
**MAGNETISM
AND FERROELECTRICITY**

Heat Capacity Study of Double Perovskite-Like Compounds $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$

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Abstract—The temperature dependence of the heat capacity of two compositions in the solid solution system $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ ($x = 0.25, 0.35$) was measured using adiabatic calorimetry. In the T – x phase diagram, these compounds occupy positions near the crossover from conventional ferroelectric behavior to the relaxor state. Both compounds reveal diffuse heat capacity anomalies: two anomalies in the temperature ranges 250–350 and 150–200 K at $x = 0.35$ and one anomaly within the range ~150–320 K at $x = 0.25$. The results obtained are discussed together with structural and dielectric measurements. © 2005 Pleiades Publishing, Inc.

1. INTRODUCTION

Relaxor ferroelectrics have been attracting research interest for a long time due to their remarkable dielectric and piezoelectric properties and the application potential they demonstrate in various areas of technology.

Dielectric, structural, spectroscopic, and other studies have established that the main relaxor features originate from the compositional and structural inhomogeneities of these materials and the presence of interacting polar nanodomains in a nonpolar matrix. The possible mechanisms responsible for these nonuniformities and for the formation of polar nanodomains have been debated intensely in the literature and are apparently different in different relaxor ferroelectric groups [1–3].

Most of the relaxors are mixed lead-containing perovskites. However, reports have recently appeared on the discovery of several groups of compounds which feature relaxor properties and are derivatives of BaTiO_3 with substituted isovalent or heterovalent cations [4–6]. The intense research interest in barium compounds stems to a considerable extent from their being more environmentally friendly.

Conventional relaxor ferroelectrics, which are similar to classical relaxors such as $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN) or $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ (NBT), possess three distinctive features: the presence in their composition of positionally disordered Pb^{2+} or Bi^{3+} ions, which occupy position *A* of the perovskite lattice because of their electronic structure; heterovalent disorder (at any rate, in one position, *A* or *B*); and, unlike solid solutions, the tendency to form a chemical compound with a fixed composition.

The solid solution system $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ with $\text{Ti}^{4+} \rightarrow \text{Zr}^{4+}$ ion substitution in position *B* exhibits none of these features, which makes its relaxor behavior all the more remarkable [7–9]. Moreover, a continuous variation from typically ferroelectric to relaxor behavior is a unique characteristic of lead-free solid solutions.

Mixed compounds with Zr concentrations $x < 0.1$ – 0.12 exhibit permittivity anomalies corresponding to three phase transitions, as is the case with the original BaTiO_3 . As the zirconium concentration increases, the temperature of the transition from the cubic to tetragonal phase decreases, while the temperatures of the other two transitions between distorted phases increase. In the range $0.12 < x < 0.25$, there occurs only one fairly strong permittivity anomaly, which corresponds to a direct transition from the cubic to rhombohedral phase and exhibits a weakly pronounced frequency dispersion. For $x > 0.25$, these compounds reveal only one broad peak in $\epsilon(T)$ with a maximum at T_m . Note that the values of the maximum permittivity and T_m depend markedly on the measuring field frequency, as should be expected in relaxors. The phase diagram of compounds with slight additions of Ca^{2+} has a narrow region of concentrations x within which, in addition to the maximum in $\epsilon(T)$ at T_m , a classical transition to the ferroelectric state is observed at $T_3 < T_m$ [7, 10]. The $T_m(x)$ and $T_{VF}(x)$ (the Vogel–Fulcher temperature) lines in the relaxor region join smoothly with the $T_c(x)$ line for compositions that exhibit conventional ferroelectric behavior. The reasons for this relation and the mechanisms governing the relaxor behavior in barium-containing relaxors are discussed in [6].

Studies of barium-containing relaxors have placed major emphasis on the behavior of the dielectric properties of these materials near T_m . The interval about the Burns temperature T_d where polar nanodomains form and the mechanisms governing the formation of these domains have not been considered up to now.

The present study was aimed at establishing the main features in the behavior of the heat capacity of $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ solid solutions with zirconium concentrations close to the crossover from the ferroelectric to relaxor state. The calorimetric method makes it possible to reveal anomalies in the heat capacity of any origin associated with changes in both the electrical and elastic subsystems and determine the energy characteristics of these changes. The temperature range covered by our studies extends over all characteristic temperatures of relaxors, namely, T_d , T_m , and T_c (the temperature of transition to the ferroelectric state), thus opening up the possibility of refining the $T(x)$ diagram.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ samples with $x = 0.25$ and 0.35 chosen for the study belong to different regions of the phase diagram and undergo transitions to the conventional ferroelectric and the relaxor state, respectively.

$\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ solid solutions were obtained in powder form by solid-phase synthesis in an oxygen environment from oxides in the reaction $\text{BaCO}_3 + (1-x)\text{TiO}_2 + x\text{ZrO}_2 \rightarrow \text{Ba}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3 + \text{CO}_2$ at temperatures of 1100–1200°C.

Ceramic samples ~10 mm in diameter and 4- to 7-mm thick were likewise synthesized in a dry oxygen atmosphere at 1250–1400°C from oxides without any sintering additives in 4 h. The grain size was about 1–2 μm , and the density reached 90–95% of the calculated value. X-ray diffraction analysis confirmed that the samples were single-phase and that the compounds had cubic structure $Pm\bar{3}m$ [11, 12].

The heat capacity studies in the range 100–370 K were carried out by adiabatic calorimetry, a method providing high accuracy in absolute measurements. The sample mass was 2.7 g for $x = 0.35$ and 4.9 g for $x = 0.25$. Measurements were made using the traditional method of discrete heating ($\Delta T = 1.5$ – 2.5 K) and in automated regime of continuous heating at a temperature variation rate $dT/dt \approx (0.2$ – $0.3)$ K/min [13]. The accuracy of total heat capacity measurements depends on the heating regime chosen and is 0.1–0.5%.

3. EXPERIMENTAL RESULTS

Figure 1a presents the results of the heat capacity measurements of $\text{BaTi}_{0.65}\text{Zr}_{0.35}\text{O}_3$. It has been reported that the permittivity of this compound exhibits one frequency-dependent anomaly near 200 K [6]. The $C_p(T)$

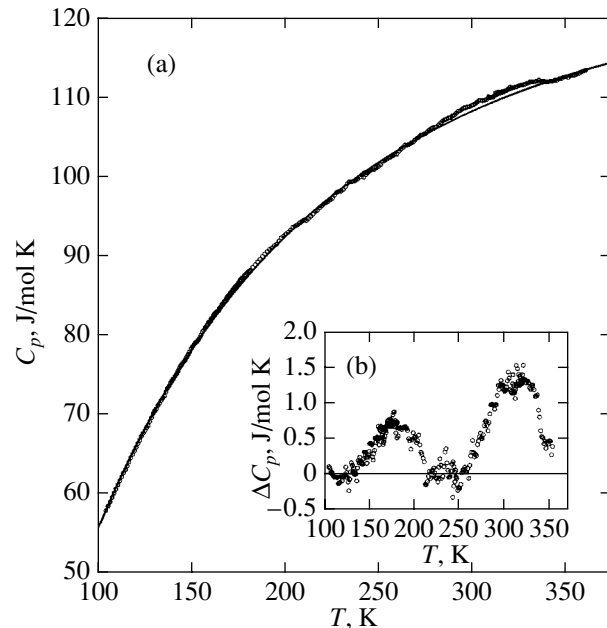


Fig. 1. (a) Temperature dependence of the specific heat of $\text{BaTi}_{0.65}\text{Zr}_{0.35}\text{O}_3$; the solid line is the lattice specific heat. (b) Anomalous specific-heat component.

curve did not reveal any clearly pronounced anomalies characteristic of traditional phase transitions. In the temperature ranges 250–350 and 150–200 K, however, one observes broad diffuse features in the heat capacity, which stand out distinctly in the temperature dependence of the excess heat capacity (Fig. 1b).

The lattice (C_L) and anomalous (ΔC_p) contributions to the specific heat of our compounds were separated using a simple model in which the lattice heat capacity is described by a combination of the Debye and Einstein functions. In the temperature region of interest, the heat capacity is only weakly sensitive to fine features in the lattice vibration spectrum, which justifies, in our opinion, the approximation of the lattice contribution in the above way. The anharmonic contributions and the difference between C_p and C_V were neglected because this difference, as a rule, is small as a result of the smallness of the thermal expansion coefficients of the compounds under study [14].

Reverting now to Fig. 1b, we note that the high-temperature anomaly is located near the temperature where the permittivity curve starts to deviate from the Curie–Weiss law [6], i.e., near the Burns temperature T_d . The temperature of the low-temperature anomaly is close to that of the maximum in permittivity T_m .

$\text{BaTi}_{0.75}\text{Zr}_{0.25}\text{O}_3$ undergoes a conventional phase transition to the ferroelectric phase [6, 11]. The small dispersion in permittivity was assigned to inhomogeneities of the samples. Compositionally, the compound is close to the point of crossover from the conventional to relaxor behavior. The temperature dependence of the

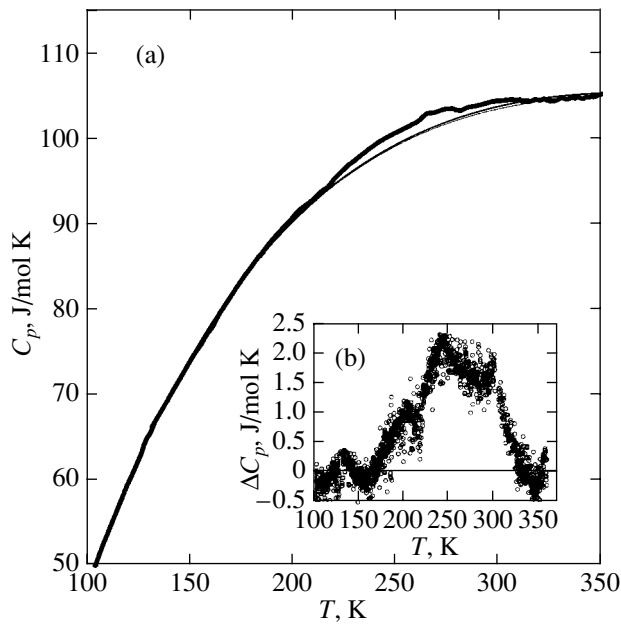


Fig. 2. (a) Temperature dependence of the specific heat of $\text{BaTi}_{0.75}\text{Zr}_{0.25}\text{O}_3$; the solid line is the lattice specific heat. (b) Anomalous component of the specific heat.

specific heat plotted in Fig. 2a reveals a broad region of anomalous behavior of $C_p(T)$ extending from ~ 150 to ~ 320 K.

We believe that the fairly large scatter of experimental points observed for $\text{BaTi}_{0.75}\text{Zr}_{0.25}\text{O}_3$ (Fig. 2b) is intimately connected with the specific features of this compound, namely, its being close to the practically vertical boundary separating the relaxor phase from the ferroelectric phase in the T - x diagram [6]. The $C_p(T)$ curves in the anomalous region were obtained in several series of measurements. In each series, the sample was cooled to nitrogen temperature and then heated at a high rate (~ 1 – 2 K/min) to the starting temperature in the series. This could bring about a lack of reproducibility in the results because of the attainment of equilibrium in the sample being a slow process. The main difficulty experienced in separating the lattice and anomalous contributions is associated with the fact that the regions of the normal behavior of $C_p(T)$ below 150 K and above 320 K are very narrow, and it is this factor that accounts for the lower reliability of $\Delta C_p(T)$ determination.

The anomalous component of the specific heat $\Delta C_p = C_p - C_L$, shown in Figs. 1b and 2b, is only 2 J/mol K, or $\sim 2\%$ of the lattice specific heat C_L .

The entropy changes related to the anomalous behavior of the specific heat and defined as $\Delta S = \int (\Delta C_p/T) dT$ are shown graphically in Fig. 3. The small values $\Delta S_{0.25} \approx 0.8$ J/mol K and $\Delta S_{0.35} \approx 0.5$ J/mol K imply that the processes involved are not of the order-disorder type, regardless of what reasonable fraction of the polar phase they are identified with. This is no sur-

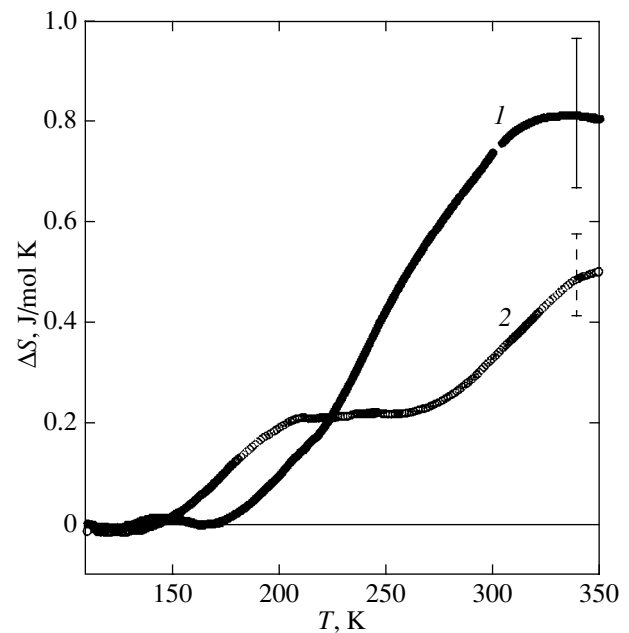


Fig. 3. Temperature dependence of the change in entropy of the $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ compounds with x equal to (1) 0.25 and (2) 0.35.

prise, because in barium compounds, unlike in compounds containing lead, the Ba^{2+} cation does not contribute noticeably either to the polarization or to the transition entropy.

4. DISCUSSION AND CONCLUSIONS

In order to gain insight into the origin of the broad anomalies in the temperature dependence of the specific heat, we consider the specific features in the structure of these materials and the corresponding models of the phenomena involved.

In a solid-solution system, according to the Vegard law, the unit cell parameter of the mixed compound varies linearly with increasing concentration of the second component. This involves a change in the interaction parameters in the lattice and, accordingly, changes in the temperatures and sequences of the phase transitions.

This is exactly what occurs in the BaTiO_3 - BaZrO_3 system at low zirconium concentrations. The unit cell parameter varies in a linear manner [15], the intermediate tetragonal and orthorhombic phases gradually vanish, and the temperature of transition from the cubic phase decreases.

Starting, however, with zirconium concentrations $x > 0.2$ – 0.3 , the temperature and frequency dependences of the permittivity change. The anomaly becomes strongly diffuse, and its temperature T_m is heavily dependent on the measuring frequency. Note that the macroscopic spontaneous polarization does not

appear below T_m in this case. This behavior is typical of relaxors.

This transition coincides in concentration with the appearance of additional reflections in the x-ray diffraction patterns and a change in the pattern of the concentration dependence of the cell parameter [15], which apparently indicates a multiphase state of the samples and a breakup of the solid solutions. In this concentration range, the samples may be assumed to consist of nanoregions with different zirconium concentrations. The long-range order characteristic of the low-temperature phase of pure barium titanate and solid solutions with $x < 0.2$ breaks down. Regions rich in Ti^{4+} become polar below the Burns temperature T_d , whereas regions with a high Zr^{4+} content remain paraelectric, like pure BaZrO_3 , so that finally only polar nanodomains are left in the samples.

Thus, for $x \geq 0.25$, the situation in $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ becomes similar in a certain sense to that observed earlier in $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$, where compositional inhomogeneities were reliably detected on the nanoscopic level and where regions with local Mg/Nb = 1 stoichiometry were observed [16].

The measured temperature dependence of the specific heat of $\text{BaTi}_{0.65}\text{Zr}_{0.35}\text{O}_3$ is likewise similar to $C_p(T)$ of lead magnesium niobate, where anomalies in the specific heat have been observed near the maximum in permittivity at T_m [17, 18] and at the temperature T_d of formation of polar nanodomains [18].

A model of relaxors for the temperature range $T < T_d$, namely, the spherical random bond–random field model (SRBRF), was proposed in [2]. This model considers a system of randomly interacting reorienting nanoclusters in the presence of random electric fields. Both random interactions (bonds) and random electric fields are assumed to have a Gaussian distribution. With no external field applied ($E = 0$), the system allows two sets of solutions. One of them, where the mean cluster polarization $\langle P \rangle = 0$ and the rms polarization $\langle P^2 \rangle \neq 0$, corresponds to a phase with no long-range order (spherical glass, SG). The other solution, with $\langle P \rangle \neq 0$ and $\langle P^2 \rangle \neq 0$, can be identified with a long-range-order phase, i.e., the ferroelectric (FE) phase.

If the mean interaction strength J_0 is less than a critical value, no long-range order sets in and the system remains in the SG state down to 0 K but the permittivity and the heat capacity pass through a maximum at a temperature T_m . If J_0 is larger than the critical value, long-range order may appear as a result of a phase transition into an inhomogeneous ferroelectric phase at $T_c < T_m$.

In $\text{BaTi}_{0.65}\text{Zr}_{0.35}\text{O}_3$, the interaction parameter J_0 is apparently less than the critical value and the ferroelectric transition with the formation of a macroscopic order parameter (polarization) does not occur. Accordingly, no classical heat capacity anomalies appear. However, the existence of the parameter $\langle P^2 \rangle \neq 0$ and its

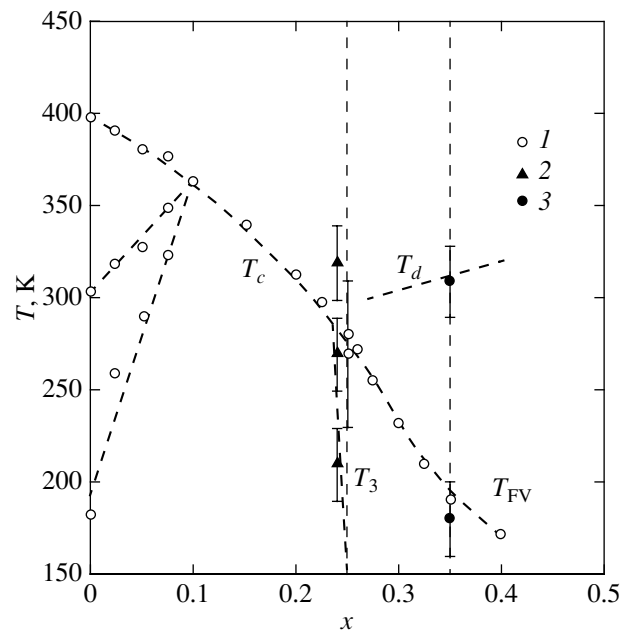


Fig. 4. Phase diagram of the $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ system. (1) Dielectric measurements [6, 12], (2) calorimetric studies of $\text{Ba}_{0.92}\text{Ca}_{0.08}\text{Ti}_{0.76}\text{Zr}_{0.24}\text{O}_3$ [14], and (3) present study.

variation with temperature give rise to an additional contribution to the free energy and heat capacity. The temperature dependence of the heat capacity was calculated numerically in [17] for various parameter values of the model proposed in [2]. It was found that, even in the absence of the ferroelectric transition, the heat capacity passes through a broad anomaly peaking at T_m .

In $\text{Ba}_{0.92}\text{Ca}_{0.08}\text{Ti}_{0.76}\text{Zr}_{0.24}\text{O}_3$, J_0 exceeds the critical value and this compound reveals, besides anomalies in the permittivity and heat capacity at $T_m \approx 270$ K, the long-range order and the phase transition to a nonuniform ferroelectric phase at $T_3 = 210$ K [7, 14].

Unfortunately, the anomalous heat capacity components, as already mentioned, are fairly small, with the associated uncertainties reaching as high as 20–30%, which precluded any attempt at quantitative treatment.

Thus, the temperatures of the heat capacity anomalies observed in our study may be identified, in our opinion, with T_d , T_m , or T_{VF} .

The data obtained suggest that the temperature versus composition phase diagram [6] should be complemented by one more line, namely, $T_d(x)$. Figure 4 sums up the results reported in [6], the results obtained in this study for $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ with $x = 0.25$ and 0.35 , and the characteristic temperatures for $\text{Ba}_{0.92}\text{Ca}_{0.08}\text{Ti}_{0.76}\text{Zr}_{0.24}\text{O}_3$ [14].

An increase in zirconium concentration above a certain critical level $x_{f-r} \approx 0.25$ – 0.27 [6] initiates, in our opinion, the formation of compositionally nonuniform nanoregions, part of which, that with a lower Zr content, transfers to the polar state at the Burns temperature

T_d . The value of T_d depends both on the actual composition of a nanoregion and on its size; so we have here a range of Burns temperatures. This suggestion is corroborated by the results obtained in a study of BaTiO₃ thin films and nanopowders [19]. Interaction among polar nanoregions gives rise to the appearance of maxima in the permittivity and heat capacity at T_m , followed by a ferroelectric transition at T_3 . As the zirconium concentration is increased further, the interaction among the polar nanoregions decreases and the transition to a phase with macroscopic polarization does not occur.

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REFERENCES

1. G. A. Samara, *J. Phys.: Condens. Matter* **15** (9), R367 (2003).
2. R. Pirc and R. Blinc, *Phys. Rev. B: Condens. Matter* **60** (19), 13 470 (1999).
3. W. Kleemann, *J. Non-Cryst. Solids* **307–310**, 66 (2002).
4. J. Ravez and A. Simon, *Phys. Status Solidi A* **178** (2), 793 (2000).
5. J. Ravez and A. Simon, *J. Solid State Chem.* **162**, 260 (2001).
6. A. Simon, J. Ravez, and M. Maglione, *J. Phys.: Condens. Matter* **16** (6), 963 (2004).
7. J. Ravez, R. von der Muhll, A. Simon, and P. Sciau, *J. Mater. Chem.* **9** (11), 2829 (1999).
8. Ph. Sciau and A. M. Castagnos, *Ferroelectrics* **270** (1), 259 (2002).
9. J. Kreisel, P. Bouvier, M. Maglione, B. Dkhil, and A. Simon, *Phys. Rev. B: Condens. Matter* **69** (9), 092104 (2004).
10. P. Sciau, G. Calvarin, and J. Ravez, *Solid State Commun.* **113** (2), 77 (1999).
11. J. Ravez and A. Simon, *Eur. J. Solid State Inorg. Chem.* **34**, 1199 (1997).
12. R. Farhi, M. El. Marssi, A. Simon, and J. Ravez, *Eur. Phys. J. B* **9** (4), 599 (1999).
13. V. S. Bondarev, A. V. Kartashev, A. G. Kozlov, I. Ya. Makievskii, I. N. Flerov, and M. V. Gorev, Preprint No. 829, F (Kirensky Institute of Physics, Siberian Division, Russian Academy of Sciences, Krasnoyarsk, 2005).
14. M. V. Gorev, I. N. Flerov, V. S. Bondarev, Ph. Sciau, and J.-M. Savariault, *J. Phys.: Condens. Matter* **16** (39), 7143 (2004).
15. R. Pantou, C. Dubourdieu, F. Weiss, J. Kreisel, G. Kobernik, and W. Haessler, *Mater. Sci. Semicond. Process.* **5** (2–3), 237 (2002).
16. S. Miao, J. Zhu, X. Zhang, and Z.-Y. Cheng, *Phys. Rev. B: Condens. Matter* **65** (5), 052101 (2002).
17. M. V. Gorev, I. N. Flerov, V. S. Bondarev, and Ph. Sciau, *Zh. Éksp. Teor. Fiz.* **123** (3), 599 (2003) [*JETP* **96**, 531 (2003)].
18. Y. Moriya, H. Kawaji, T. Tojo, and T. Atake, *Phys. Rev. Lett.* **90** (20), 205 901 (2003).
19. B. A. Strukov, S. T. Davitadze, S. N. Kravchun, S. A. Taraskin, B. M. Goltzman, V. V. Lemanov, and S. G. Shulman, *J. Phys.: Condens. Matter.* **15** (25), 4331 (2003).

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