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## The piezoelectric effect in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ceramics

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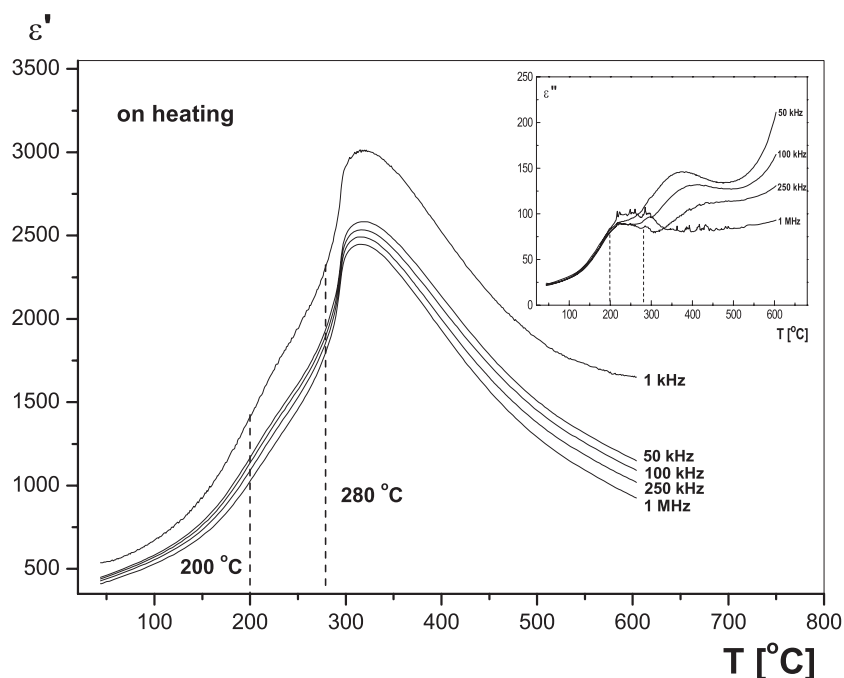
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### Abstract

Piezoelectric properties of  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  ceramics have been investigated over a broad temperature range using a resonance technique. The thermal behaviours of the piezoelectric tensor coefficients  $d_{31}$ ,  $d_{33}$  and  $d_{15}$  confirm that there is a distinct phase transformation at 200 °C. For the first time it has been found that a piezoelectric signal connected with the tensor component  $d_{33}$  is observed up to 280 °C. This corresponds to earlier neutron and x-ray diffraction data on the point of transition from rhombohedral to tetragonal symmetry.

### 1. Introduction

The perovskite sodium–bismuth titanate  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  (NBT) was discovered by Smolensky *et al* (1960). The optical and dielectric studies reported so far show that NBT behaves in an unusual manner in comparison with ordinary  $\text{ABO}_3$  perovskites (e.g. see Siny *et al* (1991a, 1991b); Suchanicz and Kwapuliński (1995); Suchanicz *et al* (1988, 1996, 1998); Tu *et al* (1994); Geday *et al* (2000); Jones and Thomas (2000, 2002); Roleder *et al* (1989)). After four decades of investigations there is still controversy concerning the basic properties of NBT, such as the number of different crystallographic phases, their polar order, the temperature range of phase existence and even coexistence. Among the numerous literature reports only a few are related to detailed structural investigations. Recently Jones and Thomas (2000) using neutron diffraction confirmed that above 540 °C NBT belongs to the cubic phase (space group:  $Pm\bar{3}m$ ). In the temperature range 400–500 °C a tetragonal phase (space group:  $P4bm$ ) is found and then below 255 °C a rhombohedral phase appears (space group:  $R3c$ ). In a temperature interval of about 40° (500–540 °C) coexistence of the cubic and tetragonal phases was found; similarly, coexistence of the rhombohedral and tetragonal phases was observed over a range of 20° (300–320 °C). These results are in close agreement with earlier x-ray data on the phase



**Figure 1.** The low-frequency temperature dependence of the dielectric permittivity for NBT ceramics (dashed lines indicate points at which piezoelectric anomalies were observed). The inset presents the temperature dependence of the imaginary part of the dielectric permittivity. It is worth noting that real and imaginary parts of  $\epsilon$  do not fully reflect points at which anomalies of structural properties have been reported.

transition points in NBT (e.g. Zvirgzds *et al* (1982); Suchanicz and Kwapuliński (1995)). In the recent paper by Jones and Thomas (2000) it was however established that structure of the tetragonal phase exhibits a unique combination of in-phase oxygen octahedral tilts and anti-parallel Ti and Na/Bi cation displacements along the polar  $c$ -axis. The non-centrosymmetric weakly polar nature of the tetragonal phase was also confirmed by the observation of a small second-harmonic-generation signal in the tetragonal phase (Jones and Thomas 2002). To the best of our knowledge this is the first perovskite structure shown to possess a ferroelectric polar order.

Controversy about this material has also focused on its polar properties. Although pure NBT is often classified as a relaxor material (Siny *et al* 1995), the temperature dependence of the dielectric permeability does not resemble that found for classical relaxors (figure 1); in particular, the broad maximum at the lower transition is not frequency dependent. Usually, NBT is taken to show the characteristic features of ferroelectric-like behaviour below about 200 °C when observing dielectric hysteresis loops (Suchanicz 1998) and pyroelectric effects (Molak and Suchanicz 1996). However, there are very few data available on the piezoelectric properties accompanying each non-centrosymmetric phase. According to Emelianov *et al* (1984) pure NBT shows piezoelectric activity ( $d_{31}$  and  $d_{33}$ ) in the low-temperature phase and is present up to 200 °C. Hence we considered it to be important to study the piezoactivity of NBT in detail throughout at least one phase transition. Observation of the piezo-effect was carried out using the well-known dynamic method, which is based on piezoelectric resonance detection. This technique allows simultaneous determination of the complex elastic coefficients, the piezoelectric tensor and electromechanical coupling factors.

## 2. Experimental conditions

The measurements were performed on NBT ceramics. The density of this material was equal to 6000 kg m<sup>-3</sup>. Samples in the shapes of bars with dimensions of about 4 × 1 × 1 mm<sup>3</sup> were poled, depending on the geometrical configuration needed to determine the relevant tensor coefficients (Bauer *et al* 1976). The respective surfaces were electroded with gold and electrical contact was made by means of thin silver wires glued in the centres of the electrodes. The most effective poling was obtained under a dc external electric field of 2 kV cm<sup>-1</sup> from 280 °C to room temperature. From the piezoelectric mechanical resonance the complex elastic coefficients  $s_{11}$ ,  $s_{33}$ ,  $s_{55}$  were determined. From theoretical considerations, we know that the piezoelectric tensor for ceramics has five non-zero coefficients, which are reduced to three because of the symmetry relations  $d_{32} = d_{31}$  and  $d_{24} = d_{15}$ . Thus  $d_{31}$ ,  $d_{33}$  and  $d_{15}$  are the independent piezoelectric tensor coefficients.

To find the piezoelectric frequencies, the complex admittance  $Y$  was measured as a function of frequency by means of a Hewlett-Packard 4192A impedance analyser. The measurements of the absolute  $Y$  and phase angle  $\theta$  were carried out with a sinusoidal voltage of 1 V. A small frequency step was used to detect accurately sudden changes of the admittance near the resonance frequencies. The values of the conductance  $G = \text{Re } Y$  and resistance  $R = \text{Re}(\frac{1}{Y})$  were ascertained and the experimental results  $\frac{G}{\omega}(f)$  and  $R\omega(f)$  obtained were then fitted using the following equations:

$$\frac{G}{\omega} = \beta \frac{\omega\Gamma}{(\omega_0^2 - \omega^2)^2 + \omega^2\Gamma^2} + C_0'' \quad (1)$$

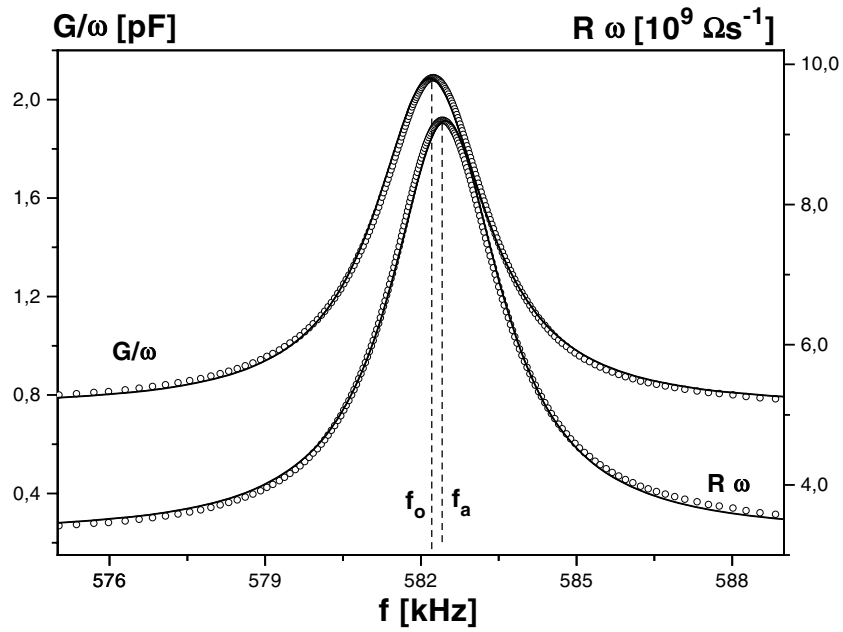
$$R\omega = \xi \frac{\omega\Gamma}{(\omega_a^2 - \omega^2)^2 + \omega^2\Gamma^2} + \zeta. \quad (2)$$

These equations enable direct determination of the resonance,  $f_0$  ( $\omega_0 = 2\pi f_0$ ), and anti-resonance,  $f_a$  ( $\omega_a = 2\pi f_a$ ), frequencies and damping coefficient  $\gamma$  ( $\Gamma = 2\pi\gamma$ ).  $C_0''$  is the imaginary part of the complex sample capacity  $C_0$ .  $\beta$ ,  $\xi$  and  $\zeta$  are constants. The formulae used for the calculation of the real part of the elastic coefficients  $s'_{ij}$ , the piezoelectric constant  $d_{ij}$  and the coupling factor  $k_{ij}$  are well known (*IEEE Standard on Piezoelectricity* 1987). The imaginary part of the complex elastic coefficient  $s''$  was estimated from the following relation:

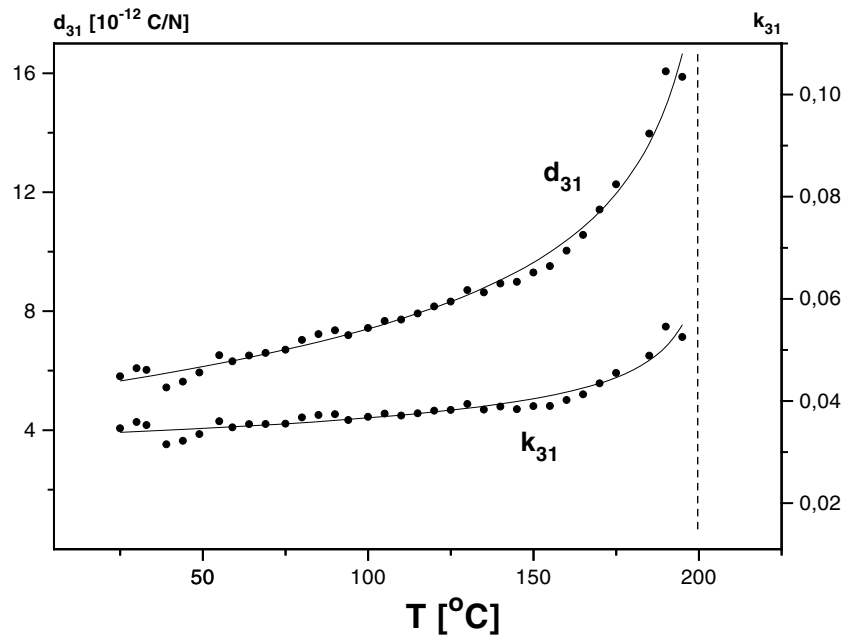
$$\frac{s''}{s'} = \frac{\gamma}{f_0}. \quad (3)$$

## 3. Piezoelectric resonance below 200 °C

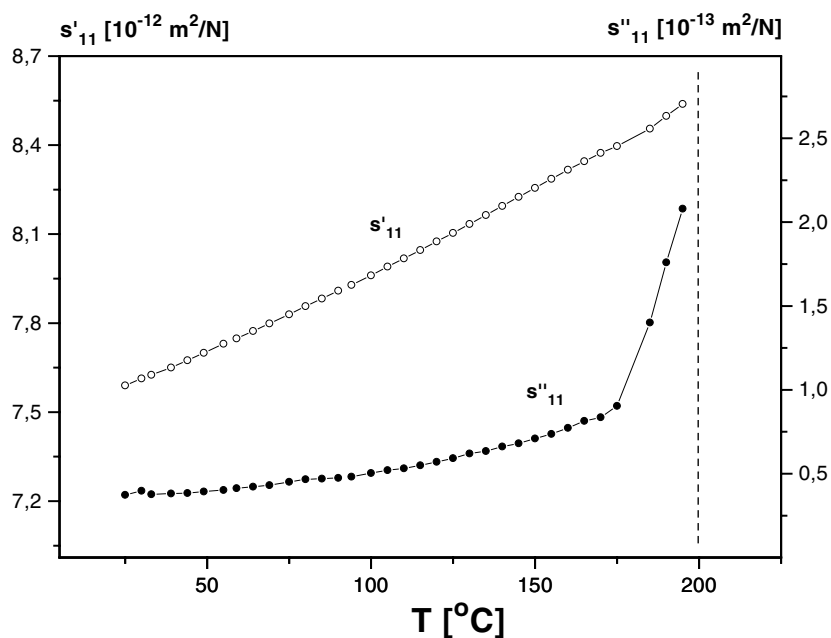
An example of the piezoelectric signal near mechanical resonance is shown in figure 2. It is seen that the experimental data obey closely the relations (1) and (2). Using the parameters from equations (1) and (2), values of the piezoelectric modulus and the real and imaginary parts of the elastic coefficients were determined. As shown in figures 3 and 4 the thermal behaviour of these coefficients indicates that at 200 °C piezoelectric properties related to  $d_{31}$  disappear (figure 3) and the imaginary part increases strongly. At the same time, the real part of  $s_{11}$  changes linearly with temperature, while the imaginary term suggests an anomaly in the elastic properties at this temperature. Similar behaviour was obtained for  $d_{15}$ . At room temperature the values of the elastic and piezoelectric tensor coefficients were as follows:  $s_{11} = 7.6 + i0.035$  ( $10^{-12}$  m<sup>2</sup> N<sup>-1</sup>),  $s_{33} = 7.7 + i0.042$  ( $10^{-12}$  m<sup>2</sup> N<sup>-1</sup>),  $s_{55} = 219 + i3.5$  ( $10^{-12}$  m<sup>2</sup> N<sup>-1</sup>),  $d_{31} = 5.9$  ( $10^{-12}$  CN<sup>-1</sup>),  $d_{33} = 8.9$  ( $10^{-12}$  CN<sup>-1</sup>),  $d_{15} = 39.1$  ( $10^{-12}$  CN<sup>-1</sup>).



**Figure 2.** The fit of the functions  $G/\omega(f)$  and  $R\omega(f)$  (continuous curves) to the experimental data. The maximum values of these functions correspond to the piezoelectric resonance ( $f_0$ ) and anti-resonance ( $f_a$ ) frequencies.



**Figure 3.** Temperature runs for the piezoelectric coefficient  $d_{31}$  and the coefficient of electromechanical coupling  $k_{31}$ . A clear increase is seen for both coefficients close to 200°C. Above this temperature the piezoelectric  $d_{31}$ -signal disappears.



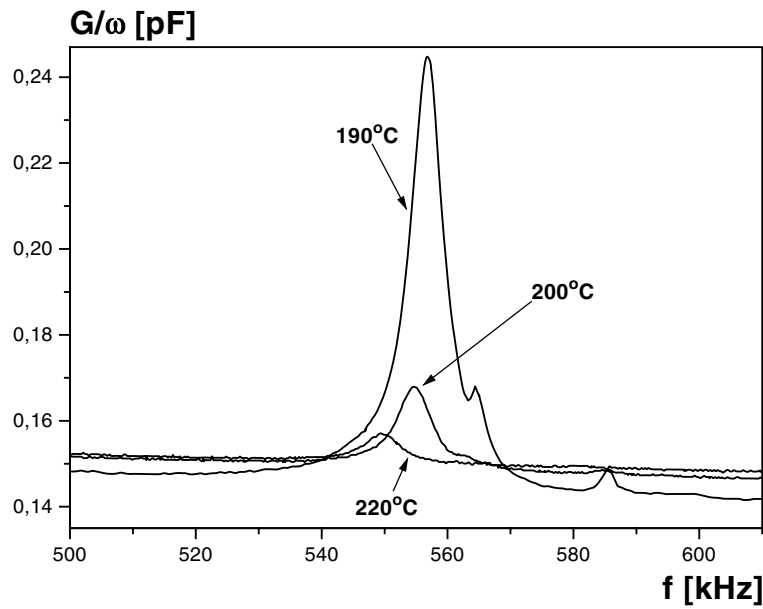
**Figure 4.** Temperature dependences of the real ( $s'_{11}$ ) and imaginary ( $s''_{11}$ ) parts of the elastic tensor coefficient below 200 °C.

#### 4. Piezoelectric resonance above 200 °C

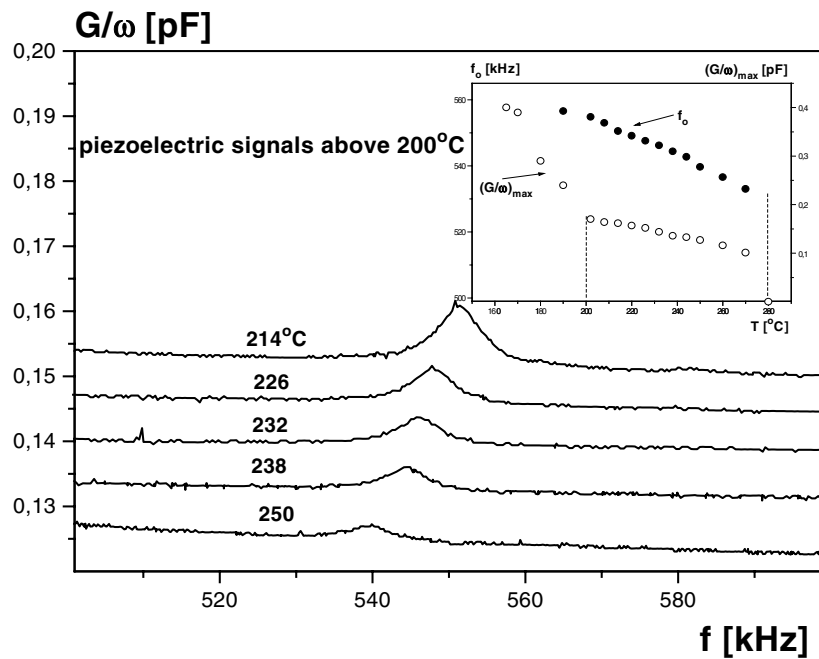
Above this temperature only the piezoelectric signal connected with  $d_{33}$  was observed up to about 280 °C. At 200 °C a strong drop in the intensity of the piezoelectric activity was observed (figure 5). Nevertheless, we stress the fact that above this temperature, a small piezoelectric response still persisted, which is consistent with the observation by Jones and Thomas (2002) of a weak second-harmonic-generation signal. Its thermal behaviour is shown in figure 6 (the inset in this figure shows the changing resonance frequency  $f_0$  and maximum of the  $G/\omega$  function against temperature).

It might be thought that the piezoelectric effect existing above 200 °C is an effect of space charge polarization produced during poling. Indeed Sessler (1980) has proposed just such a hypothesis for electret materials. In our case, the method of observing the piezoelectric effect in NBT involved a poling procedure that was one of those used in producing thermoelectrets. We would then expect a piezoelectric response to be detected in measurements carried out for  $d_{15}$ -determination, since the polar state of the sample and its geometrical size were the same as those for the  $d_{33}$ -determination. However, as already mentioned above, the signal corresponding to the  $d_{15}$ -coefficient disappeared at 200 °C.

It is worth pointing out that the notion of piezoelectricity arising from space charge polarization failed also in the case of the perovskite  $\text{PbZrO}_3$  ceramics. At room temperature, lead zirconate is antiferroelectric with a centrosymmetric point group and is known as a material in which space charge, caused by the volatility of the atoms of lead and oxygen during the technological processing, appears and is difficult to avoid. The numerous poling experiments, from the temperature of the paraelectric phase to room temperature, have never revealed any piezoelectric signal for the coefficients  $d_{31}$ ,  $d_{33}$  and  $d_{15}$ . These experiments seem to confirm that the piezoelectric signals in NBT above 200 °C are not generated by space charge polarization



**Figure 5.** Drastic changes of the piezoelectric response represented by the  $G/\omega(f)$  function, related to the coefficient  $d_{33}$ , near the transition at  $200^\circ\text{C}$ . (Additional small peaks in the  $G/\omega(f)$  results at  $190^\circ\text{C}$  probably appeared because of incomplete polarization states in the ceramics.) The estimated values of the  $d_{33}$  below and above  $200^\circ\text{C}$  are equal to  $14.5 (10^{-12} \text{CN}^{-1})$  and  $13.35 (10^{-12} \text{CN}^{-1})$ , respectively.



**Figure 6.** The temperature behaviour of the piezoelectric activity connected with the coefficient  $d_{33}$  above  $200^\circ\text{C}$ . The inset shows the disappearance of the frequency  $f_0$  of the mechanical piezoelectric resonance and the maximum of the  $G/\omega(f)$  function (after subtraction of the background) near  $280^\circ\text{C}$ .

(an electret effect).

Assuming then that the change of crystal structure is the source of the piezo-signal, we poled the ceramics under the external electric field at temperatures ranging from 440 to 230 °C. As a result, the piezoelectric signal appeared and was of the same intensity as that observed after the previous poling. This also shows that the weak piezoelectric effect above 200 °C is not an effect of a transition leading to, say, an uncompensated polydomain state. Moreover it means that the structure above 200 °C has a polarization state that is reversible in an external electric field. Therefore this lends support to the idea that the phase evolving between 200 and 280 °C possesses real piezoelectric properties and is thus non-centrosymmetric, in agreement with the determination by Jones and Thomas (2000).

## 5. Discussion

In the piezoelectric investigations described above, two temperatures have been distinguished: 200 and 280 °C. In earlier reports it was assumed that 200 °C is the temperature at which the quite strong ferroelectric properties vanish and 280 °C is the point at which the volume contribution of the tetragonal phase compared with the rhombohedral phase starts to play an essential role (Suchanicz and Kwapuliński 1995). The recent neutron diffraction and non-linear optical investigations of Jones and Thomas (2000, 2002) proved that a distinct rhombohedral phase exists at least up to 255 °C. There is no doubt that the piezoelectric properties, corresponding to the rhombohedral  $R3c$  symmetry in which the  $d_{31}$ ,  $d_{33}$  and  $d_{15}$  should be present and have different values, change drastically at 200 °C:  $d_{31}$  and  $d_{15}$  completely vanish while  $d_{33}$  diminishes considerably. However, a stable piezoelectric signal, but only for the  $d_{33}$ -geometry, was observed up to a temperature of 280 °C. It is known that there is no point group represented by a piezoelectric tensor with only one non-zero coefficient. Since one cannot exclude the possibility that the coefficients  $d_{31}$  and  $d_{15}$  may happen to have very small values and thus at the same time be difficult to detect, it might be supposed that either coexistence of the rhombohedral and tetragonal states inhibits the piezoelectric activity or pure rhombohedral symmetry is present up to 280 °C. On the other hand, in any non-centrosymmetric point group the same consideration would be valid and a similar piezoelectric response could be expected. Piezoelectric responses in ceramics cannot be used to distinguish this structural difference (on the other hand it is very difficult to make experiments on a single-domain single crystal undergoing several phase transitions; this would need different geometrical sample configurations in the different structural phases, and in any case phase coexistence and twinning would invalidate the measurements). Hence the experiments described above lead to the conclusion that the NBT phase developing in the range 200–280 °C has different properties from that below 200 °C.

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