Influence of Sn doping in Zn_2GeO_4 structure and optical properties

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Motivation

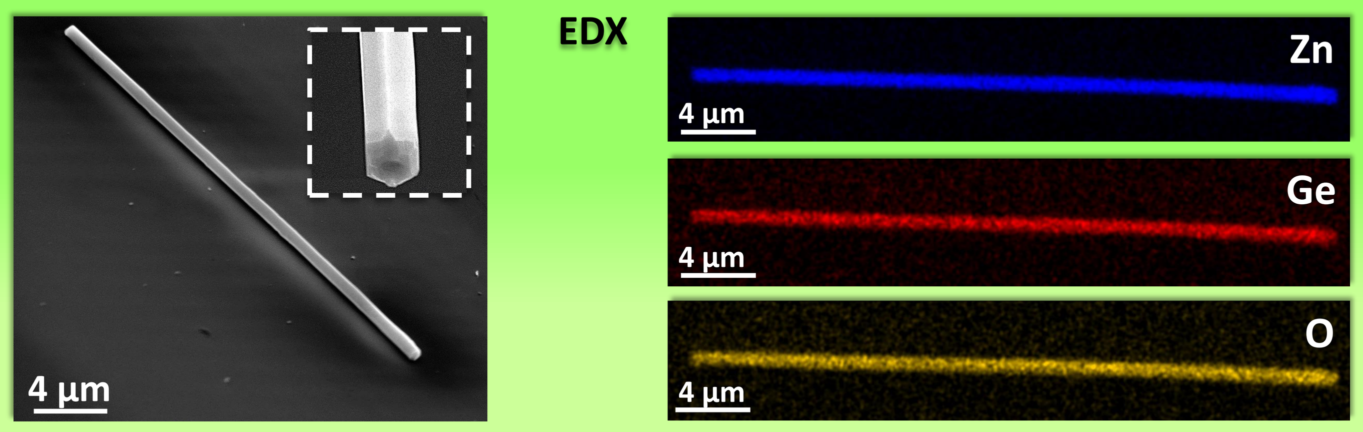
Germanates have emerged as a new family of transparent conducting oxides (TCOs), which are materials with a high electrical conductivity and a high optical transparency in visible light, due to their wide band gap. Their properties make them of interest in applications like nanoelectronics, optical nanodevices, sensing or catalysis, which has made the activity on nanostructured germanates increases in the last few years [1,2,3]. On the other hand, the role of dopants is of paramount importance in the design of materials at the nanoscale, because impurities may influence both morphology, architecture and physical properties.

Objectives

We have chosen Sn as dopant for several reasons: i) tin often acts as a catalyst during the thermal growth process and would modify the final morphology of the nanostructures. ii) Impurities often tend to out-diffusion in nanowires, hence surface properties could be affected as well. iii) Tin may locally modify the crystal lattice and the native defects structure, which would add electronic levels in the band gap and/or alter oxygen vacancies related states. In this work, we have characterized the chemical, microstructural and optical properties of Zn_2GeO_4:Sn nanostructures.

Previous Work [2,3]

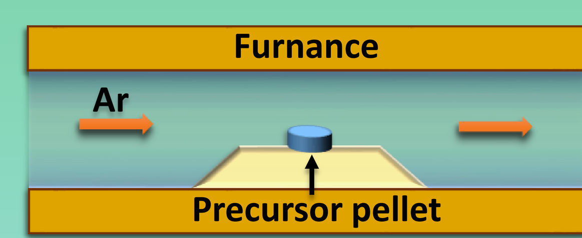
Undoped



Synthesis Method

Tin doped Zn_2GeO_4 structures have been grown by a thermal evaporation method on a catalyst free basis. Samples were annealed under argon flow in a tubular furnace at 800°C for 8h.

Samples	Precursor
Undoped Zn_2GeO_4	ZnO + Ge + C (2:1:2)
Zn_2GeO_4:Sn	ZnO + Ge + C (2:1:2) + 5, 10 and 15% of SnO_2 in the ZnO+Ge weight

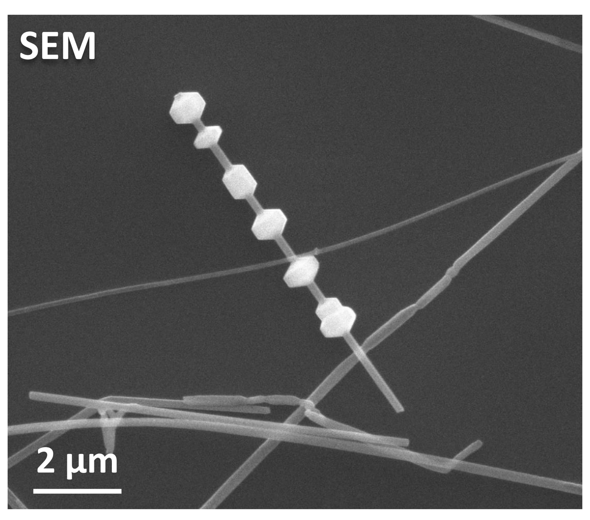


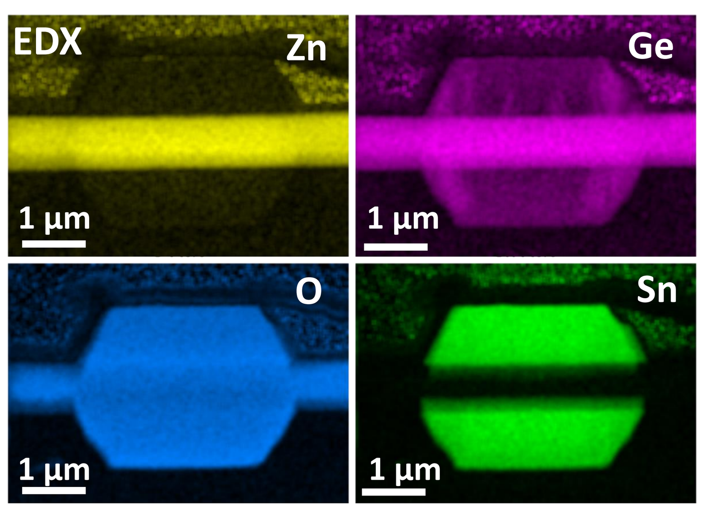
Tin doped

- High density of structures when we add tin in the precursor pellet (the amount of structures grown changes with the concentration of SnO_2).
- In addition to simple nanowires, **complex structures** appear.

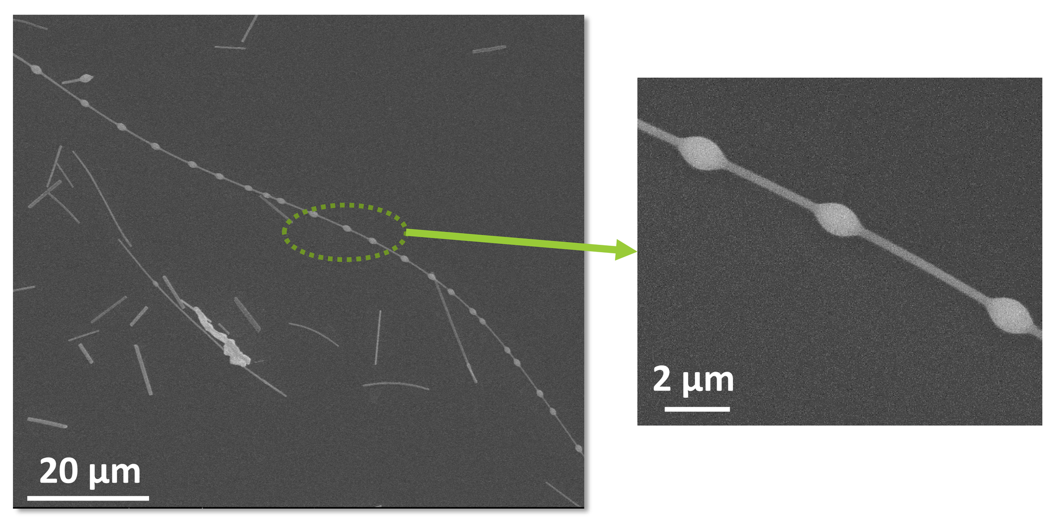
SnO_2 particles ← Axis: Zn_2GeO_4 NWs → GeO_2 beads

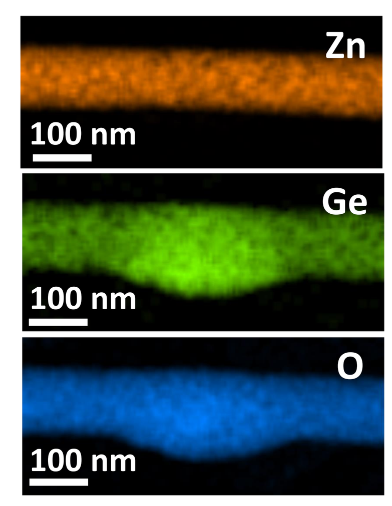
Skewer-like | Necklace-like



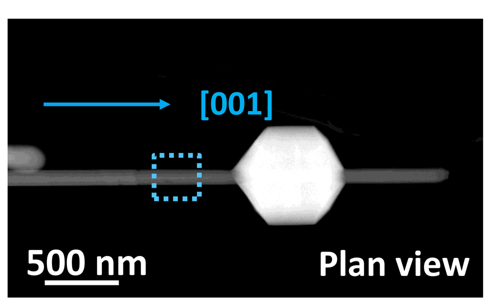


Morphology and Composition

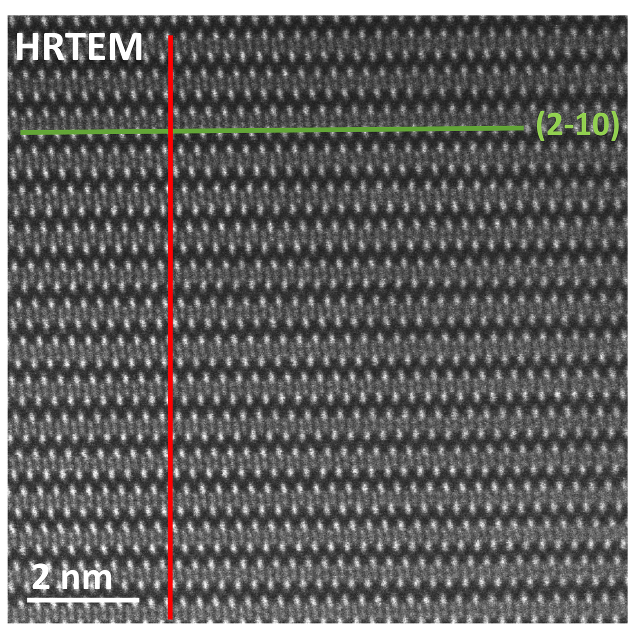


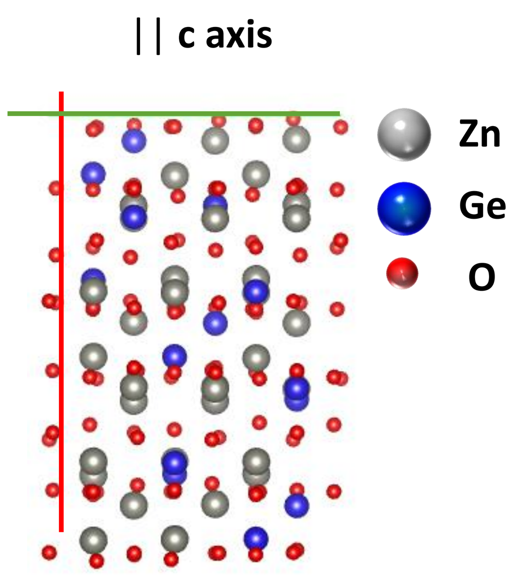


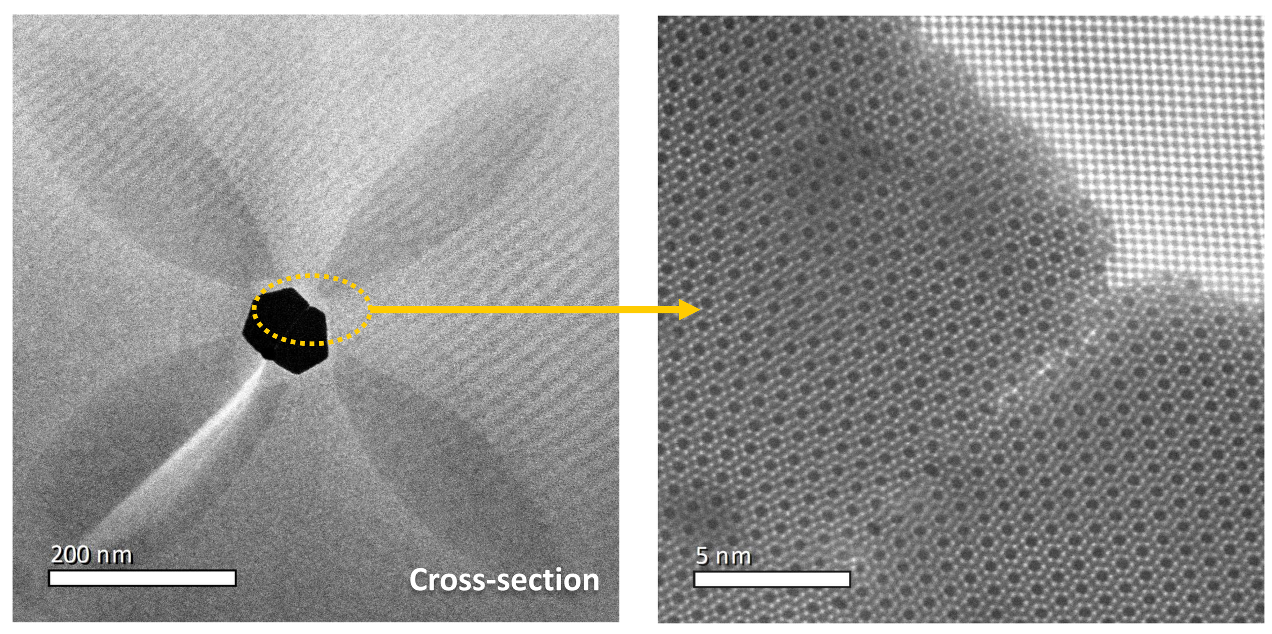
Microstructural study

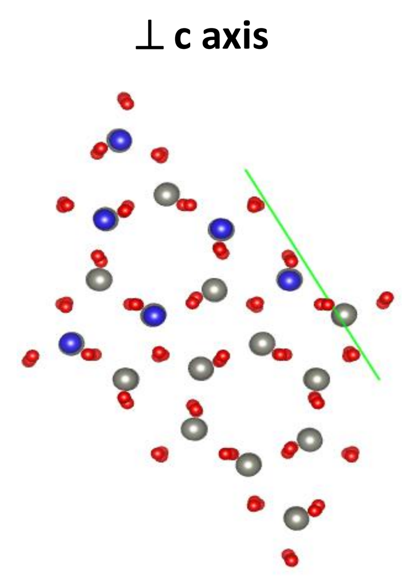


The growth direction of undoped Zn_2GeO_4 NWs is [001] [2].

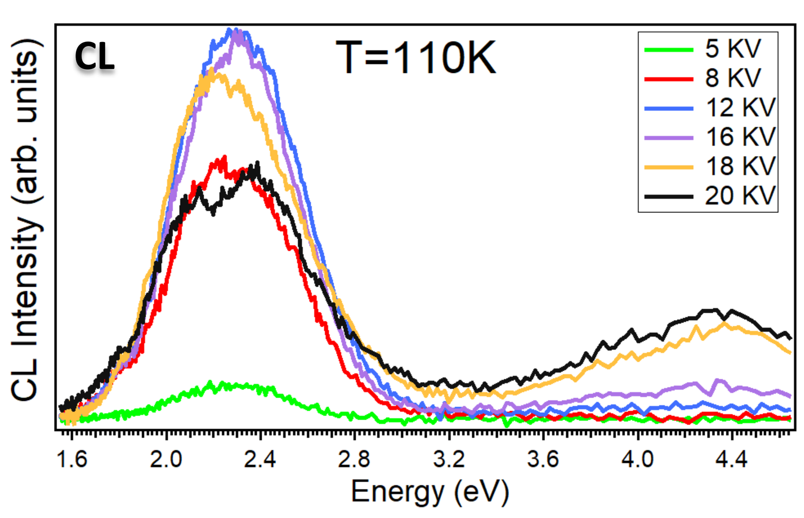


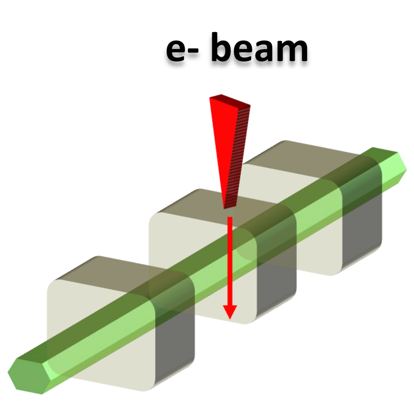






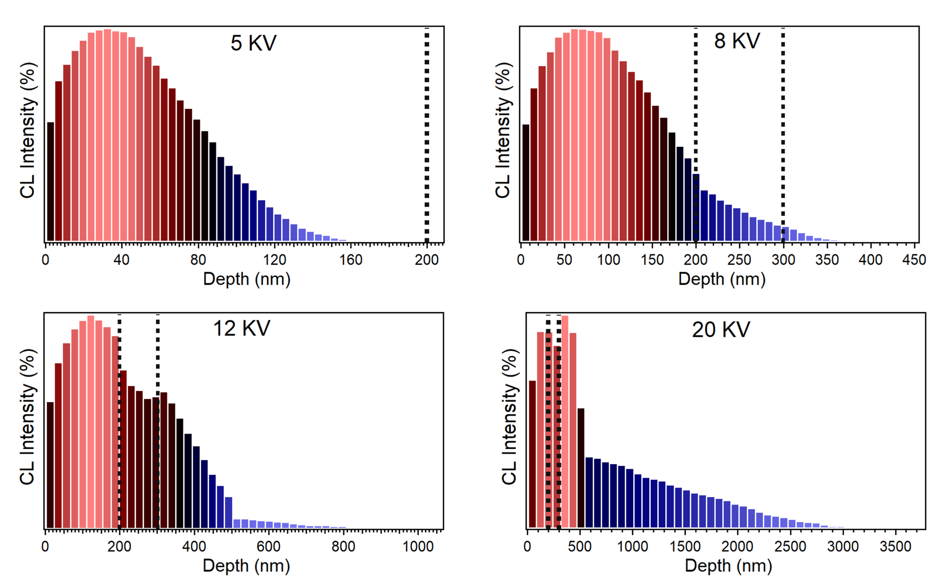
Optical properties



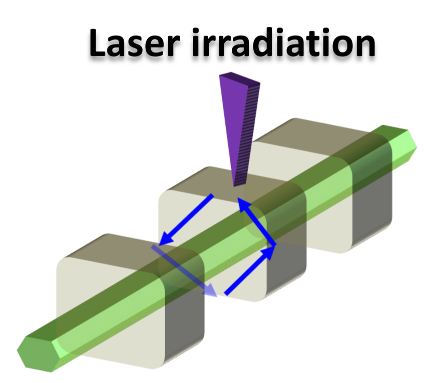


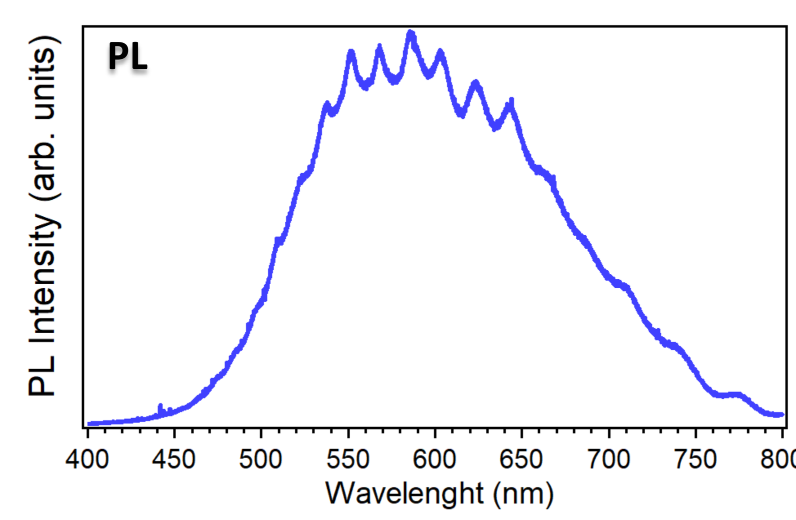
SnO_2-Zn_2GeO_4-SnO_2 (200-100-200nm)

Monte Carlo Simulation



Resonant Cavities





Conclusions

- The presence of tin during the growth favours the creation of structures (the more concentration of SnO_2, the more structures).
- Doping with tin influences the morphology. In particular, complex structures have been formed, such as Zn_2GeO_4 NWs with SnO_2 particles or GeO_2 beads attached to the nanowire stem.
- Microstructural study of complex structures with SnO_2 particles revealed that the core nanowire grows in the [001] direction and the SnO_2 adheres in the planes with the greatest amount of oxygen.
- Optical properties of these structures have been studied: Cathodoluminescence measurements at different excitation potentials fit with the Monte Carlo simulations. Moreover, photoluminescence measurements uncover that the SnO_2 coating acts as a resonant cavity.

References

[1] Mizoguchi, H.; Kamiya, T.; Matsuishi, S.; Hosono, H., A germanate transparent conductive oxide. *Nature Communications* **2011,** *2*, 470.

[2] Hidalgo, P.; López, A.; Méndez, B.; Piqueras, J., Synthesis and optical properties of Zn_2GeO_4 microrods. *Acta Materialia* **2016,** *104*, 84-90.

[3] Dolado, J.; Hidalgo, P.; Méndez, B., Correlative study of vibrational and luminescence properties of Zn2GeO4 microrods. Physica Status Solidi (a) **2018**, 215(19), 1800270.