Anisotropic spin-flip-induced multiferroic behavior in kagome Cu$_3$Bi(SeO$_3$)$_2$O$_2$Cl


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Compared to the previous report on Cu$_3$Bi(SeO$_3$)$_2$O$_2$X ($X = \text{Cl, Br}$) by Wang et al. (arXiv:1604.04249), where no dielectric anomaly was observed without magnetic field near $T_N \sim 25.6$ K, we further present the dielectric behaviors without and with magnetic field in Cu$_3$Bi(SeO$_3$)$_2$O$_2$Cl. At zero field $H = 0$, an antiferromagnetic transition from magnetization and specific heat measurements is clearly established at $T_N$, while no dielectric anomaly was observed. Those results are similar to the previous report [V. Gnezdilov et al., (arXiv:1604.04249)]. Above the critical field $H_c \sim 0.8$ T, a metamagnetic spin-flip transition from antiferromagnetic to ferrimagnetic order at $T \sim T_N$ is induced anisotropically only for $H \parallel c$. Meanwhile, a ferroelectric behavior from dielectric and pyroelectric current measurements is observed below $T \sim T_N$; then a corresponding type-II multiferroics emerges above $H_c$. The key mechanism of the anisotropic spin-flip-induced multiferroicity in Cu$_3$Bi(SeO$_3$)$_2$O$_2$Cl can be ascribed to the breaking of magnetic twofold symmetry in the $bc$ plane above $H_c$.

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I. INTRODUCTION

Multiferroic materials have received a tremendous amount of research interest in the past decade because of their potential application in spin-based devices [1]. Physical insights into the coupling of the multiferroic property can be assigned to the correlation between the charge, spin, orbital, and lattice degrees of freedom [2]. To date, multiferroic behaviors have been demonstrated in a number of systems with the aid of theoretical calculations, along with the advancement of experimental techniques [3–7]. Several mechanisms such as the Dzyaloshinskii-Moriya (DM) interaction [3], exchange striction, geometric frustration [4,5], and metal-ligand hybridization ($p$-$d$ interaction) [6,7] have been theoretically established to explain the multiferroic properties. Geometrical strain frustration systems such as triangular lattice, kagome lattice, pyrochlore lattice, and spinel structure play a major role in condensed matter to achieve diverse physical properties [8–12]. In addition to these frustrated materials, the mineral francisites of kagome Cu$_3$Bi(SeO$_3$)$_2$O$_2$X ($X = \text{Cl, Br}$) possess the antiferromagnetic ordering temperature near 24 and 27.4 K and trigger a metamagnetic transition accompanied with a spin-flip behavior under the critical magnetic fields $H_c = 0.74$ T and 0.8 T parallel to the $c$ axis [9,12]. More recently, Wang et al. [13] reported the magnetoelectric phase diagrams of multiferroic CuO using a high magnetic field up to 50 T, indicating that the magnetization, polarization, magnetocapacitance, and magnetostriiction are closely related to the spin-flip phenomenon. Furthermore, there were only a few reports on field-induced electrical polarization such as hexaferrites [14], DyFeO$_3$ [15], and NdCrTiO$_3$ [16]. This motivates us to study the magnetodielectric coupling in Cu$_3$Bi(SeO$_3$)$_2$O$_2$Cl in the presence of spin-flip behavior.

The mineral francisite Cu$_3$Bi(SeO$_3$)$_2$O$_2$X ($X = \text{Cl, Br}$) possesses a complex, layered structure with Cu$^{2+}$ spin 1/2 chains and crystallizes in an orthorhombic structure with the $Pmmn$ space group [17]. It consists of two types of [CuO$_4$] square plackets, sharing apices to form copper-oxygen layers reminiscent of a buckled kagome lattice [17]. Two Cu ions form an alternative chainlike structure in the $ab$ plane. The Cu$_1$ chains are connected to Se$^{4+}$ ions, whereas the Cu$_3$ chains contain selenium lone-pair electrons and chloride/bromide ions [17]. Besides the complex crystal structure, Cu$_3$Bi(SeO$_3$)$_2$O$_2$X ($X = \text{Cl, Br}$) exhibits intriguing physical properties such as anisotropic magnetism. This property was explored in the dc magnetic studies below $T_N$ [9,12]. When a critical magnetic field, $H_c \sim 0.8$ T, was applied perpendicular to the $ab$ plane in Cu$_3$Bi(SeO$_3$)$_2$O$_2$Br, a metamagnetic transition jump from antiferromagnetic (AFM) to ferromagnetic (FM)/ferrimagnetilike (FIM) behavior was reported; every second layer flipped its spin orientation along the field direction [9,12]. Despite the lack of detailed studies of magnetic structure for Cu$_3$Bi(SeO$_3$)$_2$O$_2$Cl, similar magnetic features of Cu$_3$Bi(SeO$_3$)$_2$O$_2$X ($X = \text{Cl, Br}$) were explored according to first-principles calculations, which suggest that the spin direction of the Cu$_1$ site deviates from the $c$ axis with the $bc$ angles $\theta = 50.1^\circ$ and $53.8^\circ$ for Cu$_3$Bi(SeO$_3$)$_2$O$_2$X ($X = \text{Cl, Br}$) [18]. More recently, based on Raman studies, Cu$_3$Bi(SeO$_3$)$_2$O$_2$X ($X = \text{Cl, Br}$) was shown to present quantum magnetic fluctuations owing to the interplay of polar phonon modes [19]. In addition, only Cu$_3$Bi(SeO$_3$)$_2$O$_2$Cl undergoes a second-order structural phase and its structure becomes polar with ferroelectricity [19]. However, Cu$_3$Bi(SeO$_3$)$_2$O$_2$Cl was investigated for antiferroelectric distortion below 115 K with nonpolar $Pcmn$ symmetry using low-temperature synchrotron powder diffraction, while Cu$_3$Bi(SeO$_3$)$_2$O$_2$Br does not exhibit low-temperature structural transformation down to 10 K [20]. In this article, magnetodielectric and pyroelectric measurements were further conducted to study the coupling between magnetism and electricity and the possible multiferroic behavior in Cu$_3$Bi(SeO$_3$)$_2$O$_2$Cl single crystals.

II. EXPERIMENTAL METHODS

Single crystals of Cu$_3$Bi(SeO$_3$)$_2$O$_2$Cl were grown using the chemical vapor-phase method and the detailed synthesis...
process is described in Ref. [9]. The typical crystal thickness was 2 mm with the crystal orientated with the c axis along the surface normal. The measurements of dc magnetization (M) and ac susceptibility (χ') with respect to the field (H) and temperature (T) were performed using a Quantum Design MPMS system (MPMS-XL 7). The low-temperature heat capacity C (T, H) was collected with a 3He heat-pulsed thermal relaxation calorimeter. The platelike Cu$_3$Bi(SeO$_3$)$_2$O$_2$Cl single crystal was coated with silver paint as the electrodes (E || c). The dielectric permittivity was obtained using commercial systems (MPMS-XL 7 and PPMS Quantum design 6200) with homemade capacitance probes and was collected using an Agilent 4294A precision impedance analyzer with an ac excitation voltage of 1 V. A maximum field of 5 T was employed during the temperature- and field-dependent dielectric measurements. The electrical polarization was obtained from the pyrocurrent data. A 300 V electrical poling was applied during the cooling process, and the pyrocurrent was collected using a Keithley 6517 B electrometer. Temperature-dependent synchrotron x-ray patterns were taken by the Taiwan Photon Source (TPS) 09A beamline with a step of angle 0.004° in the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan.

### III. RESULTS AND DISCUSSION

#### A. De magnetization

Figure 1(a) displays the M-T curves of single-crystal Cu$_3$Bi(SeO$_3$)$_2$O$_2$Cl with an external magnetic field (100 Oe) applied along the directions parallel (H || c) and perpendicular to the c axis (H ⊥ c). Both curves display a sharp maximum at 25.6 K, indicating a paramagnetic (PM) to antiferromagnetic (AFM) transition. The M-H curves of Cu$_3$Bi(SeO$_3$)$_2$O$_2$Cl at 5 K for H || c and H ⊥ c are shown in the inset of Fig. 1(a). The linear variation of the M-H curve for the H ⊥ c orientation demonstrates strong AFM behavior. However, for the H || c orientation, an abrupt metamagnetic jump occurs at critical field $H_c$ ∼ 0.8 T, and a near-saturation behavior is thereafter noticed and can be ascribed to a spin-flip transition under a critical magnetic field. To further explore the spin-flip phenomena, temperature-dependent magnetization measurements were performed for the H || c orientation under different magnetic fields shown in Fig. 1(b). For $H = 0.01$ and 0.5 T, the magnetic properties exhibit AFM behavior with $T_N$ shifts towards lower temperatures as increasing $H$. For $H = 1$ and 2 T, the magnetization curves indicate saturation as $T < T_N$, demonstrating the spin-flip and FM/FIM-like behavior. The field-induced metamagnetic transitions recorded at different temperatures are shown in the inset of Fig. 1(b). It can be observed that the critical field for the field-induced spin-flip behavior decreases with increasing temperature. These results are consistent and similar to those reported in some studies [9,12]. Above $T_N$, the spin flip entirely disappears and a linear M-H curve at 35 K exhibits PM behavior.

#### B. Ac susceptibility and specific heat

To elucidate the nature of the phase transition below and above $H_c$, temperature-dependent ac susceptibility (χ'') and specific heat (C) measurements of Cu$_3$Bi(SeO$_3$)$_2$O$_2$Cl were performed for H || c. The results are presented in Figs. 2(a) and 2(b). In the zero-magnetic field, a frequency-independent [inset in Fig. 2(a)] sharp peak in χ'' vs $T$ is observed. Furthermore, a pronounced λ-type anomaly in C/T vs $T$ signifies a long-range order below 26 K. For $H > H_c$, the field-induced metamagnetic transition suddenly diminishes the sharp anomalies in χ'' and C/T (data not shown) suggests a second-order phase transition with respect to $T$. For $H = 0.5$ T, the peak is slightly shifted to a lower temperature in both χ'' vs $T$ and C/T vs $T$ curves, as expected for an AFM order. Indeed, a smeared peak in χ'' is observed and shifted to a higher temperature with an increase in $H$. As for C/T, the pronounced peak suddenly becomes a broad anomaly at $H > H_c$. This broad feature also shifts to higher $T$ with increasing $H$. In actuality, the above-described evolution of C/T in $H$ is similar to that in MnSi skyrmions, where the high-field regime is a...
FIG. 2. (a) Temperature-dependent ac susceptibility ($\chi'_{ac}$) of Cu$_3$Bi(SeO$_3$)$_2$O$_2$Cl with the application of dc magnetic fields 0, 0.5, 1, and 2 T for $H \parallel c$. The inset shows $\chi'_{ac}$-T of Cu$_3$Bi(SeO$_3$)$_2$O$_2$Cl at a frequency of 10 and 1000 Hz. (b) Temperature-dependent specific heat ($C/T$) of single-crystal Cu$_3$Bi(SeO$_3$)$_2$O$_2$Cl with magnetic fields 0, 0.5, 0.8, 1, and 2 T for $H \parallel c$. Field-polarized one [21]. Moreover, the broad feature above $H_c$ indicates a crossover line between the paramagnetic phase and field-polarized (or ferrimagnetic) regime. There have been several other metamagnetic systems such as Pr$_{0.63}$Ca$_{0.37}$MnO$_3$, Y$_2$CoMnO$_6$, and (Eu$_{0.4}$La$_{0.6}$)(Se$_{0.4}$Cu$_{0.6}$)MnO$_3$, where the field-forced AFM order to FM- or FIM-like phase is ascribed to the first-order phase transition [22–24]. The present case of Cu$_3$Bi(SeO$_3$)$_2$O$_2$Cl is likely reminiscent of some of them.

C. Dielectric, magnetodielectric, and pyrocurrent measurements

To observe the anisotropic effects on the magnetodielectric property, temperature-dependent dielectric measurements were performed using several magnetic fields with both $H \perp c$ and $H \parallel c$ orientations. As illustrated in Fig. 3(a), the dielectric permittivity for the $H \perp c$ orientation does not exhibit an anomaly near $T_N$ with the magnetic field region between 0 and 6 T. However, there is a significant enhancement in the low-temperature dielectric permittivity for the $H \parallel c$ orientation when $H = 1$ and 2 T, as indicated in Fig. 3(b). The anisotropic dielectric behavior is very similar to the magnetization behavior, suggesting that the metamagnetic spin-flip transition triggers a large anisotropic magnetodielectric on the system.

Furthermore, the field-dependent dielectric and polarization measurements for $H \parallel c$ at 10 K were performed to explore the coupling between magnetism and electricity in Cu$_3$Bi(SeO$_3$)$_2$O$_2$Cl. The spin flip at $H_c$ induces a step jump in the $M$-$H$ curve [Fig. 4(a)]. From the schematic diagram shown in Fig. 7, the Cu$_1$ and Cu$_2$ spins at alternative layers exhibit a flip for $H \parallel c$, which leads to an abrupt jump in magnetization. However, as $H_c \sim 0.8$ T, the magnetization reaches 0.68 $\mu_B$/Cu$^{2+}$, which is smaller than the expected magnetization of 1 $\mu_B$/Cu$^{2+}$, indicating that the spin-flip transition does indeed alter the magnetic state from AFM to FIM ordering. When $H > H_c$, the magnetization exhibits a slow variation because of the field-forced alignment of FIM.

Figure 4(b) displays the field-dependent dielectric property for $H \parallel c$. As $H < H_c$, the dielectric permittivity is insensitive to the field variation. However, as $H_c \sim 0.8$ T, an abrupt drop in dielectric property is noticed, reminiscent of the magnetization jump, suggesting that the spin flip plays an important role in the observed variations. Furthermore, the field-dependent electrical polarization also exhibits a finite peak near the $H_c$ value, as shown in Fig. 4(c), indicating that the spin flip triggers a ferroelectric property in Cu$_3$Bi(SeO$_3$)$_2$O$_2$Cl. In other words,
the magnetic field induces type-II multiferroic behavior with
the coexistence of ferrimagnetism and ferroelectricity at
$T < 25$ K and $H > 0.8$ T. In contrast to magnetization, dielec-
tric permittivity and polarization display a finite hysteresis with
the field variation above $H_c$. This difference might be related
to the high inertia of electric dipoles compared to magnetic
spins, indicating that electric dipoles could be more difficulty
to controlled than magnetic spins. A similar kind of type-II
multiferroic behavior was noticed in the orthorhombic DyFeO$_3$
2. Field-forced spin reorientation of Fe moments below Dy
ordering creates an exchange striction between the Dy and Fe layers,
leading to ferroelectric ordering for $T = 3$ K and $H_c \geq 2.4$ T [15].
However, in the present case, the type-II multiferroic occurs
at a much higher temperature ($T < 25$ K) and lower field
($H_c \geq 0.8$ T) than in the case of DyFeO$_3$ [15].
Because of the coexistence of FIM and FE ordering in Cu$_3$Bi(SeO$_3$)$_2$O$_2$Cl as $H > H_c$ and $T < T_N$, its multiferroic nature is now demonstrated. The magnetic properties of Cu$_3$Bi(SeO$_3$)$_2$O$_2$Cl indicate a strong anisotropy below $T_N$. This anisotropy stems from the microscopic details of the magnetic structure. Cu$_3$Bi(SeO$_3$)$_2$O$_2$Cl has a layered crystal structure with complex magnetic interactions. The two Cu$_1$O$_4$ and Cu$_2$O$_4$ sites, respectively, occupy two different crystallographic positions in the $ab$ plane; these form two-dimensional (2D) magnetic layers [17]. Cu$_1$ and Cu$_2$ ions are connected to each other similar to a pseudo-kagome lattice in the $ab$ plane. The Cu$_1$-O$_1$-Cu$_1$ and Cu$_1$-O$_1$-Cu$_2$ bonds almost have similar bond lengths and angles that exhibit superexchange FM behavior [12]. The former magnetic interaction is backed by an additional exchange path via a lone-pair Bi$^{3+}$ ion, i.e., Cu$_1$-O$_1$-Bi$^{3+}$-O$_1$-Cu$_1$. This magnetic interaction along with the magnetic frustrations by the kagome geometry creates a sizable AFM interaction between the Cu$_1$-Cu$_1$ ions. The competing FM and AFM interactions form an unconventional FIM state, where spins arrange in a canting configuration with the magnetic moments oriented $50^\circ$ from $c$ towards $b$ [12]. However, the spin of Cu$_2$ is oriented strictly parallel to the $c$ axis with an antiparallel alignment between the layers along the $c$ axis. The spin structure in the $bc$ plane exhibits a twofold rotation symmetry. From neutron diffraction studies, when $H \perp ab$, the first-order-like metamagnetic spin-flip nature for the critical field of 0.8 T emerges [12]. Similar field-induced phenomena in the dielectric and FE behaviors (Fig. 4) might indicate the origin of the multiferroic nature hidden in the same single magnetic building block [26]. The canted ferrimagnetic magnetic structure in the $ab$ plane is represented in the schematic diagram of Fig. 7. Spin moments within each layer form the spin structure; they are denoted by solid orange lines in Fig. 7. The spin structure is out of phase between the layers. Spin canting within each layer produces a finite DM interaction vector that creates the electric polarization parallel to the spin moment, denoted by large blue arrows in Fig. 7. In the low-magnetic field ($H < 0.8$ T), the twofold symmetry of the magnetic structure creates a net zero electric polarization due to the cancellation between the $ab$ layers. However, for $H > H_c$, the field-induced spin flip breaks the twofold symmetry and generates a nonzero electric polarization along the $c$ axis as illustrated in Fig. 7. Recent theoretical studies by Rousochatzakis et al. suggested that the dominating DM vector along the Cu$_1$-O$_1$-Cu$_2$ bond is crucial in determining
the microscopic details of the magnetic structure, i.e., Cu₁ spin canting and anisotropic magnetic properties [27]. In addition, for the lower-temperature part, the $H-T$ phase diagram of single-crystal Cu₃Bi(SeO₃)₂O₂Cl shown in Fig. 8 could be plotted using magnetization, ac susceptibility, dielectric constant, and pyroelectric current measurements.

**IV. CONCLUSION**

A unique type-II multiferroic system in kagome Cu₃Bi(SeO₃)₂O₂Cl at $T<25$ K and $H \geq 0.8$ T is established with a magnetic field-induced coexistence of ferromagnetism and ferroelectricity. The magnetic-field-dependent magnetization measurements and magnetodielectric effects of Cu₃Bi(SeO₃)₂O₂Cl demonstrate a strong anisotropic behavior. The spin-flip-induced ferroelectricity was confirmed from the magnetic-field-dependent dielectric constant and electric polarization. The mechanism of field-induced multiferroic phenomena in Cu₃Bi(SeO₃)₂O₂Cl could be related to the breaking of twofold symmetry of the magnetic blocks. These findings provide an interesting insight into the multiferroics in spin-flip metamagnetic materials.

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