전기장에서 Zr0.98Sn0.02TiO4 의 Lifshitz point
(Lifshitz point of Zr0.98Sn0.02TiO4 in an applied electric field)

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Recently, there has been great interest in the dielectric resonator of Sn-doped $ZrTiO_4$ for satellite telecommunication ranging from cellular telephones to global positioning systems.[1] The existence of an incommensurate phase in $ZrTiO_4$ has influence on the microwave dielectric properties, the quality factor (*Q*) and temperature coefficient of resonance frequency (τf).[2]

Incommensurate (*I*) phases in dielectric ceramics, which show low-temperature-commensurate (*C*) phases, are strongly influenced by applied external electric fields. In $ZrTiO_4$ a new intermediate *C* phase was induced by an applied field.[3] In $NaNO_2$ it has been observed that the *I* phase is suppressed by a field *E* which is above a certain critical field.[4] In both cases the incommensurate-commensurate (*IC*) transition is discontinuous.

In the cases where the *I* phsae disappears in large bias fields *E*, a multicritical point could exist in the *E-T* phase diagram. There, a line of continuous *normal(N)-I* transitions merges with the lines of *IC* transitions and the *normal(N)-C* transitions, which are both general discontinuous. It has been pointed out that in the crystals with the degeneracy parameter of the *C* state *n* is being 4, the multicritical point (*EL, TL*) is in fact a Lifshitz point (LP) where the modulation wave vector *q* in the *I* phase vanishes continuously on approaching LP and the *normal(N)-C* transition is continuous.[5] Until now LP was accessible experimentally only in few systems, namely in helicoidal magnetic structures [6] and in ferroelectric liquid crystals, both in the presence of the external magnetic field.[7]

$ZrTiO_4$ have been known to undergo two successive phase transitions: (i) from a high temperature phase (normal phase) to incommensurate phase [8-17] at 1125 ± 10 ℃ (*TI*) and (ii) from commensurate to incommensurate[9,18] at 845 ± 5 ℃ (*Tc*). In the temperature range between *TI* and *Tc*, the $ZrTiO_4$ ceramic is in an incommensurate structure modulated by a displacement wave with a wave vector of $qo = (0.5+\delta)a^*$ [14], along orthorhombic *a*-axis. It has been demonstrated in authors' previous studies not only that the dielectric constant measurements at the dc electric field showed a split anomaly at 875±5 ℃ [3], but also that Sn addition prevent the intermediate commensurate phase ($q0 = 26/50a^*$).[18]

Zr0.98Sn0.02TiO4 was synthesized by conventional solid-state reaction from individual powders; ZrO_2 (99.5% low grade Hf) and TiO_2 (99.9%). The starting materials were mixed, calcined at 1050 ℃ for 4h, ground and dried, and fabricated as multilayer ceramic capacitors. Pt paste was applied on an internal electrodes and the ceramic thickness between the electrodes was approximately 50μm. After holding at 1400 ℃ for 30min, 1KHz dielectric constant versus temperature was measured under the dc electric field at 0, 4, 20, 50, 100 kV/cm.

The Landau free-energy density in the presence of an external electric field *E*, for $ZrTiO_4$, has been argued to be

$$f(\quad) = \frac{}{2}|Q|^2 + \frac{}{4}|Q|^4 - i\frac{}{2}\left[q\frac{dQ^*}{d} - Q^*\frac{dQ}{d}\right]$$
$$-\frac{}{2}(Q^4 + Q^{*4}) + \frac{K}{2}\left|\frac{dQ}{d}\right|^2 + P(Q^2 + Q^{*2}) +$$
$$\frac{P^2}{2_{\ 0}} - PE \text{------}(1)$$

where *Q(x)* is a complex one-dimensionally modulated order parameter and *P(x)* is the polarization along *a*-axis. Here, $\alpha = \alpha o(T - To)$ whereas other parameters are assumed to be temperature independent and positive. By analyzing the equation (1) it has been shown that the *N-I* transition temperature *TI* changes with *E* as

$$T_I - T_0 = (T_I^0 - T_0)(1 + \frac{E^2}{E_L^2}) \text{----}(2)$$

where $Ti^o = TI\,(E = 0)$ and *EL* denotes the critical Lifshitz field which can be expressed in terms of the free-energy parameters $EL = \delta^2/2\kappa\xi\chi o$. The modulation seems to remain always of the plane-wave type so that the *I-C* transition is of first order for all applied electric fields. In this case the width *TI - Tc* exhibits a quadratic dependence on *EL - E:*

$$T_I - T_C = \frac{T_I^0 - T_0}{1-}[1 - \frac{E}{E_L}]^2 \text{----}(3)$$

where $\eta^2 = (2\text{-}8\gamma/\beta)/3$ and $\gamma = \gamma + \xi^2\chi o$, $\beta = \beta - 4\xi^2\chi o$. In the plane-wave regime we can also calculate the dielectric constant which is given by

$$-1 = \frac{2\ \ _0\ _0}{3\ E_L}[T_I - T + 3(T_I^0 - T_0)\frac{E^2}{E_L^2}] \text{--}(4)$$

According to Landau theory the dielectric constant ε should show a linear variation with temperature in the *I* phase, with a maximum at *Tc*. The height $\Delta\varepsilon max = \varepsilon(Tc) - \varepsilon(T > Tc)$ at *Tc* is, from equation (4), proportional to *TI-Tc* and from equation (3) we get $\Delta\varepsilon max \propto (EL - E)^2$.

We measured the dielectric constant ε in Zr0.98Sn0.02TiO4 ceramics at the frequency of 1KHz. The presented results were obtained on cooling rate of less than 0.3 ℃/h. Figure 1 shows the results for the temperature variation of dielectric constant ε at different bias electric fields. In the plot we have determined the *I-C* transition temperature *Tc* from the position of the peak in ε. In view of the rather small value of the dielectric constant no anomaly in the first derivative of dielectric constant could be observed at *TI*. *TI* was determined by differential scanning calorimetry (DSC).

The results for *Tc* and *TI*, as can be seen in Fig. 2, can be described with the equations (2) and (3) by assuming $Ti^o - To \approx 28K$, $\eta \approx 0.9$, and $EL = 100 \pm 4$ kV/cm. The agreement between the theoretical and experimental *E-T* phase diagrams is rather good and demonstrates the presence of Lifshitz point. The fact that the *N-I* and *I-C* transition merge tangentially excludes the possibility of an interpretation in terms of triple point.

The Lifshitz field *EL* can be as well determined from the behavior of the maxima of dielectric constant at the *I-C* transition. Figure 3 shows the field dependence of the dielectric anomaly Δεmax calculated as a difference between the value ε(*Tc*) and the background ε curve as determined in strong fields at which the dielectric anomaly at *Tc* vanishes. The variation of Δεmax (*E*) seems to be consistent with the equation (4). From the dependence $\Delta\varepsilon max \propto (E - EL)^2$ we then get $EL = 100 \pm 4$ kV/cm which agrees with the previous value within the experimental uncertainty.

Our experimental results suggest that the LP has really been reached in Zr0.98Sn0.02TiO4 ceramics, which is thus the first incommensurate ceramics having this property in the accessible experimental range. It should be pointed out that the narrow *I* phase and the rather small Lifshitz field $EL \approx 100$ kV/cm are both closely connected with the value of the *I* part of the modulation wave vector, which is here an order of magnitude smaller than in other incommensuratre ceramics.

In summary, we have demonstrated the existence of a Lifshitz point at the critical field $EL \approx$ 100kV/cm in Zr0.98Sn0.02TiO4 ceramics. The *E-T* diagram was determined by dielectric constant measurement. As we have indicated in Fig. 3, this curve was consistent with the theoretical equation (4).

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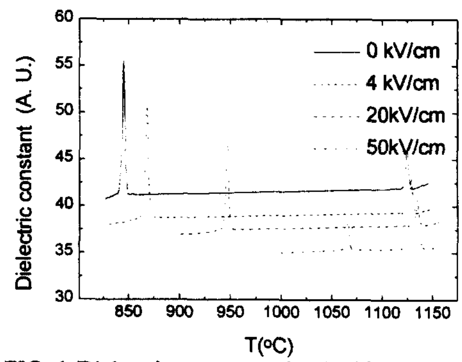

FIG. 1 Dielectric constant of Zr0.98Sn0.02TiO4 ceramics as a function of temperature at various dc bias electric fields.

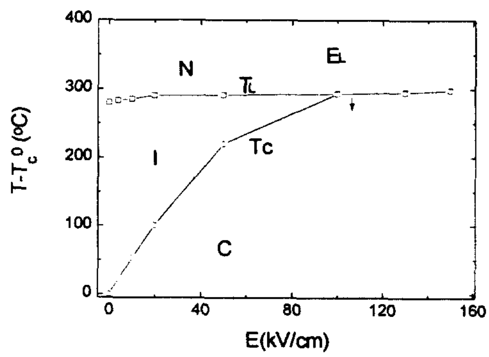

FIG. 2 The *E-T* phase diagram of Zr0.98Sn0.02TiO4 ceramics. The data for *TI* are the DSC results. The solid curves represent the theoretical *E-T* phase diagram according to Eqs. (2) and (3). The three transition lines merge at the Lifshitz point.

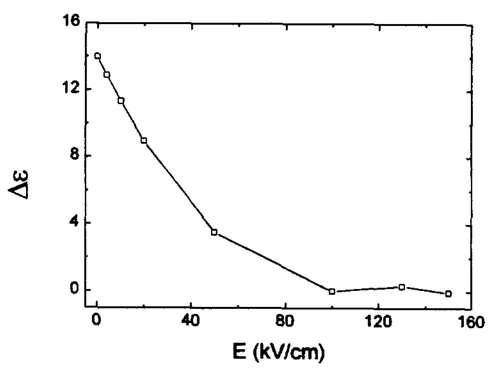

FIG. 3 The magnitude of the peak of dielectric constant Δε at the *I-C* transition as a function of the bias electric field.