SUPPLEMENTARY MATERIAL

Evidence for a dynamics crossover and its implication on the freezing temperature determination of relaxor ferroelectrics

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S1 Experimental procedure

A precision LCR meter (Agilent E4980A) is used to obtain the real and imaginary parts of the permittivity of unpoled $(Pb_{0.91}La_{0.09})(Zr_{0.35}Ti_{0.65})O_3$ (PLZT) and $SrNaBi_2Nb_3O_{12}$ (SNBN) at selected frequencies from 100 Hz to 1 MHz. The PLZT sample was placed in a programmable tubular oven for measurement cooling down from 550K to room temperature, while the SNBN sample was placed in a closed loop cold finger cryogenic system to scan the temperature from 400 K to 50 K. The temperature dependence of the permittivity was measured at a cooling rate of 0.5 K/min, slow enough to avoid thermal gradients inside the sample. The results of the measurements for the real permittivity are shown in Fig. S1.
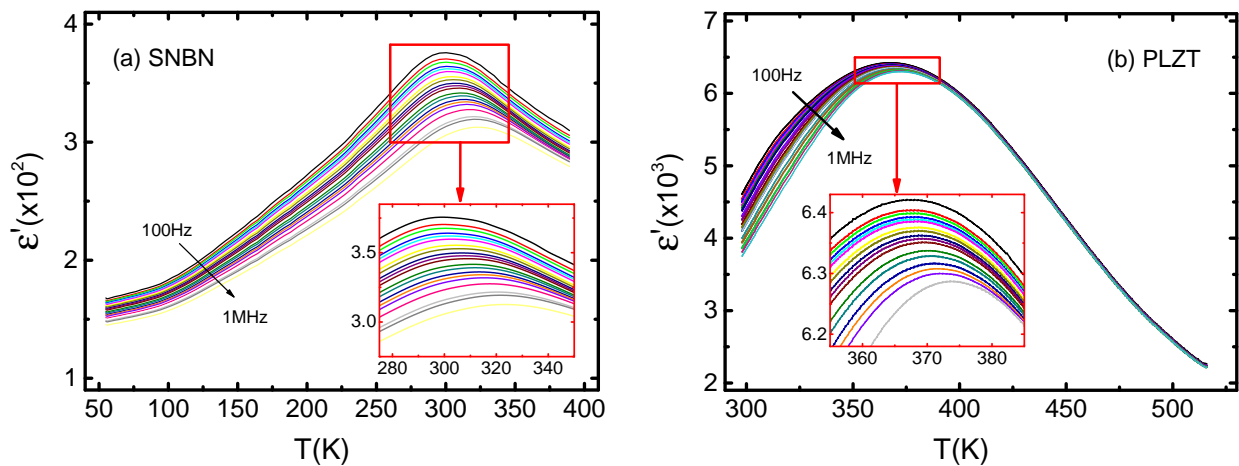
Figure S1: **Dielectric relaxation curves.** Dielectric constant (real permittivity) versus temperature curve for (a) SNBN and (b) PLZT relaxor ferroelectrics, at several frequencies ranging from 100 Hz to 1 MHz. The insets display a zoom of the region highlighted with a red rectangle in the main panel.

A quadratic fitting near the maximum of the real permittivity, ϵ', was performed for each curve in order to obtain the temperature T_{max} corresponding to the maximum value of ϵ'. Taking into account the quality of the data and to avoid bias-processing, none smooth or interpolation was performed to the raw data. For simplicity, all references to T_{max} temperatures are expressed in the main manuscript as T. Furthermore, the measurement frequencies are represented by the corresponding relaxation time, $\tau = (2\pi f)^{-1}$.

S2 Parameterization of dielectric relaxation data

The Vogel-Fulcher-Tammann (VFT) phenomenological equation is probably the most commonly used approach for parameterizing the super-Arrhenius behavior in relaxor ferroelectrics. By means of three parameters (τ_0, E_A, T_0), the VFT equation describes the temperature dependence of the relaxation times in the following way:

$$\tau^{VFT}(T) = \tau_0 \exp\left[\frac{E_A}{k_B(T - T_0)}\right], \tag{S2.1}$$

T_0 being a singular divergence temperature usually regarded as the freezing temperature of a freezing phenomenon. The parameter E_A denotes the Arrhenius activation energy and τ_0 defines the relaxation time at high temperatures.
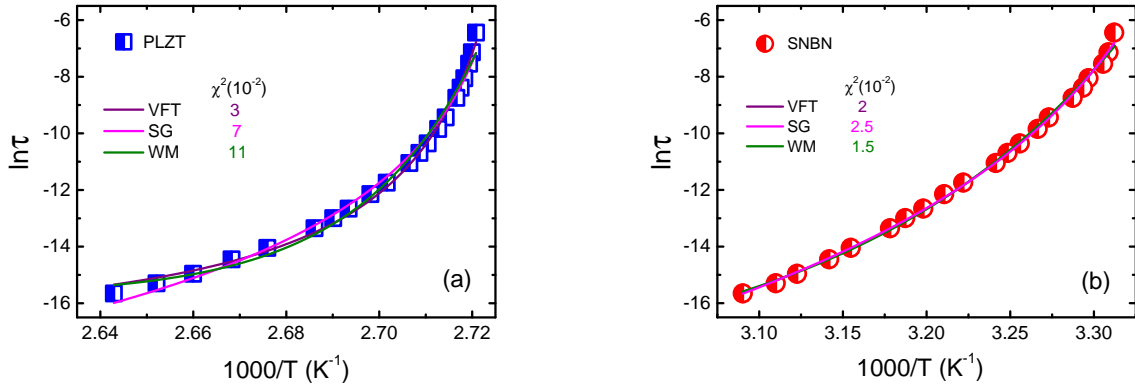
Figure S2: **Typical relaxation data representation.** Logarithm of relaxation time versus temperature for (a) PLZT and (b) SNBN relaxor ferroelectrics. A clear super-Arrhenius behaviour is displayed. The data are fitted by using Vogel-Fulcher-Tammann (VFT), spin-glass (SG), and Waterton-Mauro (WM) equations. The values of chi-square (χ^2) resulting from the fittings are shown as a measure of the statistical goodness of fit. No prevalent fitting quality is revealed.

Figure S2 show a typical representation of the relaxation data for both PLZT and SNBN. The data fitting according to VFT equation is also plotted. The low values of chi-square (χ^2) resulting of this fitting evidence the good quality of the VFT fit for both materials. Despite the indisputable good result offered by the VFT equation, the data are also fitted according to other two model equations using for describing the SA

behavior in relaxor systems. These are the power law spin-glass (SG) and the Waterton-Mauro (WM, also called MYEGA) equations.

On the one hand, the SG equation is used to describe the dynamic of systems such as glass-forming liquid crystals, orientationally disordered crystals (plastic crystals), spin-glass-like systems and others,[1–3] where a remarkable dynamic divergence is observed. The SG equation can be written as:

$$\tau^{SG}(T) = \tau_0 \left(\frac{T - T_C}{T_C} \right)^{-\phi},$$ (S2.2)

which is also a three-parameter equation, where τ_0 is here the value of the relaxation time for $T = 2T_C$, T_C being a critical temperature comparable to T_0 in the VFT equation. The exponent ϕ is related to an order parameter, often associated to the orientational order-disorder of the system.

On the other hand, the non-divergent WM equation:

$$\tau^{WM}(T) = \tau_0 \exp\left[\frac{K}{T} \exp \frac{C}{T} \right],$$ (S2.3)

where τ_0 has the same meaning as in the VFT equation, and K and C are related to an effective activation barrier and to the energy difference between two-states in the system, respectively, has proven to be the best way to unravel the dielectric relaxation of glass-forming liquids.[4]

The results from the VFT, SG and WM fitting show an equally reasonable fitting quality, without a clear prevalent parameterization for the relaxation data of relaxor ferroelectrics. In fact, the WM equation leads the lowest χ^2 value for SNBN, although WM is a non-divergent model. The apparently good fits for all the non-Arrhenius equations is not a surprising result, since these are three fitting-parameter equations. These results put in evidence that there are no statistical criteria that make one parameterization prevail over the other two.

S3 Dielectric relaxation data processing

The super-Arrhenius (SA) behavior can be described by a temperature dependent apparent activation energy, such as:

$$\tau(T) = \tau_0 \exp\left[\frac{E_A(T)}{k_B T} \right].$$ (S3.1)

The Eq. (S3.1) can be easily transformed by the first derivative, assuming $x = T^{-1}$:

$$\frac{d}{dx} \ln \tau(x) = x \frac{d}{dx} \left(\frac{E_A(x)}{k_B} \right) + \frac{E_A(x)}{k_B}.$$ (S3.2)

According to Drozd-Rzoska *et al.*[5], the apparent activation enthalpy can be defined as:

$$H_a(x) = \frac{d}{dx} \ln \tau(x). \tag{S3.3}$$

Thus, the Eq. (S3.2) can be rewritten as a Bernoulli-type equation:

$$F(x) = \frac{dy(x)}{dx} + \frac{y(x)}{x}, \tag{S3.4}$$

where $y(x) = \frac{E_A(x)}{k_B}$, and

$$F(x) = \frac{1}{x} H_a(x) \tag{S3.5}$$

is a temperature-dependent function that can be obtained directly from dielectric relaxation data. The numerical solution of the Eq. (S3.4) allows us to obtain the activation energy function, $E_A(T)$, from the experimental data.

S4 Determination of dynamics regions from the Stickel plot

More than a decade ago, Stickel *et al.*[6–8] indicated that the validity of VFT equation has to be associated with the linearity of the "Stickel function":

$$\varphi(T) = \left(-\frac{d}{dT} \ln \tau \right)^{-\frac{1}{2}}, \tag{S4.1}$$

which can be easily obtained directly from the experimental data.

The VFT equation relates the relaxation times with the temperature as follow:

$$\ln \tau = \ln \tau_0 + \frac{B}{T - T_0} \tag{S4.2}$$

such that:

$$\frac{d}{dT} \ln \tau = -\frac{B}{(T - T_0)^2}. \tag{S4.3}$$

Thus, the Stickel function:

$$\varphi(T) = \frac{T}{\sqrt{B}} - \frac{T_0}{\sqrt{B}}, \tag{S4.4}$$

turns out to be a linear temperature-dependent function.

Consequently, the Stickel plot became a key tool for estimating the so-called dynamic crossover temperature between two dynamic domains. The application of such analysis showed that at least two VFT equations are desired for describing "previtrificational" slowing down in a broader range of temperatures. Therefore, the

Stickel plot represents a valuable tool for predicting the crossover temperature from a simple linearization of the classical VFT equation. The computed $\varphi(T)$ as a function of the temperature for the studied PLZT and SNBN relaxor ferroelectrics are showed in Fig. S3. Two dynamic domains are identified, which are in accordance with the two dynamic regions evidenced from the derivative-based representation of the relaxation data (i.e., Fig. 2 of the main manuscript).
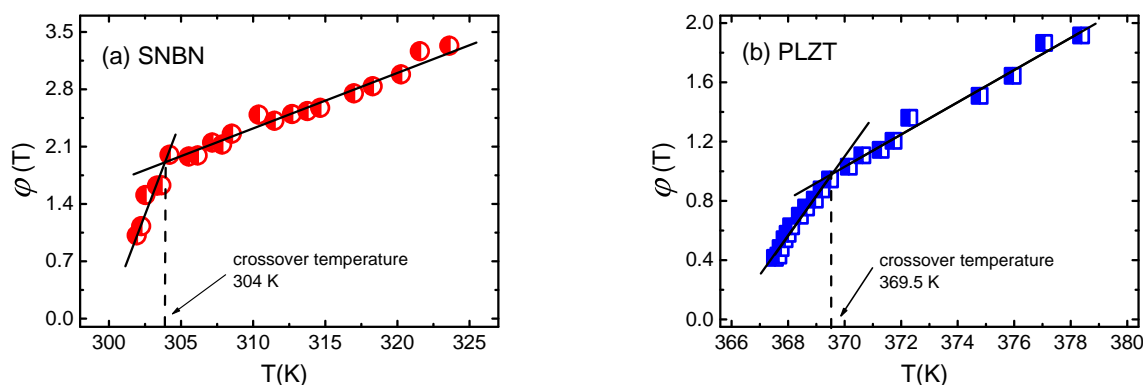
Figure S3: **Stickel plot.** Stickel function versus temperature for the tested (a) SNBN and (b) PLZT materials. Two linear regions for $\varphi(T)$ may be easily identified. A linear fitting for the two linear patterns are plotted. The crossover temperature between the two dynamic regions can be estimated as indicated.

Supplementary Bibliography

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