# An Investigation into Tellurium doping of single crystals $Cu_2OSe_{1-x}Te_xO_3$

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## What is a skyrmion?

A skyrmion is a topologically protected quasiparticle, where the magnetic moments are arranged two-dimensionally in a spiral fashion and is related to helical domains is a one-dimensional structure with magnetic moments canted.

$Cu_2OSe_3$ is the first multiferroic material shown to host skyrmion. The skyrmions are stable at a narrow temperature and magnetic field range (57 K and 200 Oe). These skyrmions are packed hexagonally.[1,2]

Magnetic skyrmions could provide a new novel data storage devices that is faster, more stable and energy efficient than currently used magnetic hard drives. Recent studies have also shown that it is possible to insert and delete a skyrmion with an injection of electrons.[3]

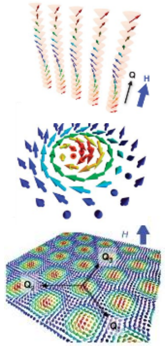

Fig 1. Helical domain (top), skyrmion (middle) and hexagonally packed skyrmion lattice.[1]

$Cu_2OSe_3$ consists of magnetically active $Cu^{2+}$ ions with two different site, Cu1 site being trigonal bipyramidal and Cu2 square pyramidal. The magnetic moment of the Cu sites are arranged where the Cu1 and Cu2 sites consist of a 3up-1down structure and is a large contributor to the formation of the magnetic helical domains and skyrmions.[1,2,4,5]

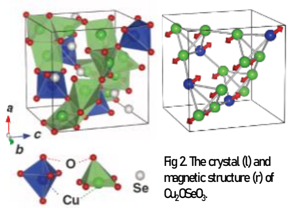

Fig 2. The crystal (l) and magnetic structure (r) of $Cu_2OSe_3$.

## Crystal Synthesis

Single crystals were grown by chemical vapour transport. Stoichiometric amounts of precursor were sealed in a quartz tube with transport agent ($NH_4Cl$). Large dark green crystals were obtained with larger crystals synthesized by leaving in the furnace for a longer period.

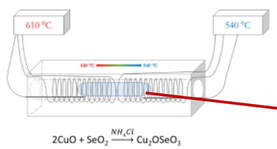


Fig 3. Schematics of two-zone furnace used to grow $Cu_2OSeO_3$.

## Elemental Analysis

The Te content was determined using both neutron and X-ray diffraction along with energy dispersive spectroscopy (EDS) and inductively coupled-mass spectroscopy (ICP-MS). The EDS and ICP-MS shows that Te was successfully doped into the crystals.

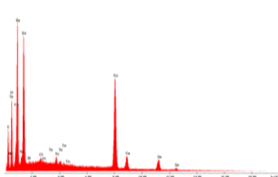

Fig 4. Schematics of two-zone furnace used to grow $Cu_2OSeO_3$.

Table 1. Te content obtained from EDS.

| Nominal Doping | Te content |
|---|---|
| Pure $Cu_2OSeO_3$ | 0% |
| 5% Te doped $Cu_2OSe_{1-x}Te_xO_3$ | 4.7% |
| 10% Te doped $Cu_2OSe_{1-x}Te_xO_3$ | 3.3% |
| 20% Te doped $Cu_2OSe_{1-x}Te_xO_3$ | 13.7% |
| 30% Te doped $Cu_2OSe_{1-x}Te_xO_3$ | 7.2% |
| 50% Te doped $Cu_2OSe_{1-x}Te_xO_3$ | 10.7% |

# Improving the skyrmion stability range in $Cu_2OSeO_3$

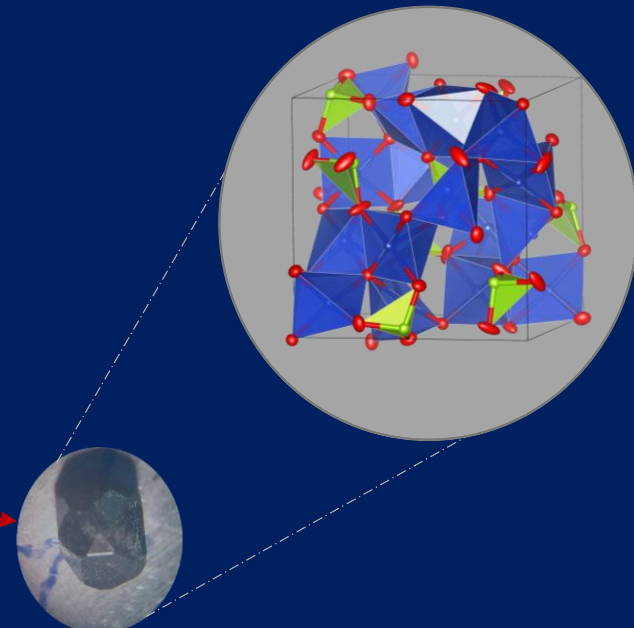

Figure 5. Photo of $Cu_2OSeO_3$ single crystal and crystal structure modelled using VESTA[6]

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REFERENCES
1. Ni, Y.; Nakajima, T.; Kikkawa, A.; Yamasaki, Y.; Ohishi, K.; Suzuki, J.; Taguchi, Y.; Arima, T.; Tokura, Y.; Iwasa, Y. Uniaxial Stress Control of Skyrmion Phase. Nat. Commun. 2015, 6 (1), 8539.
2. Ogawa, N.; Seki, S.; Tokura, Y. Ultrafast Optical Excitation of Magnetic Skyrmions. Sci. Rep. 2015, 5 (1), 9552. https://doi.org/10.1038/srep09552.
3. Ni, Y.; Nakajima, T.; Kikkawa, A.; Yamasaki, Y.; Ohishi, K.; Suzuki, J.; Taguchi, Y.; Arima, T.; Tokura, Y.; Iwasa, Y. Uniaxial Stress Control of Skyrmion Phase. Nat. Commun. 2015, 6 (1), 8539. https://doi.org/10.1038/ncomms9539.
4. Rov, R. The Effect of Tellurium Doping on the Skyrmion Hosting Multiferroic Material $Cu_2OSeO_3$. Thesis, ResearchSpace@Auckland, 2019.
5. Gnezdilov, V. P.; Lamonova, K. V.; Pashkevich, Yu. G.; Lemmens, P.; Berger, H.; Bussy, F.; Gnatchenko, S. L. Magnetoelectricity in the Ferrimagnetic $Cu_2OSeO_3$: Symmetry Analysis and Raman Scattering Study. Low Temp. Phys. 2010, 36 (6), 550–557.
6. Momma, K. and Izumi, I. VESTA3 for three-dimensional visualization of crystal, volumetric and morphology data, J. Appl. Crystallogr., 44, 1272-1276 (2011)
7. Piltz, R. O. Accurate data processing for neutron Laue diffractometers. J. Appl. Crystallogra. 51, 635-645 (2018)
8. Sheldrick, G. M., A short history of SHELX. Acta Crystallographica Section A: Foundations of Crystallography 2008, 64 (1), 112-122.

## Structural Analysis

X-ray and Laue Neutron diffraction were both employed to study the crystal structure of the crystals from room temperature and the effects of temperature as well as determine the Te doping. Single crystals of pure and doped $Cu_2OSeO_3$ were also analysed using the Laue Neutron Diffractometer KOALA at ANSTO. The data sets were reduced and corrected using the program LaueG and subsequently solved and refined using SHELX.[7,8]

XRD data showed that Te was successfully doped into the crystal structure with approximately ¼ actually doped of the nominal doped. Measurements for XRD down to 100 K and Laue Neutron Diffraction down to 10 K revealed no significant structural distortion from room temperature, no significant changes to the Cu-Cu distances and retained the cubic structure.

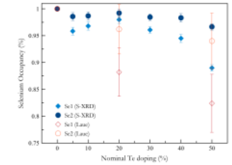

Fig. 6. Cu-Cu distances as a function of temperature

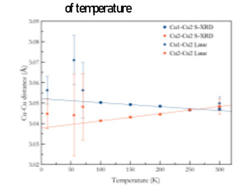

Fig. 7. Te content derived from XRD & Laue Neutron Diffraction

## Magnetic Field-Temperature phase diagram

Small angle neutron scattering (SANS) was used to detect the magnetic structures in the single crystals. The polarized neutrons are diffracted from the regular structure resulting in a reciprocal space diffraction pattern (for a hexagonally packed skyrmion phase this is a ring of 6 intensity peaks. The temperature-magnetic field phase diagram mapping was completed using the SANS instrument QUOKKA.

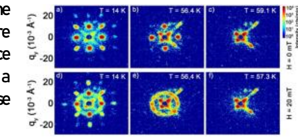

Fig. 8. Selected SANS scans of pure $Cu_2OSeO_3$ at various temperatures and magnetic field.

Fig 8 & 9. shows selected scans at various temperatures and magnetic fields. The pure crystal was orientated along the 100 direction and 10% Te doped $Cu_2OSeO_3$. In the skyrmion stability range there is a ring of intensity indicating that there is multiple skyrmion lattice orientated differently.

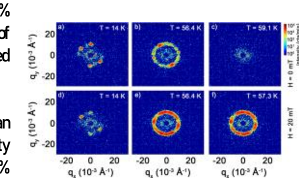

Fig. 9. Selected SANS scans of 10% nominal Te doped $Cu_2OSeO_3$ at various temperatures and magnetic field.

The effect of doping is evident in the phase diagrams below with an increase in nominal Te doping resulting there is an increased stability range for both the helical domain and skyrmion phase up to 20% nominal doped. For the 50% nominal doped the helical domain increases however the skyrmion phase appears to decrease in stability

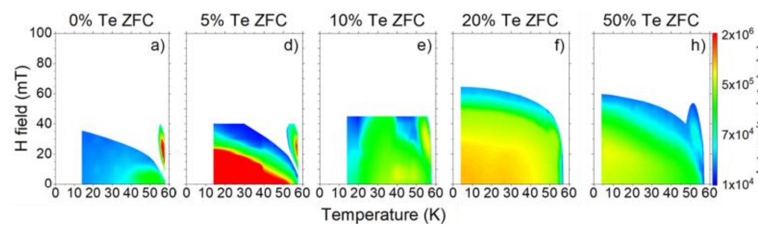


Fig. 10. Magnetic field-Temperature phase diagram for pure, 5%, 10%, 20% and 50% nominal Te doped $Cu_2OSeO_3$ under a zero-field cooling.

## What Next?

$Cu_2OSeO_3$ was shown to retained the cubic space group $P2_13$ down to 10 K as well as upto 10% Te doping. Though further studies are still needed to determine the homogeneity of the synthesis method. The exact Te content needs to be accurately determined using techniques such as ICP-MS. The use of Te doping dramatically effected the skyrmion stability range.

Further study would involve the synthesis, structural and magnetic studies of Cu site doping with various transition metal dopants. Previous studies on polycrystalline doped $Cu_2OSeO_3$ has shown that doping influences the stability range of the skyrmion range with shifts and enlarged stability range.