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Atomic Structure Transformations of C-Doped $Ge_2Sb_2Te_5$ Thin Films Using *In Situ* X-Ray Scattering

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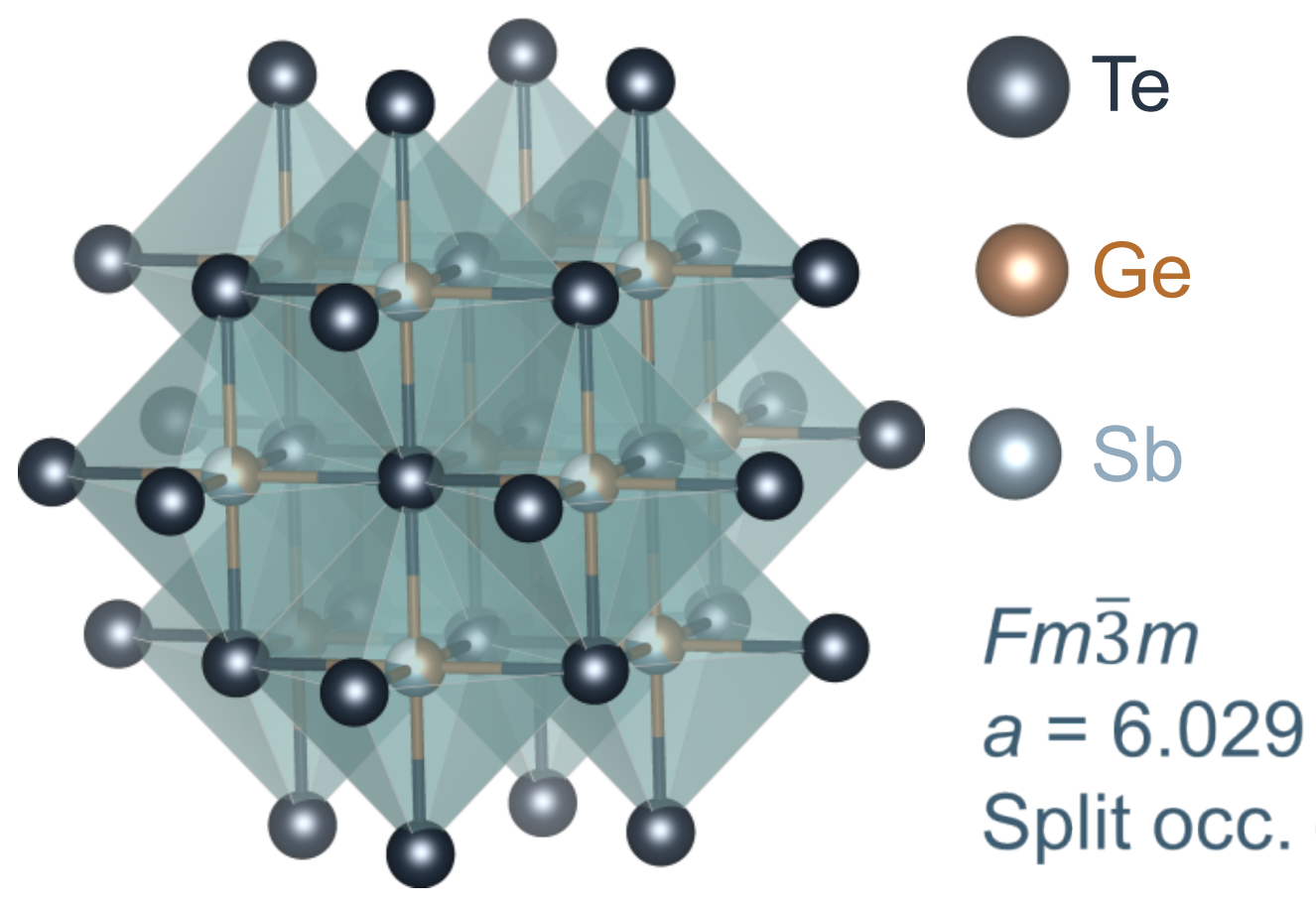
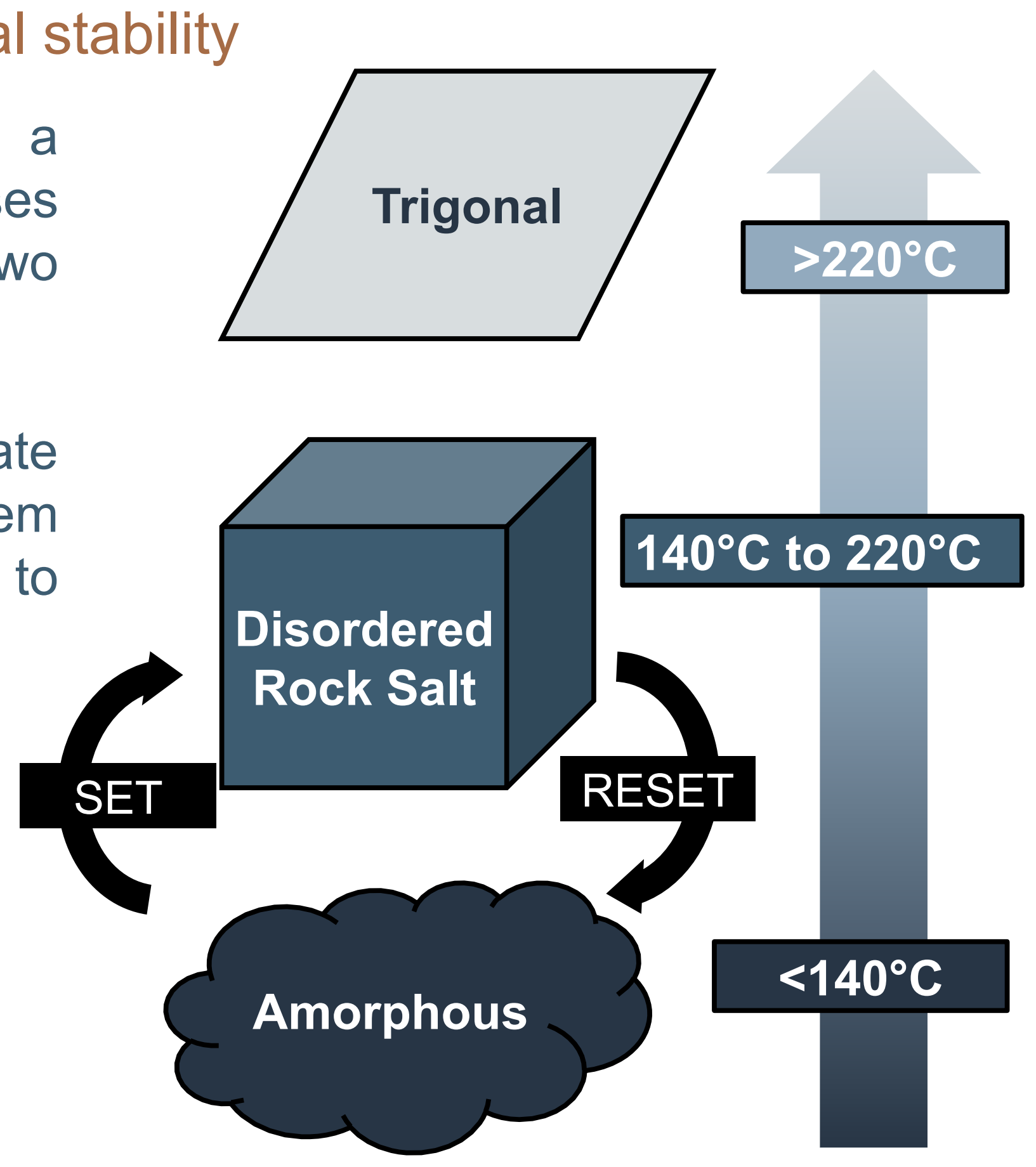
$Ge_2Sb_2Te_5$ (GST) is a candidate for future memory devices, but is limited by poor thermal stability

PCRAM (Phase-Change RAM) is a nonvolatile memory application that uses the resistivity difference between two phases. [1]

GST has two states with appropriate contrast and fast switching between them but risks unintended crystallization due to its low crystallization temperature.



Fm$\bar{3}$*m*
a = 6.029 Å
Split occ. of Ge, Sb, and vacancy



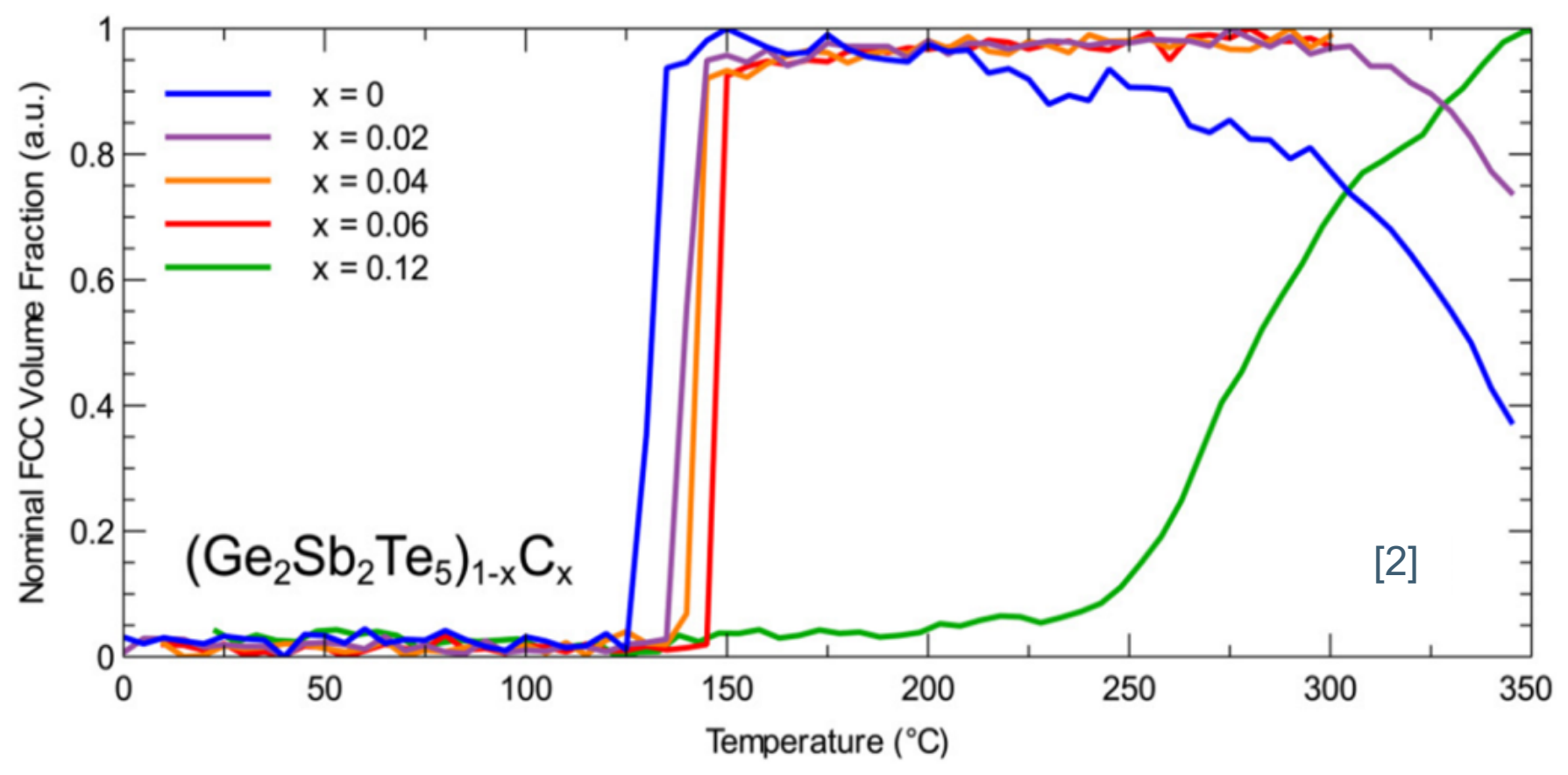
- Hard to amorphize
- Ordered structure
- Thermally stable

- Low Resistivity
- Metastable
- Disordered
- Octahedrally-coordinated Ge
- Easy to amorphize

- High Resistivity
- Easy to crystallize
- Tetrahedrally-coordinated Ge

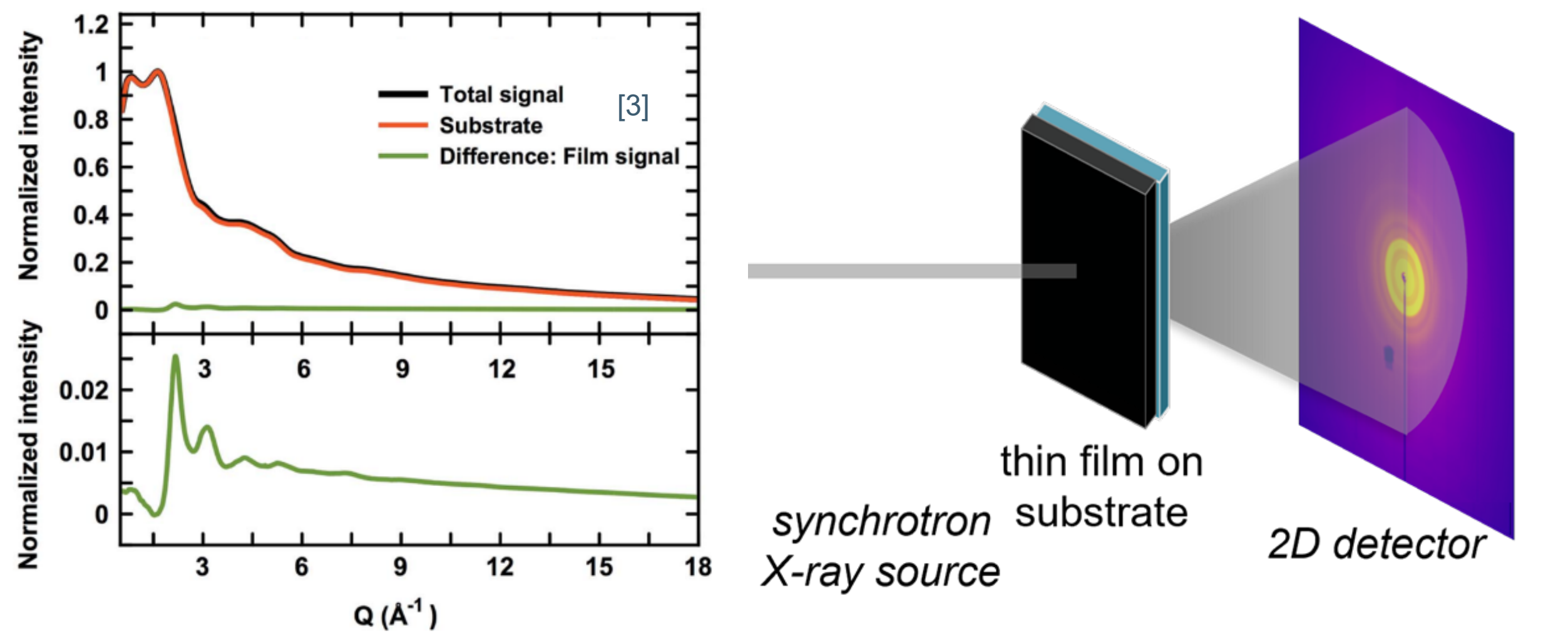
C-doping can increase the crystallization temperature of GST, but the mechanism of this change remains unknown

Dopants can increase crystallization temperature, improving thermal stability. However, how dopants are incorporated and the mechanism by which they modify the kinetics and thermodynamics of the transformation remain poorly understood [2].



The local, mid, and average structures are accessible through a modified pair distribution function

X-ray pair distribution function (PDF) is helpful to understand local and mid-range structures of disordered materials.
Though less conventional, PDF can be applied to disordered thin films to access multi-lengthscale structure-property relationships.[3]



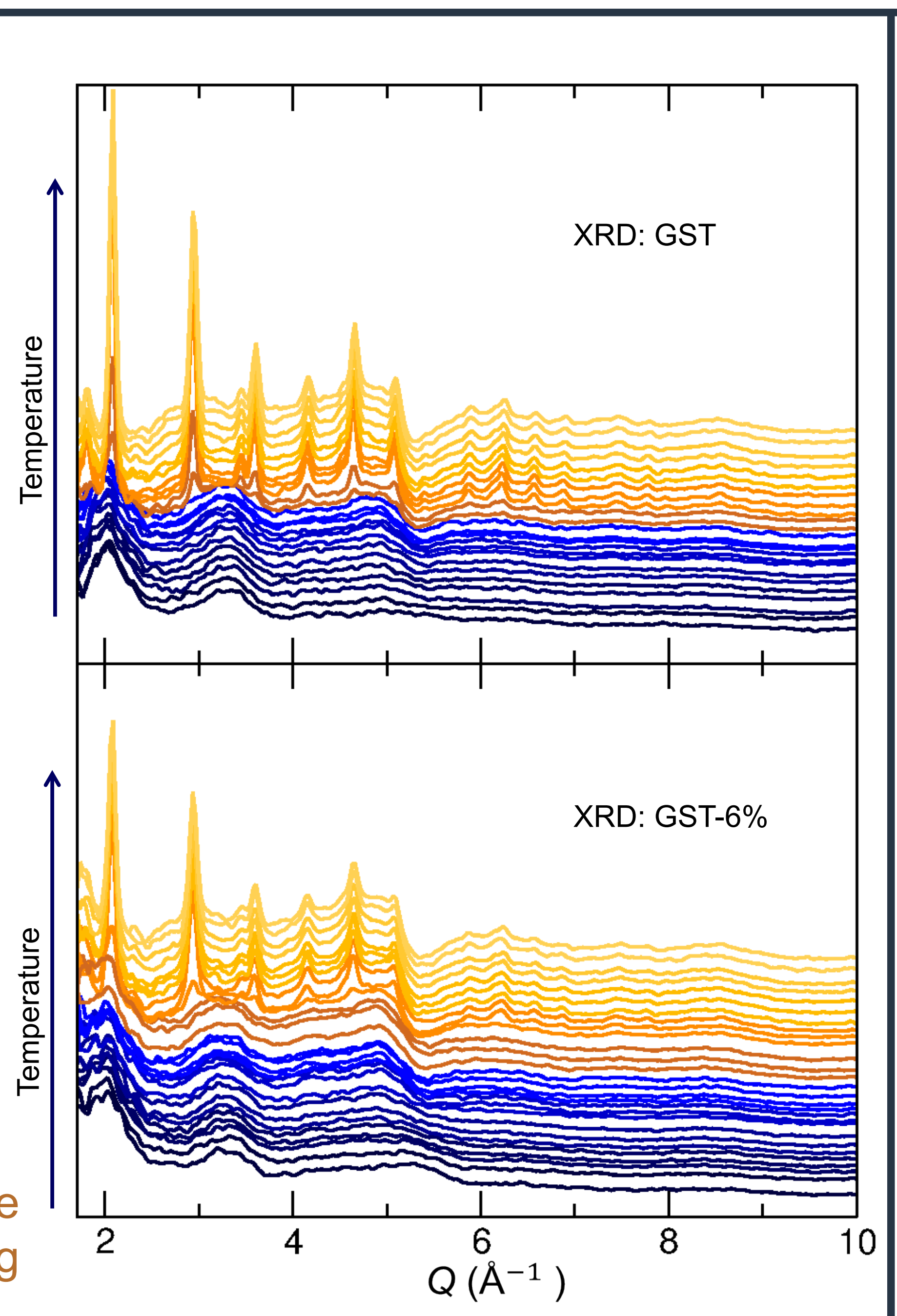
Using in situ atomic structure characterization during crystallization, we find that mid-range structure during the amorphous to crystalline transformation varies most between GST and C-GST.

The average structure has an abrupt phase transformation between the amorphous and crystalline states

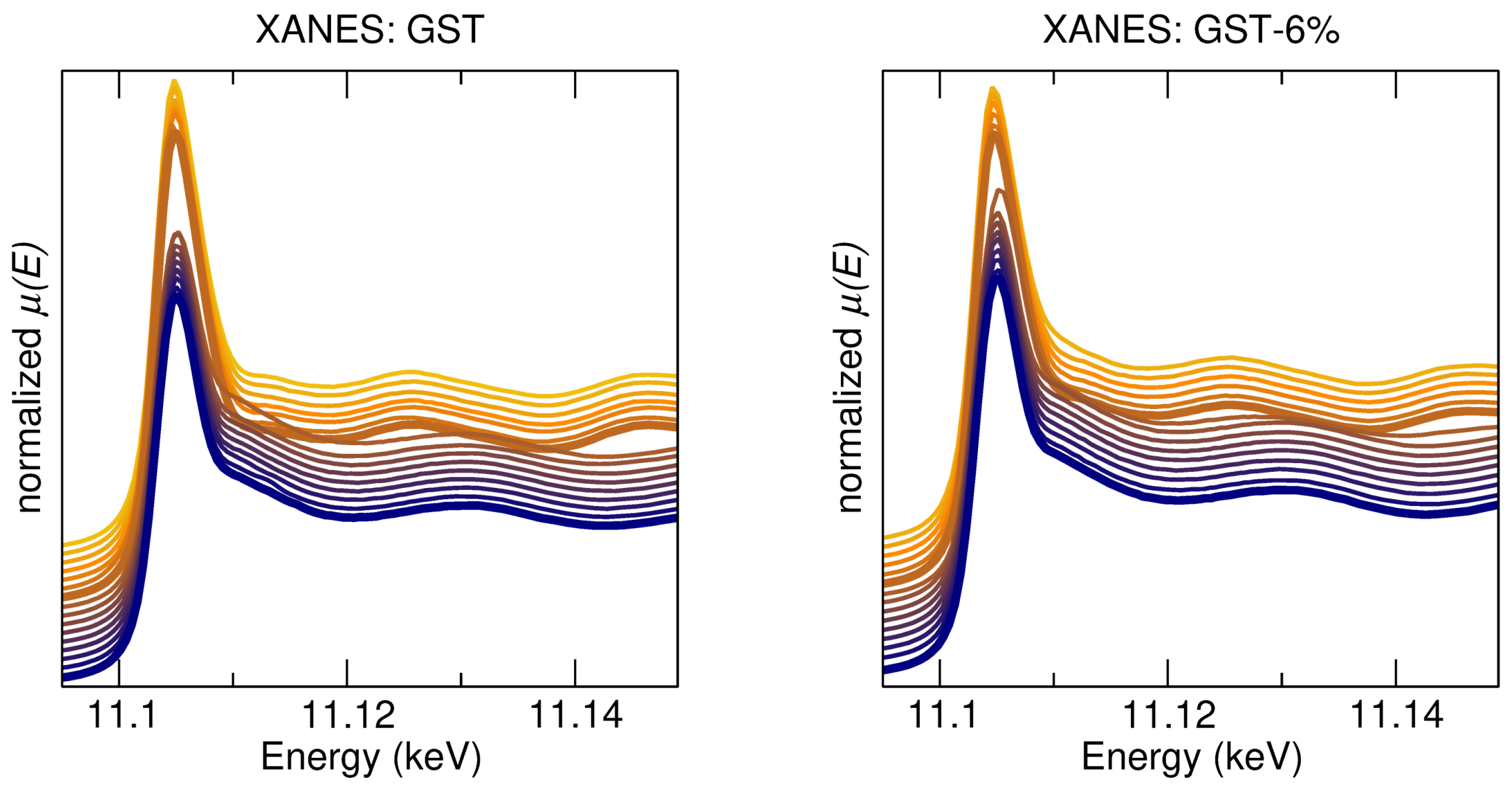
Temperature dependent *in situ* XRD on GST and C-GST films shows sudden crystallization. The C-GST has a more gradual change and crystallizes at a higher temperature.

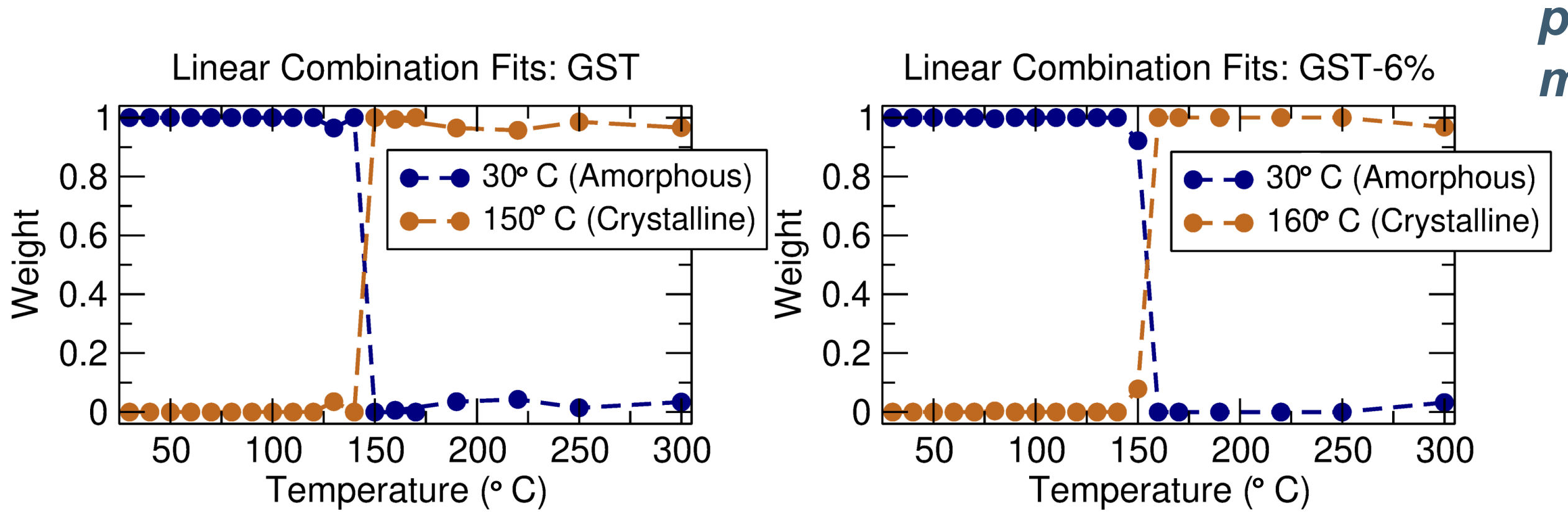
While XRD clearly indicates when a crystalline phase is present, it does not provide quantitative insights to the amorphous structure.

Crystallization temperature increases with increasing C content



Local coordination environment of Ge also shows an abrupt change during crystallization for GST and C-GST

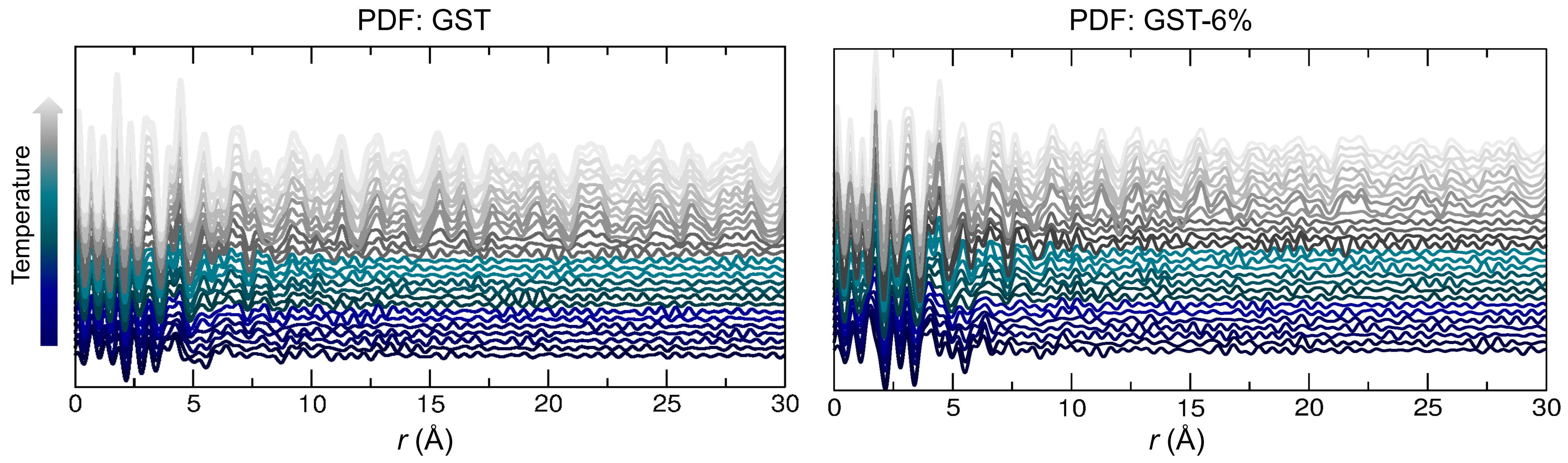




In situ X-ray absorption near edge structure (XANES) data and linear combination fits of the lowest and highest temperature edges show the crystallization temperatures.[4]

The crystallization process for C-GST is more gradual than GST.

PDF data confirm the abrupt phase transformation for GST in the high *r* range, and shows relatively gradual changes in the local- and mid-range structure



With heating, correlations at higher *r*-ranges (10 Å to 30 Å) change suddenly, corresponding to crystallization.

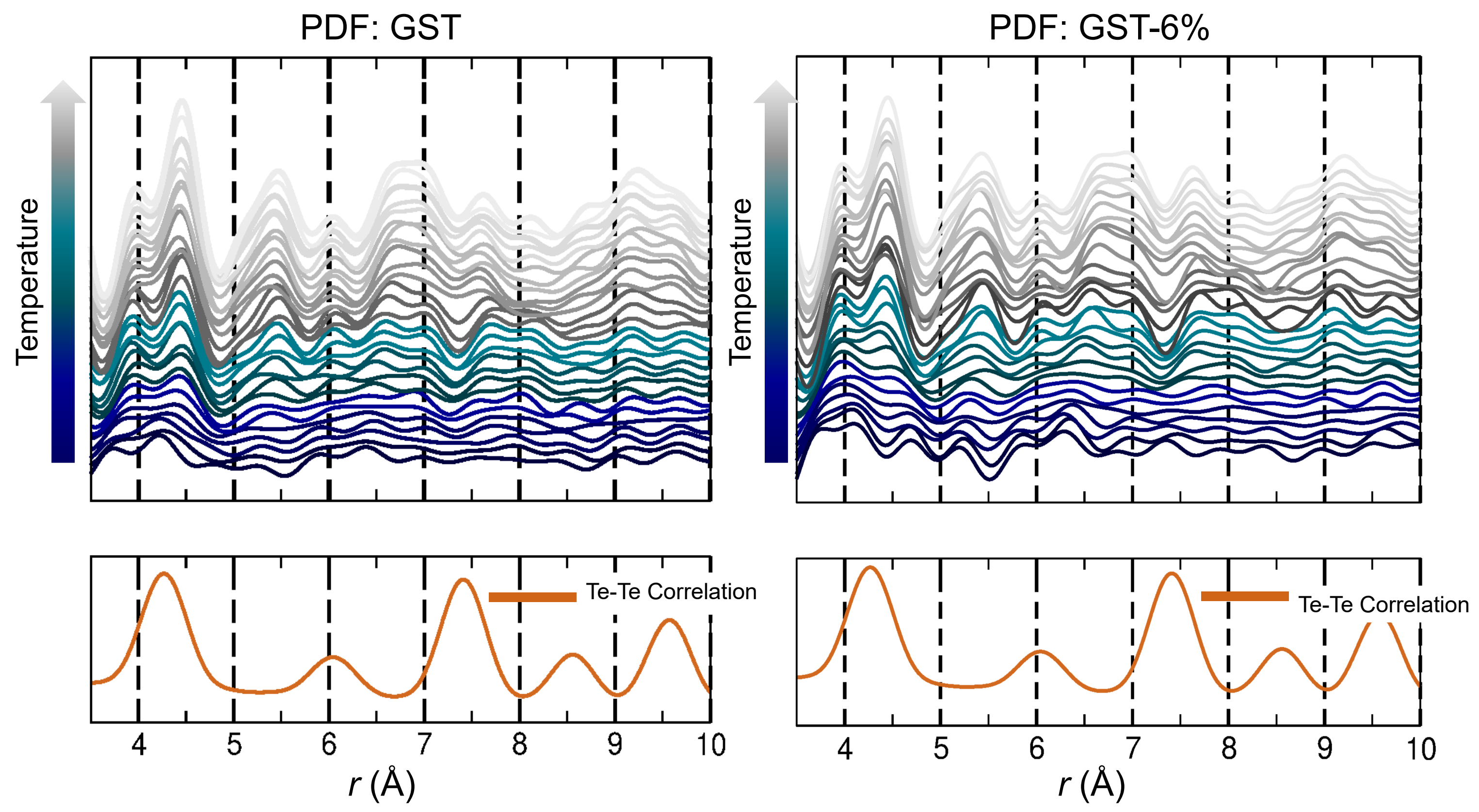
Correlations at lower *r*-ranges (2 Å to 7 Å) gradually evolve with heating, indicating local structure changes precede crystallization.

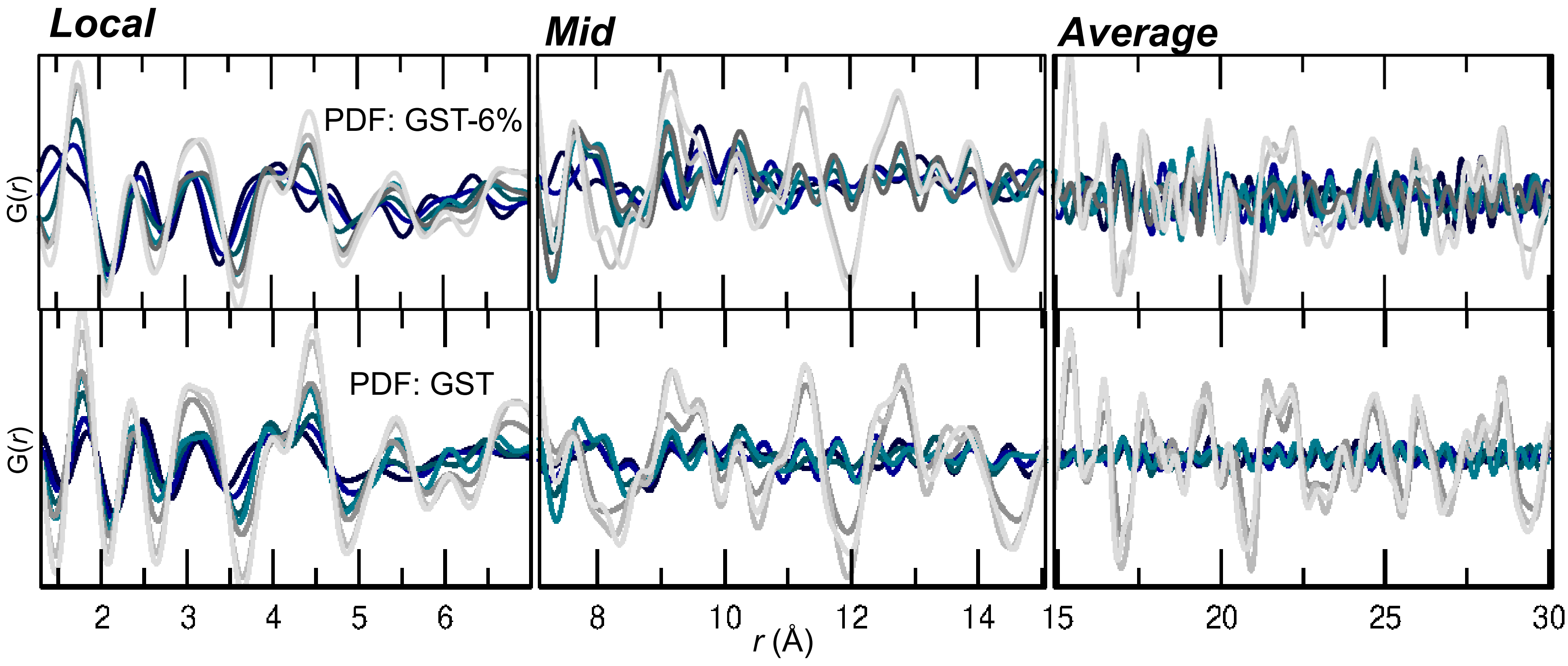
The Te framework continuously evolves during heating, including at mid-range length scales before crystallization

The mid-range structure has correlations associated with the Te-Te framework before crystallization that are not seen in the average structure or the local Ge coordination.

The addition of carbon slows the formation of the Te framework during heating. These mid-range effects, may be the origin of the elevated crystallization temperature with C-doping.

Carbon doping disrupts the Te framework, and thus stabilizes the amorphous state.





Carbon doping of the GST structure affects disorder, crystallization temperature, and trigonal phase formation

For all compositions, local structure changes are similar and continuous during heating.

The mid-range structure changes for GST occur at lower temperatures than C-GST. This includes correlation splitting suggestive of the trigonal phase (in GST).

High *r*-ranges show more gradual changes for C-GST than for GST.

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Conclusions

Using tfPDF, we gain new insights into the structural phase evolution of GST that are not accessible through either XRD or XAS. We find supporting evidence of an increase in amorphous phase stability, leading to a rise in the crystallization temperature, as well as evidence of the trigonal phase transformation. Through tfPDF, we have observed that the Te framework develops before crystallization, which could play a significant role in the fast transformation speed between the amorphous and crystalline phases. We speculate that the slow formation of Te correlations with carbon doping could be due to Ge forming strong bonds with C instead of with Te, thus increasing the amorphous phase stability.

References

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