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Phase transition of displacive type in $\text{PbZr}_{0.94}\text{Ti}_{0.06}\text{O}_3$

K Wieczorek, Z Ujma, K Popek, I Gruszka, M Górny, J Koperski, A Soszyński and K Roleder

Institute of Physics, University of Silesia, ulica Uniwersytecka 4, 40-007 Katowice, Poland

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Abstract

In this paper the electrostrictive properties above $T_{\varepsilon\text{max}}$, represented by the field-related M and polarization-related Q coefficients, have been reported for $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ ceramics with $x = 0.03\text{--}0.10$. Among $M_{11}(T)$ and $Q_{11}(T)$ dependences, those found for $\text{Pb}(\text{Zr}_{0.94}\text{Ti}_{0.06})\text{O}_3$ have been clearly distinguished. In this case, the $Q_{11}(T)$ dependence is linear in the whole temperature range above $T_{\varepsilon\text{max}}$. Experimental and theoretical analysis of the $M_{11}(T)$ dependences has shown that the phase transition to the ferroelectric phase in $\text{Pb}(\text{Zr}_{0.94}\text{Ti}_{0.06})\text{O}_3$ ceramics seems to be of the displacive type.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT), where $x = 0.03\text{--}0.10$, solid solutions belong to the ABO_3 perovskites with high temperature structural transitions between the paraelectric and ferroelectric phase. In the literature the existence of the tricritical point in PZT has been considered for $x = 0.06$. It means that around this concentration the change from the first to second order phase transition takes place. Numerous experiments revealed distinct differences in physical properties of ceramics with x below and above 0.06 but did not prove the existence of such a change. In spite of the numerous literature reports on these classical materials, there is a lack of detailed experimental data on their electrostrictive properties. For the first time, the electrostrictive properties of those solid solutions were reported in paper [1]. In solutions with x close to 0.06, a distinct change in the temperature dependence and values of the electrostrictive coefficients have been found. In particular the changes were connected with the coefficient describing coupling between the polarization and spontaneous strain. The observed anomaly corresponded well to the PZT with Ti content $x = 0.06$ for which the tricritical point (TP) has been postulated [2]. However, the existence of the TP is still not resolved. One of reasons is that the existence of a phase transition of the second order for PZT with $x = 0.06$ has not, up to now, been proved. That is why precise investigations of the temperature dependence of the electrostrictive properties have been undertaken for PZT solid solutions with Ti content $x = 0.03\text{--}0.10$. The goal was to find the temperature

dependence of the electrostrictive coefficients M_{11} and Q_{11} above $T_{\varepsilon\text{max}}$.

2. Theoretical background

Above $T_{\varepsilon\text{max}}$, the electrostrictive strain η is quadratically coupled with the polarization P and electric field E (indexes are omitted):

$$\eta = QP^2 \quad \text{and} \quad \eta = ME^2. \quad (1)$$

The polarization is described as

$$P = \varepsilon_0 \varepsilon E. \quad (2)$$

Now, from (1) it appears that $QP^2 = ME^2$ and thus, using relation (2), the electrostriction coefficient M can be calculated as

$$M = \frac{Q\varepsilon_0^2 \varepsilon^2 E^2}{E^2} = Q\varepsilon_0^2 \varepsilon^2. \quad (3)$$

Assuming that the dielectric permittivity fulfils the Curie–Weiss law,

$$\varepsilon = \frac{C}{T - T_0} + \varepsilon_\infty \quad (4)$$

and that there is a linear temperature dependence of the polarization-related coefficient Q [3], i.e.

$$Q = aT + b \quad (5)$$

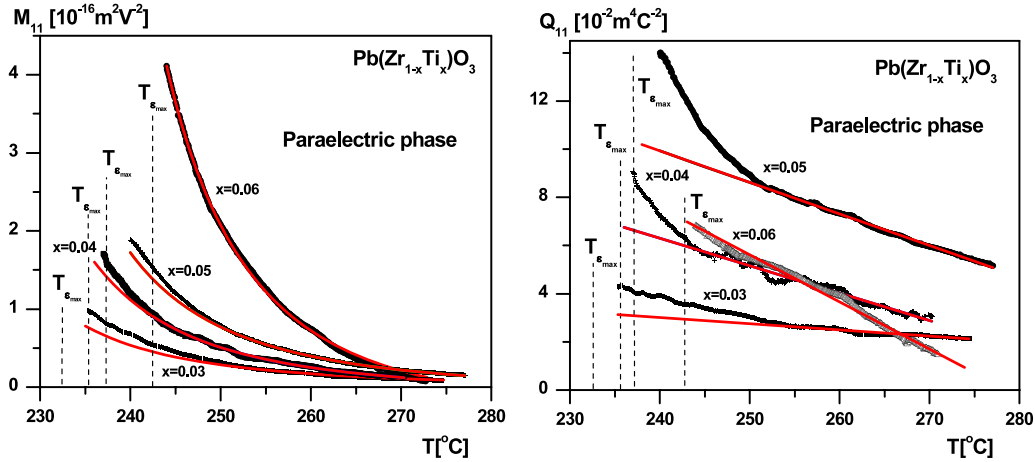


Figure 1. Electrostrictive coefficients M_{11} as a function of temperature for $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ceramics with $x = 0.03\text{--}0.06$. An alternating strain of 320 Hz was induced by an ac electric field with $E_{\sim} = 4 \text{ kV cm}^{-1}$ and frequency 160 Hz.

one can show—based on (3)–(5) and neglecting ε_{∞} in (4) since $\varepsilon''\varepsilon_{\infty}$ above $T_{\varepsilon \text{ max}}$ —that

$$M(T) = \varepsilon_0^2 C^2 \frac{(-aT + b)}{(T - T_0)^2}. \quad (6)$$

Assuming the ε_0 , C , a and b are constant parameters one can check in which temperature interval the relation (6) is fulfilled.

3. Strain measurement

Measurements were conducted on PZT ceramics with $x = 0.03\text{--}0.10$. The ceramics have been obtained by the conventional thermal procedure. In all experiments, the samples were electroded with gold. To determine the strain η , a very sensitive capacitance method has been applied. A detailed description of the technique used is described in [4]. It enables strain measurements of the order 10^{-7} in the wide and high temperature interval. Here, only basic comments are made of the technique applied. Namely, an alternating electric field of frequency $f = 160 \text{ Hz}$ was applied perpendicular to the sample. The electrostrictive strain η of double frequency $f = 320 \text{ Hz}$ ($\omega = 2\pi f$) was transferred via a quartz rod with one end placed on the sample surface and the second one connected to the measurement condenser plate. The measurement condenser C was connected to the resistance R and constant voltage source U . The electrostrictive vibrations of the sample cause variations of charge in the condenser C and induce a flow of alternating current I in the circuit RC . At a defined temperature the magnitude of strains η was calculated knowing the value of potential drop U_{\sim} at resistance R measured at 320 Hz:

$$\eta = \frac{l_0}{d_0} \frac{U_{\sim}}{\omega RUC} \quad (7)$$

where l_0 is the distance between the plates of condenser C and d_0 is the sample thickness.

4. Experimental results

Experiments were made in the phase above $T_{\varepsilon \text{ max}}$ of the macroscopic cubic symmetry. In the cubic phase, the electrostrictive strain η_1 can be described by

$$\eta_1 = M_{11} E_1^2 \quad (8)$$

and

$$\eta_1 = Q_{11} P_1^2 \quad (9)$$

where M_{11} and Q_{11} denote respectively the field-related and polarization-related electrostrictive coefficients. Using equations (8) and (9) the temperature variations of $M_{11}(T)$ and $Q_{11}(T)$ in the phase above $T_{\varepsilon \text{ max}}$ were determined, as shown in figures 1 and 2. The M_{11} monotonically decreases with temperature but its value increases with increasing x in the solutions. The $Q_{11}(T)$ dependence reveals very similar behaviour. While the values of Q_{11} decrease with increasing temperature, it is worth noting that at high temperatures the $Q_{11}(T)$ runs are the linear functions of T , as predicted by theory. However, the most important observations are very distinct nonlinearity in $Q_{11}(T)$ functions, in the range of tens of centigrade above $T_{\varepsilon \text{ max}}$. This nonlinear $Q_{11}(T)$ behaviour coincides with the non-classical runs of $M_{11}(T)$ functions, in the same temperature region. In figure 1 the continuous line represents fit with formula (6) that strongly deviates from the experimental points. The closer the $T_{\varepsilon \text{ max}}$ the stronger is the deviation of experimental points from the $M_{11}(T)$ foreseen by the theory (see section 2, equation (6)).

Very good agreement between the experimental data and theoretical dependence $M_{11}(T)$ is observed only for $\text{PbZr}_{0.94}\text{Ti}_{0.06}\text{O}_3$ ceramic (figure 1). For this material, $Q_{11}(T)$ is a linear function in the whole temperature range. As it was assumed, the polarization-related coefficient Q_{11} is a linear function of T , i.e. $Q_{11} = -aT + b$ in the case of the pure (classical) paraelectric phase. From the experiments performed it was possible to find the variations of coefficients a and b as a function of Ti content in the $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$. In figure 3 it is seen that there is a sharp change of both coefficients for

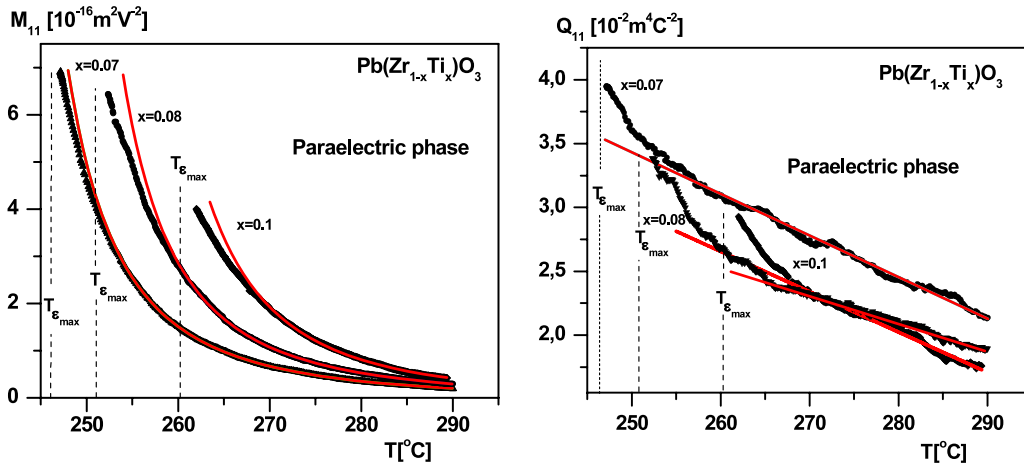


Figure 2. Electrostrictive coefficients M_{11} as a function of temperature for $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ceramics with $x = 0.07\text{--}0.10$. An alternating strain of 320 Hz was induced by an ac electric field with $E_{\sim} = 4 \text{ kV cm}^{-1}$ and frequency 160 Hz.

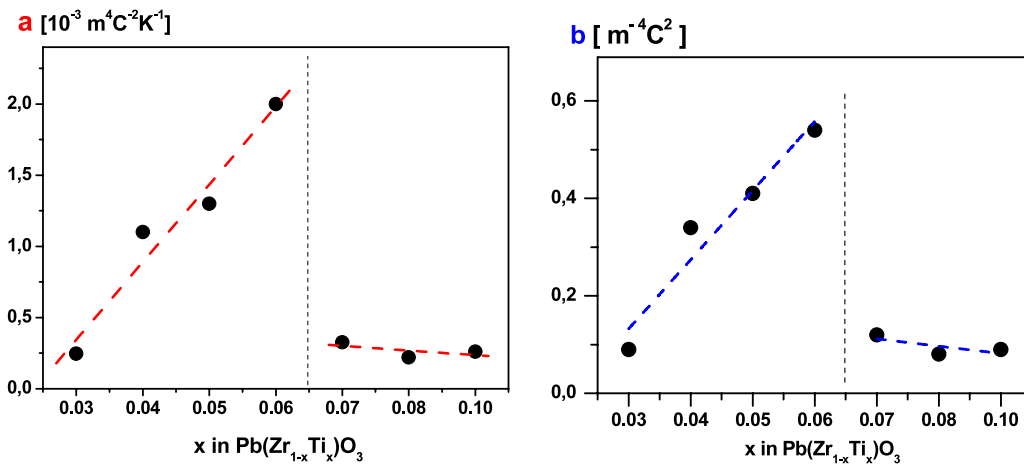


Figure 3. Coefficient a and b as a function of Ti content in $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ solid solutions.

a concentration $0.06 < x < 0.07$. In the similar range of concentration x , anomalous physical properties of PZT ceramics and single crystals have been observed by Whatmore *et al* [5], who considered the existence of the TP.

By means of a scanning electron microscope ISM-5410, with an energy dispersion x-ray spectrometer (EDS), the chemical composition of the ceramics used in experiments was determined. Quantitative microanalysis with the implementation of SEMQuant programs elaborated by Oxford Instruments (Link ‘ISIS’ Series System) was made, taking into account the radiation intensity from the excited Pb, Ti and Zr ions. Scanning was performed on several grains for each ceramic under investigation and the ratio Ti:Zr was determined. It is seen in figure 4 that in separate grains there is a fluctuation of the Ti:Zr ratio for each ceramic. In fact, the fluctuation is decreasing monotonically, i.e. the higher Ti content in a solution the lower is the change in Ti concentration in grains. It has to be stressed that there is no distinct change in the Ti fluctuations near the nominal value x at which a very clear anomaly in the electrostrictive properties has been found. Hence, one of the main results for the performed

investigations is that fluctuation in the chemical composition does not influence the specific behaviour of the electrostriction.

5. Discussion

The phase diagram of PZT is much more complex for ceramics with low Ti content [6]. Below $x = 0.06$ these ceramics undergo two transitions between the antiferroelectric–ferroelectric and ferroelectric–paraelectric phase. Above $x = 0.06$ the PZT ceramics below $T_{\epsilon \text{max}}$ are ferroelectric in the whole range of x . While the most explored are PZT compounds from the morphotropic phase boundary ($x \sim 0.50$), the part of the phase diagram for low Ti content is related to transitions of as yet unknown nature. Although there is no convincing proof for the tricritical point existence for ceramics with $x = 0.06$, distinct differences in the physical properties of PZT solid solutions with x below and above 0.06 were experimentally observed. Among those properties, the electrostriction has not been investigated. Results presented in this paper showed that the coefficients M_{11} and Q_{11} , except those for $\text{PbZr}_{0.94}\text{Ti}_{0.06}\text{O}_3$, behave in a non-classical

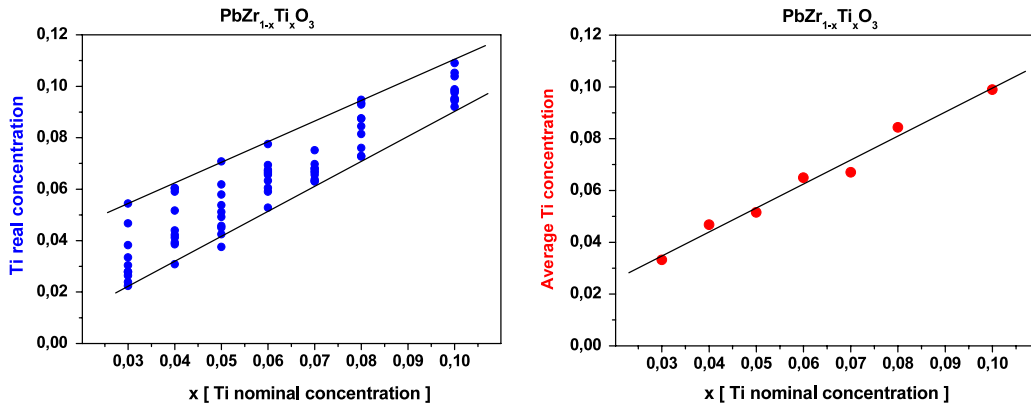


Figure 4. Real and average concentration of Ti measured for ten different grains of each of the $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ceramics.

way. Especially interesting is the field-related M_{11} coefficient, which directly couples the strain with the electric field that produces it. With the supposition that the Curie–Weiss law and linear temperature dependence of the electrostrictive coupling between strain and polarization is fulfilled, the derived $M_{11}(T)$ formula has been fitted to the experimental data. While experimental $M_{11}(T)$ runs are above the theoretical curves for $x < 0.06$, above this Ti content the experimental results lie below the curves. This evolution clearly points out an x value for which there would not have been a discrepancy between the theoretical and experimental $M_{11}(T)$ functions. It would also mean that the $Q_{11}(T)$ dependence is linear in the whole temperature range above $T_{\varepsilon \text{ max}}$.

It is known that the mechanism of phase transitions in ferroelectric perovskites is of both displacive and order–disorder character. This distinction has been made in terms of whether the paraelectric phase was macroscopically non-polar or only polar in a macroscopic or thermally averaged sense [7]. In all investigated ceramics, except for that with $x = 0.06$, nonlinear dependences of $Q_{11}(T)$ have been observed and could be accounted for by the presence of stable polar micro/nano-regions. The fact that in the range of that nonlinearity a piezoelectric activity has been detected is in favour of this supposition.

Only in the case of solid solution $\text{PbZr}_{0.94}\text{Ti}_{0.06}\text{O}_3$ is this nonlinearity not present. It can be supposed that the appearance of a special point at $x = 0.06$ on the PZT phase diagram is connected with an interplay between the two above-mentioned mechanisms of phase transitions. This composition seems to exhibit more displacive character of phase transition as compared to the neighbouring compositions. The extent of departure from a Curie–Weiss relationship for the selected compositions correlates well with the departures of the electrostrictive coefficients from the predicted theoretical equations (figure 5). No such departure for the ceramics with $x = 0.06$ would be expected. Although this departure from the Curie–Weiss law in figure 5 is still noticeable for $x = 0.06$, the fitted $Q(T)$ and $M(T)$ curves show no departure from the theoretical relations, particularly for $M(T)$ (figure 1) which makes use of the Curie–Weiss relationship. A reason for this discrepancy is the following. The electrostrictive response comes from a area of about $30 \mu\text{m}^2$ that is related to the quartz

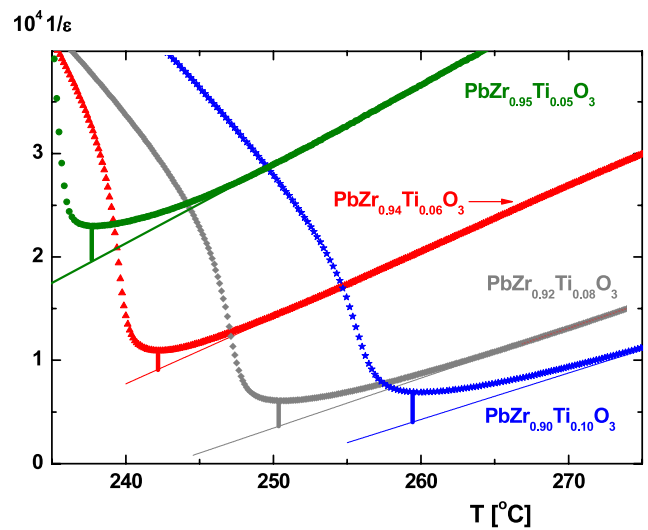


Figure 5. Temperature dependence of the inverse of the law-field dielectric permittivity for $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ceramics with $x = 0.04, 0.06, 0.08$ and 0.10 . Vertical lines connecting the linear fit with point $\varepsilon^{-1}(T_{\varepsilon \text{ max}})$ represent discrepancy from the Curie–Weiss law.

rod end contacting the sample surface and transmitting the electrostrictive deformation, while the temperature dependent weak-field permittivity $\varepsilon(T)$ is related to the much larger area of about 9 mm^2 . Taking into account the results presented in figure 4, these two different areas may correspond to two slightly different Ti concentrations, i.e. to two slightly different values of x . In this context, the above-mentioned discrepancy can be comprehended.

In figure 6 a comparison of the T_0 and C values obtained from the fit to the $M(T)$ and $\varepsilon(T)$ data is presented. Very similar values of $T_0(x)$ and $C(x)$ have been obtained from both fits.

In earlier investigations of electrostriction in ferroelectrics with perovskite-type structure, it was supposed that the value of coefficient Q_{ij} depends on the degree of ions ordering in the lattice [8]. The present results for electrostriction in PZT have shown that Q_{11} suffers a distinct decrease in its values above Ti concentration $x = 0.06$. Thus, it could be related to the strong disappearance of internal stresses arising inside

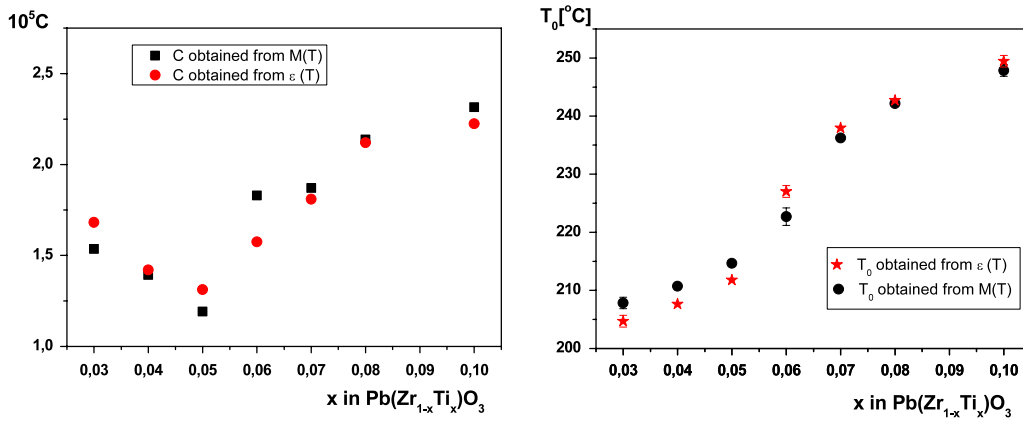


Figure 6. Values of Curie–Weiss temperature T_0 and constant C obtained respectively from the fit to the $M(T)$ and $\varepsilon(T)$ data in figures 1, 2 and 5.

the crystal lattice due to disorder in Ti and Zr sites. Thus for $\text{PbZr}_{0.94}\text{Ti}_{0.06}\text{O}_3$ a perfect disorder, not leading to a local polarity above $T_{\varepsilon\text{max}}$, would be expected. If polar regions are present above $T_{\varepsilon\text{max}}$, they interact between themselves in a non-trivial way and constitute a polar sub-system in the paraelectric matrix. Such a sub-system has been proved to exist above $T_{\varepsilon\text{max}}$ in barium titanate [9] and in lead zirconate crystal [10]. The Brillouin scattering experiment [11] has recently confirmed this for barium titanate crystals.

In fact the literature reports on the TP in PZT are not coherent from the point of view of parameter x . For example, the paper by Eremkin *et al* [12] is the only one reporting two PTs in single PZT crystals for $x = 0.22$ and 0.55 . Haun *et al* [13] suggested the appearance of TP between the pure PbTiO_3 and solid $\text{PbZr}_{0.88}\text{Ti}_{0.12}\text{O}_3$ solution. On the other hand Rossetti and Navrotsky [14] reported on TP in the range $0.30 < x < 0.40$. In the paper by Whatmore *et al* [5], already mentioned, the TP was considered for $x = 0.06$. The experiments described here have been performed for $x = 0.03$ – 0.10 and proved that distinct changes of physical properties taking place for PZT with $x = 0.06$ seem not to be connected with TP. The question remains as to the character of the phase transition for $x = 0.06$. First, the fact that there is no discrepancy between the theoretical and experimental $M_{11}(T)$ functions means that the phase transition is of displacive character. Second, the relation (5) contains the Curie–Weiss temperature T_0 and a fit of the $M_{11}(T)$ dependence gives $T_0 < T_C(T_{\varepsilon\text{max}})$. This means

that in this compound the phase transition to the ferroelectric state is of the first order.

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