New Cu-Based Multiferroic Materials

Neutron powder diffraction is a useful tool to characterize the magnetic structures of multiferroic materials.

Multiferroics, exhibiting two or more ferroic orders, are extensively investigated in condensed-matter physics because of their potential applications in spintronics and low-power-based microelectronics, especially multiferroics type II, of which the magnetic order and electric order are mutually coupled. Among all currently known multiferroics, materials containing Cu^{2+} spin-1/2 are placed in a special class due to their unconventional spin structures, involving spin frustrations or quantum effects. CuO and $CuCl_2$ are well known multiferroic materials; compounds from the CuO-$CuCl_2$-SeO_2 ternary phase diagram have also been reported to exhibit exotic quantum magnetic states and multiferroic properties. Hung-Duen Yang (National Sun Yat-sen University) and his co-workers studied the properties of various Cu-based materials, such as Cu_2OSeO_3 and Cu_2OCl_2. They recently reported the structural, magnetic and dielectric properties of α-$Cu_5O_2(SeO_3)_2Cl_2$ and $Cu_9O_2(SeO_3)_4Cl_6$,[1,2] which belong to the CuO-$CuCl_2$-SeO_2 ternary system.

Single crystals of α-$Cu_5O_2(SeO_3)_2Cl_2$ and $Cu_9O_2(SeO_3)_4Cl_6$ were synthesized using a chemical vapor-transport method. The mixture of raw materials was sealed in an ampoule (length 10 cm), which was placed horizontally in a tubular two-zone furnace, as illustrated in **Fig. 1(a)**. Single crystals of α-$Cu_5O_2(SeO_3)_2Cl_2$ and $Cu_9O_2(SeO_3)_4Cl_6$ formed in the hot and cold ends, respectively. The crystal structures of α-$Cu_5O_2(SeO_3)_2Cl_2$ and $Cu_9O_2(SeO_3)_4Cl_6$ are both monoclinic with space groups $P2_1/c$ and $C2/m$, respectively. Both compounds were characterized with synchrotron radiation X-ray powder diffraction (**TPS 09A**), magnetometry, specific heat, dielectric measurements and neutron powder diffraction.

The magnetic Bragg peaks from the Cu^{2+} spin structures are typically weak because of small magnitudes of magnetic moment and quantum fluctuation. The magnetic structures of these two compounds were hence studied with the high-intensity neutron powder diffractometer, **WOMBAT**. **Figure 1(b)** shows magnetic diffraction patterns of α-$Cu_5O_2(SeO_3)_2Cl_2$ obtained on subtracting the high-temperature diffraction pattern from the low-temperature one. The propagation vector is determined as $q = (1/2\ 0\ 0)$, which indicates that the magnetic

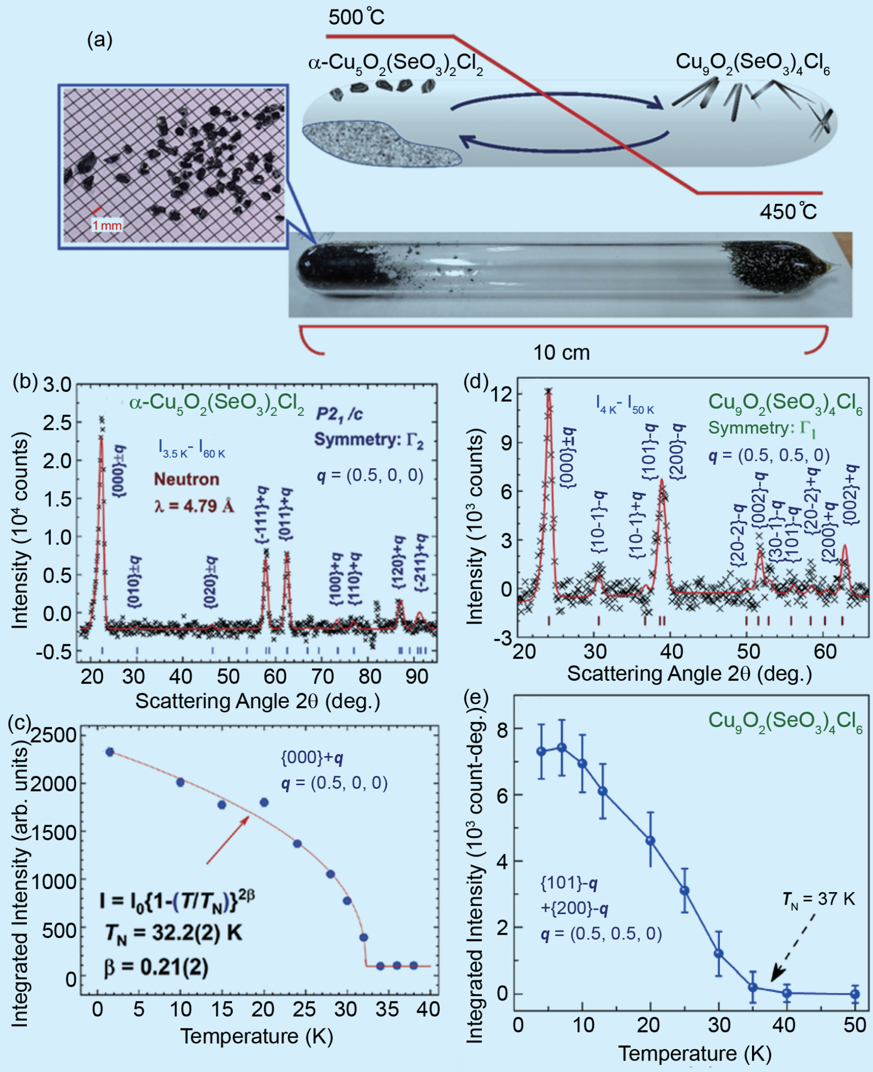

Fig. 1: (a) Experimental two-zone growth of α-$Cu_5O_2(SeO_3)_2Cl_2$ and $Cu_9O_2(SeO_3)_4Cl_6$ single crystals: pictorial representation and photograph of the quartz ampoule. A red line denotes the temperatures of the hot and cold ends of the two-zone furnace. Brownish α-$Cu_5O_2(SeO_3)_2Cl_2$ and green $Cu_9O_2(SeO_3)_4Cl_6$ single crystals grown at hot and cold ends, respectively. (b) and (d) show the fit of magnetic neutron diffraction patterns of α-$Cu_5O_2(SeO_3)_2Cl_2$ and $Cu_9O_2(SeO_3)_4Cl_6$, respectively. (c) and (e) show the order magnetic peak intensities as a function of temperature. [Reproduced from Ref. 1 and Ref. 2]

unit cell is double the nuclear unit cell. The temperature dependence of the magnetic peak intensity is plotted in **Fig. 1(c)**; the magnetic structure is illustrated in **Figs. 2(a) and 2(b)**. The ordered Cu^{2+} moments are about 0.75 μ_B at 3.5 K and lie in plane *a*-*c*. The typical spin structure of the frustrated bow-tie lattice is realized in the Cu2-Cu3 layer, in which the Cu3 spins form sequence (++--) along axis *a*, which might invoke magnetoelectric coupling through the exchange-striction effect.

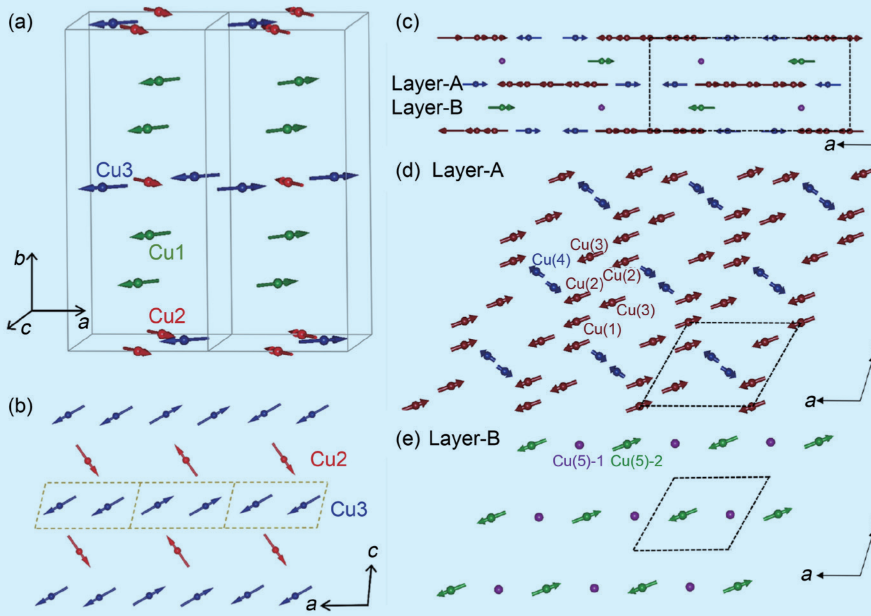

Fig.2: Magnetic structure of α-$Cu_5O_2(SeO_3)_2Cl_2$ illustrated as (a) stacking along the crystallographic *b*-axis direction and (b) projection of Cu2 and Cu3 spins in crystallographic plane *a*-*c*. Dashed rectangular blocks indicate ferromagnetic spin-dimers that form along the *a*-axis direction. Non-collinear antiferromagnetic structure of $Cu_9O_2(SeO_3)_4Cl_6$: (c) stacking of Cu layers along the crystallographic *b*-axis direction, (d) Cu spin configuration in layer A, and (e) Cu spin configuration in layer B. [Reproduced from Ref. 1 and Ref. 2]

In the case of $Cu_9O_2(SeO_3)_4Cl_6$, the propagation vector is found to be *q* = (1/2 1/2 0), indicating that the magnetic unit cell is double the nuclear unit cell along axes *a* and *b* (**Fig. 1(d)**). The temperature dependence of the magnetic peak intensity is plotted in **Fig. 1(d)**; the magnetic structure is illustrated in **Figs. 2(c)–2(e)**. The magnetic moments lie in plane *a*-*c* forming a non-collinear antiferromagnetic structure. Half of Cu(5) ions carry no moments as required by the magnetic symmetry group, showing that the spins of Cu(5) ions still fluctuate, even below T_N, and carry no static magnetic moment.

In summary, Yang's group successfully synthesized α-$Cu_5O_2(SeO_3)_2Cl_2$ and $Cu_9O_2(SeO_3)_4Cl_6$ single crystals with a chemical vapor-transport method and investigated the structural, magnetic and dielectric properties. Neutron powder diffraction provided information about the magnetic order and magnetic structures. (Reported by Chin-Wei Wang)

This report features the work of Hung-Duen Yang and his collaborators published in Mater. Adv. ***2****, 7939 (2021) and Phys. Rev. B* ***100****, 245119 (2019).*

TPS 09A Temporally Coherent X-ray Diffraction
ANSTO WOMBAT – High-intensity Powder Diffractometer

- XRD, NPD
- Condensed-matter Physics

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