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Article

Multiferroic Hysteresis Loop

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Abstract: Multiferroics, showing both ferroelectric and magnetic order, are promising candidates for future electronic devices. Especially, the fundamental understanding of ferroelectric switching is of key relevance for further improvements, which however is rarely reported in literature. On a prime example for a spin-driven multiferroic, $LiCuVO_4$, we present an extensive study of the ferroelectric order and the switching behavior as function of external electric and magnetic fields. From frequency-dependent polarization switching and using the Ishibashi-Orihara theory, we deduce the existence of ferroelectric domains and domain-walls. These have to be related to counterclockwise and clockwise spin-spirals leading to the formation of multiferroic domains. A novel measurement – multiferroic hysteresis loop – is established to analyze the electrical polarization simultaneously as a function of electrical and magnetic fields. This technique allows characterizing the complex coupling between ferroelectric and magnetic order in multiferroic $LiCuVO_4$.

Keywords: Multiferroicity; $LiCuVO_4$; Spin-driven improper ferroelectricity; Hysteresis in magnetic fields, Multiferroic Hysteresis Loop

1. Introduction

In the last years, multiferroic materials established a very important field of materials science as they host inherent functionalities for novel electronic and magnetic devices [1]. Among these materials, those who exhibit both, ferroelectric and (anti-)ferromagnetic order, are most prominent as they usually exhibit large magnetoelectric effects [2,3]. Controlling the magnetic order via an electric field and vice versa is a challenging task. Especially, systems with spin-driven ferroelectric order formed by spiral or helical spin structures enable this approach [4,5,6]. The electrical polarization arises directly from the non-collinear spin structure, for which $LiCuVO_4$ is a prototypical example [4,6,7,8]. As proposed, e.g., in Refs. [9,10,11], the presence of tilted spins (S_i and S_{i+1}) at neighbouring atomic sites (i and $i + 1$) breaks the inversion symmetry via spin-orbit coupling and is the microscopic mechanism for multiferroicity in these systems. This spin-driven improper ferroelectricity leads to the following relation for the electrical polarization: $P \propto e \times Q$, where Q denotes the propagation vector of the spin spiral and $e = (S_i \times S_{i+1})$ corresponds to the spiral axis, i.e., the normal vector of the spiral spin plane [7,10,11,12].

The spin-driven multiferroic compound $LiCuVO_4$ provides a complex (H,T)-phase diagram for the polarization at low temperatures [7]. An external magnetic field ($H_1 \approx 2.5$ T $< H < H_2 \approx 7.5$ T) is able to from conical spin structures leading to a polarization perpendicular to the magnetic field direction. For increased magnetic fields ($H > H_2$) a modulated collinear spin structure is induced [13], which suppress the helical spin state. Without an external magnetic field the spin spiral in $LiCuVO_4$ is formed below $T_N = 2.5$ K in the ab-plane (spiral axis $e \parallel c$) and propagates in the crystallographic b direction (i.e., $Q \parallel b$) [7,8]. As predicted by theory (e.g., Refs. [10,12]) and confirmed by experiments (e.g., Refs. [7,14]) this leads to a ferroelectric polarization along $P \parallel a$. Above H_1, e aligns along the external magnetic field direction. This allows switching of the electrical polarization according to $P \propto e \times Q$. Accompanied by the transition into the modulated collinear spin state above H_2 the ferroelectric state vanishes. Interestingly, not only the magnetic field has an impact on the

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polarization of a $LiCuVO_4$ single crystal but also an external electrical field [14]. This field can switch the ferroelectric polarization implying that the spin helicity switches from clockwise to counter-clockwise and vice versa. Such ferroelectric hysteresis loops have only rarely been documented in spin-spiral multiferroics [3,4,14,15,16].

In the present work, we thoroughly analyze the *electric and magnetic* field dependent ferroelectric hysteresis loops of single crystalline $LiCuVO_4$. Special emphasis is put on two aspects: firstly, the frequency dependence of ferroelectric hysteresis shows that the polarization varies with respect to frequency and coercive field. We provide a fundamental basis, using Ishibashi-Orihara theory for domain-wall movements [17], to explain the presence of multiferroic domains (clockwise and counterclockwise spin-spirals). This allows further insights into the dynamics of multiferroic switching processes. Secondly, on $LiCuVO_4$ we demonstrate a novel multiferroic hysteresis loop measurement, which enables unraveling the complex coupling of ferroelectric and magnetic order, e.g., in the vicinity of the critical magnetic field H_2. So far, only magnetic biasing fields are used for ferroelectric hysteresis loop measurements in multiferroics [14,18].

2. Results and Discussion

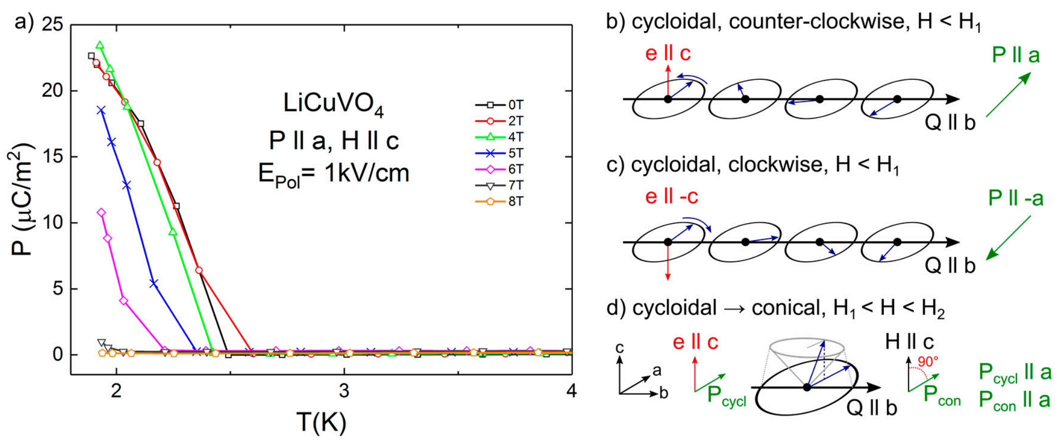

Figure 1. Temperature dependent polarization along the *a* direction of a $LiCuVO_4$ single crystal, measured during heating after a poling field of 1 kV/cm was applied while cooling. The pyrocurrent measurements were performed for various magnetic fields (up to 8 T) along the **c** direction. (b) – (d) illustrate possible spin-spiral configurations in $LiCuVO_4$, also including the directions of polarization, applied magnetic field, spiral-axis and the modulation direction of the spin-spiral.

Figure 1a shows the temperature dependent polarization along the *a* direction, measured after polarizing the sample during cooling down to 1.8 K with an electric field of 1 kV/cm. In addition, the polarization was determined for different magnetic fields up to 8 T applied in *c* direction of the sample. A polarization of up to 24 µC/m² for $H < 4$ T at low temperatures is for this specific measurement configuration explained in terms of ferroelectric ordering, as described in Refs. [7,14]. For instance, in the absence of an external magnetic field the polarization appears at the long-range magnetic order at $T_N = 2.5$ K. For magnetic fields exceeding 2 T the ferroelectric transition shifts to lower temperatures, which is in perfect agreement with reports of anomalies in temperature dependent dielectric constants [14]. Finally, the electrical polarization vanishes for magnetic fields above H_2 coinciding with the paraelectric phase as consequence of the modulated collinear spin state [7]. Hence, $LiCuVO_4$ single crystal investigated in this work is an illuminating example for spin-driven ferroelectric ordering for $T < T_N$. The figures 1b-d illustrate possible spin-spiral states of $LiCuVO_4$ for zero and applied magnetic fields. We assume, that for $H < H_1$ (figs. 1b and 1c) purely cycloidal spin states in the *ab*-plane exist, which allow the switching of the electrical polarization from $+P$ to $-P$ in the *a* direction due to the helicity of the spin-spiral (rotation sense). These are the

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so-called clockwise and counter-clockwise spin helicities. In an applied magnetic field $H_1 < H < H_2$ out of the spin-spiral a transvers conical configuration is formed gradually with increasing magnetic field (figure 1d). Here, the polarization arises in the *a* direction in a distinct relationship to the direction of the applied magnetic field [6]. Tilting the spin out of the *ab*-plane reduces on the one hand the polarization based on the cycloidal state, but on the other hand may increase the polarization of the conical configuration. The polarization derived from magnetocurrent measurement (i.e., measuring the pyrocurrent signal at constant temperature but changing magnetic field) [7] confirms this assumption, as the polarization changes from 0 to 24 μC/m² between H_2 and H_1.

An inherent property of conventional ferroelectricity is by definition the switchability of the spontaneous electric polarization by an external electric field. Ruff *et al.* [14] demonstrated, that even for $LiCuVO_4$ the improper ferroelectric order could be controlled by an electric field. As a consequence of the relation $P \propto e \times Q$, the spin helicity (containing both: modulation direction and spin spiral axis) of multiferroic $LiCuVO_4$ has to switch between counterclockwise and clockwise direction [5,16]. Here, we investigate the electric polarization of these *multiferroic* domains as a function of the frequency of the applied electric switching pulse. The switching kinetics in conventional ferroelectrics are often interpreted using the Kolmogorov-Avrami-Ishibashi (KAI) model [19,20,21,22]. In this case, ferroelectric domains grow unrestrictedly from nucleation centers in an applied electric field. While switching the polarization, the domains start to overlap. Hence, the overall switched volume fraction is based on: switching time, density of nucleus of reversed domains, mobility of domain walls, dimension of domain growth, and the impact of the electric field on moving domains. Ishibashi and Orihara (IO) [17,20] derived from the KAI model a more simplified scenario, especially in the case of deterministic nucleation. Here, the volume fraction of reversed polarization depends purely on the frequency of the applied field and its waveform (normally sinusoidal). It turns out, that the analysis of coercive fields derived from hysteresis loops measurements performed with various frequencies, can provide strong hints for the underlying ferroelectric switching mechanism [20].

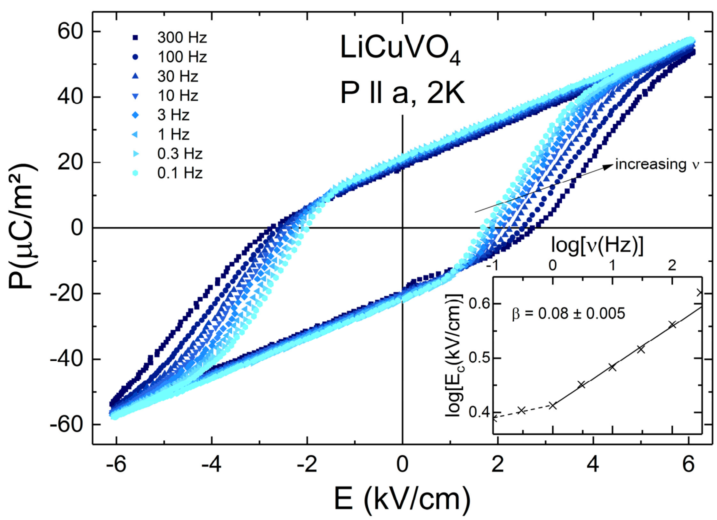

Figure 2. Frequency dependent ferroelectric hysteresis loops of a $LiCuVO_4$ single crystal. The polarization *P* was measured along the *a* direction at $T = 2$ K and in electric fields *E* up to 6 kVcm^{-1}. The inset shows a double-logarithmic representation of the coercive field E_c *vs.* frequency ν. The line denotes a linear fit representing IO model resulting in a slope of $\beta = 0.08$.

In the scope of the IO scenario, we conduct a thorough analysis of frequency dependent (0.1 Hz < ν < 300 Hz) ferroelectric hysteresis loops *P(E)* of multiferroic $LiCuVO_4$ as shown in figure 2 for $T = 2$ K (no magnetic field applied). For the lowest frequency ($\nu = 0.1$ Hz) of the applied

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sinusoidal electric field pulse a fully saturated hysteresis loop emerges. The tilt of the curve arises from linear capacitance contributions. Positive-up-negative-down measurement reported within Ref. [14] exclude for $LiCuVO_4$ extrinsic effects, e.g., leakage current, giving rise to an artificial hysteresis loop [23,24]. The remnant polarization of about 22 μC/m² confirms the polarization derived from pyrocurrent measurements (Fig. 1). With increasing frequency the remnant polarization only slightly decreases, while the coercive field rises from E_c (0.1 Hz) = 2.45 kV/cm to E_c (300 Hz) = 4.18 kV/cm. The inset of figure 2 presents this ν-dependence of E_c in a double-logarithmic scale. For higher frequencies $\nu > 1$ Hz, log[$E_c(\nu)$] shows an almost linear increase in the log(ν) representation. For ν = 300 Hz slight deviations are expected as the full saturation is not reached when applying an electric field pulse of E_{max}(300Hz) = 6 kV/cm (c.f. Fig. 2). In the scope of the IO model, E_c should follow a simplified power law relation: $E_c \propto \nu^\beta$ [20]. We use this model to describe $E_c(\nu)$ and reveal a β–parameter of 0.08 (± 0.005), which is quite similar to β–values of domain-wall movement in conventional ferroelectrics, like PZT (β = 0.05) [25] and SBT (β = 0.12) [26]. Hence, the frequency dependent hysteresis loops of $LiCuVO_4$ can be comprehensible explained in the framework of the IO model. Consequently, the volume fraction of reversed polarization has to be directly linked to the magnetic order of counterclockwise and clockwise spin helicity. Thus, multiferroic domains are formed in $LiCuVO_4$, which can be controlled by an external electric field.

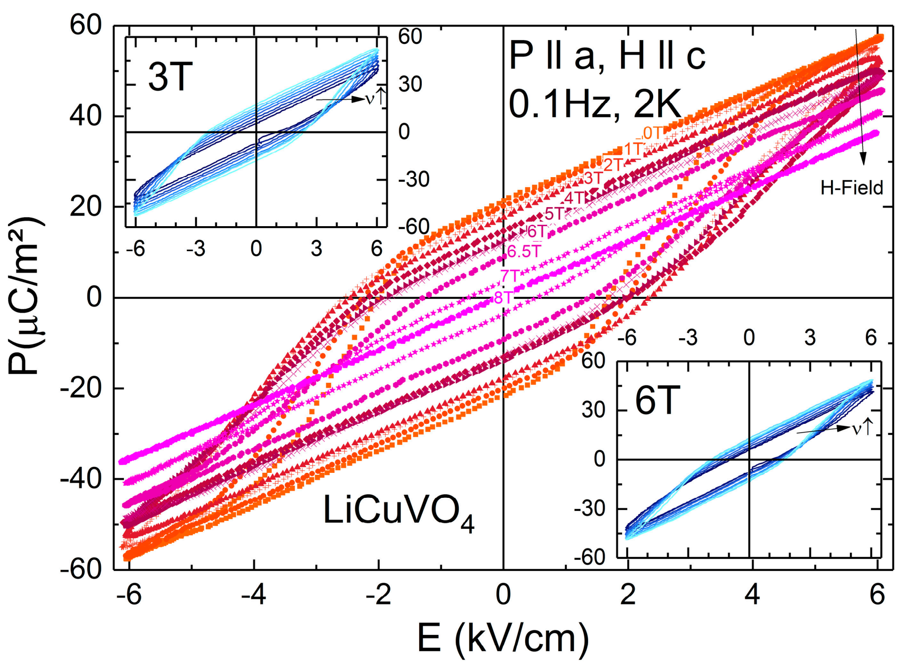

Figure 3. Ferroelectric hysteresis loops of a $LiCuVO_4$ single crystal measured at 2 K and 0.1 Hz in electrical fields up to 6 kV/cm⁻¹. *P* is measured along the *a* direction. Static magnetic fields of up to 8 T are applied along *c* direction. Insets (upper and lower) show the frequency dependent hysteresis loops (0.1 Hz < ν < 300 Hz) in magnetic fields of 3 T and 6 T, respectively.

However, not only electric fields have an impact on the multiferroic domains but also applied magnetic fields do so. Figure 3 shows *P(E)* measured in static external magnetic fields up to 8 T. The magnetic field *H* is applied in the direction of the spiral axis $e \parallel c$, allowing $P \parallel a$ even for $H_1 < H < H_2$ [14]. For the frequency of *P(E)* we chose ν = 0.1 Hz, because the magnetic field enhances E_c. So, if E_c is rather low, a fully saturated hysteresis loop can be achieved even in the presence of applied magnetic fields. For increasing magnetic fields, but still below H_1, the remnant polarization P_r slightly decreases, while the coercive field strongly increases (from 2.45 kV/cm at 0 T to 3.91 kV/cm at 3 T). In the regime $H_1 < H < H_2$ the remnant polarization declines until zero for $H > H_2$. In contrast, the coercive field has a reversal point at about 4 T leading to a decreasing E_c for higher magnetic

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fields. The linear behavior of *P(E)* at *H* = 8 T points towards the absence of non-linear contributions, which denotes the capacitive background of the complete system (sample and measurements devices). Hence, this curve was used as *background* for all other measurements to determine the intersection revealing the coercive fields. So, in a nutshell, we observe that external magnetic fields lead to a strong decrease of the remnant polarization of multiferroic $LiCuVO_4$. It seems that the coupling of the external magnetic field on the spin spiral impedes, especially if the magnetic field exceeds H_1, the switchability of the multiferroic domains, which are accompanied with multiferroic domain-wall movements. Indeed, frequency dependent *P(E)* loops with applied static magnetic fields *H* ∥ *c* of 3 T and 6 T (two insets in figure 3), at increasing external magnetic fields and higher frequencies of the *P(E)* loops reveal a strongly reduced P_r and a shift of E_c to higher values. However, probably the applied electrical field is too low to reach saturation polarization. It seems plausible that due to the multiferroicity, the external magnetic field influences the domain-wall movement leading to deviations of the simple IO model.

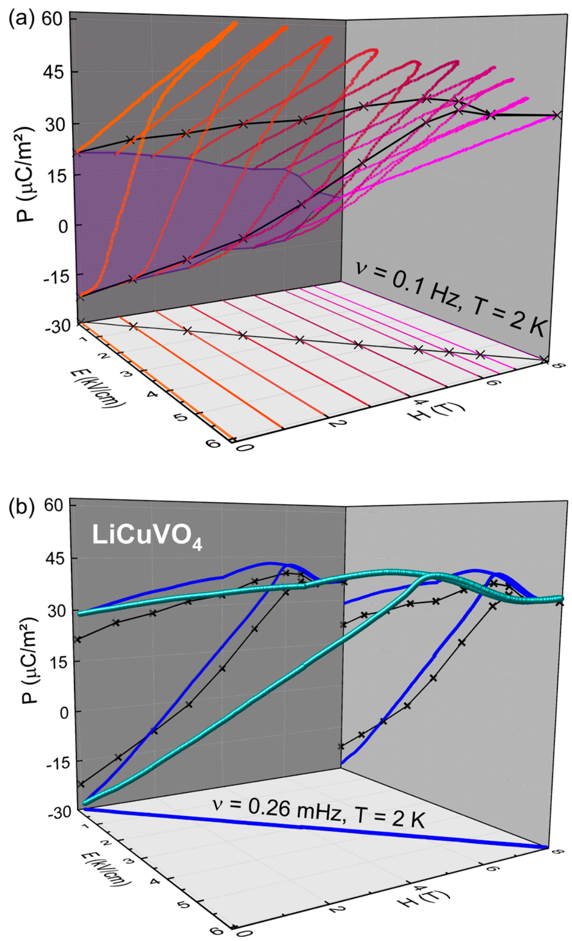

Figure 4. (a) *P(E)* loops of a $LiCuVO_4$ single crystal, which are the same as shown in figure 3. The color-coded lines (orange to magenta) represent the positive half of the hysteresis loops at static magnetic field. The crosses depict the intersection with the bisecting line in the *E*,*H*-plane. The *P*-values of these intersections forms a multiferroic hysteresis loop derived in static magnetic fields (shown also in (b)). (b) Multiferroic hysteresis loop of a $LiCuVO_4$ single crystal measured at *T* = 2 K and 0.26 mHz, again with *P* along the *a* direction and magnetic fields along the **c** direction. The dark-blue lines are projections of the multiferroic hysteresis loop in *P(E)*, *P(H)* and within *H*,*E* planes.

Hence, we performed a novel experiment measuring the polarization when varying simultaneously the *magnetic and electric* fields with the same rise-time and waveform. This multiferroic hysteresis loop is compared to *P(E)* loops detected in static external magnetic fields.

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Figure 4a shows the results of the hysteresis loop measurements of figure 3 in a *P(E,H)* representation. The lines in the *E,H*-plane denote the applied static magnetic field. As proof of concept, we show in figure 4b a multiferroic hysteresis loop (MHL) at low frequencies, to reach saturation polarization, and in magnetic fields up to 8 T to detect the ferroelectric to paraelectric transition at H_2. We apply an electrical pre-poling pules at zero magnetic field to start at $-P_r$. The same limits (E_{max} = 6 kV/cm^{-1} and H_{max} = 8 T) are used to derive a multiferroic hysteresis loop from intersections of *P(E)* loops (static magnetic fields) with a theoretical bisecting line in the *E,H*-plane (c.f. black line and crosses in figure 4a). The derived *P*-values of that loop reflect roughly the curve progression of the dynamic multiferroic hysteresis loop (figure 4b). The switching process of the polarization from $-P_r$ to $+P_r$ takes place over a broad range of electrical and magnetic fields differing significantly from typical *P(E)* loops in static magnetic fields below H_2. Approaching H_2 the MHL shows a clear peak like feature (i.e., $E = 4.6$ kV and $H = 6.1$ T) indicating an accelerated rise of *P* before the polarization approaches zero in the non-collinear state. Above H_2, the polarization resembles the pure paraelectric background (about 36 μC/m² at 2 K and for 8 T). Interestingly, for decreasing (*E,H*)-fields the peak-feature in *P* arises again. Below H_2, the overall *P* for zero electrical and magnetic fields reaches a value of about 29 μC/m², which agrees with results of pyrocurrent (figure 1) and magnetocurrent (figure 4a of Ref. [7]) measurements. A pronounced MHL requires the possibility to switch the polarization. For a cycloidal state this is allowed due to the formation of clockwise and counter-clockwise spin spirals. However, for $H > H_1$ we assume the emergence of a transverse conical spin structure, for which an electrical poling seems to be impeded. This novel MHL technique enables now to distinguish between switchable and non-switchable polarization (via an electric field): In figure 4a the violet-shaded area in the *P(H)*-plane denotes the switchable polarization for an applied electric field of E_{max} = 6.1 kVcm^{-1} and $\nu = 0.1$ Hz. If we subtract from the MHL-data (figure 4b) the paraelectric background, the switched polarization as a function of increasing electrical and magnetic fields emerge and purely the electric contribution remains for decreasing fields below H_2 (c.f. *P(H)* in figure 4b). As a consequence, polarization switching of multiferroic domains is limited at high magnetic fields due to the formation of transvers conical spin structures. One can speculate, that this complex interplay of electric and magnetic order in multiferroic $LiCuVO_4$ allows poling of *P* by electrical and reversed switching via magnetic fields. Further detailed measurements are required to analyze this coupling. Finally, a distinct benefit of the novel MHL technique is the precise measurement within a certain *E,H* parameter set enabling the analysis of multiferroic coupling in the vicinity of critical electric and magnetic fields.

3. Summary

In summary, we have performed a thorough characterization of the switching polarization of $LiCuVO_4$, which is a prime-example of spin-driven multiferroicity, by investigating the ferroelectric hysteresis loops as function of frequencies and magnetic fields below the ordering temperature. From the frequency dependence of the coercive fields and using the Ishibashi-Orihara model, we conclude the existence of ferroelectric domains. Magnetic domains of counter-clockwise and clockwise spin-spirals representing rarely observed multiferroic domains accompany these ferroelectric domains. To determine the complex interplay of this multiferroic state we establish a novel technique: multiferroic hysteresis loop measurement. Therefore, both fields vary with the same waveform and frequency allowing the analysis of *P(E,H)*-loops. From these measurements we deduce the existence of a switchable polarization in the cycloidal state ($H < H_1$). This is gradually reduced by the formation of a polarization arising from the magnetic-field induced transvers-conical state ($H_1 < H < H_2$), which only allows polarization switching via magnetic field. Hence, this novel technique enables unraveling complex coupling phenomena in multiferroic systems and, if a magnetic field of high rise-time is available also frequency dependent multiferroic hysteresis loop measurements, which can provide promising insights to the switching kinetics of multiferroic domains.

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Materials and Methods

Sample Preparation: Single crystals of the orthorhombic distorted spinel compound $LiCuVO_4$ were grown from a $LiVO_3$-based flux as described in detail in Refs [27,28]. Even a slightly variation in the composition results in different sample properties. Therefore, the single-phase and stoichiometry of the crystal was checked by X-Ray diffraction and differential dissolution technique, respectively. A crystal with almost ideal Li and Cu sublattices [13] and a size of approximately 3 × 1 × 1 mm^3 was chosen and oriented by Laue diffraction technique.

Polarization measurements: The pyroelectric current and the hysteresis-loop measurements were performed for electrical fields along the *c* direction and are in perfect agreement with previous measurements on that sample [7,14]. For polarization measurements silver paint contacts were applied to the single crystal in sandwich geometry to measure P along the *a* direction. For measurements between 1.5 and 30 K and in external magnetic fields up to 9 T, a Quantum Design Physical Property Measurement System and an Oxford cryostat equipped with a superconducting magnet was used. To probe the ferroelectric order the pyroelectric current at fixed magnetic fields was measured as a function of temperature between 1.8 K and 30 K utilizing a Keithley Electrometer 6517A. A typically temperature rate of 5 K/min was used. The spontaneous polarization was obtained by integrating the current over the time. Further, in order to align the ferroelectric domains a poling field of about 1 kV/cm was applied during cooling the sample through the magnetic transition temperature. Hysteresis-loop measurements were made using an Aixacct TF2000 ferroelectric analyzer equipped with a high-voltage booster. All hysteresis curves show a certain slope, which is independent of temperature and external magnetic fields, at least in the measured ranges of the present work. This is due to the contribution of a linear capacity, which can be neglected by subtraction a straight line with an appropriate slope leaving only the non-linear electric contributions. In this manuscript we only use the corrected curves to evaluate the frequency dependent coercive fields E_c. Furthermore, the coercive fields were calculated using $E_c = (|E_{c+}| + |E_{c-}|)/2$, where E_{c+} and E_{c-} are the positive and negative coercive fields.

Multiferroic hysteresis loop: For the multiferroic hysteresis loop measurement *P(E,H)* simultaneously an electric and magnetic field with the same frequency was applied to the sample while the polarization was determined. The frequency was limited by the maximum sweeping rate of the magnetic field of 0.5 T/min of the Oxford Cryostat.

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Author Contributions: A.R. and S.K. designed the experiments. A.R. performed the measurements and analyzed the data. A.R. and S.K. wrote the paper with contribution of A.L. S.K. supervised the project.

Conflicts of Interest: The authors declare no conflict of interest.

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