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THE INFLUENCE OF UNIAXIAL PRESSURE ON THE DIELECTRIC PROPERTIES OF Co- AND Cu- DOPED TGS CRYSTALS

The results of the experimental investigation of the effect of uniaxial pressure on dielectric properties of TGS crystals doped with metallic impurities of Co^{2+} and Cu^{2+} in the vicinity of the ferroelectric structural phase transition are presented. The obtained results are compared with published data for undoped TGS crystal. The results of experimental measurements show that for the TGS:Co^{2+} and TGS:Cu^{2+} crystals the uniaxial pressure σ_2 leads to decreasing the maximum values of the dielectric constant and reducing the phase transition temperature with a coefficient of $dT_c/d\sigma_2 = -5.2$ K/kbar and $dT_c/d\sigma_2 = -5.3$ K/kbar, respectively. The shift of the phase transition temperature under the influence of uniaxial pressure along the ferroelectric axis *b* for investigated crystals is lower than for undoped ones due to the existence of internal electric fields in doped crystals, whose value is determined by the presence of impurities. The phase σ_2, *T*-diagrams are constructed.

Keywords : TGS, uniaxial pressure, metal impurities, dielectric constant, ferroelectric crystals.

Наведено результати експериментального дослідження впливу одновісного тиску на діелектричні властивості кристалів ТГС, легованих металічними домішками Co^{2+} та Cu^{2+}, в околі структурного сегнетоелектричного фазового переходу. Отримані результати порівнюються з літературними даними для нелегованого домішками кристалу ТГС. Результати експериментальних вимірювань показали, що для кристалів ТГС:Co^{2+} і ТГС:Cu^{2+} одновісний тиск σ_2 приводить до зменшення максимальних значень діелектричної проникності та зменшення температури фазового переходу з коефіцієнтами: $dT_c/d\sigma_2$ = -5.2 К/кбар та $dT_c/d\sigma_2$ = -5.3 К/кбар, відповідно. Зміщення температури фазового переходу під дією одновісного тиску вздовж сегнетоелектричної осі досліджуваних кристалів є меншим, ніж для нелегованих кристалів, що пояснюється існуванням внутрішніх електричних полів у легованих кристалах, величина яких визначається наявністю домішок. Побудовано фазові σ_2, *T*- діаграми.

Ключові слова: ТГС, одновісний тиск, металічні домішки, діелектрична проникність, сегнетоелектрики.

Приведены результаты экспериментального исследования влияния одноосного давления на диэлектрические свойства кристаллов ТГС, легированных металлическими примесями Co^{2+} и Cu^{2+}, в окрестности структурного сегнетоэлектрического фазового перехода. Полученные результаты сравниваются с литературными данными для нелегированного примесями кристалла ТГС. Результаты экспериментальных измерений показали, что для кристаллов ТГС:Co^{2+} и ТГС:Cu^{2+} одноосное давление σ_2 приводит к уменьшению максимальных значений диэлектрической проницаемости и уменьшению температуры фазового перехода с коэффициентами: $dT_c/d\sigma_2$ = -5.2 К/кбар и $dT_c/d\sigma_2$ = -5.3 К/кбар, соответственно. Смещение температуры фазового перехода под действием одноосного давления вдоль сегнетоэлектрической оси исследуемых кристаллов меньше, чем для нелегированных кристаллов объясняется существованием внутренних электрических полей в легированных кристаллах, величина которых определяется наличием примесей. Построены фазовые σ_2, *T*-диаграммы.

Ключевые слова: ТГС, одноосное давление, металлические примеси, диэлектрическая проницаемость, сегнетоэлектрики.

1. Introduction

The most important in understanding the mechanisms of phase transitions (PT) in ferroelectric crystals with hydrogen bonds is a study of their behavior under the influence of external factors such as pressure or electric field [1]. In particular, the external pressure is the only way to continuously modify the geometric characteristics of hydrogen bonds, break their equivalence etc., which makes possible to investigate the role of hydrogen bonding in the mechanisms of the phase transition and dielectric response of crystals. Significant part of ferroelectrics with hydrogen bonds has piezoelectric properties in the paraelectric phase. Applying the mechanical stress provides an opportunity to examine the piezoelectric interactions in phase transformations and formation of the physical characteristics of crystals [2]. Herewith, taking into account the effects, related to the lattice deformations, that occur spontaneously or are caused by external pressures, gives an opportunity to obtain more consistent description of the behavior of crystals.

Among the ferroelectric crystals with hydrogen bonds triglycine sulfate $(NH_2CH_2COOH)_3 \cdot H_2SO_4$ (TGS), despite the complexity of the chemical formula and crystal structure, investigated the most fully. Such crystals are ferroelectrics with second order phase transition of "order-disorder" type. The crystal has monoclinic symmetry and belongs to centrosymmetric class 2/m above the Curie temperature T_C = 322 K. Below T_C the mirror plane disappears and the crystal belongs to the polar point group 2 of the monoclinic system. Unlike ferroelectrics of KDP-type, triglycine sulfate has dielectric properties, which are poorly affected by deuteration. It follows, that despite the structural complexity, ferroelectric character of triglycine sulfate can be quite simple in general terms and can be described by a theoretical model with the absence of tunneling [1].

To change the properties of these crystals they are doped by metallic or organic impurities. The relevance of such studies for TGS crystals caused by the absence of experimental data of the influence of uniaxial pressure on dielectric properties of Co- and Cu-doped TGS crystals.

The aim of this paper is to investigate the influence of uniaxial pressure on the dielectric properties of TGS crystals doped with metallic impurities of Co^{2+} and Cu^{2+} in the vicinity of the ferroelectric structural phase transition. The concentrations of impurities for both crystals are 2 %.

2. Experimental technique

The dielectric constant of the crystals was determined by the results of experimental measurements of the capacitance of samples and was calculated by using the formula for a plane capacitor. The capacitance of samples was directly measured by using an AC bridge LCR E7-12 at a frequency of 1 MHz with a measuring field of 1.25 V/cm.

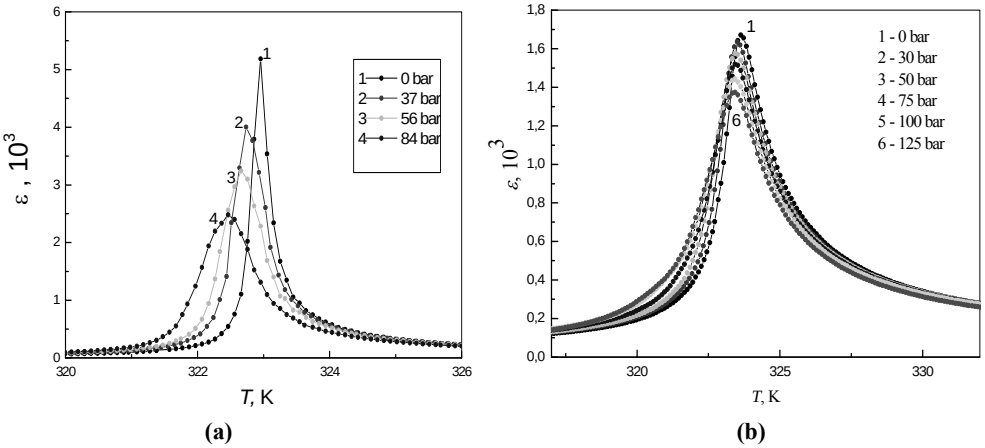
Samples were made in the form of a parallelepiped oriented according to the crystallographic axes. At the edge, which are perpendicular to the polar direction, electrical contacts were applied with silver paste.

Uniaxial mechanical stress was created by a spring dynamometer and was transferred on sample through a punch with floating heads. The accuracy of registration of the uniaxial pressure was ± 5%. The sample was placed in a specially designed thermostat which allowed adjusting the temperature of sample gradually. The temperature was measured by the copper-constantan thermocouple with an accuracy of ± 0.1 K. To improve heat transfer and to prevent contact with air the sample and thermocouple were filled by silicone oil. The device for investigating the ferroelectric crystals under uniaxial pressure allows to perform measurements over a wide temperature range (77÷370 K) and

efforts (up to 45 kg). Uniaxial pressure was applied along the ferroelectric axis *b* corresponding to the mechanical stress σ_2 [3].

3. Experimental results

Fig. 1 shows the temperature dependences of the dielectric constant of studied crystals under the influence of the uniaxial pressure σ_2.



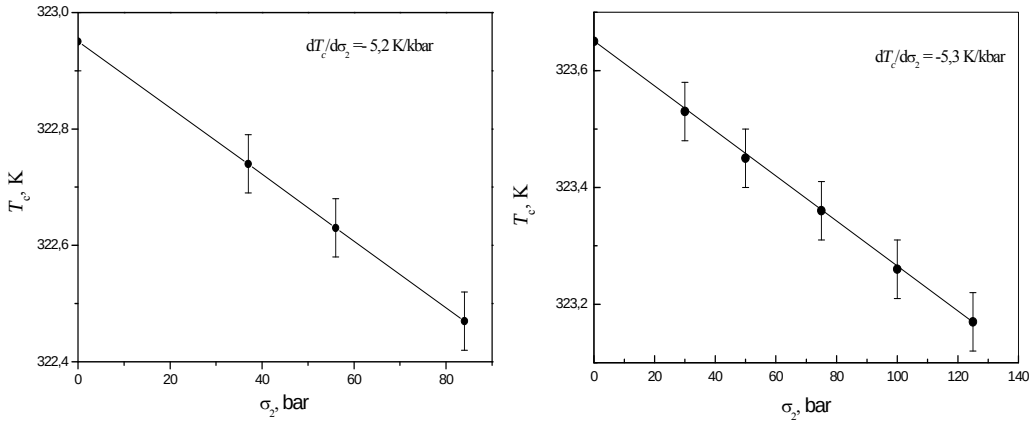
(a) **(b)**

Fig. 1. Temperature dependences of the dielectric constant of TGS:Co^{2+} (a) and TGS:Cu^{2+} (b) crystals for different values of uniaxial pressure.

It can be seen that the application of mechanical stress decreases the maximum value of the dielectric constant and the temperature of this maximum, which in the absence of mechanical stress was 322.9 K and 323.6 K for TGS:Co^{2+} and TGS:Cu^{2+} crystals, respectively.

Effects related to the pinning domains on charged impurities were not observed in the temperature dependences of dielectric permeability.

Fig. 2 shows the phase σ_2,*T*-diagram of TGS crystals doped with metallic impurities of cobalt and copper. To construct the phase diagrams the extrapolating of the inverse temperature dependence of the dielectric constant to zero in the paraelectric phase was performed [2].



(a) **(b)**

Fig. 2. Phase σ_2,*T*-diagrams of TGS:Co^{2+} (a) and TGS:Cu^{2+} (b) crystals.

The pressure coefficients of the shift of the phase transition temperature for TGS:Co^{2+} and TGS:Cu^{2+} crystals were – 5.2 and – 5.3 K/kbar, respectively. The displacement of the phase transition temperature under the influence of uniaxial pressure along the ferroelectric axis of doped crystals was less than for undoped ones. This effect can be accounted for by the existence of internal electric fields in doped crystals, the value of which is determined by the presence of impurities [4, 5]. The nature of such internal fields has a relaxing character, and the presence of such internal field, along with the changes of the temperature maximum of dielectric constant, leads to the blurring of $\varepsilon(T)$ dependencies.

It is known, that the shift of the temperature maximum of dielectric constant depending on the applied electric field is nonlinear: $T_m \sim E^{2/3}$. Therefore, the effect of the influence of the electric field created by the uniaxial compression due to piezoelectric effect is lower. It can be explained by overlaying such electric field on an existing field which is created by defects in the crystal lattice.

4. Conclusions

The shift the PT temperature towards the lower temperatures is found for doped TGS crystals. It is due to the existence of internal electric fields, the value of which is determined by the presence of impurities (Co^{2+} and Cu^{2+}).

It is experimentally shown that for the TGS:Co^{2+} and TGS:Cu^{2+} crystals the uniaxial pressure σ_2 results in decreasing the maximum values of the dielectric constant and reducing the phase transition temperature with a coefficient of $dT_c/d\sigma_2 = -5.2$ K/kbar for TGS:Co^{2+} and $dT_c/d\sigma_2 = -5.3$ K/kbar for TGS:Cu^{2+} crystals, respectively. The phase σ_2,T-diagrams are constructed.

We found that increasing the atomic mass of dopants leads to an increase in the phase transition temperature. Thus, for TGS, TGS:Co^{2+} and TGS:Cu^{2+} crystals it was, respectively, 321.9 K, 322.9 K and 323.6 K.

References

1. **Lines**, **M.** Ferroelectrics and Related Materials. / M. Lines, A. Glass/ M.: Mir. 1981. – 736p (in Russian).

2. **Kiyoyasu Imai**. Effect of Uniaxial Pressure on the Ferroelectric Phase Transition of Tri-Glycine Sulfate. / I. Kiyoyasu / Journal of the Physical Society of Japan. – 1974. – Vol. 36. №4. – P.256 – 259.

3. **Kedyulich, V. M**. Condensed Matter Physics. – 2000. – Vol. 3, N4 (24). – P. 851-856.

4. **Kedyulich, V. M.** Influence of spatially inhomogeneous electric fields on dielectric constant in ferroelectrics / V. M. Kedyulich, E. I. Gerzanich, A. G. Slivka, P. M. Lukach // Scientific Bulletin of the Uzhhorod University, ser. Physics. – 1999. – № 3. – P. 79-81.

5. **Slivka, A. G.** Influence of electric field on the ferroelectric phase transition in $Sn_2P_2S_6$ / A. G. Slivka, V. M. Kedyulich, E. I. Gerzanich, V. S. Shusta, P. P. Guranich // Ukr. Journal of Physics. – 2000. – V. 45, № 3. – P. 328-331.

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