



Unveiling Local Structural Distortions and Band Gap Narrowing in Oxysulfide Pyrochlore $\text{Sn}_2\text{Nb}_2\text{O}_{7-x}\text{S}_x$

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MOTIVATION

Desired Inorganic Pigment

- Structurally stable
- Non-toxic
- Resistant to chemical attack and fading
- Band gap for red pigment ~ 2.0 eV

Conventional use



CADMIUM YELLOW

Cadmium sulfide, CdS



CADMIUM ORANGE

Cadmium sulfoselenide, Cd_2SSe_2



CADMIUM RED

Cadmium selenide, CdSe

CHROME YELLOW

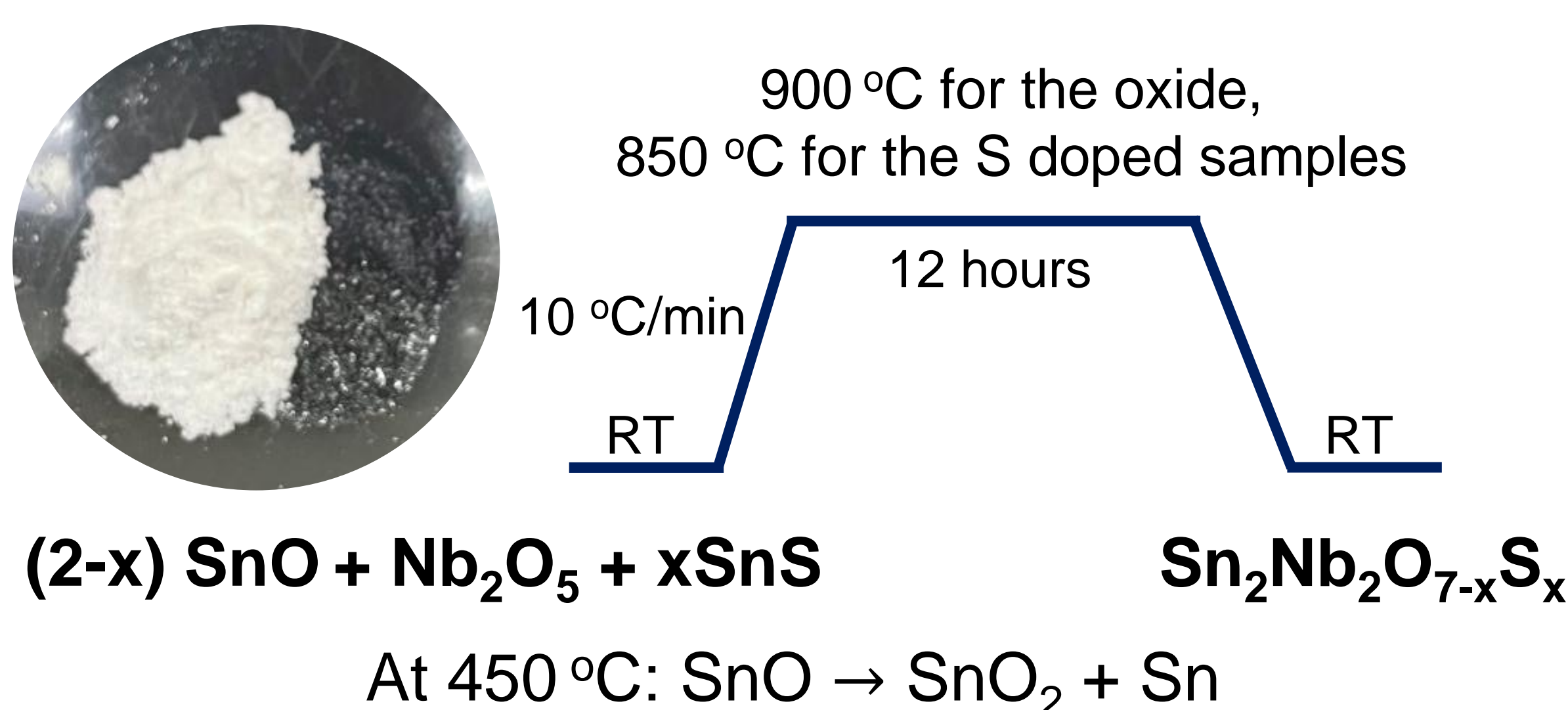
Lead chromate, PbCrO_4

RED OCHRE

Iron (III) oxide, Fe_2O_3

Contain toxic heavy metals
→ Severely restricted

SYNTHESIS



PRODUCTS AND OPTICAL BAND GAP

Increasing S content

$x = 0.0$



$x = 0.2$



$x = 0.4$



$x = 0.6$



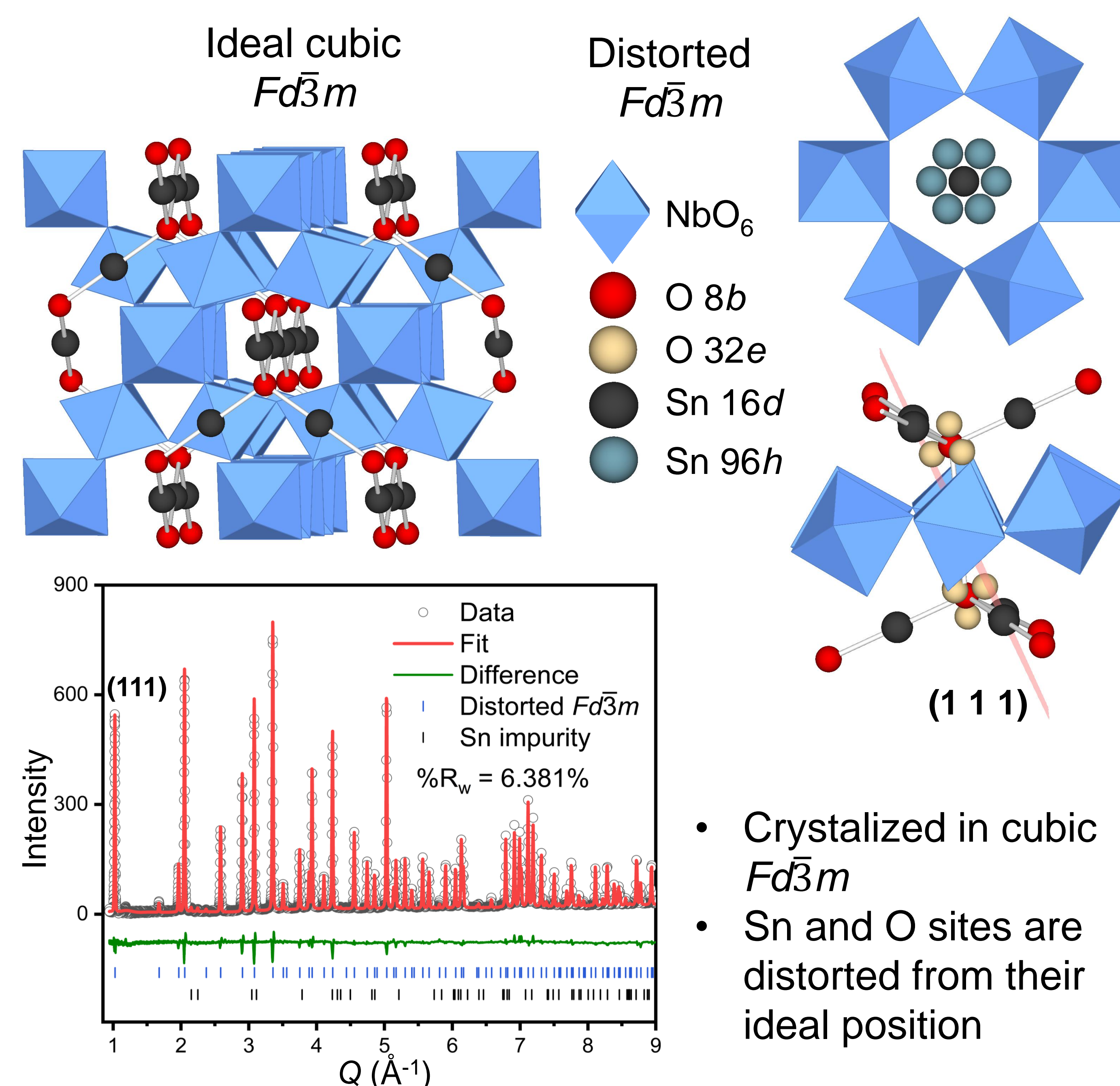
Band gap: 2.39 eV

2.14 eV

2.12 eV

2.10 eV

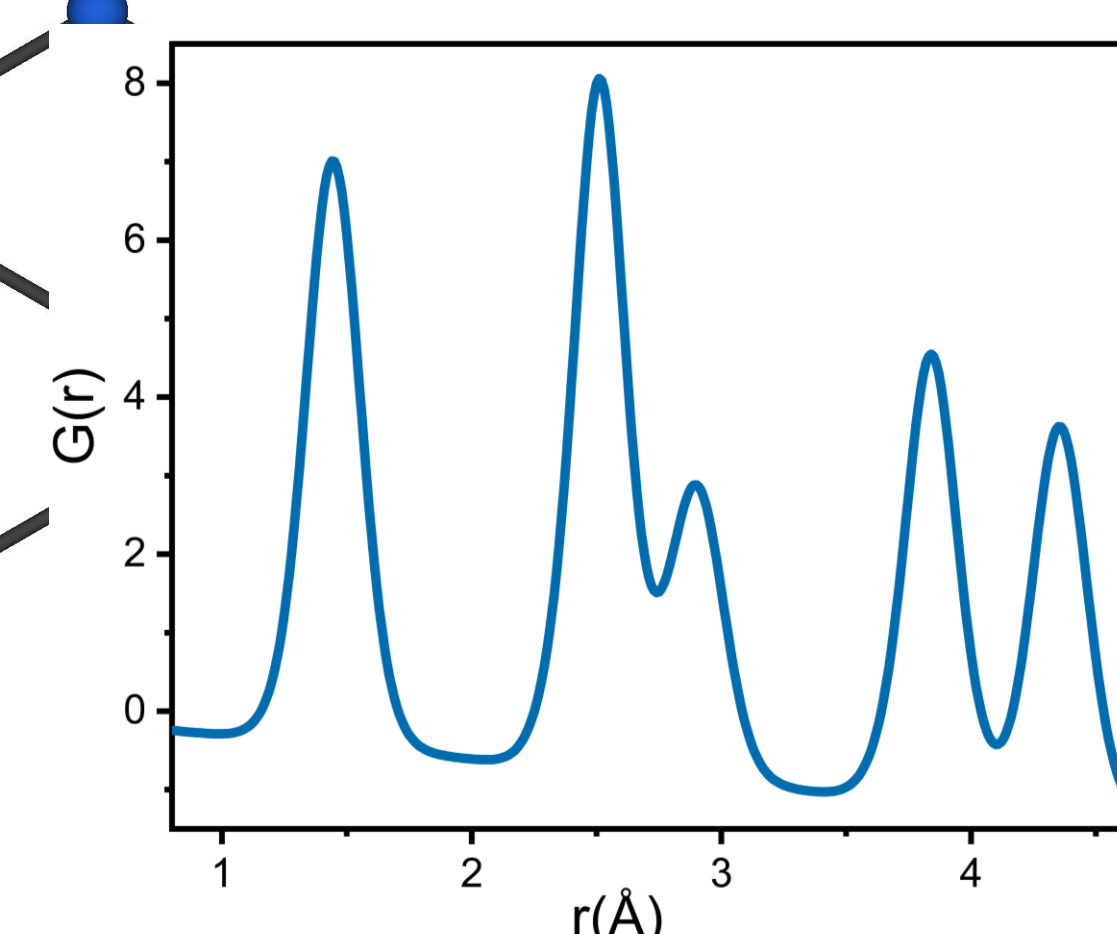
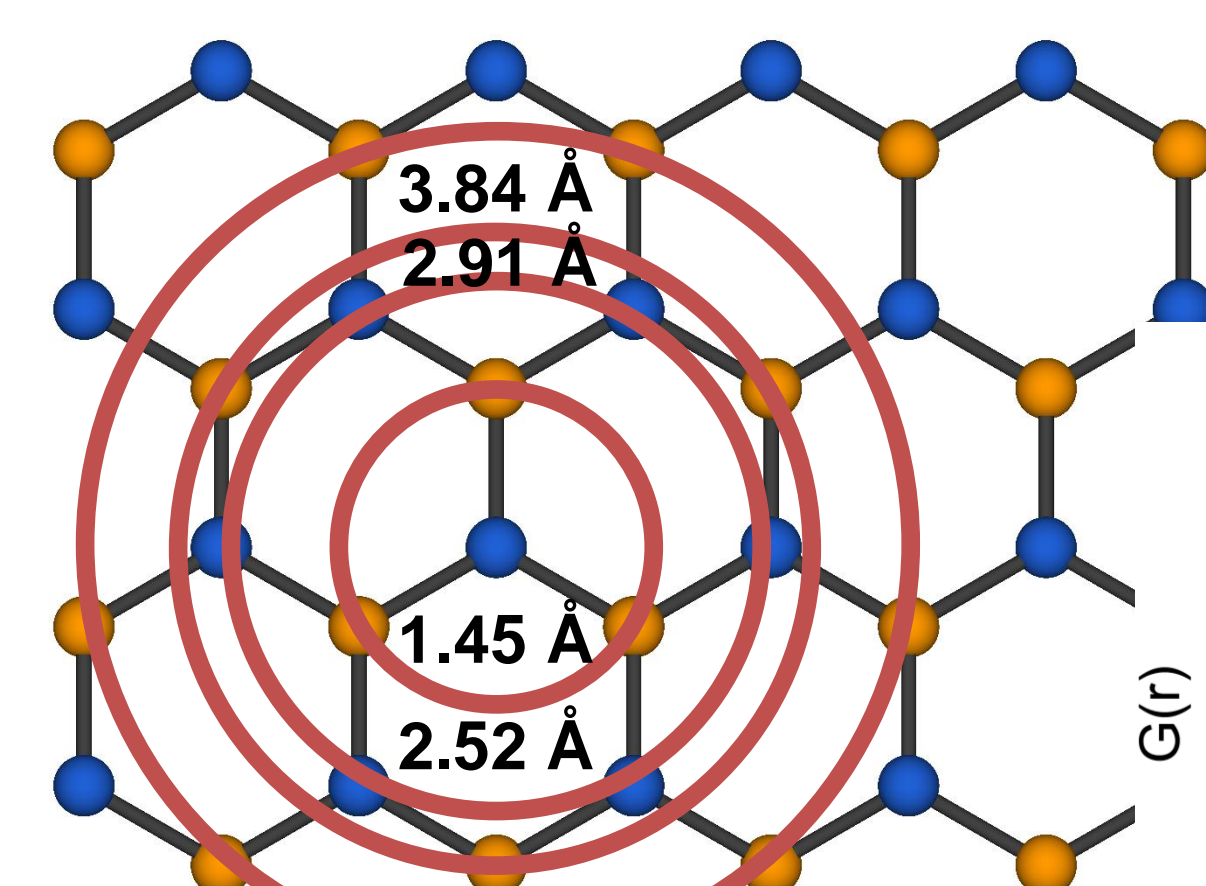
AVERAGE CRYSTAL STRUCTURE



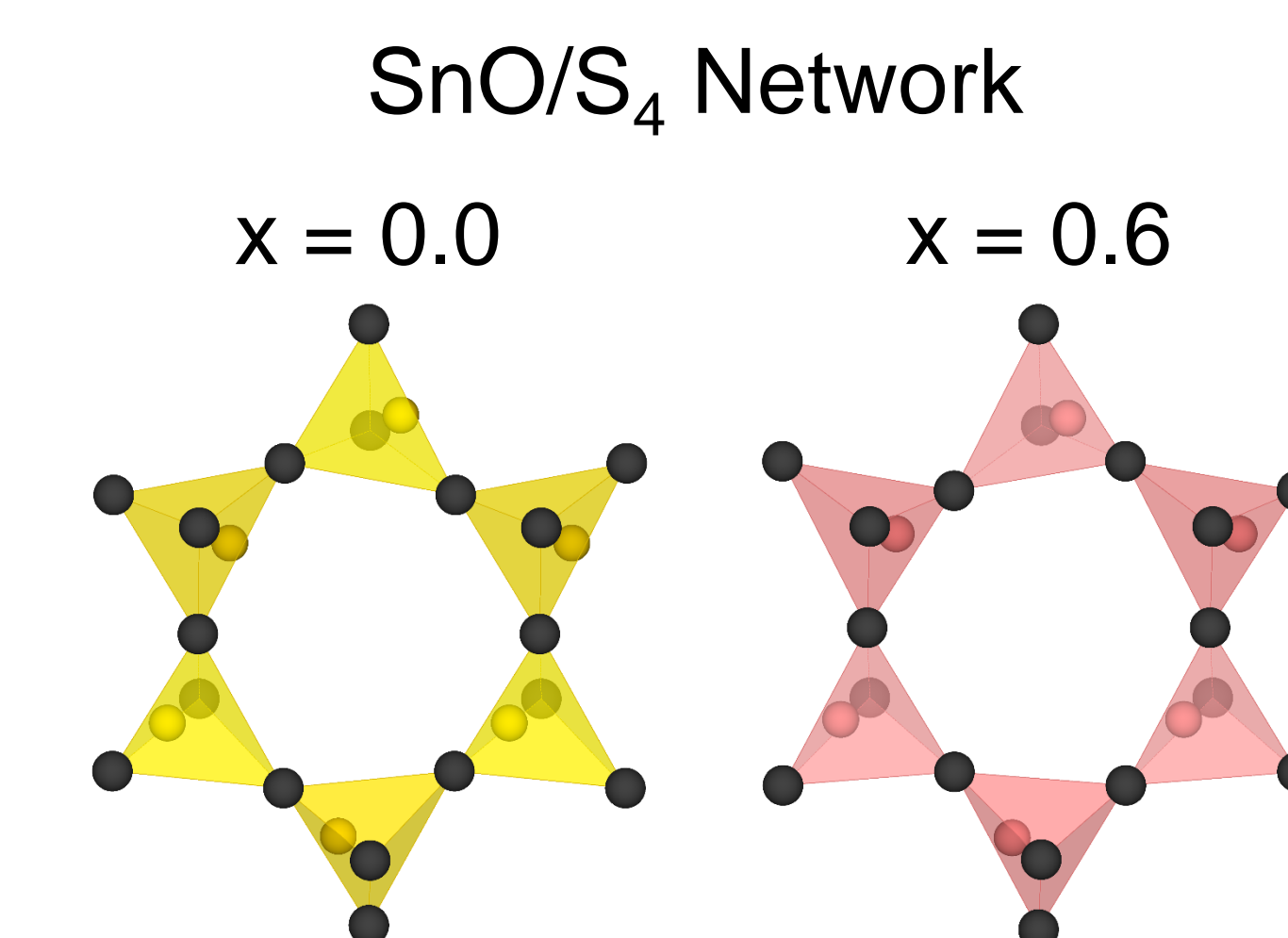
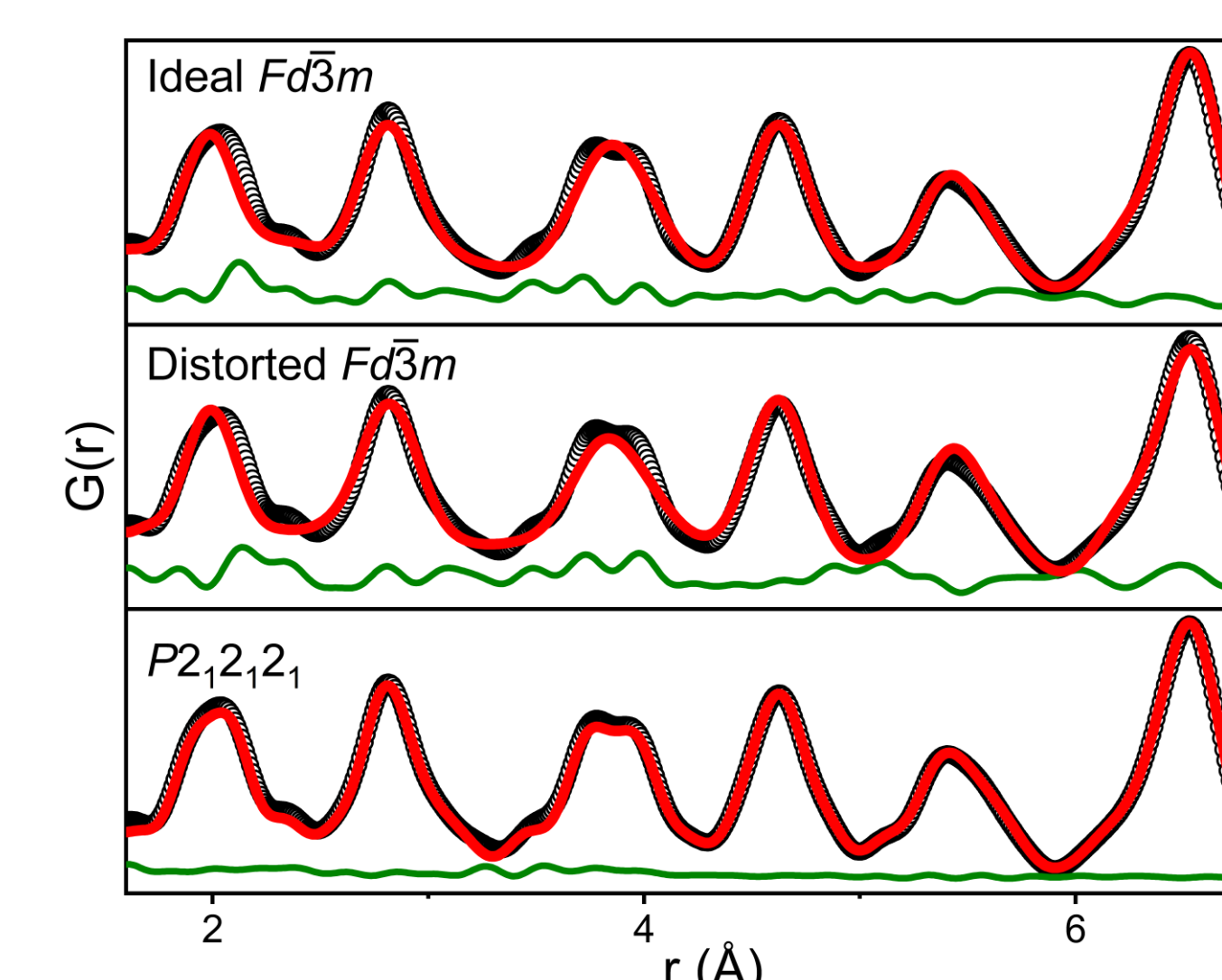
PAIR DISTRIBUTION FUNCTION (PDF)

PDF represents the probability of finding atomic pairs at a given distance.

- Short-range atomic correlations
- Distortions and disorder
- Require high-energy synchrotron (28-ID-1 at BNL) or neutron (POWGEN at ONL) beamlines



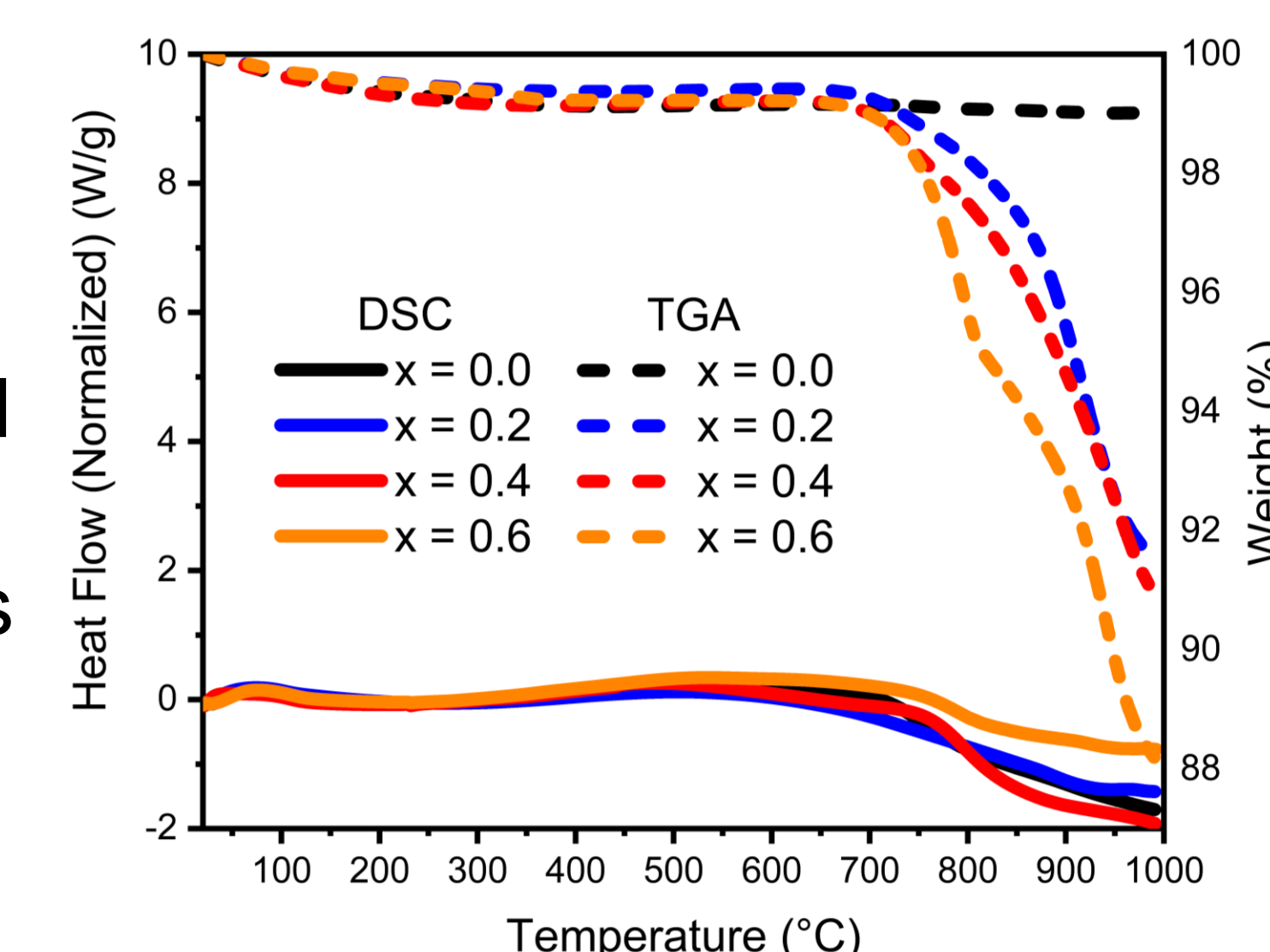
LOCAL DISTORTIONS



- Local Distortions Revealed: PDF analysis fits better with the lower-symmetry space group $P2_12_12_1$, highlighting distortions undetectable by laboratory XRD.
- Effect of Sulfur Doping: Replacing oxygen with sulfur alters covalency and modifies Sn lone pair interactions, impacting the overall electronic structure and band gap.

THERMAL STABILITY

- Stable up to 650 °C under an inert nitrogen environment
- Higher sulfur content results in greater weight loss around 650 °C
- Sulfur loss at ~ 650 °C causes a red-to-yellow color change



CONCLUSION

- Increasing sulfur content shifts the color from yellow (oxide) to orange/red
- Sn and O shift from ideal positions in the average structure
- PDF analysis confirming lower-symmetry ($P2_12_12_1$) space group indicates local distortion in the Sn-O/S network
- Offer a non-toxic alternative to yellow and red pigments, with a thermally stable structure up to 650 °C.

REFERENCES

- Solid State Sci.* **2018**, 81, 32–42.
- Philos. Transact. A Math. Phys. Eng. Sci.* **2019**, 377 (2147), 20180413.

ACKNOWLEDGEMENT

