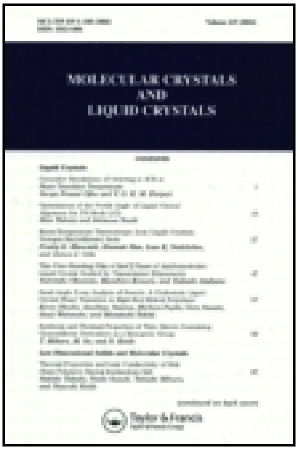

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Ferroelectric Particles in Liquid Crystals: Recent Frontiers

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Ferroelectric Particles in Liquid Crystals: Recent Frontiers

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In this article we describe electro-optical properties of recently discovered ferroelectric particles/liquid crystal colloids. We show that the presence of ferroelectric particles in a liquid crystal changes its birefringence and dielectric anisotropy. In contrast to the traditional time consuming and expensive chemical synthetic methods, this method to create liquid crystals with enhanced properties is relatively simple and has a great potential. We also demonstrate the performance of these new materials in various devices, including displays, light modulators, and beam steering devices.

Keywords: birefringence; dielectric constants; ferroelectric particles; high contrast; high speed; liquid crystal properties; low voltage; order parameter

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INTRODUCTION

Long-range forces between ultra-fine dielectric particles embedded in liquid crystal (LC) matrices result in intriguing colloids [1–7]. Large ($\sim\mu$m) colloidal particles form defects in LC matrices due to strong director deformations and ensembles of these particles and defects can form complex structures [8–15]. Small ($<<\mu$m) nano-particles do not significantly perturb the director field and defects do not form. However, if the concentration of small particles is large enough (>2–3% by weight), even the weak deformations in the director create an almost rigid suspension [4–6]. Heterogeneous liquid crystal suspensions of ferromagnetic-particles in nematic liquid crystal have also been reported [16,17]. These suspensions reveal unique sensitivity to magnetic fields; reorientation of the ferro-particles in the field also reorients the liquid crystal. In these heterogeneous systems the particles produce director distortions that extend over macroscopic scales.

Also, Barner with co-workers [18] found that the sensitivity of isotropic liquids to an applied electric field can be increased by doping with ultra-fine (less than 1 μm size) ferro-electric particles. They showed that a long milling process of ferro-electric $BaTiO_3$ particles (with spontaneous polarization of $0.26\,C/m^2$) in the presence of surfactant results in a stable suspension of ultra-fine particles of $BaTiO_3$ in heptane. The particles had an average radius of about 10 nm. These particles consist of ferroelectric single crystals. The induced birefringence in the isotropic heptane host, was controlled by application of an electric field.

Our approach disperses low-concentrations of ferroelectric nanoparticles in a liquid crystal host. These dilute dispersions are stable. The dispersions are macroscopically homogeneous and appear similar to a pure liquid crystal with no readily apparent evidence of dissolved particles. Clearly the nanoscale of the particles does not significantly disturb the liquid crystal orientation, i.e., create defects. At the same time, the doping particles are large enough that they maintain their ferroelectricity and share these intrinsic properties with the liquid crystal matrix.

In this work, we continue studying the electro-optical properties of the ferroelectric particles/liquid crystal suspensions. We show that this new approach, in contrast to the traditional time consuming and expensive chemical synthetic methods, dramatically enhanced the electro-optical performance of many liquid crystal materials. By changing a concentration and a type of ferroelectric particles, we were able to control many physical properties of liquid crystals, including the dielectric constants and birefringence.

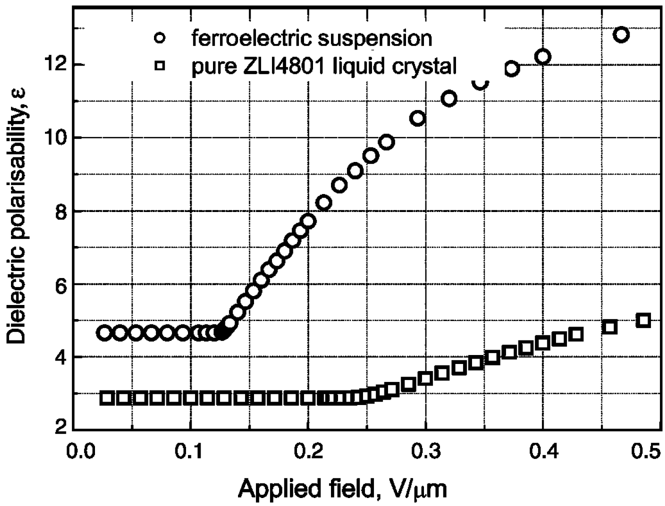

FIGURE 1 The dependence of the effective dielectric constant ε^{eff} of the pure liquid crystal material and the ferroelectric nematic suspension on the applied field. By comparing the electro-optical response of the planar cell filled with the pure LC ZLI-4801 and the particle suspension, we verified the increase in the dielectric anisotropy of the suspension.

SOME RELEVANT PRIOR WORK

Before, we observed that embedding sub-micron ferroelectric particles of $Sn_2P_2S_6$ in a nematic liquid crystal host at the volume concentration of 0.3% resulted in an enhanced dielectric response [19]. In particular, we found the dispersed particles increased the dielectric anisotropy by a factor >2 resulting in a decrease of the Freedericksz transition voltage and acceleration of the director reorientation in the electric field (Fig. 1). Also, we found that in the ferroelectric suspension the direction of the director reorientation is sensitive to the sign of the applied electric field, a property intrinsic to ferroelectric liquid crystals rather then for nematics. We therefore induced ferroelectric properties in a nematic host.

MATERIALS AND CELL PREPARATION

In this work, we used two kinds of ferroelectric naanoparticles: tin-hypodiphosphate ($Sn_2P_2S_6$) particles and barium titanate ($BaTiO_3$) particles. The $Sn_2P_2S_6$ particles are slightly anisotropic and their size is about 200 nm. $Sn_2P_2S_6$ single crystals have a spontaneous polarization of 14 μC/cm^2 parallel to the [101] direction of the monoclinic cell. The dielectric constant of the $Sn_2P_2S_6$ along the main axis strongly depends on the quality of the samples and varies from 200 for ceramic samples to 9000 for monodomain crystals [20]. The detail preparation process of the $Sn_2P_2S_6$ particles was described in another publication [19]. $BaTiO_3$ single crystals have tetragonal crystal structure with [001] polar axis and a spontaneous polarization of 26 μC/cm^2 at room temperature [21]. The dielectric constant of the $BaTiO_3$ single crystal is 168 in the direction parallel to polar axis and 2,920 perpendicular to the polar axis [21]. We used $BaTiO_3$ nanopowder (99+%, Aldrich). This $BaTiO_3$ particles have an average size of 30–50 nm and isotropic polyhedron particle shapes. We used the nematic model liquid crystal 5CB which has a dielectric anisotropy of $\varepsilon_a = \varepsilon_{\|} - \varepsilon_{\perp} = 18 - 7 = 11$.

We used a liquid crystal with negative dielectric anisotropy (NGLC) and a standard nematic 5CB, which has a positive dielectric anisotropy.

Planar or homeotropic cells were filled with the liquid crystal/ferro electric particles suspension or pure liquid crystal at a temperature higher than the NI transition temperature of the corresponding liquid crystal. The cells consisted of two indium tin oxide (ITO) coated glass substrates with a rubbed polyimide layer assembled for anti-parallel alignment. Calibrated rodlike spacers controlled cell spacing. Cells with the suspension or pure liquid crystal had identical alignment quality. Within experimental error, we measured equal value of the pretilt angle for both cells.

RESULTS AND DISCUSSIONS

We measured the phase retardation of a homeotropically or a planarly aligned cell as a function of applied field using the experimental set-up shown in Figure 2. We measured the dependence of transmitted light intensity at $\lambda = 0.632$ μm passing through the cell, placed between two crossed polarizers, with the optical axis oriented 45° to the polarization axes. The transmitted intensity will be at a minimum when the phase retardation, Δnd, is an even multiple of the incident light wavelength. The change of phase retardation of the cell can therefore be easily determined from a graph of the transmitted intensity relative to the applied voltage.

Figure 3 shows the increase in phase retardation of the cells which is the result of an increase in the birefringence of the particle dispersions. The effective birefringence of the ferroelectric particle $BaTiO_3$/NGLC liquid crystal dispersions is increased more than 20% (0.148 for the colloid, 0.116 for the pure liquid crystal). We did not find any

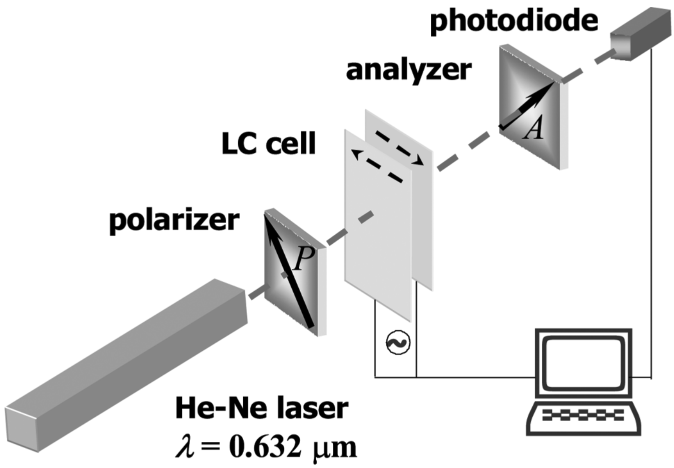

FIGURE 2 Experimental setup for phase retardation measurement for a liquid crystal cell.

increase of the birefringence when the NGLC liquid crystal is doped with $Sn_2P_2S_6$ ferroelectric particles. At the same time, both kinds of particles work with 5CB liquid crystal (Fig. 4). Both $BaTiO_3$ and

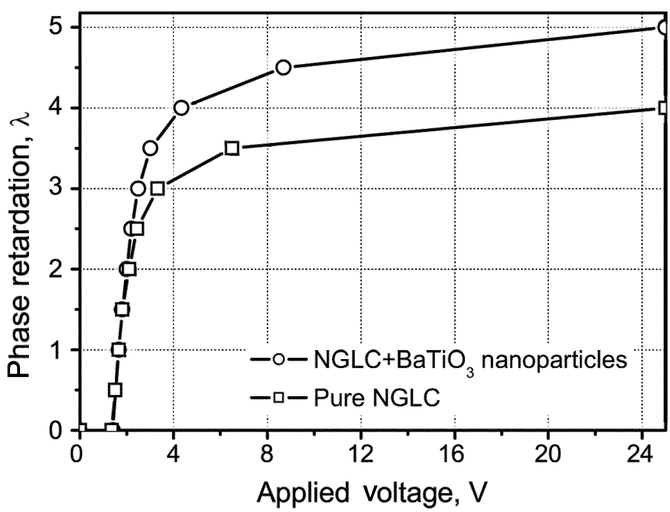

FIGURE 3 The phase retardation and birefringence of the liquid crystal NGLC and a ferroelectric particles/liquid crystal suspension at different voltage. Total achievable phase retardation for the suspension is increased by 25% due to the increase of the effective birefringence Δn_{eff}.

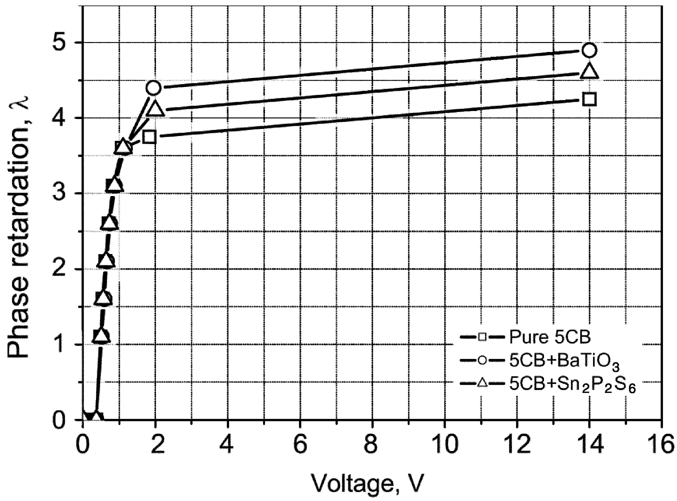

FIGURE 4 Phase retardation and effective birefringence for the pure 5CB liquid crystal cell and the cell filled with the mixture of the 5CB and $Sn_2P_2S_6$ ferroelectric nanoparticles and the 5CB and $BaTiO_3$ particles.

$Sn_2P_2S_6$ ferroelectric nanoparticles will enhance the birefringence of 5CB; addition of $BaTiO_3$ particles results in higher increase of the birefringence.

Figure 5a shows that the Freedericksz transition voltage of a 5CB liquid crystal suspension of $Sn_2P_2S_6$ ferroelectric nanoparticles is 10% lower than that of the pure 5CB liquid crystal cell, as expected for the higher dielectric anisotropy suspension. We did not find any decrease of the Freedericksz transition voltage when we used $BaTiO_3$ ferroelectric particles with 5CB liquid crystal, Figure 5b. At the same time, the $BaTiO_3$ particles clearly influence the dielectric anisotropy of the mixture, as it is seen from the capacitance measurements (Fig. 6). In contrast, while mixed with the NGLC liquid crystal, $BaTiO_3$ particles decreases the Freedericksz transition (Fig. 7).

The described results raise many questions and further study is necessary to explain the observed effects. We believe the improved characteristics of liquid crystals doped with ferroelectric particles (increase of the birefringence and dielectric anisotropy) are caused by a strong dipole-dipole interaction between the ferroelectric particles and the surrounding liquid crystal molecules. The properties of the mixtures may be varied by changing the type of the nanoparticles and adjusting their interaction with the surrounding liquid crystal molecules by modifying the surfaces of particles.

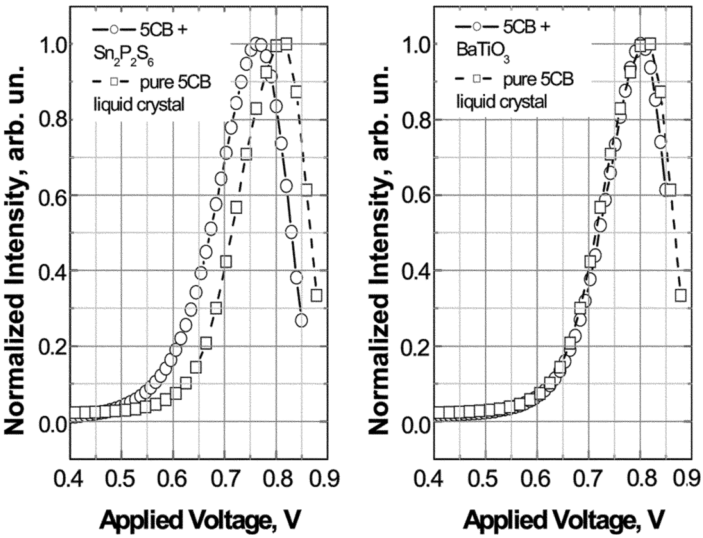

FIGURE 5 Electro-optic response to the applied voltage for the pure 5CB liquid crystal cell and the cell filled with the mixture of the 5CB and 1.0 wt.% of $Sn_2P_2S_6$ ferroelectric nanoparticles and the 5CB and $BaTiO_3$ particles.

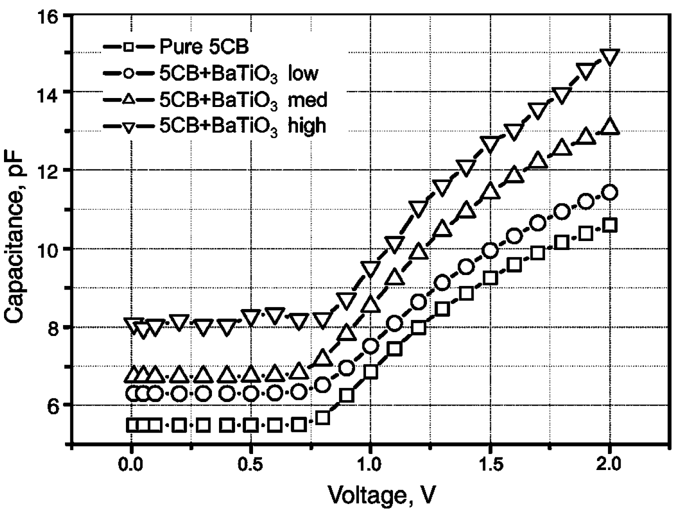

FIGURE 6 The dependence of the effective capacitance for the pure 5CB liquid crystal cell and a cell filled with a mixture of the 5CB and $BaTiO_3$ particles. Three different concentrations of $BaTiO_3$ particles are used: low, medium, and high. Basically, the $BaTiO_3$ particles do not change the threshold voltage of the 5CB but significantly influence the dielectric constants.

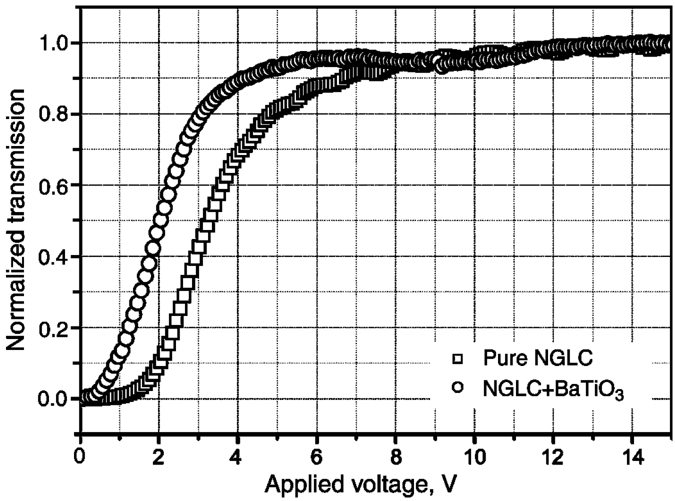

FIGURE 7 Comparison of T-V characteristics of vertically aligned cells filled with the NGLC liquid crystal and the NGLC/$BaTiO_3$ suspension.

This is an entirely new direction in the nano-scale soft matter. Below we demonstrate that appearance of these new materials may lead to astonishing new applications.

Performance of a Bistable Cholesteric Mode

We have doped cholesteric liquid crystal BL118 with ferroelectric nanoparticles $Sn_2P_2S_6$ and used these materials to make bistable cholesteric displays. We adjusted the concentration of the chiral additive to produce materials reflecting in the visible. A small percentage of the NOA65 monomer was then added and mixed uniformly into the cholesteric liquid crystal mixture before it was vacuum filled. An electric field was applied to the filled cell sufficient to align the liquid crystal molecules in the homeotropic state while ultraviolet radiation is applied to the cell. The photo-polymerized cell has two stable states: the highly reflecting quasi-planar (multi-domains with slightly different helix directions) texture and the weakly scattering (essentially non-reflecting) focal-conic texture.

The particles produced a sharp increase in the steepness of the focal conic-planar transition and improved the contrast of this transition, Figure 8. The particles produce higher reflective properties in the imperfect-planar state and are more transparent state in the focal

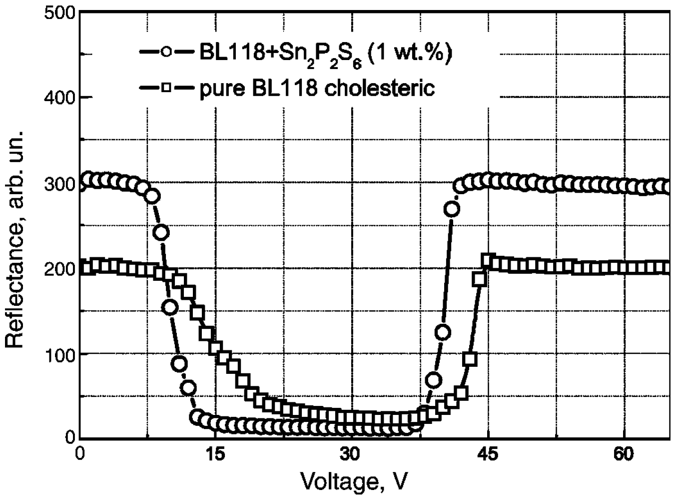

FIGURE 8 Electro-optics of a cholesteric bistable cell made of pure BL118 cholesteric and a mixture of the BL118 liquid crystal with $Sn_2P_2S_6$ ferroelectric particles. The reflectance is measured 800 ms after the corresponding voltage with a 20 ms pulse applied and then grounded. The initial state was in the quasi-planar state. The cell with particles demonstrates lower driving voltages, more profiled dependence of the reflectance vs. applied voltage and better contrast.

conic state (Fig. 9). Clearly, the overall performance of these devices is improved when using the ferroelectric particle dispersions.

Performance of a Bistable Smectic Mode

We checked influence of the ferroelectric nanoparticles on a classical smectic liquid crystal 8CB. We did not find any increase in the dielectric anisotropy when 8CB is doped with $BaTiO_3$ nanoparticles. We did find the predicted effect when $Sn_2P_2S_6$ ferroelectric particles are used. We produced scattering in a 16 μm thick cells by heating the cell above the clearing temperature and cooling into the smectic phase. Application of an electric field orients the liquid crystal in a homeotropic state and the scattering disappears. Figure 10 shows dependence of the intensity of the light passing through such a cell as a function of applied voltage. The threshold voltage for a cell filled with the pure 8CB liquid crystal was almost 10 V higher then the corresponding voltage for a cell filled with the mixture of 8CB and $Sn_2P_2S_6$ particles when their concentration was 0.36 wt.%.

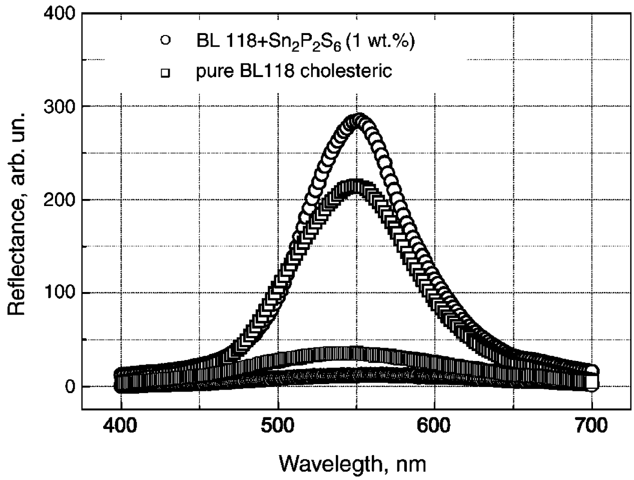

FIGURE 9 Reflectance measurement of the bistable cholesteric cell filled with pure BL118 cholesteric and a mixture of the BL118 liquid crystal with $Sn_2P_2S_6$ ferroelectric particles. The cell with the particles demonstrates higher reflective properties in quasi-planar state and more transparent state in a focal conic state. This explains a great value of a contrast in the case when the cell is filled with the mixture of the cholesteric liquid crystal and the ferroelectric particles.

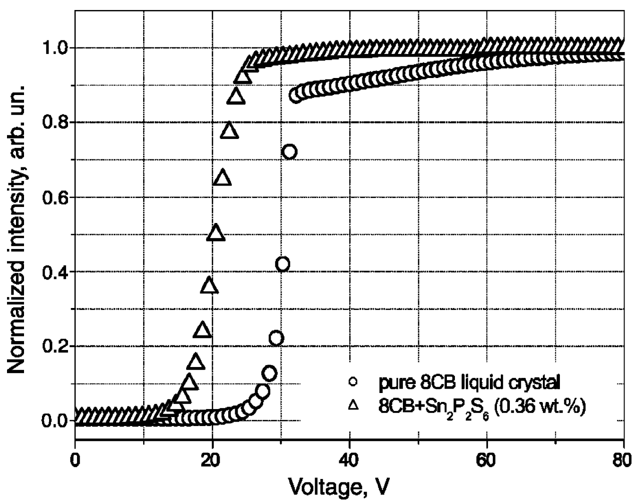

FIGURE 10 Comparison of the electro-optic response of the cells filled with pure SmA 8CB liquid crystal and a mixture of the 8CB with $Sn_2P_2S_6$ ferroelectric particles. The graph shows transition from scattering orientation of the liquid crystal in the cells to its defect-less homeotropic orientation.

CONCLUSION

The sensitivity of liquid crystals to applied electric fields may be enhanced by doping them with ferroelectric nanoparticles. Doping also may increase the effective birefringence, enhancing the performance of the liquid crystal mixtures. The reason for this behavior may be an enormous local electric field created around each ferroelectric particle due to the presence of the permanent dipole moment of the particle. We are continuing our studies to understand the mechanism of this behavior.

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