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COMMENT

Comment on "Growth and characterization of unidirectional benzil single crystal for photonic applications"

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Abstract
The benzil crystal has at room temperature symmetry with the space group $P3_121$ without a polar axis, thus ferroelectricity cannot exist at RT. Unsaturated P-E hysteresis loop is due to dielectric loss not to ferroelectric properties. The large values of dielectric constant and dielectric loss measured for low frequencies are unreliable because the apparatus used gives erroneous results.

Keywords Ferroelectricity · Hysteresis loop · Phase transitions · Dielectric constants

1 Introduction

Benzil single crystal was obtained from aqueous solution and its crystallographic structure and symmetry with space group $P3_121$ were determined by Brown and Sadanaga [1] at RT in 1965. Esherick et al. redetermined its structure in 1973 [2]. This crystal undergoes the first order phase transition at 84.3 K changing its symmetry from $P3_121$ into C2 [3]. This phase transition was confirmed by Raman scattering [4, 5], Brillouin scattering [6, 7], infrared spectra [8] and dielectric constant studies [9].

The ferroelectric properties in the benzil crystal was discovered by Almeida et al. in 1988 [10]. The values of spontaneous polarization measured by pyroelectric method are $P_S = 4.10^{-5}$ and $1.3.10^{-5}$ C/m^2 at 65 and 80 K. The intensity of electric field used was 100 V/mm,.

Many other optical properties as absorption spectra [11], Raman scattering [12–15] and optical activity [16, 17] have been applied to the study of this crystal. These publications were not mentioned in the references of the commented paper.

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2 Comment

2.1 P-E hysteresis loop

Saranraj et al. [18] reported on unusual properties of the benzil crystals at room temperature. Unfortunately, the results reported should be critically approached. In the introduction the authors write that the benzil crystals have trigonal symmetry with the space group $P3_121$ and claim that the P-E loop presented in Fig. 3b is an evidence of ferroelectricity. However, in this symmetry group, there is no polar axis which is a prerequisite for spontaneous polarization. Thus, the authors ignored the basic principles of condensed phase physics. Also in this paper there is no information about the measurement method and frequency of the electric field used. The authors write: "area of the P–E loop decreases with respect to the decreasing applied electrical field". This statement means that the authors did not measure spontaneous polarization, but dielectric polarization caused by the *ac* electric field. In addition, the value of dielectric susceptibility can be easily calculated from the P *vs*. E relationship—it is about 30.

The authors write: „the hysteresis loop obtained in the present investigation is elliptical, which confirms the ferroelectric behavior of the material". Only a saturated P-E hysteresis loop informs about ferroelectric properties of crystals. The hysteresis loop presented in the paper commented on is not ferroelectric loop. The P-E loops of this type are typical of lose dielectrics and arises from the energy loss when the imperfect dielectric samples are subjected to

ac electric field. Scott, the authority in ferroelectricity, has proved in his work ‘‘Ferroelectrics go bananas” that even in the banana skin covered with electrodes a hysteresis loop appears in a strong alternate electric field, but it would not be a ferroelectric hysteresis loop like that recorded for the well-known BaNaNb crystal [19, 20].

2.2 Impedance studies

The authors measured the complex dielectric constant in the frequency range from 1 Hz to 2 MHz—however, they did not specify the intensity of the measurement field. Figures 5 and 6 illustrate the real part of the dielectric constant and the dielectric loss, but the results obtained at temperatures of 35, 55 and 75 °C do not show any temperature dependence. The large values of dielectric constant and dielectric loss measured in the frequency range from 1 to 100 Hz are unreliable because the apparatus used gives erroneous results for low frequencies.

The sentences: “the defect concentration increases exponentially with varying temperature and accordingly the electrical conduction also increases and thereby the dielectric constant decreases” and ‘‘as the frequency increases, dipoles of the materials will tend to orient along the field direction and show constant dielectric value” are contrary to basic physical principles.

2.3 Optical transmission studies

The result of the optical transparency measured in the range of 200–800 nm has been presented at Fig. 4. This result is a repetition of the previous result obtained by Sulthana et al. [21].

The only novelty of the commented paper was the determination of the values of the nonlinear refractive index and the nonlinear absorption coefficient using the z-scan method.

Author contributions Z. Tylczyński is the only author of this comment

Data availability No datasets were generated or analysed during the current study.

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