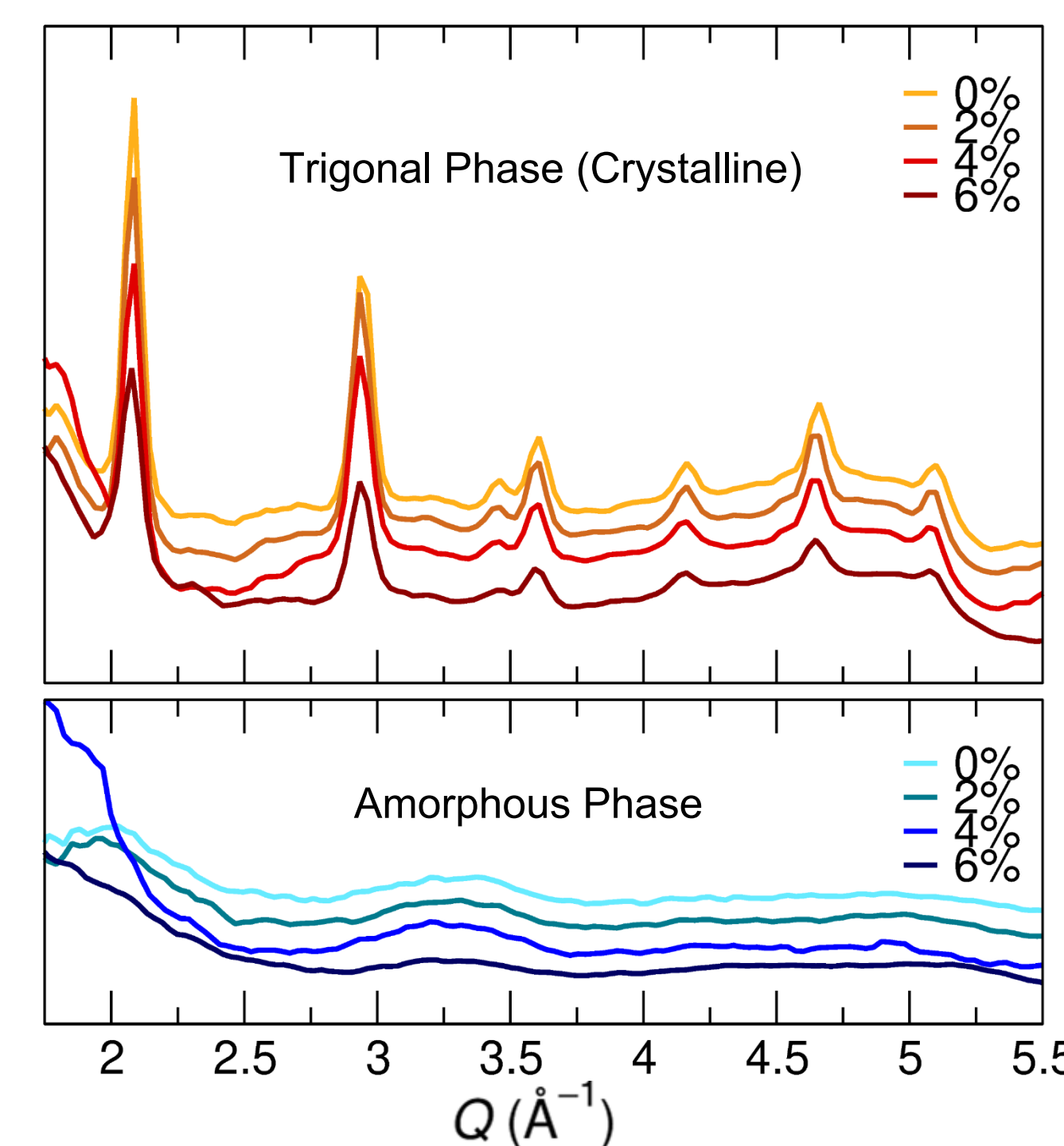
DNA, JL, and MMB acknowledge support through LDRD with Sandia National Laboratories and contributions of DA. We thank collaborators DO and BR at NSLS-II for incredible X-ray scattering data and for supporting student development. We acknowledge insights into GST and complementary Raman data from TB. We thank MMB for mentorship, guidance, and encouragement. This work was supported by the Sandia National Laboratory Directed Research and Development (LDRD) program. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under Contract No. DE-NA0003525. This work describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the U.S. Government. SAND2022-XXXX

In-Situ temperature dependent X-ray diffraction shows the increased stability of the amorphous phase with carbon doping



With carbon doping, the phase transformation temperature increases.

In addition, the peaks that form have reduced intensity relative to those in undoped GST.



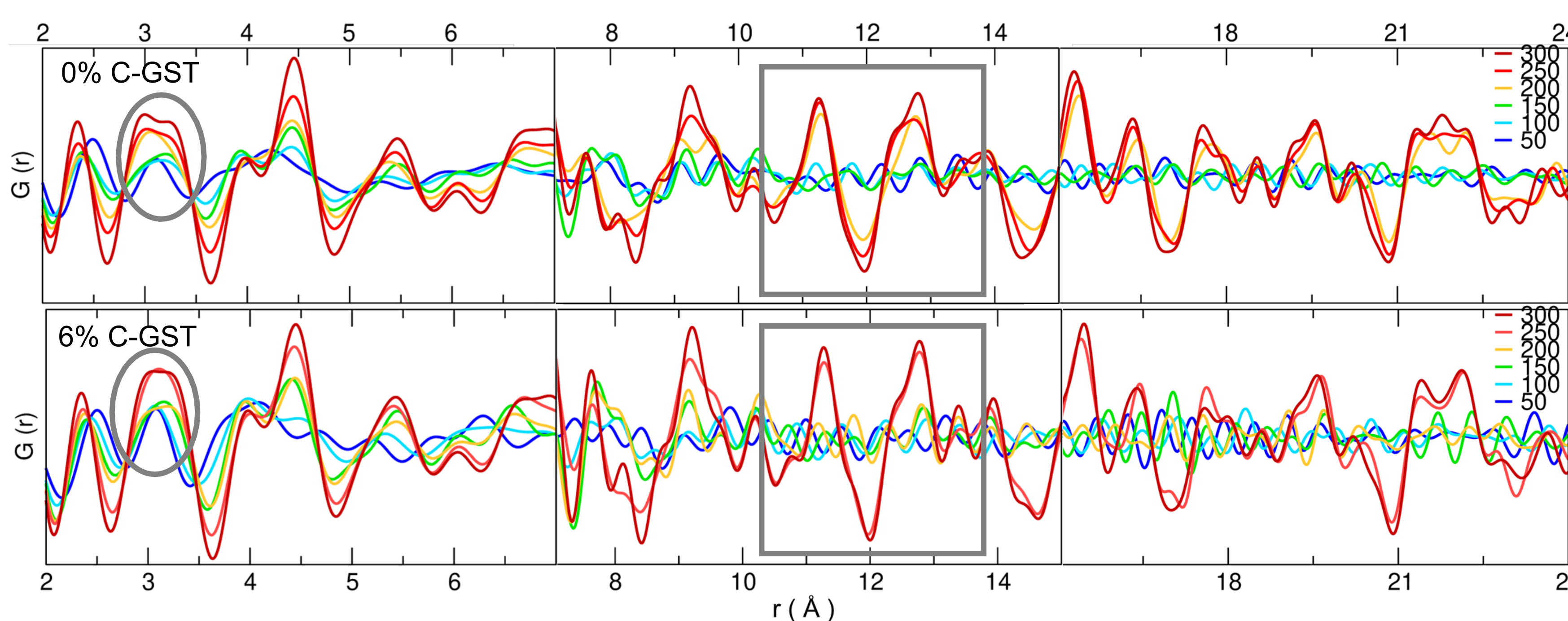
Carbon content increases the temperature of the cubic-to-trigonal phase transformation, and results in broader, lower intensity Bragg peaks

At the maximum temperature (approximately 300°C) films with carbon content ≤ 4% undergo a crystalline-crystalline phase transformation to the trigonal phase. This transformation is suppressed for the 6% carbon-doped film.

As expected, XRD cannot be used to capture changes between amorphous structures of GST films. This applies to changes in temperature and doping.

Thin-film pair distribution function (tPDF) data indicate the effect of carbon doping and temperature on the amorphous structure

The effect of carbon on the atomic structure on the local and long-range structure of amorphous and crystalline states is evident in differences of the position, shape, and intensity of correlations[3]. Differences at high r (right panel) reflect the formation of long-range order upon crystallization. Local structure changes within the amorphous phase are evident at lower r , revealing that local changes within the amorphous phase occur before crystallization.



Conclusions

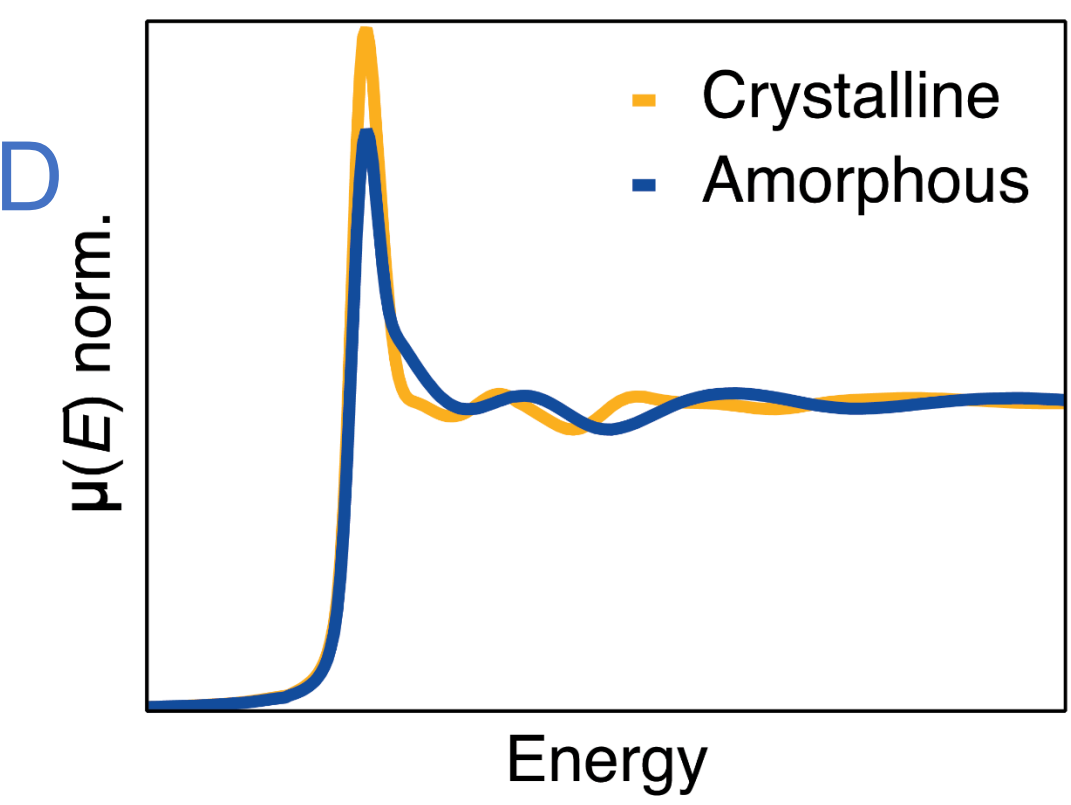
The effect of Carbon alloying in GST plays a significant role in the phase stabilization of the amorphous phase that yields beneficial structure-property relationships has previously been unknown in local structure analysis. Carbon replaces Ge-Ge bonds with (stronger) Ge-C bonds in a -GST, thus leading to the stabilization. Formation of C-C chains at high doping levels implies an ideal carbon doping concentration at ~5%.

Future Work

Future work entails quantitative analysis on high density in-situ temperature dependent PDF measurements to identify a "primed state" (or states) and EXAFS analysis at higher temperatures with doped samples to analyze effect of carbon on the priming state.

X-ray Absorption Fine Structure reveals local structure changes not evident in XRD

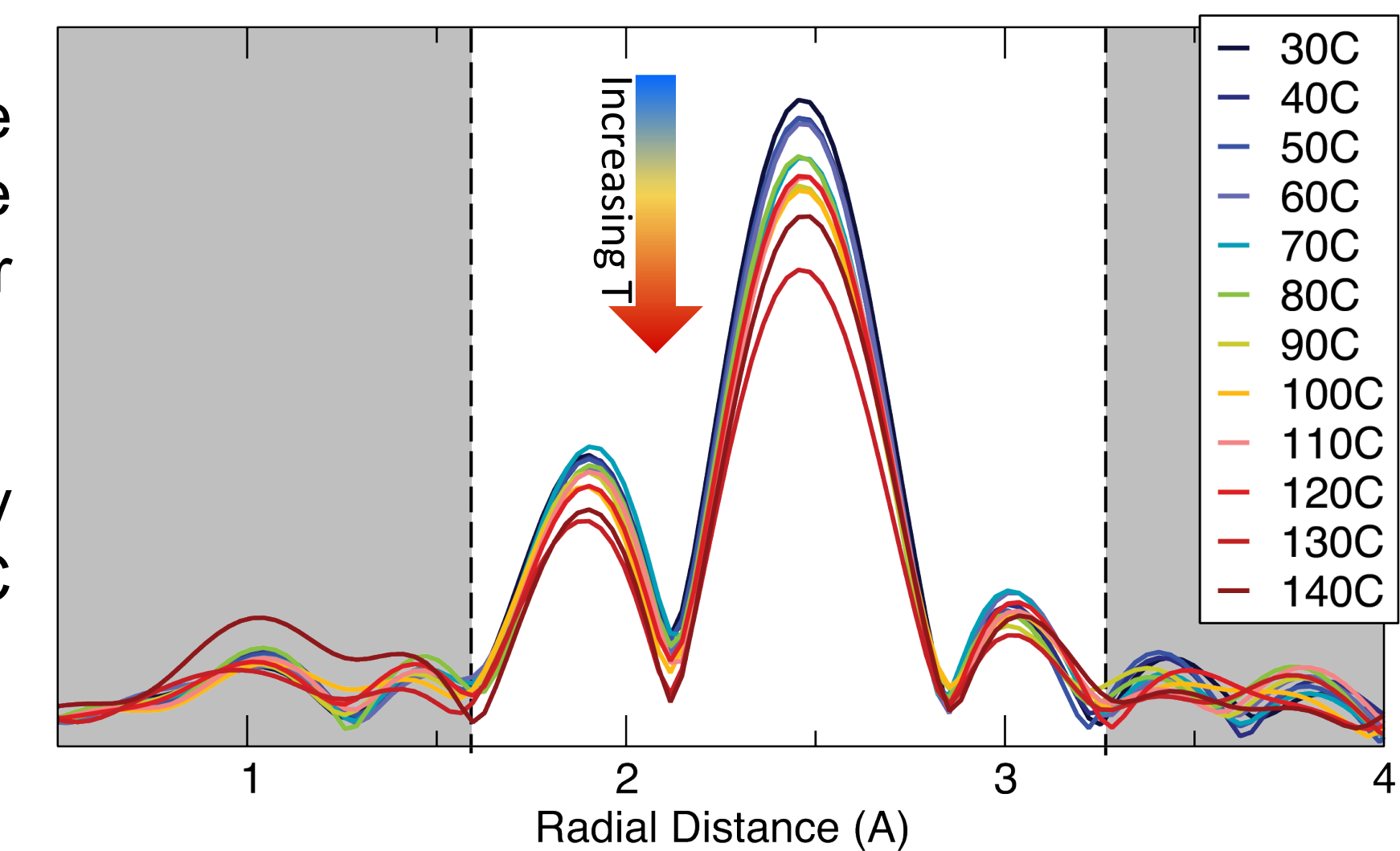
X-ray absorption near edge structure (XANES) qualitatively shows a binary change in Ge local structure upon phase transformation[4].



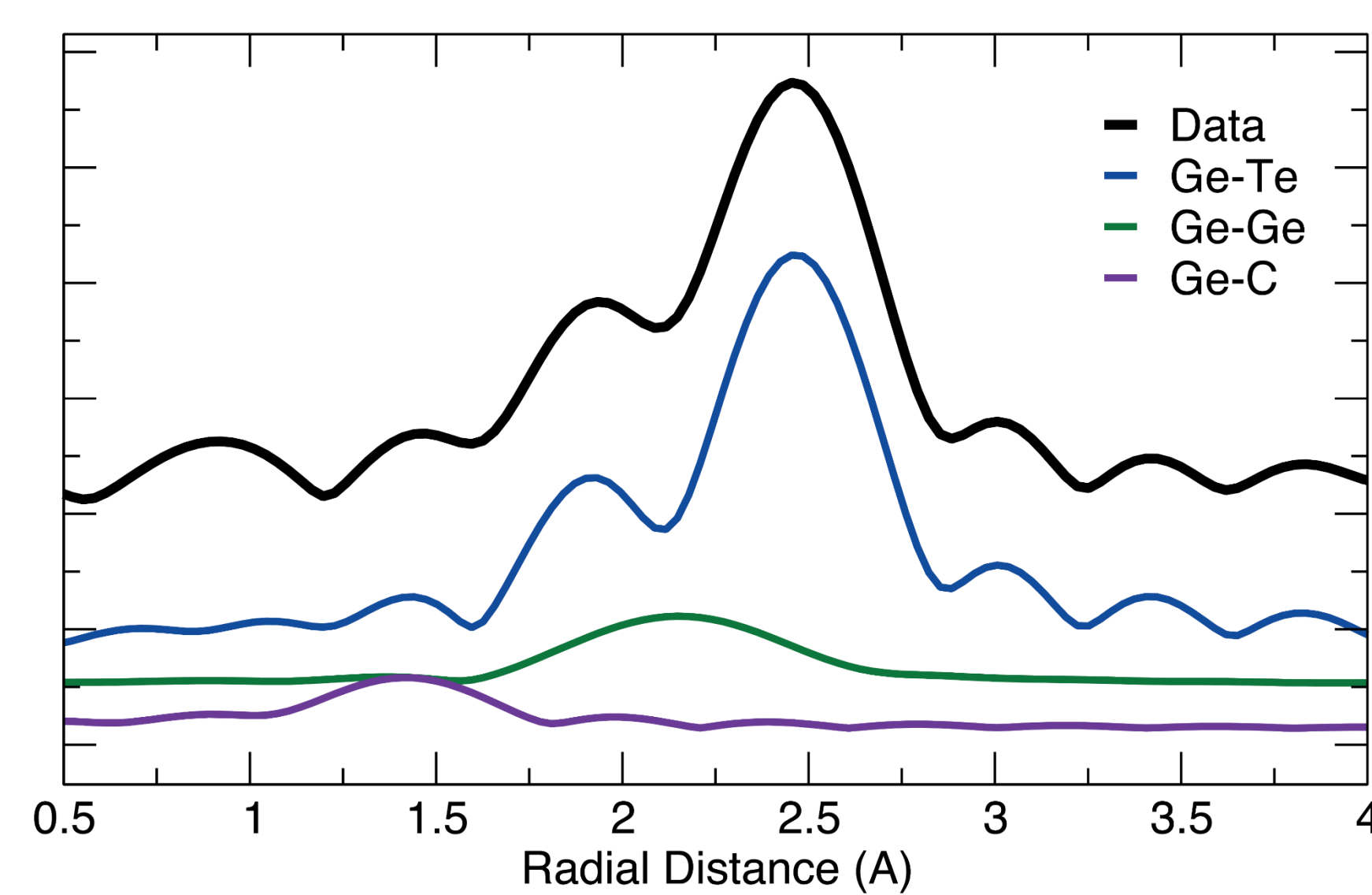
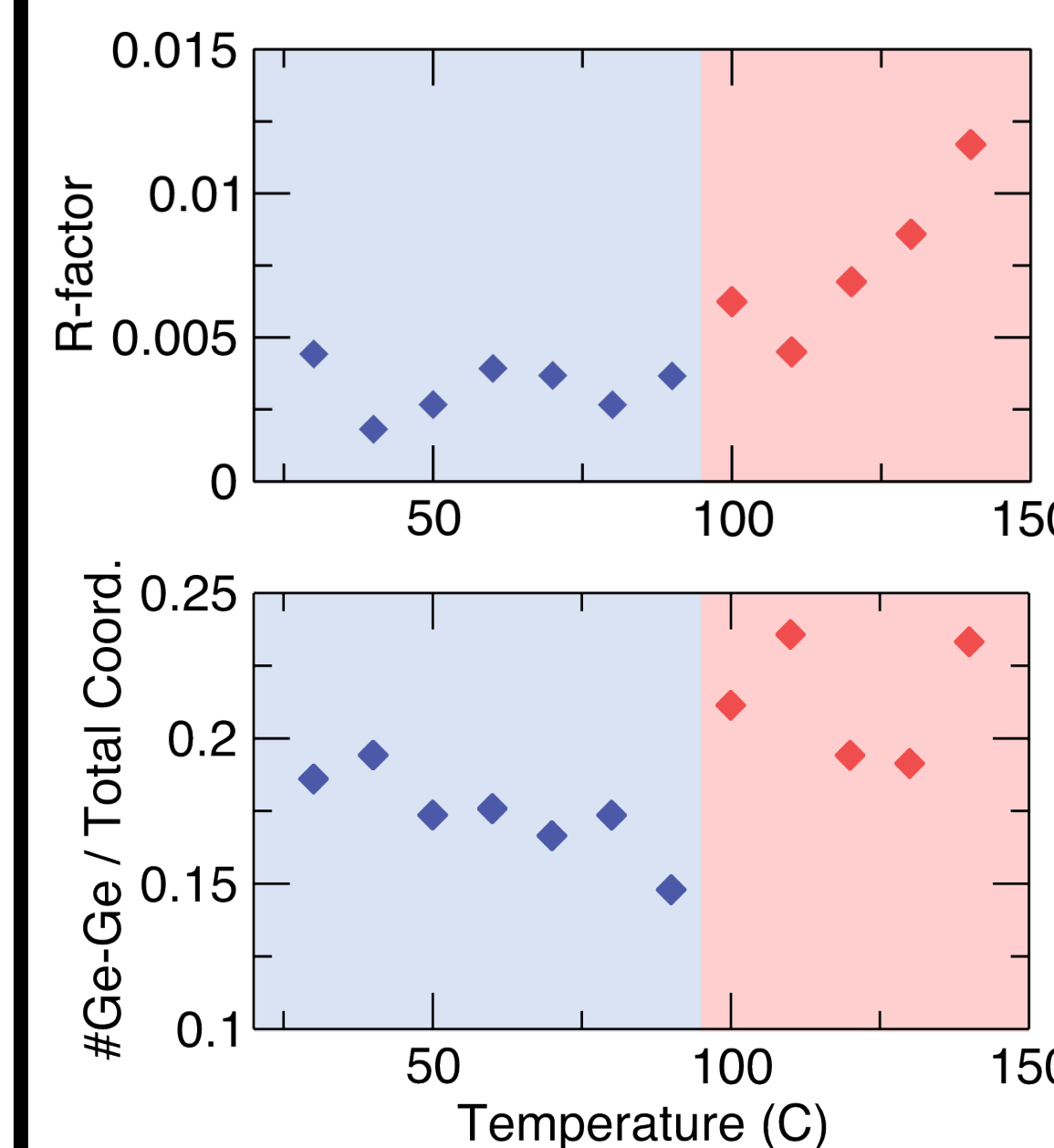
Extended X-ray Absorption Fine Structure (EXAFS)

Meanwhile, EXAFS qualitative reveals subtle changes in the Ge bonding environment prior to crystallization.

These changes are especially noticeable between 100°C and 140°C[4].



By modelling average signal contributions of adjacent atoms to Ge in amorphous GST, bond lengths and coordination numbers can be quantitatively determined [4].



The local structure model that fits the data well at low temperatures starts to fall apart above 100° C, before crystallization occurs.

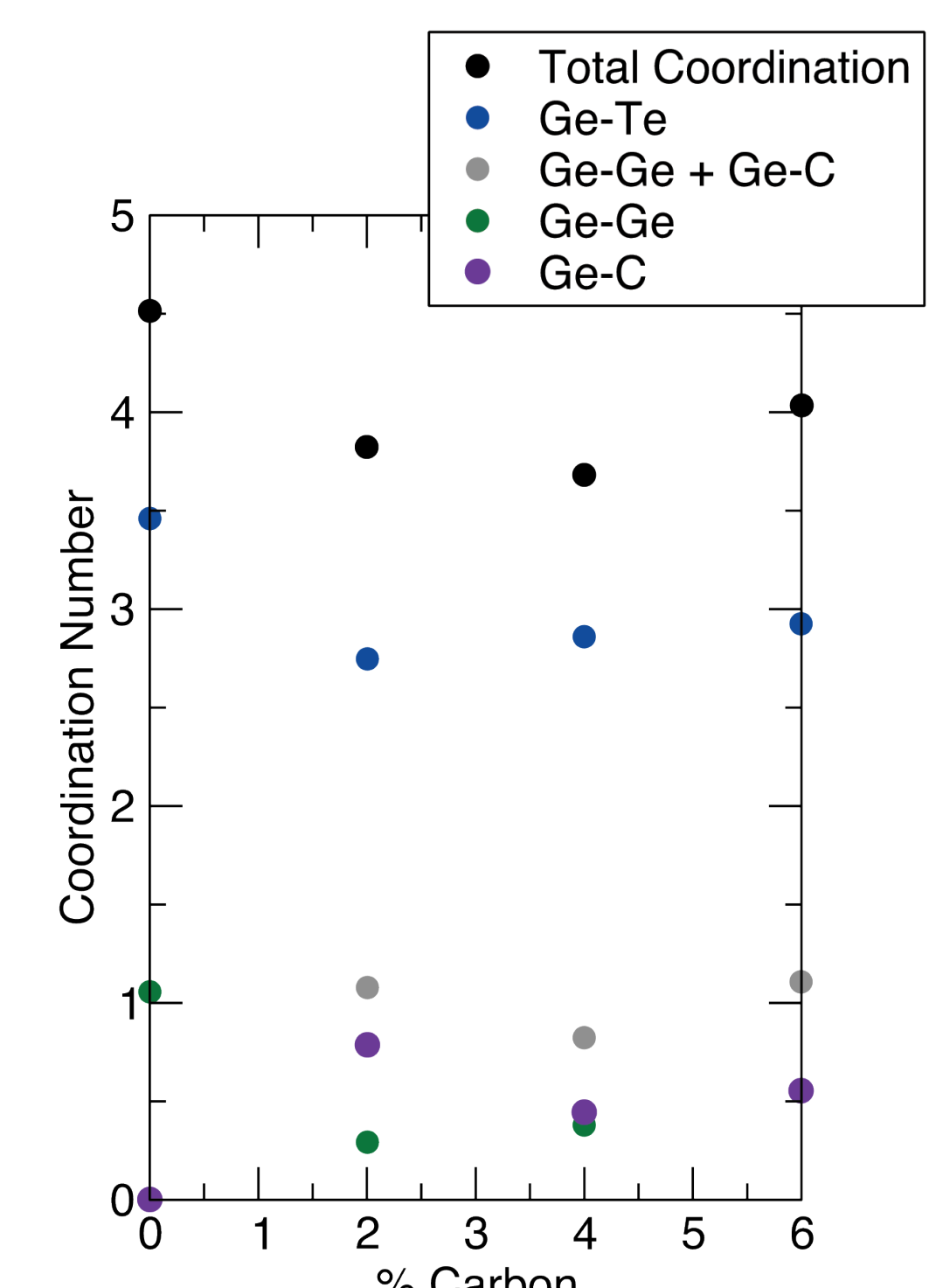
Similarly, parameters like Ge coordination number deviate sharply. This could indicate a distinct state that precedes crystallization.

EXAFS suggests the role of C in modifying the amorphous network, impacting crystallization kinetics

Carbon replaces Ge-Ge bonds with Ge-C bonds, which are shorter and stronger.

Ge-C bonds encourage Ge to form tetrahedral over distorted octahedral bonding schemes, lowering the average coordination number.

At higher doping levels, C forms chains with itself, and Ge-C bonds begin to disappear.



References

- S. Raoux, F. Xiong, M. Wuttig, and E. Pop, *Phase change materials and phase change memory*, *MRS Bull.*, vol. 39, no. 8, Art. no. 8, Aug. 2014, doi: [10.1557/mrs.2014.139](https://doi.org/10.1557/mrs.2014.139).
- E. A. Scott *et al.*, *Thermal conductivity of (Ge₂Sb₂Te₅)_{1-x}C_x phase change films*, *J. Appl. Phys.* **128** (2020) doi: [10.1063/5.0023476](https://doi.org/10.1063/5.0023476)
- K. M. Ø. Jensen *et al.*, *Demonstration of thin film pair distribution function analysis (tPDF) for the study of local structure in amorphous and crystalline thin films*, *IUCr*, vol. 2, no. 5, Art. no. 5, Sep. 2015, doi: [10.1107/S205252515012221](https://doi.org/10.1107/S205252515012221).
- B. Ravel & M. Newville, *ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT*, *J. Synch. Rad.* **12** (2005) doi: [10.1107/S0909049505012719](https://doi.org/10.1107/S0909049505012719)