Zn_2GeO_4: A promising material in optoelectronic applications and energy storage

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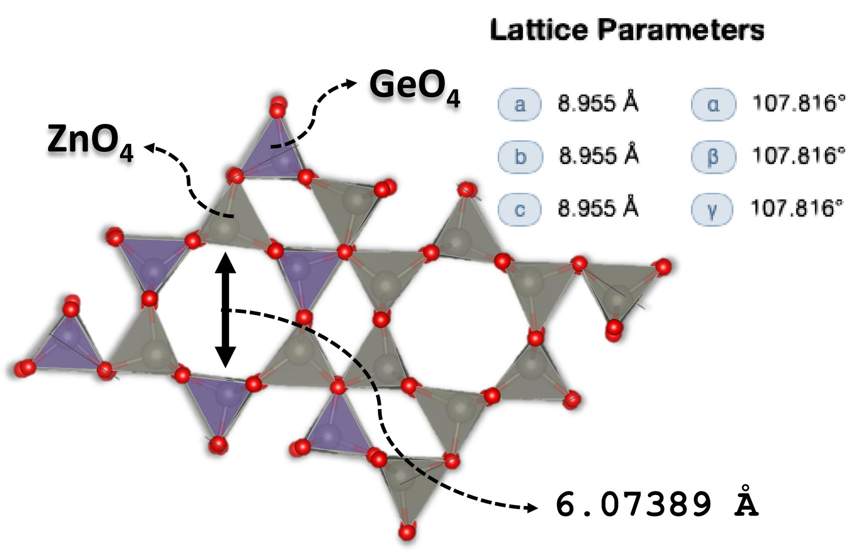
Motivation

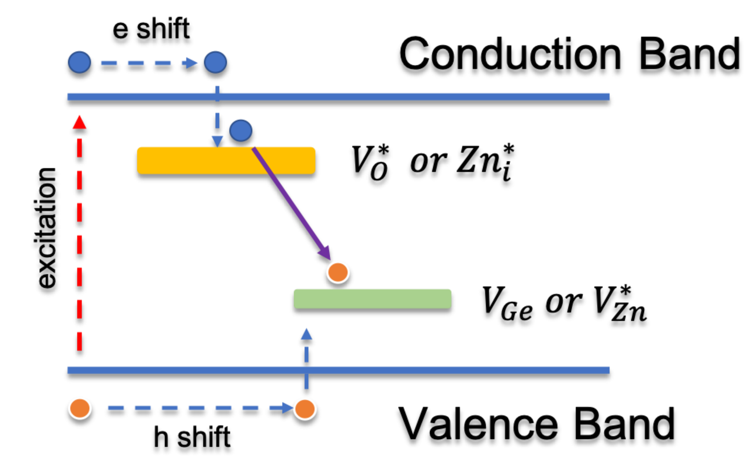
Transparent conducting oxides (**TCO's**), which exhibit both high electrical conductivity and high optical transparency in visible light, are necessary for a variety of optoelectronic application. Not only binary but also ternary oxides have been explored as TCO materials [1], being Zn_2GeO_4 with a wide-bandgap (4.7 eV) one of the most appealing.

Crystal Structure



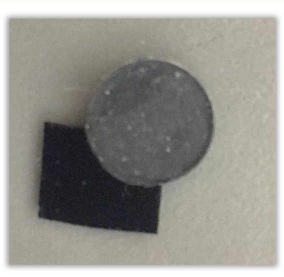
Besides the optical transparency Its crystalline structure consists of corner-shared ZnO_4 and GeO_4 tetrahedra forming six-member rings with room enough for interstitial atoms. This configuration made Zn_2GeO_4 a promising material for application in **metal-ion batteries** as a high-capacity anode material [3].

Native Defects

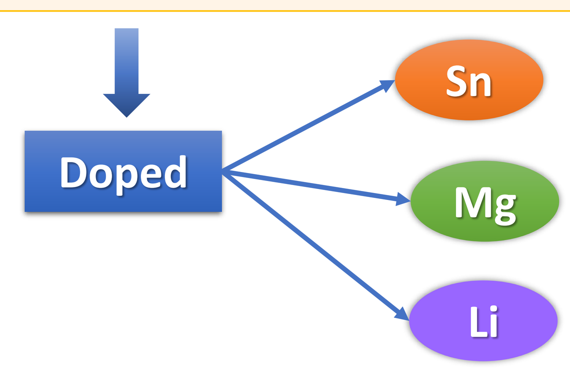


Native defects usually play a fundamental role in the physical properties in semiconducting oxides, e.g. optical properties, photocatalytic properties or ionic transport, which is very important for batteries. The native defects in Zn_2GeO_4 are oxygen vacancies and zinc interstitials, with a donor character, and zinc and germanium vacancies as acceptors. They are responsible for the **luminescence** spectra observed in Zn_2GeO_4 [2].

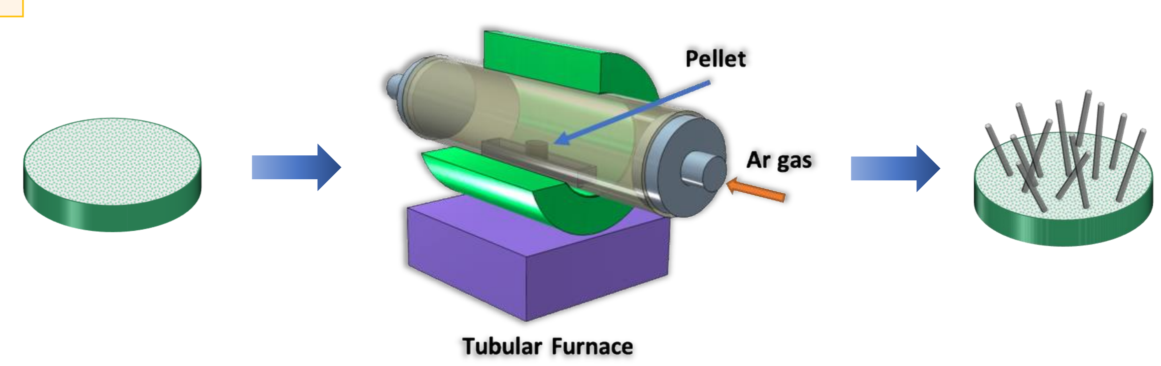
Synthesis

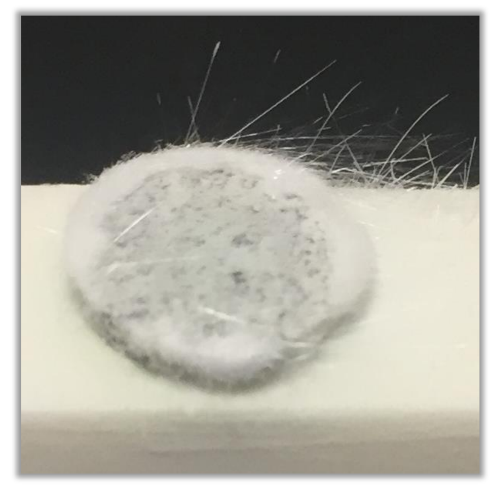


Compacted Mixture	Treatment
ZnO + Ge + C (2:1:2 wt.%)	800°C, 8h, Ar 1,5 l/min



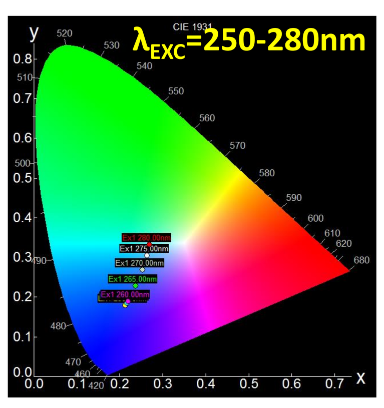
Single step thermal evaporation





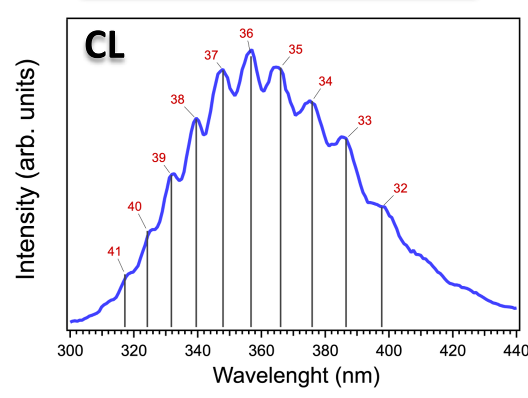
Experimental Results

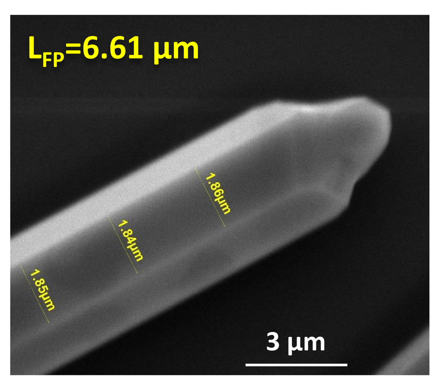
Intense white luminescence



Its luminescence is about **40%** higher than the ZnO based phosphors.

Resonant cavities

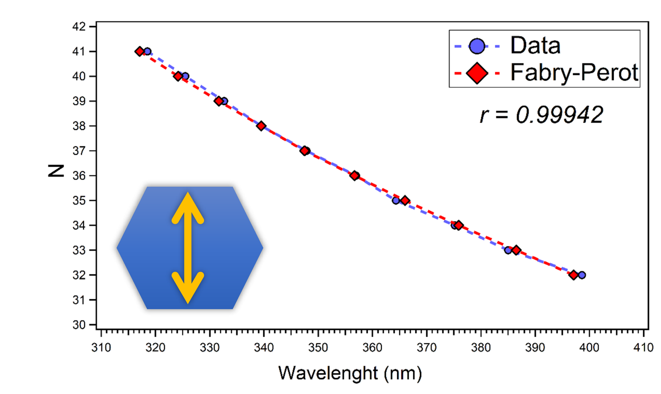




Fabry-Perot resonance condition

$$\lambda_{FP} = \frac{nL_{FP}}{N}$$

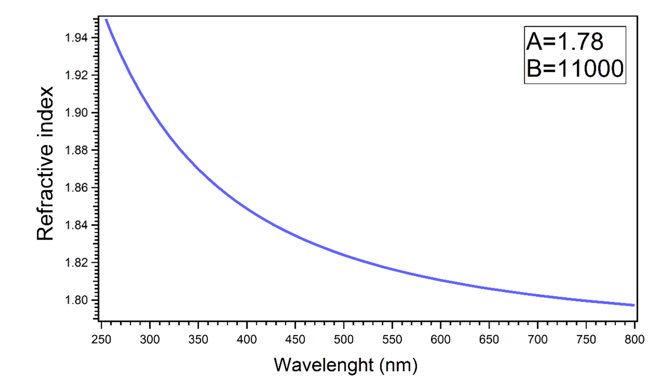
n = Refractive Index
L_{FP} = Length of th optical path
N = Mode number



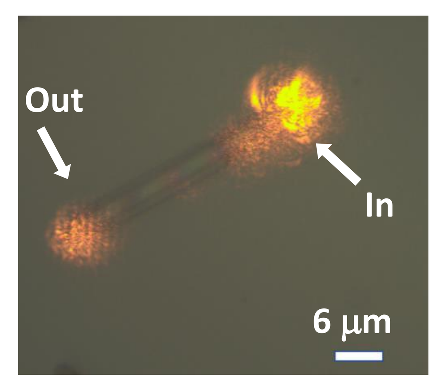
An analysis of the optical resonances, permit determine the **refractive index** of the Zn_2GeO_4.

The refractive index adjusts perfectly to the **Cauchy's expression**:

$$n = A + \frac{B}{\lambda^2}$$



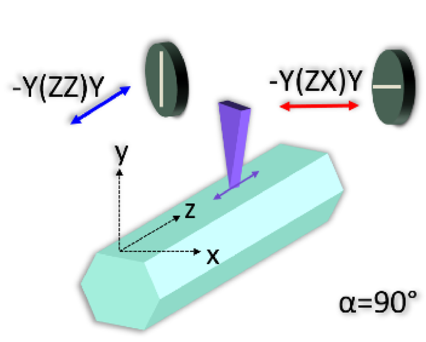
This high value for the refractive index permit the Zn_2GeO_4 microrods to act as a **waveguides**:

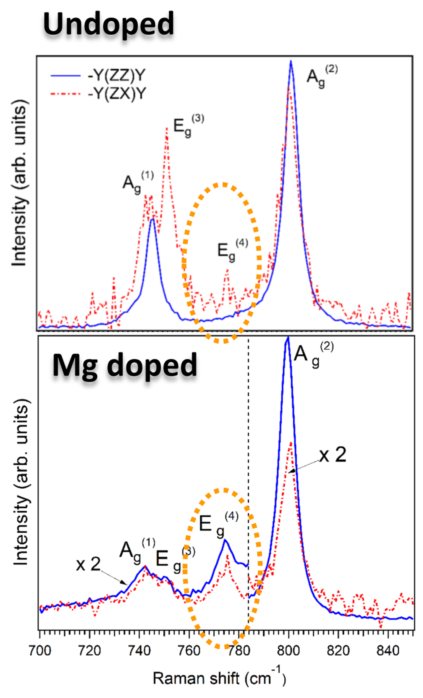


Waveguide behavior

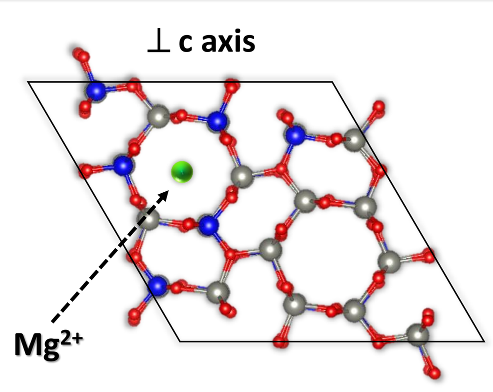
Mg doped

Polarized Raman





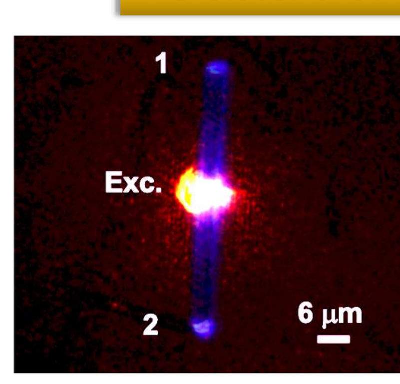
The different behavior of the Eg[4] mode (related to the Zn_i [2]) between undoped and Mg doped samples suggests that some Mg ions could be sited at the center of rings as an interstitial impurity [3], which could be interesting for **metal-ion batteries** applications.

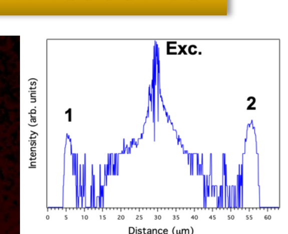


Element	r_{ion} (Å)
Mg^{+2}	0.86

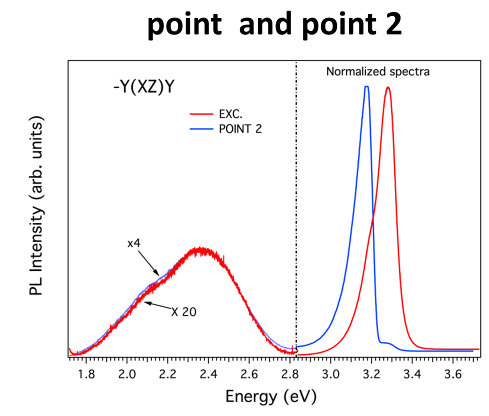
Promising candidate for batteries applications

Persistent luminescence





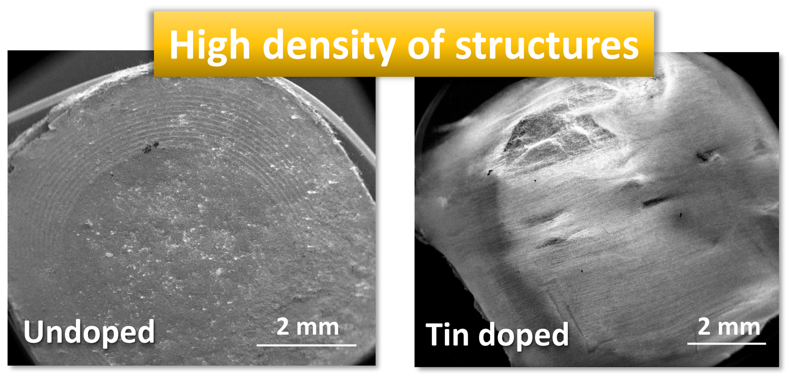
PL Recorded generation point and point 2

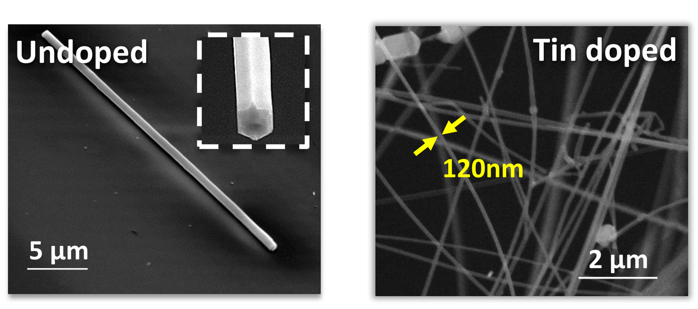


Mg doped microwire shows **persistent photoluminescence** in the UV region not observed in undoped samples. We suggest that this feature is due to the presence of Mg in interstitial position [3].

Sn doped

High density of structures

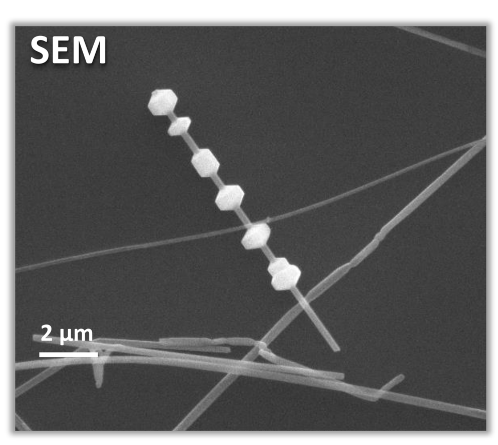




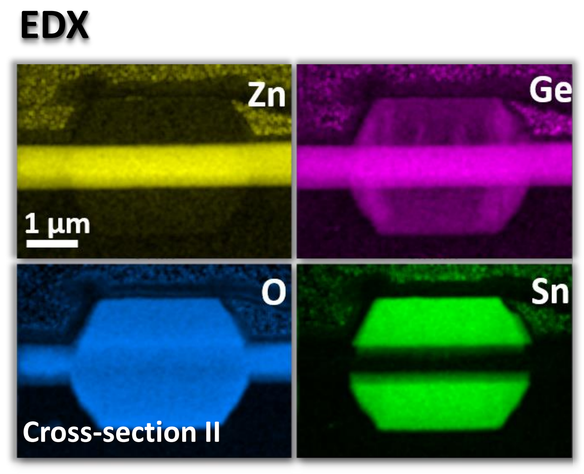
Cross section 1-4µm	Cross section 100-300nm

Nanowires thickness reduction

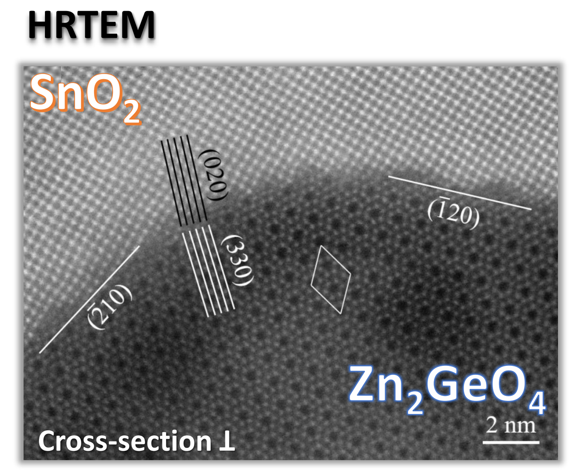
Heterostructures [4]



EDX



HRTEM



References

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

[2] **Dolado, J.**; Hidalgo, P.; Méndez, B., Correlative study of vibrational and luminescence properties of Zn_2GeO_4 microrods. *Physica Status Solidi (a)* **2018**, 215(19), 1800270.

[3] Hidalgo, P.; **Dolado, J.**; Méndez, B., Efficient white-light emission from Zn_2GeO_4 nanomaterials. *Oxide-based Materials and Devices X. International Society for Optics and Photonics* **2019**, p. 109192D.

[4] **Dolado J.**; Renforth K.; Nunn J.E.; Hindsmarsh S.A.; Hidalgo, P.; Sánchez A.M.; Méndez, B., Zn_2GeO_4/SnO_2 nanowire heterostructures driven by Plateau-Rayleigh instability. *Nano Letters* (**under review**).