Details of the experiment

Single crystals of Ni$_3$TeO$_6$ (NTO) were grown by chemical vapor transport method [1]. Magnetization ($M$) above 13 T was measured in a pulse magnet by recording the induced voltage in a triply-compensated coil [2] and calibrated by vibrating sample magnetometry measurements in a superconducting magnet (PPMS-14, Quantum Design). Magnetoelectric current and integrating it over time was obtained under pulsed-field conditions by measuring the magnetoelectric current and integrating it over time [3]. During the magnetoelectric measurement, the $ab$-plane of the sample was attached to a platform for mechanical stabilization during the rapid magnetic field pulse. The absolute value of magnetoelectric current and integrating it over time was checked and calibrated against a capacitive analyzing magnet (combination of generator- and capacitor-driven magnets) up to 92 T at NHMFL in Los Alamos. Specific heat was measured by using a relaxation method in a PPMS-14 (Fig. S2).

Linear magnetoelastic coefficient

To visualize the giant response of $P$ to the external magnetic field, we plot the ME coefficient $\alpha(=dP/dH)$ of NTO as a function of magnetic field (Fig. S3). In the case of $c$-axis magnetic field, one can immediately see that the ME coefficient value at $H_{c2}$ is almost four times greater than that at $H_{c1}$ (Fig. S3(a)) and reaches up to 6,000 ps/m which is one of very high $\alpha$ value observed among the ME materials to date [7–9].
Details of the first-principles calculations

In order to model the magnetism in NTO it is essential to know the exchange constants. They were calculated using DFT previously [10], but, unfortunately, the minimization of the energy Eq. 1 of the main text within the 6-atom magnetic unit cell using those values gives a non-collinear state at a moderate $K_2$, while experiments suggest a collinear ground state [11]. We have found that the collinear state could be stabilized by reducing the exchange constant $J_5$ by 30%. Since Ni ions are centered in similar oxygen octahedra, we assumed the anisotropy constants to be equal, $K_{2,i} = K_2$, and chose their value to match the spin flop field measured experimentally. The calculated $M(H)$ curve is very different from the experimentally observed one - the magnetization jump at the spin flop transition is overestimated, and the second transition is absent. In order to improve the model we calculated the exchange constants using the PBE0 hybrid density functional, which is known to give better estimates for exchange constants in some compounds [12]. We used the VASP code with the supplied PAW-PBE atomic files [13–20], with the plane wave cutoff of 500 eV; spin-orbit coupling was neglected; energy convergence threshold was set to $10^{-6}$ eV; total energy was evaluated using Γ-centered $4 \times 4 \times 4$ k-point grid. The PBE0 calculation was seeded with the wavefunctions, calculated using PBE+U with $U = 8$ eV applied on Ni d-orbitals. The PBE0 total energies for 10 different spin arrangements within the magnetic unit cell were fitted to the model Eq. 1 of the main text using a least-square fit. The choice of trial magnetic states ensured that the system is overdetermined. The relative error for $J_1 \ldots J_4$ was estimated below 12 %, for $J_5 \sim 37$ %. Fig. S5 compares the energies of the used spin states, calculated using PBE0 [21] and from the fit.

The obtained exchange constants result in the experimentally observed ground state and the appearance of the second transition without any additional tuning, as shown in Fig. S6. The critical field $H_{c2}$ of the second transition is not sensitive to $K_2$. The magnetization change at $H_{c2}$ is much smaller than that observed in the experiment. Starting from these values, we tuned the exchange constants to improve the agreement between the calculated and measured $M$ along the c-axis. The final result is presented on Fig. 2(g), and the values of exchange constants are summarized in Table 1 of the main text.

Due to a frustration in NTO the ground state could be sensitive to small variations of exchange constants, therefore hybrid functional calculations were required to reproduce the correct ground state. However, these calculations are computationally expensive, therefore we used a faster GGA + $U$ as implemented in VASP to estimate the polarization variations in response to changes of spin arrangement, encoded in $\alpha_n$. Hubbard $U = 4.5$ eV was applied to Ni d orbitals in these calculations. The 20-atom rhombohedral unit cell, containing 2 formula units, were relaxed with the magnetic moments of Ni initialized to be in 10 trial configurations, and we have checked that the directions of magnetic moments didn’t change during the procedure. Total energies and Berry-phase polarizations were then calculated, and the exchange-striction coefficients $\alpha_n$, shown in Table 1 of the main text, were obtained by a least-square fit of Eq. 2 to the DFT results.

![FIG. S4. Contributions to the total energy from different exchanges $J_1 \ldots J_5$, single-ion anisotropy (marked $a$) and Zeeman energy (marked $h$), calculated using the model Eq. 1 of the main text, as functions of the applied magnetic field $H_c$.](image)

![FIG. S5. The energies of trial magnetic states calculated using PBE0 and from the fit Eq. 1.](image)

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FIG. S6. The magnetization $M_c(H_c)$ under the applied magnetic field $H_c$, calculated using the model Eq. 1 of the main text, PBE0 exchange constants and $A = 0.05$ meV (blue line), and measured in the experiment (black line). The second transition obtained from the model calculations is indicated by the black arrow.