Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Phase equilibria in metastability regime in the $(C_8H_{12}NO)_2[ZnCl_4]$ ferroelectric system

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PXRD measurements

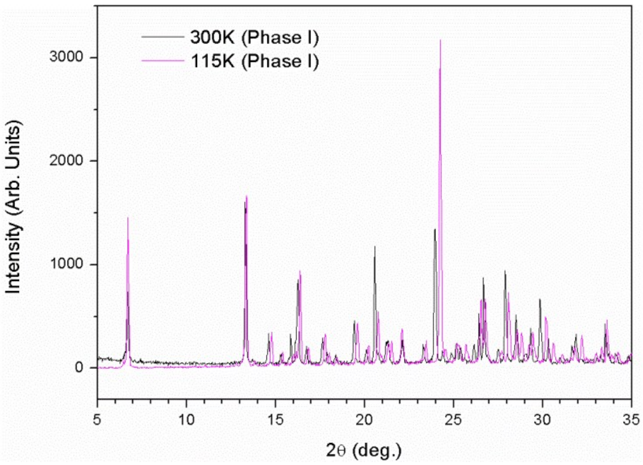

Figure S1: *PXRD patterns of the I phase collected at 300 and 115 K.*

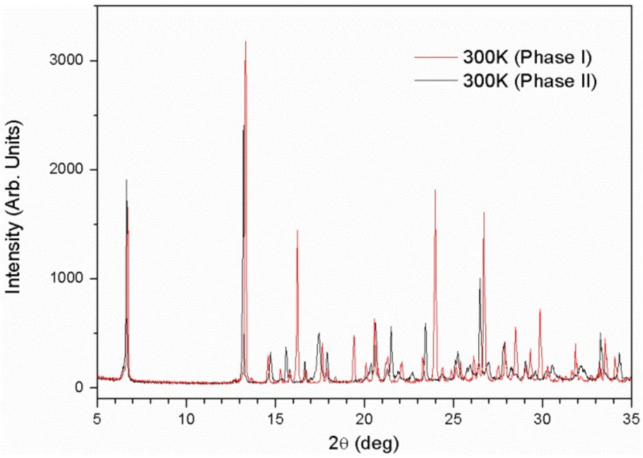

Figure S2: *PXRD patterns of the I and II phase collected at 300 K.*

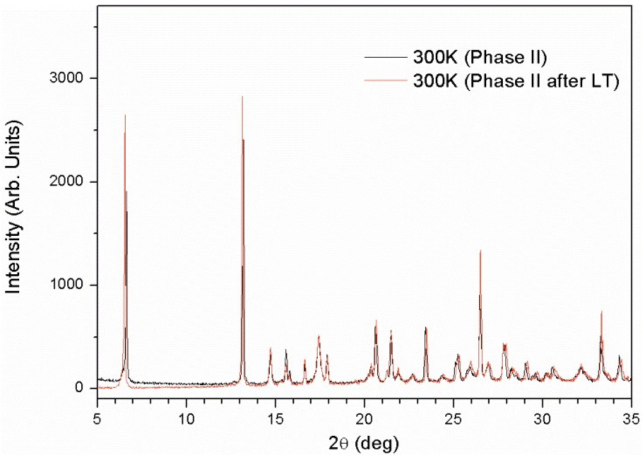

Figure S3: *PXRD patterns of the II phase collected at 300 K after a low-T thermal cycle.*

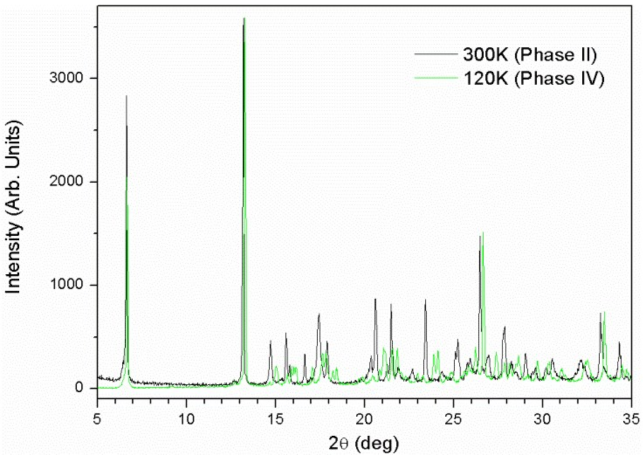

Figure S4: *PXRD patterns of the II and IV phase collected at 300 K and 120 K respectively.*

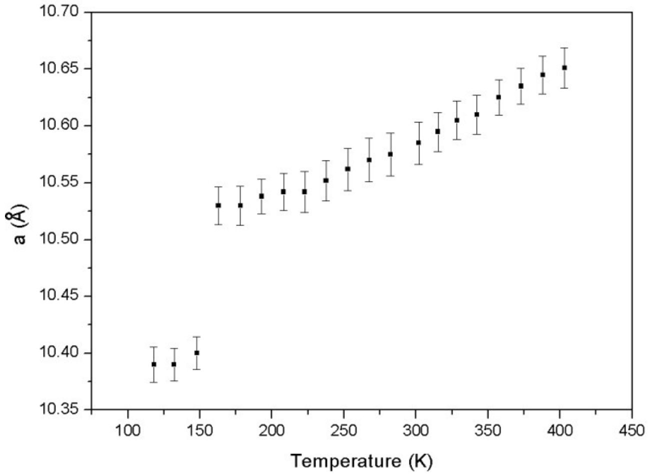

Figure S5: *Temperature evolution of the* a *lattice parameter of the heated phases.*

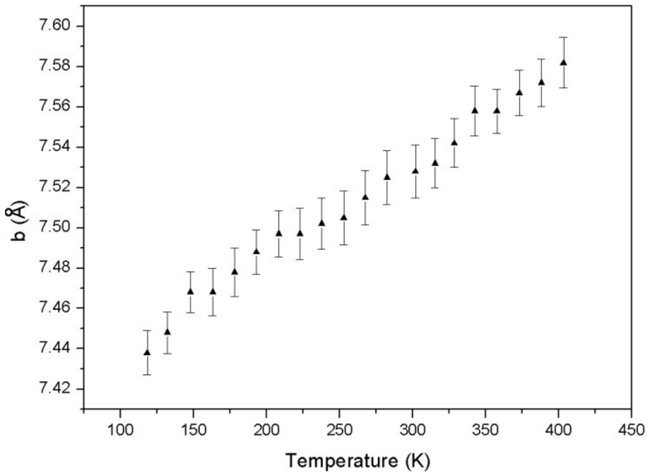

Figure S6: *Temperature evolution of the* b *lattice parameter of the heated phases.*

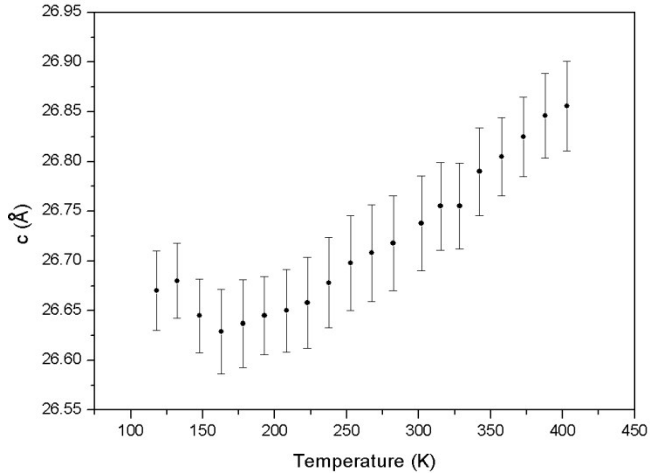

Figure S7: *Temperature evolution of the* c *lattice parameter of the heated phases.*

Pyroelectric and ferroelectric measurements

As shown in FigS8, Phase-I samples display the typical trend of a dielectric material with very low values of current (<1 pA) and a substantial invariance versus temperature. The absence of significant peaks or anomalies in the whole range states that, at least for such poling and thermal conditions, the sample does not display thermal depolarization phenomena. This behaviour can be justified in three different ways: (1) the electric field through the sample is not sufficiently intense to polarize the electric domains; (2) the ferro/pyroelectric thermal onset is located at temperatures higher than 325 K; (3) there is not a stable-macroscopic spontaneous electrical polarization arising from a concordant arrangement of the electrical dipoles present in the structure (i.e. the sample is either not ferroelectric or pyroelectric). Points (1) and (2) are both correct for Phase-I while (3) is wrong, as demonstrated by the DHM study reported in the main text, where a quite hard polarization loop was recorded at room temperature (RT) hence, phase-I is ferroelectric.

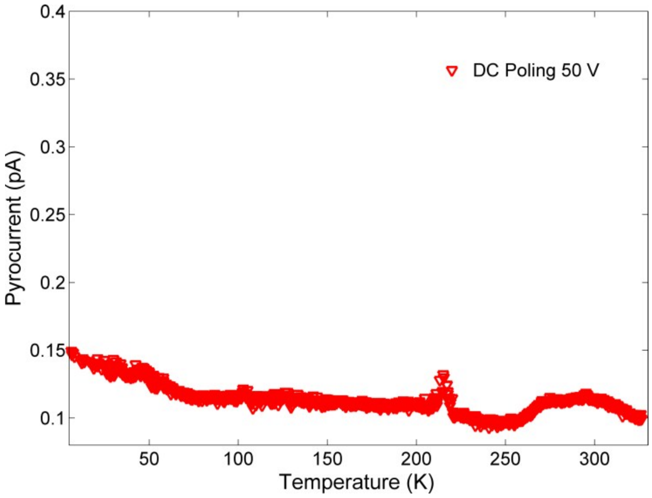

Figure S8:*. Pyrocurrent measured for the Phase-I after a slow cooling under the application of an electric DC poling.*

The curve shown in Figure S9 points out the formation of proper broad peaks (i.e. current lobes) centered at a specific field (the so called coercive field). Exchange bias is observed by a slight asymmetry in the position of the two absolute maxima of the curve, possibly suggesting the presence of pinning phenomena involving the electric dipole and the spatial structure.

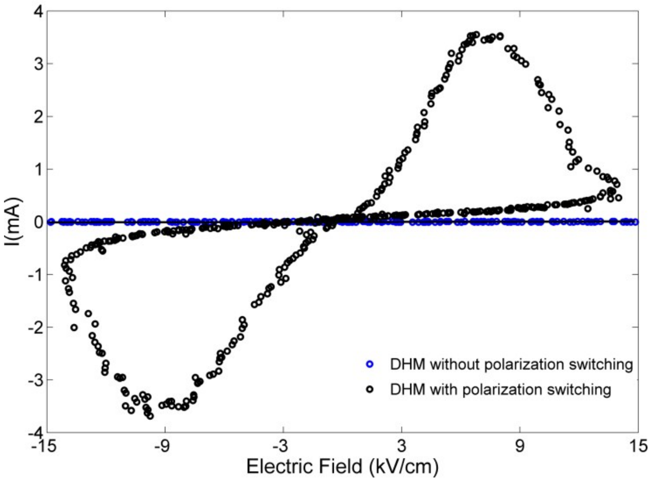

Figure S9: *Current vs. Voltage signals before the poling treatment (blue curve) and after the poling treatment when the polarization switching is obtained. The time-integral of the latter corresponds to the curve of Fig. 9 in the manuscript.*

The dielectric constant of phase I was measured above room temperature in order to fully characterize the I-II transition which, based on the ferroelectric measurements is expected to be a ferro-to-paraelectric transition. One single crystal prepared in parallel plate capacitor geometry was heated from RT to 420 K, while measuring the capacitance by applying a staircase voltage bias. In the described conditions the depolarization current released by the sample at the transition exceeds the maximum value allowed by the instrumentation, reaching its preset overflow limit. Correspondingly, since the depolarization current is integrated by the system electronics, a rapid increase of the capacitance tanδ, i.e. the resistive component of the capacitor, (not shown here) is observed. At higher temperature, when the depolarization process is complete, the system normalizes both in terms of ε_R and tanδ, recovering a pure dielectric character with voltage and temperature-invariant values. Both the diverging nature of the peak and its λ-like shape are characteristic features of a ferro-to-paraelectric transition, in agreement with the observed disappearance of ferroelectric hysteresis after the phase I-phase II transformation.

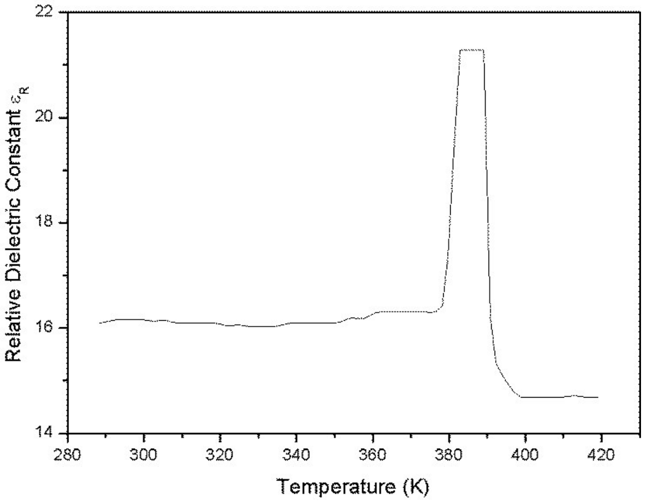

Figure S10: *Relative dielectric permittivity measured in heating on a single crystal of the as-grown phase I of* $(C_8H_{12}NO)_2[ZnCl_4]$.