



Origin of the large strain response in (K 0.5 Na 0.5) NbO 3 -modified (Bi 0.5 Na 0.5) TiO 3 – BaTiO 3 lead-free piezoceramics

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Origin of the large strain response in $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ -modified $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ - BaTiO_3 lead-free piezoceramics

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The mechanism of the giant unipolar strain recently observed in a lead-free piezoceramic, $0.92(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-0.06\text{BaTiO}_3-0.02(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ [S.-T. Zhang, A. B. Kounga, E. Aulbach, H. Ehrenberg, and J. Rödel, *Appl. Phys. Lett.* **91**, 112906 (2007)] was investigated. The validity of the previously proposed mechanism that the high strain comes both from a significant volume change during the field-induced phase transition, from an antiferroelectric to a ferroelectric phase and the domain contribution from the induced ferroelectric phase was examined. Monitoring the volume changes from the simultaneously measured longitudinal and transverse strains on disk-shaped samples showed that the phase transition in this specific material does not involve any notable volume change, which indicates that there is little contribution from a volume change due to the phase transition to the total strain response. Temperature dependent hysteresis measurements on unpoled samples of a nearby ferroelectric composition, $0.93(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-0.06\text{BaTiO}_3-0.01(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ demonstrated that the origin of the large strain is due to the presence of a nonpolar phase that brings the system back to its unpoled state once the applied electric field is removed, which leads to a large unipolar strain. © 2009 American Institute of Physics. [DOI: 10.1063/1.3121203]

I. INTRODUCTION

Research on nontoxic piezoceramics has increased sharply during the past decade since the RoHS/WEEE regulations have come into effect.¹ Although no real success in replacing commonly used lead-containing piezoceramics in a wide range of applications has been made so far, several potentially promising materials have been developed²⁻⁶ and a couple of prototypal devices such as ultrasonic motor⁷ and transducer⁸ using $(\text{K},\text{Na})\text{NbO}_3$ -based materials have been introduced. For large-strain actuator applications, materials such as $0.92(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-0.06\text{BaTiO}_3-0.02(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (Ref. 5) (referred to as 92-6-2, hereafter) appear very promising, since its large signal $d_{33}(S_{\text{max}}/E_{\text{max}})$ value is as high as 550 pm/V, comparable to that of lead zirconic titanate (PZT). Promising as it may be, the 92-6-2 has one critical drawback: the high $S_{\text{max}}/E_{\text{max}}$ can only be realized at relatively high electric fields exceeding 6 kV/mm. This high minimum actuation field must be reduced significantly before the material can be seriously considered for industrial applications. To do this, it is essential to have a clear understanding on the mechanism involved in the creation of the high strain.

Initially, it was proposed that the mechanism for the high strain be a combined effect of a volume change during a field-induced phase transition from an antiferroelectric (AFE) to a ferroelectric (FE) phase and the normal intrinsic and extrinsic piezoelectric effects from an electric field-induced FE phase.⁵ Evidence for the field-induced phase transition was indeed detected by an acoustic emission

technique⁹ and the contribution from the induced FE phase is quite evident from the measured polarization hysteresis. However, the assumption that the total strain is largely indebted to the postulated volume change during the phase transition has remained hypothetical: it was merely presumed based on the fact that other well-studied lead-based AFE materials do display a significant volume change during a field-induced AFE-FE transition.^{10,11} 92-6-2 shares several phenomenological similarities with these lead-containing AFE materials, but there is yet no experimental evidence for a significant volume change during the phase transition.

In this paper we first describe investigations of the total volume change (S_v) of 92-6-2 during the application of an electric field by measuring the longitudinal strain (S_{33}) and transverse strain (S_{11}) simultaneously. The volume change is then compared with that of $0.93(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-0.06\text{BaTiO}_3-0.01(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (referred to as 93-6-1 hereafter) whose composition lies right next to 92-6-2 but exhibits a strong FE order. The results suggest that the field-induced phase transition in 92-6-2 involves no notable volume change, indicating that the observed giant strain in 92-6-2 originates from a different phenomenon. Temperature dependent strain measurements on unpoled samples of 93-6-1, which also shows a similar level of strain at a slightly higher temperature where its FE order vanishes,¹² clearly show that the origin of the giant strain is mostly a consequence of the disappearance of the remnant strain due to the presence of a nonpolar phase at zero electric field. Note that the use of the terminology, AFE phase instead of the nonpolar phase, is intentionally avoided in this manuscript because the nature of this phase is still controversial in the literature.¹³⁻¹⁶

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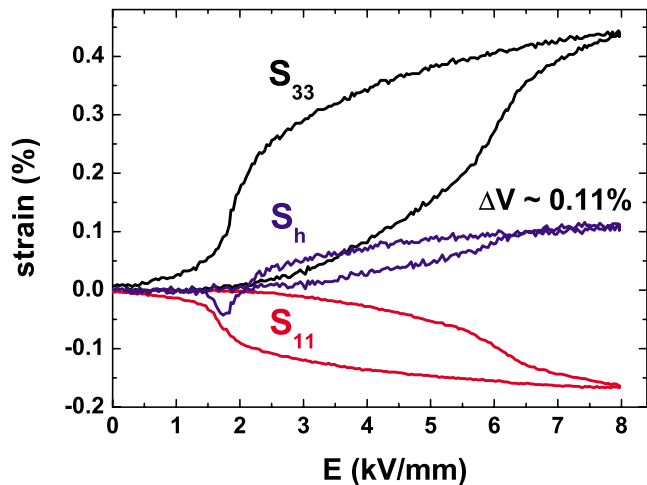


FIG. 1. (Color online) Unipolar strain hysteresis of 92-6-2 from the unpoled state. S_{33} and S_{11} are the strains simultaneously measured parallel and perpendicular to the electric field, respectively, S_h denotes the volume change.

II. EXPERIMENTAL PROCEDURE

92-6-2 and 93-6-1 ceramics were prepared by the conventional solid state reaction method. Details of the production process can be found in Ref. 5. The purity and formation of the desired single perovskite phase in the calcined powders and sintered products were monitored by powder x-ray diffraction (XRD) (STOE STADIP) using Cu $K\alpha$ radiation. The XRD patterns of both 92-6-2 and 93-6-1 showed practically no difference from our previous report.⁵ No second phase was detected and the XRD patterns of both 92-6-2 and 93-6-1 were fitted as a single phase with a pseudocubic structure. The relative densities measured by Archimedes method were $>98\%$ for all samples. The microstructure of both compositions was homogeneous and the average grain size determined by the linear intercept method was about 2 μm for 92-6-2 and 5 μm for 93-6-1.

All electrical measurements were performed in a silicone oil bath on unpoled disk-shaped specimens electroded with silver paint. The polarization hysteresis $P(E)$ was measured with a field amplitude of 6 kV/mm for 93-6-1 and 8 kV/mm for 92-6-2 at a frequency of 50 mHz using a Sawyer–Tower circuit. Simultaneously, the change of axial strain $S_{33}(E)$ and radial strain $S_{11}(E)$ was measured with linear variable differential transformers. Since both S_{33} and S_{11} are small, the volume change $S_h(E)=[V(E)-V(0)]/V(0)$ can be calculated using the relation $S_h=S_{33}+2S_{11}$. Temperature dependent measurements of $P(E)$ and $S_{33}(E)$ between 20 and 125 $^\circ\text{C}$ were separately performed in a thermal bath with a field amplitude of 6 kV/mm. All measurements were done for four bipolar and unipolar cycles to see if a fully poled state is reached during the initial poling cycle at 6 kV/mm. No notable difference in the strain level was detected after the second cycle, which means that the currently chosen conditions are appropriate enough to induce the full poling state.

III. RESULTS AND DISCUSSION

Figure 1 shows the changes in the longitudinal and transverse strain and the resulting volume change of 92-6-2 dur-

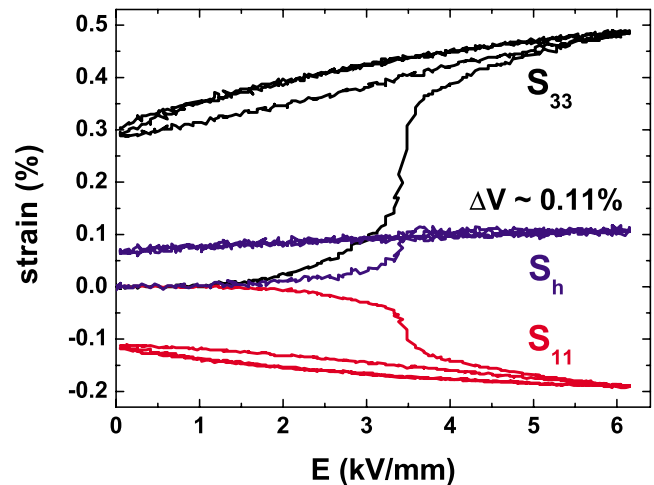


FIG. 2. (Color online) Unipolar strain hysteresis of 93-6-1 piezoceramics.

ing two unipolar cycles up to 8 kV/mm. At the maximum field, values of $S_{33}(8 \text{ kV/mm})=0.45\%$ and $S_{11}(8 \text{ kV/mm})=-0.17\%$ are observed. The corresponding large signal value is $d_{33}=S_{\text{max}}/E_{\text{max}}\approx 560 \text{ pm/V}$, comparable to the previously reported value.⁵ The total volume change during unipolar cycling is about 0.11%. It should be noted that $S_{11}(E)$ decreases smoothly and continuously with increasing field, just like a mirror reflection to the evolution of S_{33} . In the case of the well-known AFE lead lanthanum zirconate titanate stannate¹⁰ and lead niobium zirconate titanate stannate,¹¹ S_{11} is positive up to the electrical breakdown, and the volume change reaches up to 0.5% while S_{33} is only 0.35%. There, the volume contribution to the achievable S_{33} is roughly 80%. In the case of 92-6-2, the transition from a nonpolar phase at zero electric field to a polar FE phase involves no notable volume change (about 0.11%).

During the poling cycle the volume increases quadratically up to about 6.3 kV/mm; after that, the change becomes almost linear. This change in slope indicates that the phase transition from a nonpolar phase to an FE can be assumed to be completed above 6.3 kV/mm. During field reduction the volume changes almost linearly down to about 3 kV/mm, which indicates the field-induced FE phase persists till the electric field is quite small. The linear decrease undergoes an abrupt drop at 2.5 kV/mm. This sharp decrease reaches its minimum at about 1.8 kV/mm and then the volume change gradually increases back to zero.

Figure 2 shows $S_{33}(E)$, $S_{11}(E)$, and $S_h(E)$ measured in 93-6-1 during two successive unipolar cycles from an unpoled state. A total poling-induced strain $S_{\text{pol}}=0.49\%$ from the unpoled state to the maximum field level and a remnant strain $S_{\text{rem}}=0.3\%$ are observed. Despite the high value of S_{pol} , the strain $S_{33}(E)$ during the second and subsequent unipolar cycles is only about 0.19% at 6 kV/mm, corresponding to $d_{33}=S_{\text{max}}/E_{\text{max}}=320 \text{ pm/V}$. This significant reduction in $S_{\text{max}}/E_{\text{max}}$ in 93-6-1 is a direct result of the high value of S_{rem} .¹⁷ Note that the volume change from the unpoled state to the fully poled state at 6 kV/mm reaches about 0.11%, practically identical to that of 92-6-2. Since 93-6-1 does not display a phase transition, this again indicates that the large strain observed in 92-6-2 has little to do with a possible volume change during the phase transition.

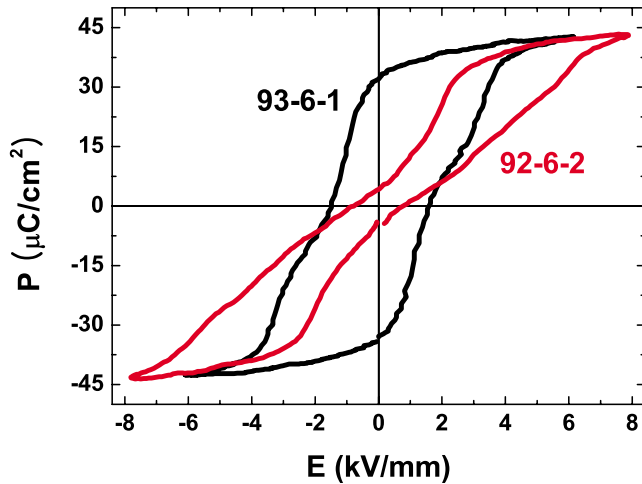


FIG. 3. (Color online) Polarization hysteresis loop of 92-6-2 at 8 kV/mm and of 93-6-1 at 6 kV/mm.

The polarization hysteresis loops for 92-6-2 and 93-6-1 are presented in Fig. 3. The maximum polarization P_{\max} and the spontaneous polarization P_{S^*} , defined as the intercept of a linear interpolation of the high-field regime of $P(E)$ with the P -axis are almost identical for both compositions. This implies that the induced FE phase in 92-6-2 can be fully poled at 8 kV/mm. Although the strain hysteresis of 93-6-1 shows typical FE features, the presence of a small fraction of a nonpolar phase cannot be excluded due to the pinched shape of the $P(E)$ curve. Similarly, the presence of traces of FE order in 92-6-2 at zero electric field is also evident, since the remnant polarization is not negligible at $P_{\text{rem}} = 4.2 \mu\text{C}/\text{cm}^2$. The coexistence of the different polarization states in a system may indicate that the free energy of both phases is so comparable that the FE phase in 92-6-2 and the nonpolar one in 93-6-1 could survive as a metastable phase. Upon heating, the nonpolar phase becomes dominant also in 93-6-1; this can be seen in the thermal evolution of $P(E)$ shown in Fig. 4. The temperature dependence of P_{\max} , P_{S^*} , and P_{rem} is summarized in Fig. 5.

As expected, P_{\max} slowly decreases with increasing tem-

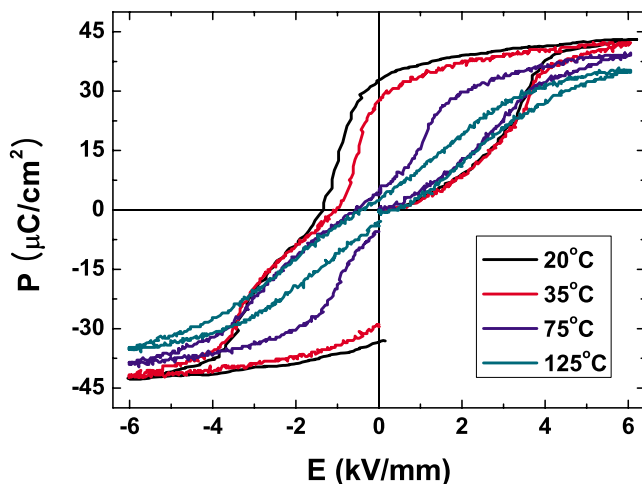


FIG. 4. (Color online) The thermal evolution of the polarization hysteresis loops of 93-6-1 piezoceramics.

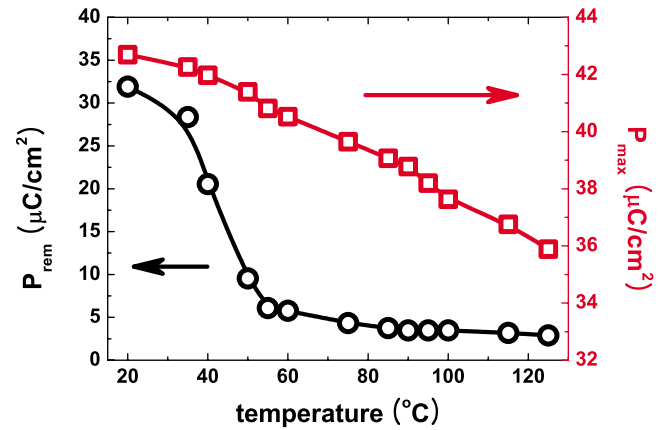


FIG. 5. (Color online) P_{\max} and P_{rem} as a function of temperature. Note that P_{rem} drops down to about $5 \mu\text{C}/\text{cm}^2$ and then gradually saturates at about $3 \mu\text{C}/\text{cm}^2$.

perature. The shape of the hysteresis loops clearly shows that the nonpolar phase becomes more pronounced with increasing temperature, in good agreement with previous reports.^{12,18} The most notable change is the sharp drop in P_{rem} , which decreases drastically from about $28 \mu\text{C}/\text{cm}^2$ at 30°C to $5 \mu\text{C}/\text{cm}^2$ at 60°C and then asymptotically converges to zero. Apparently, the FE order that is dominant at room temperature is disrupted over a relatively wide range of temperatures and does not vanish completely even at fairly high temperatures. The transition between the FE and the nonpolar phase is smeared, causing both phases to coexist over a wide range of temperatures.

The temperature dependence of bipolar strain hysteresis loops of 93-6-1 is presented in Fig. 6. It is evident that the lower the temperature, the larger the S_{pol} which can be regarded as the upper limit of the achievable unipolar strain at a given electric field. Obviously, any possible volume change due to the field-induced phase transition has no apparent consequence; otherwise, the maximum achievable unipolar strain should increase noticeably when the FE order decreases sharply between 30 and 60°C . It can be assumed that the same holds true for 92-6-2, which behaves very similarly to 93-6-1 and just shows the transition from polar to nonpolar phase at lower temperatures.

Figure 7 summarizes the thermal evolution of several key parameters related to the experimentally observed strain hysteresis loops. Just like P_{rem} , both S_{rem} and the negative strain (S_{neg}),¹⁹ which is denoted by the difference between the minimum strain and the strain at zero electric field during bipolar cycles, decrease rapidly up to 60°C and then gradually converge to zero. It should be noted that the drastic increase of $S_{\text{max}}/E_{\text{max}}$, the most important parameter for actuator applications is closely related to the drop in S_{neg} and S_{rem} , more directly to that in S_{rem} . S_{rem} is mainly represented by the amount of non- 180° domains, which are once switched during the application of the electric field and not switched back on the removal of the electric field. In this regard, S_{rem} is considered to be a measure how far away from a completely random state a system is. In that the high unipolar strain is achieved when the FE order is already significantly suppressed, the major factor influencing $S_{\text{max}}/E_{\text{max}}$

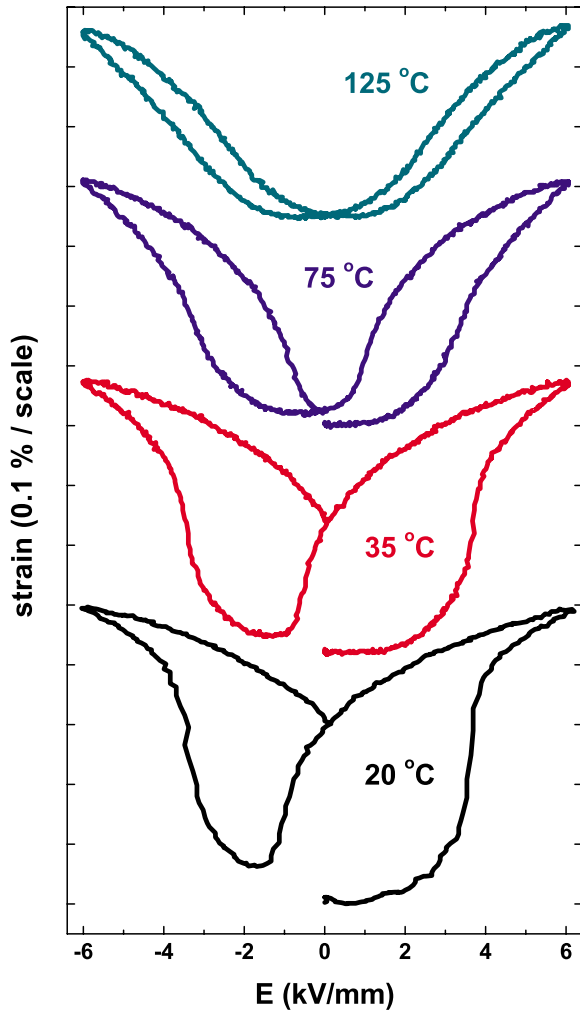


FIG. 6. (Color online) Thermal evolution of the bipolar strain response of unpoled 93-6-1 piezoceramics.

can be said to be S_{rem} . The large strain observed in 92-6-2 can thus be attributed to the significant reduction in S_{rem} due to a dominant presence of a nonpolar phase at zero electric field, which brings back the system as close to the unpoled state as possible. In other words, during each cycle, the re-

sidual and field-induced FE phase are fully poled and depoled again, resulting in large strain due to the repeated switching and back-switching of non-180°-domains. This observation is similar to that made for ordinary PZT ceramics under axial compressive loads.^{20–23} There, domain destabilization is mechanically induced, here, it is a result of a phase transition. In this way, each unipolar cycle can make the best use of the intrinsically high S_{pol} of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{-BaTiO}_3$ (BNT-BT) based systems, which results in such a high $S_{\text{max}}/E_{\text{max}}$.

IV. CONCLUSIONS

The origin of the giant piezoelectric strain in $0.92(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{-}0.06\text{BaTiO}_3\text{-}0.02(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (92-6-2) was investigated by comparing polarization and strain hysteresis with those of $0.93(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{-}0.06\text{BaTiO}_3\text{-}0.01(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (93-6-1). Using temperature-dependent measurements it was demonstrated that the enhanced unipolar strain in 92-6-2 is closely related to a reduction in the remnant strain S_{rem} due to a dominant presence of a nonpolar phase at zero electric field. Based on the results, it was proposed that the giant strain originates from a combined effect of the intrinsically high poling strain S_{pol} of BNT-BT based systems, the presence of a nonpolar phase at zero electric field which destabilizes and randomizes an electrically induced FE order, and an easy transition between the nonpolar and FE phases due to their comparable free energies. The optimum $S_{\text{max}}/E_{\text{max}}$ in BNT-BT based systems can be expected at the boundary where a rapid change in S_{rem} becomes retarded. It further suggests that adjusting the temperature showing the optimum $S_{\text{max}}/E_{\text{max}}$ near to the room temperature as in the case of 92-6-2 should expand the temperature range of usage, because once S_{rem} vanishes, $S_{\text{max}}/E_{\text{max}}$ becomes identical with S_{pol} whose temperature dependence is relatively small.

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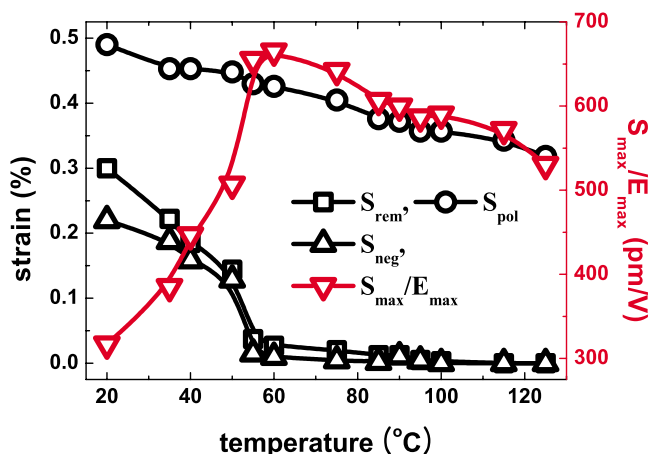


FIG. 7. (Color online) S_{rem} , S_{pol} , S_{neg} , and $S_{\text{max}}/E_{\text{max}}$ as a function of temperature. Note that a drastic increase in $S_{\text{max}}/E_{\text{max}}$ is accompanied by a sharp decrease in S_{rem} and S_{neg} .

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