

Layered Copper Metagermanate Nanobelts: Hydrothermal Synthesis, Structure, and Magnetic Properties

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One-dimensional (1D) quantum spin systems exhibit fascinating magnetic phenomena. As the first inorganic spin-Peierls (SP) material ever discovered, copper metagermanate (CuGeO₃, CGO) [$S = 1/2$] has been the focus of much excitement since it was first demonstrated by Hase et al. to undergo an SP transition at $T_{sp} = 14$ K.¹ The SP transition is one of the quantum phenomena which occurs in an $S = 1/2$ antiferromagnetic Heisenberg uniform chain system.² Below the SP transition temperature, a lattice dimerization occurs, which increases progressively as the temperature decreases, together with the concomitant appearance of an energy gap in the spectrum of magnetic excitations. This gap separates a nonmagnetic singlet ground state from a triplet of excited states. The SP transition has been found in several organic compounds.³

CGO has an orthorhombic crystal structure with lattice parameters $a = 0.481$, $b = 0.847$, and $c = 0.294$ nm, $Z = 2$, and space group $Pbmm$.⁴ The basic building blocks of the CGO structure are corner-sharing GeO₄ tetrahedra aligned along chains. These chains are linked by Cu²⁺ ions. Each Cu atom is surrounded by six oxygen atoms, forming a strongly deformed CuO₆ octahedron. The alignment of these CuO₆ octahedra provides chains made of regularly spaced Cu atoms. The two types of chains run parallel to the c -axis of the crystal. A large number of investigations have been performed using a wide variety of techniques including magnetic susceptibility, NMR, neutron scattering, and optical spectroscopy to study its structural and physical properties. All experimental results reported strongly support the fact that CGO undergoes a true SP transition. Until now, CGO and its analogues endowed with the SP transition were merely fabricated by high-temperature reaction processes, in which a floating-zone method was generally employed to ensure the growth of large single crystals.¹ In view of the strong relationship between structural, magnetic, and elastic properties in CGO, it is instructive to extend the studies of CGO in another direction, to its nanostructured analogues, such as a new discovery of beltlike 1D nanostructures.⁵ Unfortunately, no attempts were ever devoted to synthesize ternary complex oxide CGO based 1D nanostructures up to date.

In principle, the properties of a magnetic material depend critically on its chemical composition, processing route, and specific morphology, owing to the dominating role of anisotropy in magnetism.⁶ Successes in morphology control of nanocrystals have been reported in the syntheses of ferromagnetic materials.⁷ Herein, we report for the first time a facile hydrothermal route to synthesize layered CGO nanobelts, and their magnetic properties were measured and discussed.

Hydrothermal processing in the presence of CTAB at 180 °C for 1 day resulted in light blue CGO powders in a high yield (Supporting Information). The X-ray diffraction (XRD) pattern of

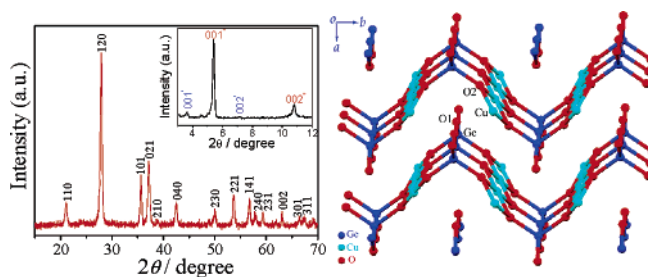


Figure 1. (Left) XRD pattern of the obtained layered CuGeO₃ nanobelts, inset is low-angle XRD pattern of sample; (right) the crystal structure of CuGeO₃.

the as-synthesized CGO nanobelts is shown in Figure 1. All the peaks can be indexed to orthorhombic structured CGO (JCPDS 74-0302). No peaks of any other phases or impurities were detected. Low-angle XRD pattern (inset in Figure 1) shows that the obtained product has a layered mesostructure with two interlayer distances. The structure of CGO can be explained as a layered structure. The unique orthorhombic crystal structure of CGO is characterized by chains of planar CuO₄ units and corner-sharing chains of GeO₄ tetrahedra running parallel to the c -axis. The [GeO₃]²⁻ chains are interconnected by short Cu–O(2) bonds, which form the rippled layers stacked in the a -direction. Because the rippled layers are bound by weak Cu–O(1) bonds, the crystal cleaves like mica in the b - c plane (Figure 1, right).⁸ Electrostatic interaction between CTA⁺ cations and [GeO₃]²⁻ chains could lead to the formation of a layered mesostructure with different CTA⁺ chains tilt angles.⁹ TGA data (Supporting Information (SI), Figure S1) shows that about 10 wt % CTAB remained in the final product.

The morphology and structure of the products were examined by scanning electron microscopy (SEM, JEOL JSM-6330F). The CGO products consist almost entirely of uniform nanobelts (see SI, Figure S2). The typical widths of the nanobelts are in the range of 20–70 nm, and lengths range from 1 to 3 μm. The rectangle-like cross section of the materials is clearly visible in the SEM image. The width-to-thickness ratios are ca. 2 to 4.

The structure of the products was further examined with transmission electron microscopy (TEM) and high-resolution TEM (JEOL-2010 at 200 kV). Figure 2a shows the typical TEM image of the obtained CGO nanobelts with uniform size. Figure 2b shows a HRTEM image of a CGO nanobelt, giving resolved lattice fringes of (001) (0.286 nm) and (120) (0.309 nm) planes, and the nanobelts grow along the [001] direction. Fast Fourier transformation (FFT) pattern (inset in Figure 2b) taken from a single nanobelt can be indexed as an orthorhombic CGO single-crystal recorded along the [2̄10] zone axis. TEM observations show that each nanobelt is a single crystal. Energy dispersive X-ray spectroscopy (EDS) analysis shows that the composition of the product is CGO (SI, Figure S3).

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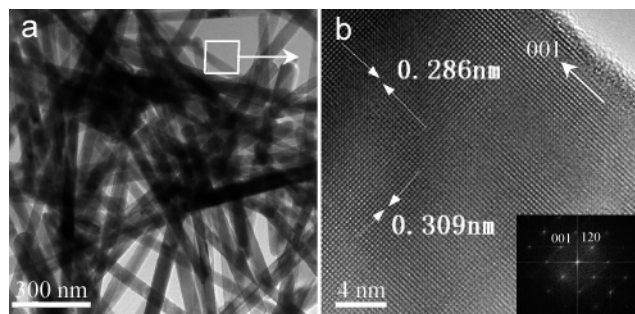


Figure 2. (a) TEM image of CuGeO₃ nanobelts; (b) HRTEM image of an individual nanobelt with clearly resolved lattices. The inset in panel b shows the FFT pattern.

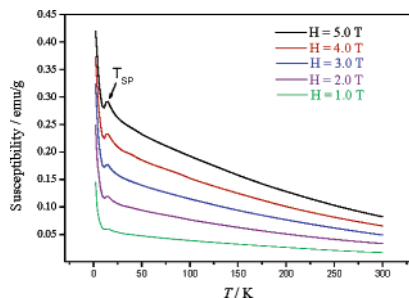


Figure 3. Plots of the magnetic susceptibility of CuGeO₃ nanobelts, measured under $H = 1.0$ – 5.0 T with a temperature range of 1.9–300 K.

Here, the growth of CGO into 1D nanostructure is obviously determined by the highly anisotropic and intrinsic nature for CGO crystals.¹⁰

Magnetic susceptibility study provides compelling evidence for the interesting magnetic property of layered CGO nanobelts. The magnetic susceptibility measurements were performed using a Quantum Design-made MPMS XL-7 SQUID magnetometer operating in the temperature range of 1.9–300 K and in a field up to 5 T. The temperature dependence of magnetic susceptibility for layered CGO nanobelts is shown in Figure 3 under various magnetic fields. A cusp in susceptibility at ca. $T_{SP} = 14$ K can be clearly observed, indicating the SP transition appeared in the obtained CGO nanobelts.¹ The SP transition appears in $S = 1/2$ one-dimensional antiferromagnetic Heisenberg chains with spin–phonon interactions. Below T_{sp} , a lattice dimerization and an alternation of exchange interaction is believed to occur, and a finite energy gap opens between singlet-ground and triplet-first-excited states.² A sharp decrease can be observed below 14 K, where the lowest point of the drop occurs at 10.4 K. Above the transition temperature, their susceptibility slowly decreases with increasing temperature. As compared to magnetic properties of bulk CGO crystals synthesized by high-temperature solid reaction (SI, Figure S4, Figure S5), a sharp peak at T_{SP} can be observed in our layered CGO nanobelts, instead of a broad peak observed for CGO bulk crystals.¹ More interestingly, there is another significant difference in the temperature dependence of the magnetic susceptibility at lower temperatures after transition. For CGO bulk crystals, susceptibilities drop to small constant values below the transition temperature.¹ On the contrary, for the CGO nanobelts, the susceptibility starts to sharply increase again after the lowest point of the drop.

The magnetic interaction is very sensitive to subtle structural variations. Previous studies show that dimerization and phonons

play a central role in the SP transition.¹⁰ In CGO bulk crystals, the dimerization lattice is doubled along the a and c -axis,¹¹ the CTA⁺ intercalation will affect the lattice dimerization along the a -axis. Below 10.4 K, the susceptibilities again sharply increase with decreasing temperature. This behavior is likely due to lattice defects induced by the intercalation of CTA⁺ cations in the CGO nanobelts,¹² leading to the decrease of a lattice dimerization and thus the weakening of the SP transition in CGO nanobelts. Through removal of CTA⁺ by calcination (SI, Figure S6), the SP transition of the calcined CGO nanobelts is similar to that of CGO bulk crystals (SI, Figures S4, S7), indicating that the presence of CTA⁺ really changed the magnetic behaviors of CGO. In addition, the intercalation of CTA⁺ cations in CGO rippled layers may largely change the magnetoelastic coupling of the CGO nanobelts. The phonon dispersion relation might be modified as a result of the phonon confinement in the 1D nanostructure, leading to changes of the spin–phonon coupling.^{10,13}

In conclusion, a simple hydrothermal route has been discovered to synthesize single-crystal CuGeO₃ nanobelts with a layered mesostructure. The produced CGO nanobelts show distinct susceptibility behaviors in comparison with CGO bulk crystals. Magnetic properties of the obtained layered CGO nanobelts are quite interesting and deserve further study in detail. The studies on the relationship between magnetic behaviors below the transition temperature and this novel material are now being carried out. This successful synthesis of CGO nanobelts provides an opportunity to study fundamental magnetic and electronic structures in 1D quantum spin and strongly correlated electronic systems at the nanoscale.

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Supporting Information Available: Experiment procedure, TGA, SEM image, EDS spectrum, magnetic data, and XRD. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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