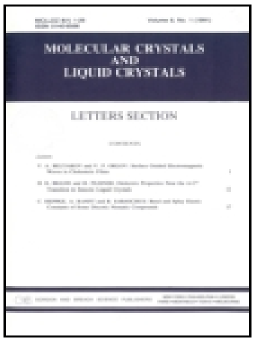
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Effect of Particle Size on Electro-Optic Properties of Liquid Crystal Devices Doped with γ-Cyclodextrin Stabilized Barium Titanate Nanoparticles

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Barium titanate stabilized by γ-cyclodextrin nanoparticles were prepared by using a microwave reactor equipped with ultrasonic nozzle mixing at 240°C in a tetraethylene glycol solution of barium ethoxide and titanium ethoxide in the presence of γ-cyclodextrin. Particles in γ-cyclodextrin-stabilized $BaTiO_3$ nanoparticles had an average diameter of 2.1 nm and mainly distributed within the range of about 1 to 4 nm. The γ-cyclodextrin-stabilized $BaTiO_3$ nanoparticles were mixed with 4-cyano-4′-pentylbiphenyl at room temperature resulting in a liquid crystal sol of 4-cyano-4′-pentylbiphenyl. The response time of liquid crystal devices in the presence of γ-cyclodextrin-stabilized $BaTiO_3$ nanoparticles was faster than that in the absence.

Keywords nanoparticles; barium titanate; cyclodextrin; response time; twisted nematic liquid crystal devices

1. Introduction

Liquid crystal devices (LCDs) are common electronic devices and are widely used any place and at any time. The modification of physical properties of liquid crystals by doping nanomaterials has received much attention from the view point of the enhancement of the performance of LCDs. Reflecting these trends several research groups reported on heterogeneous liquid crystal suspensions using; ferroelectric nanoparticles [1], ferromagnetic particles [2], fullerene [3], carbon nanotubes [4], diamond powders [5], metal nanoparticles [6,7], and metal nanorods [8]. In particular, strong activities have been reported for barium titanate ($BaTiO_3$) nanoparticles doped in nematic liquid crystalline mixtures [9]. For example, Basu have demonstrated that, when a small quantity of $BaTiO_3$ nanoparticles was dispersed in nematic liquid crystal, the hybrid in the isotropic phase exhibited an electromechanical effect which showed a significant pretransitional behavior on approaching the nematic phase from the isotropic phase [10]. A significant enhancement in the nematic

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orientational coupling by doping with BaTiO$_3$ nanoparticles was predicted by means of theoretical modeling and a remarkable increase in nematic-isotropic transition temperature has been reported by Li *et al.* [11].

Nanoparticles stabilized by organic molecules are now creating a new class of materials different from either conventional bulk materials or atoms, giving one of the smallest building blocks of matter [12]. Metal nanoparticles are stabilized by citrate ion [13], surfactants [14], polymers [15], and organic ligands [16]. For example, palladium nanoparticles obtained by UV irradiation of a tetrahydrofuran solution of palladium (II) acetate in the presence of 4-cyano-4′-pentylbiphenyl (5CB) were stabilized by 5CB and used as a dopant for a guest-host LCD [17]. Poly(*N*-vinyl-2-pyroridone)-stabilized Pd nanoparticles were prepared by refluxing of palladium(II) acetate in the mixture of water/ethanol in the presence of poly(*N*-vinyl-2-pyroridone) and worked as a dopant for twisted nematic LCD with high speed response [18]. Thus, stabilizers play important roles for not only protecting nanoparticles but also controlling properties. Cyclodextrin (CyD) is cyclic oligomers of glucose units, linked by α(1–4) bonds with a central nanocavity. The external diameter at the secondary hydroxyl side of CyD is larger than that at the primary hydroxyl side of CyD. While the outside of CyD molecule is hydrophilic, the cavity inside is a hydrophobic medium such as diethyl ether, and various hydrophobic substances in aqueous medium can be included therein as the guest, when they are spatially fitted in the nanocavity [19, 20]. The inclusion complex formation in solution is a dynamic process of the equilibrium between the inclusion state and the free state of the substrate. The time scale of the exchange of these states is faster than that of NMR spectroscopy. In previous communication [21], we preliminarily reported the preparation of silica nanoparticles using CyD, and the application of LCDs. However, to the best of our knowledge, there is no report on synthesis of BaTiO$_3$ nanoparticles by using CyD as a stabilizer.

In this paper, we report the detailed results of ultrasonic and microwave method for the preparation of γCyD-stabilized BaTiO$_3$ nanoparticles, which can improve the compatibility of BaTiO$_3$ nanoparticles with 5CB as a liquid crystal molecule. LCDs fabricated by 5CB doped with the γCyD-stabilized BaTiO$_3$ nanoparticles show an obvious fast electro-optic switching. This is the first report of γCyD-stabilized BaTiO$_3$ nanoparticles applied to LCDs resulting in a fast response compared with pure liquid crystal without dopants. In addition we discuss a relationship between the fast response and physical parameters of liquid crystal.

2. Experimental

2.1. Materials and Experimental Procedure

Gamma-cyclodextrin (γCyD), barium (II) ethoxide, titanium (IV) ethoxide and tetraethylene glycol from Wako Pure Chemical Industries, Ltd. were used without further purification. Other reagents employed here were of a commercial G.R. grade and used as received. The γCyD-stabilized BaTiO$_3$ nanoparticles were prepared by using a microwave reactor equipped with ultrasonic nozzle. Gamma-CyD (7.1 μmol in monomeric units, 0.1 times the total amount of barium titanate), barium (II) ethoxide (71 μmol), and titanium (IV) ethoxide (71 μmol) were mixed in tetraethylene glycol to form a 200 cm^3 solution. Mixed solutions filled with pure nitrogen and then exposed to the microwave (2450 MHz) and ultrasonic waves (150W, 20kHz). Contaminants like ions in the dispersions were removed by washing the dispersions three times with ethanol by using an ultrafiltration. Complete removal of the solvent and volatile byproducts by vacuum evaporation gave γCyD-stabilized $BaTiO_3$ nanoparticles.

2.2. Characterization

UV-Vis absorption spectra were measured with a Shimadzu UV-2500PC recording spectrophotometer using a quartz cell with 10 mm of optical path length. Transmission electron microscopy (TEM) images were observed with a JEOL TEM 1230 at accelerated voltage of 80 kV. An average diameter and standard deviation were calculated by counting the diameters of 200 particles on the enlarged TEM photographs. The X-ray diffraction patterns were obtained by using a Mac Science Co. M18XHF-SRA diffractometer with Cu Kα radiation for the powder samples at room temperature.

2.3. Fabrication and Electro-optic Properties of LCDs Containing γCyD-stabilized $BaTiO_3$ Nanoparticles

The γCyD-stabilized $BaTiO_3$ nanoparticles were mixed with 5CB at room temperature resulting in a liquid crystal sol of 5CB containing 0.075 wt% of total metal. The sols were injected into an empty cell for a twisted nematic mode with a cell gap of 5 μm, supplied by Sun Trading Co. Ltd. The electro-optic properties, especially applied voltage versus optical transmittance (*V-T*) curves of twisted nematic liquid crystal devices (TN-LCDs) were measured by applying the 100 Hz square wave alternating current at 25°C with a LCD evaluation system (Photal Ohtsuka Electronics, Ltd., model LCD-5200). All the experiments and measurements were carried out five times under room temperature, so that the measurements values are struck an average.

3. Results and Discussion

3.1. Characterization of γCyD-Stabilized $BaTiO_3$ Nanoparticles

The γCyD-stabilized $BaTiO_3$ nanoparticles were prepared by using a microwave reactor equipped with ultrasonic nozzle mixing at 240°C for 60 min in a tetraethylene glycol solution of barium (II) ethoxide and titanium (IV) ethoxide in the presence of γCyD. The temperature-dependent UV-Vis spectra of γCyD-stabilized $BaTiO_3$ nanoparticles are shown in Figure 1. The dispersions of γCyD-stabilized $BaTiO_3$ nanoparticles obtained after ultrasonic and microwave reaction show broad absorption spectra. The absorption spectra of dispersions of γCyD-stabilized $BaTiO_3$ nanoparticles remarkably increased with increasing reaction temperature, suggesting the formation of large particle size at high temperature.

Figure 2 exhibits TEM photograph and size distribution histogram of γCyD-stabilized $BaTiO_3$ nanoparticles at the reaction temperature of 240°C. The most γCyD-stabilized $BaTiO_3$ nanoparticles were distributed in the range of 1–4 nm, suggesting that the size of $BaTiO_3$ nanoparticles is homogeneous. The results reveal that γCyD-stabilized $BaTiO_3$ nanoparticles examined here have the average diameter of 2.1 nm (standard deviation of 0.5 nm) and relatively small standard deviation. The average diameters of γCyD-stabilized $BaTiO_3$ nanoparticles at the reaction temperature of 270°C and 300°C were 3.0 nm and 3.5 nm, respectively, with a narrow size distribution. These result are consistent with the UV-Vis spectra of γCyD-stabilized $BaTiO_3$ nanoparticles, indicating the formation of large particle size at high temperature. On the other hand, the average diameters of γCyD-stabilized $BaTiO_3$ nanoparticles prepared by solvothermal method at the reaction

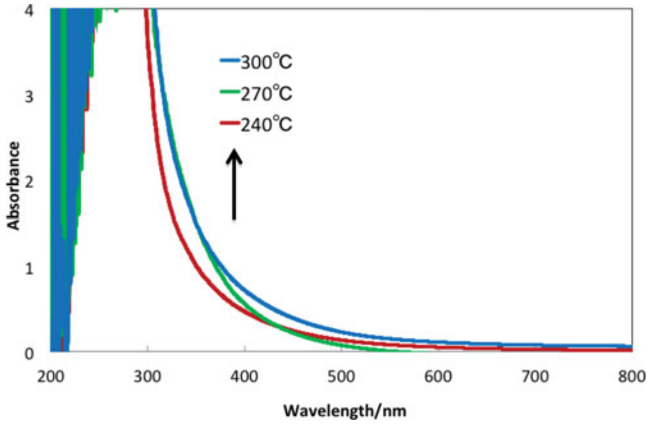

Figure 1. UV-Vis absorption spectra of a tetraethylene glycol solution of γCyD-stabilized $BaTiO_3$ nanoparticles prepared at 240, 270 and 300°C.

temperature of 240°C, 270°C and 300°C were 2.3 nm, 2.7 nm and 3.9 nm, respectively. Dang *et al*. reported the formation of $BaTiO_3$ nanoparticles by ultrasonic irradiation in the sodium hydroxide aqueous solution [22]. They described that the $BaTiO_3$ nanoparticles had the average diameter of 250 nm and showed the aggregation of 5–10 nm. Lee *et al*. reported the synthesis and size control of $BaTiO_3$ nanoparticles by facile solvothermal method [23]. The average diameters of $BaTiO_3$ nanoparticles prepared with and without the organic amines as stabilizers were found to be 80 and 100 nm, respectively. Thus, stabilizers play weighty effects for not only controlling properties but also protecting nanoparticles. Cyclodextrin exhibits their remarkable functions owing to the soluble effect, the protection effect, the conformation effect, and so on. In previous communication, we preliminarily reported the preparation of silica nanoparticles using CyD [21]. γCyD as stabilizer of nanoparticles plays an important role in the formation of single nano-order particles.

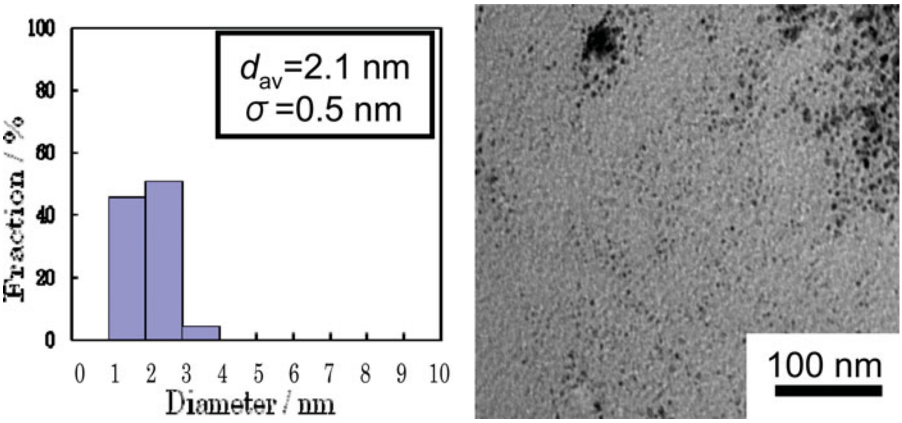

Figure 2. Transmission electron micrograph and particle size distribution histogram of γCyD-stabilized $BaTiO_3$ nanoparticles by ultrasonic/microwave method at the reaction temperature of 240°C. d_{av} = average diameter, σ = standard deviation.

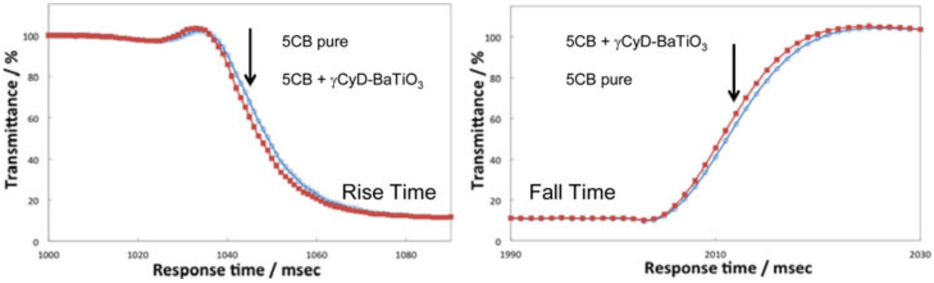

Figure 3. Relationship between response time and transmittance of TN-LCDs fabricated by 5CB sol in the absence and presence of γCyD-stabilized $BaTiO_3$ nanoparticles by ultrasonic/microwave method at the reaction temperature of 240°C.

3.2. *Electro-Optic Properties of TN-LCDs Containing γCyD-Stabilized $BaTiO_3$ Nanoparticles*

The γCyD-stabilized $BaTiO_3$ nanoparticles prepared in the present experiments were easily mixed with liquid crystal molecule 5CB at room temperature to form liquid crystal sol for TN-LCDs. The TN-LCDs fabricated by injecting the liquid crystal sol containing γCyD-stabilized $BaTiO_3$ nanoparticles into empty cells were supplied to measure the electro-optic properties. Electro-optic properties of TN-LCDs fabricated by 5CB with and without γCyD-stabilized $BaTiO_3$ nanoparticles were measured by applying voltage in alternating current at 25°C. Figure 3 shows the relationship between response time and transmittance of TN-LCDs fabricated by 5CB sol in the absence and presence of γCyD-stabilized $BaTiO_3$ nanoparticles. The response times (τ_{on}; the rise time from 90% transmittance to 10%, and τ_{off}; the fall time from 10% transmittance to 90%) of TN-LCDs fabricated by 5CB sol in the presence of γCyD-stabilized $BaTiO_3$ nanoparticles are summarized in Table 1. The fast response time is observed in the presence of γCyD-stabilized $BaTiO_3$ nanoparticles by ultrasonic/microwave method at the reaction temperature of 240°C with the τ_{on} of 58.55 msec and the τ_{off} of 14.49 msec, while the low response time was exhibited in the absence with the τ_{on} of 60.57 msec and the τ_{off} of 15.45 msec. The overdrive voltage is

Table 1. Response times of TN-LCDs fabricated by 5CB sol in the presence of γCyD-$BaTiO_3$ nanoparticles

		Response time / msec			
		5CB pure	5CB + γ CyD-$BaTiO_3$ (240°C)	5CB + γ CyD-$BaTiO_3$ (270°C)	5CB +γ CyD-$BaTiO_3$ (300°C)
Ultrasonic /	τ_{on}	60.57	58.55	60.75	62.97
Microwave	τ_{off}	15.45	14.49	15.57	16.10
Method	Total	76.01	73.04	76.32	79.08
	τ_{on}	59.82	58.78	59.81	60.47
Solvothermal	τ_{off}	14.26	14.56	14.51	14.64
Method	Total	74.08	73.34	74.32	75.11

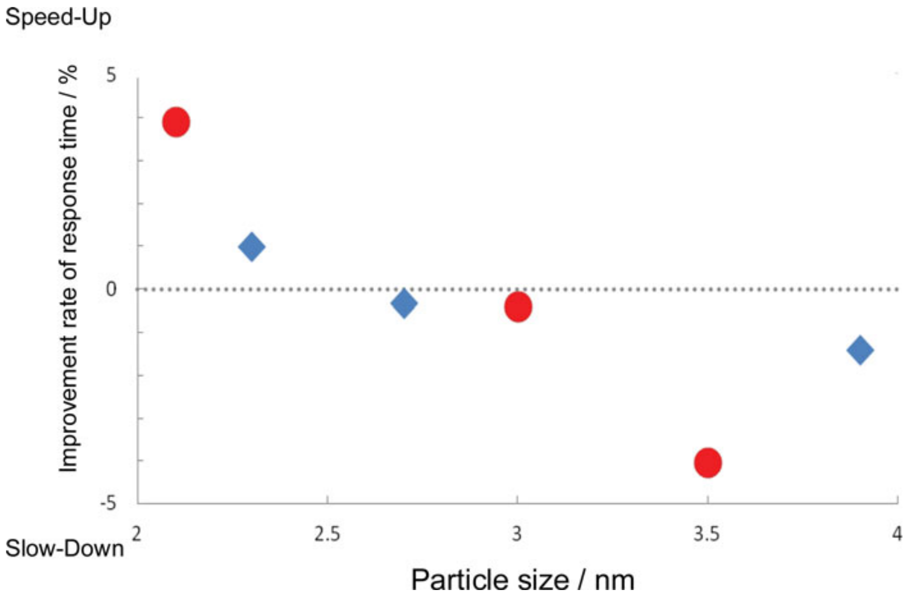

Figure 4. Relationship between improvement rate of response time and particle size of γCyD-stabilized BaTiO$_3$ nanoparticles by ultrasonic/microwave method (●) and solvothermal method (◆).

generally achieved on fast rising response of LCDs. The fast response on the rise time of TN-LCDs doped with nanoparticles was driven by overdrive voltage [24]. On the other hand, the fast response on the fall time have been hard. However, the fall time of TN-LCDs in the presence of γCyD-stabilized BaTiO$_3$ nanoparticles was faster than that in the absence. Dependence of particle size on the improvement rate of response time in the case of γCyD-stabilized BaTiO$_3$ nanoparticles prepared by the ultrasonic/microwave method and the solvothermal method is shown in Figure 4. The improvement rate of response time increases with decreasing particle size of γCyD-stabilized BaTiO$_3$ nanoparticles and is maximum when the average particle size is 2.1 nm. We reported that the catalytic activity for hydrogenation depended on the metal size of polymer-stabilized metal nanoparticles [25]. In general the catalytic activity gradually increased with decreasing metal size for rather large rhodium nanoparticles, and then rapidly increased when the average metal size was less than about 2.2 nm. A similar tendency was observed in this dependence of particle size on the improvement rate of response time of TN-LCDs fabricated by 5CB sol in the presence of γCyD-stabilized BaTiO$_3$ nanoparticles.

In order to examine the fast response of TN-LCDs doped with γCyD-stabilized BaTiO$_3$ nanoparticles by the ultrasonic/microwave method at the reaction temperature of 240°C, X-ray diffraction analyses were performed, as shown in Figure 5. Although the diffraction pattern of γCyD-stabilized BaTiO$_3$ nanoparticles by ultrasonic/microwave method (average particle size; 2.1 nm) is clearly consistent with a cubic BaTiO$_3$, that by the solvothermal method (average particle size is; 2.3 nm) is broad peak. Thus, the ultrasonic/microwave method is the effective tool to prepare the homogeneous nanoparticles. The response time of TN-LCDs in the presence of γCyD-stabilized BaTiO$_3$ nanoparticles by ultrasonic/microwave method at the reaction temperature of 240°C is faster than that in

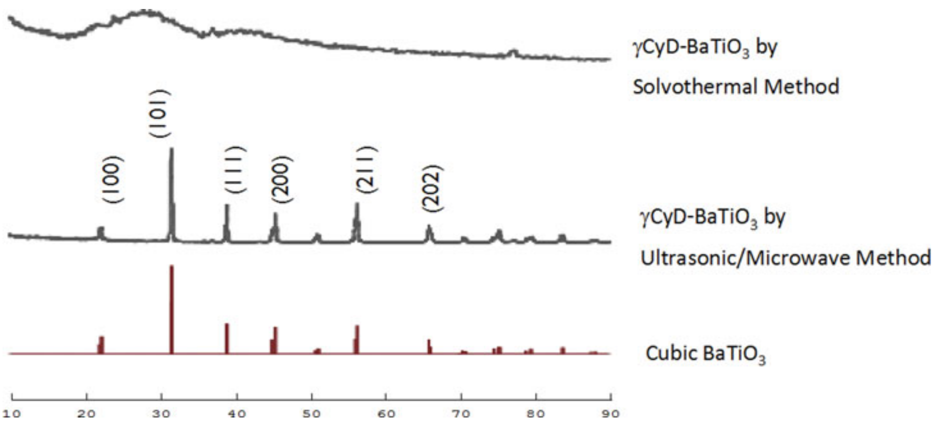

Figure 5. X-ray diffraction patterns of γCyD-stabilized BaTiO$_3$ nanoparticles.

the absence. The response time is given by

$$\tau_{\rm on} = (\gamma_1 d^2)/\varepsilon_0 \Delta\varepsilon (V_{\rm on}^2 / - V_{\rm th}^2)$$
$$\tau_{\rm off} = (\gamma_1 d^2)/(\pi^2 K_{\rm eff})$$

where γ_1, d, ε, $V_{\rm th}$ and $K_{\rm eff}$ are rotational viscosity, a thickness of host LCD, dielectric constant, threshhold voltage, and elastic constant, respectively. To consider this fast response, we measured the rotational viscosity of 5CB sol in the absence and presence of γCyD-stabilized BaTiO$_3$ nanoparticles, as shown in Table 2. This measurement was done for an electrically controlled birefringence (ECB) mode cells by a Model 6254 (Toyo). The rotational viscosity obtained in this manner were 77.0 and 75.0 mPa·s for LCDs in the absence and presence of γCyD-stabilized BaTiO$_3$ nanoparticles, respectively. Yasuda *et al.* reported cyclodextrin derivatives reduced the viscosity of liquid crystal [26]. These results suggest that the presence of γCyD-stabilized BaTiO$_3$ nanoparticles in liquid crystal makes it easy for liquid crystal molecules to change the viscosity probably due to the inclusion effect of γCyD upon intermolecular interactions among liquid crystal molecules.

Liquid crystal devices doped by liquid crystal molecule-stabilized nanoparticles have some issues to be practically realized as a TFT (thin film transistor)-driven liquid crystal display, which include generation of screen burn-in phenomena, and low specific resistance [27]. These issues may be caused by low long-term stability of nanoparticles and/or presence of contaminated ions. We previously measured voltage holding ratio (VHR) for TN-LCD fabricated by doping CyD derivative stabilized-Rh nanoparticles [28]. The VHRs were 98.9 and 98.9 for TN-LCD without dopant and doped with CyD derivative stabilized-Rh nanoparticles, respectively. The VHR after 2 month in the presence CyD derivative stabilized-Rh nanoparticles was in good agreement with that before 2 month in the presence of nanoparticles, suggesting the stability of CyD derivative stabilized nanoparticles in LCD.

Table 2. Rotational viscosity of 5CB doped with γCyD-BaTiO$_3$ nanoparticles

	5CB pure	5CB + γCyD-BaTiO$_3$
γ_1/ mPa·s	77.0	75.0

Table 3. Response times of TN-LCDs fabricated by NTN01 sol in the presence of γCyD-BaTiO$_3$ nanoparticles

		NTN01 pure	NTN01 + γCyD-BaTiO$_3$	
		Response time / msec	Response time /msec	Improvement rate /%
25°C	τ_{on}	10.43	9.82	5.84
	τ_{off}	4.86	4.86	0.02
	Total	15.29	14.68	3.99
0°C	τ_{on}	18.61	16.42	11.81
	τ_{off}	10.24	10.29	−0.50
	Total	28.86	26.71	7.44

Since a joint research enterprise requested the fast response speed, we can select field-sequential-color (FSC) LCDs. The FSC-LCDs are a long-expected technology because of its potential advantages such as high resolution, high legibility under high-ambient lighting conditions, and low power consumption. Hasebe and Kobayashi reported a flat-panel-type FSC-LCDs using narrow-gap TN-LCDs and ferroelectric LCDs together with color CRT tubes connected by a bundle of optical fibes [29]. Recently, several papers were presented on the reduction of color break-up and power reduction of FSC-LCDs. Then, the FSC practical liquid crystal NTN01 from DIC Corp. was used as the host liquid crystal. Table 3 shows the time course of transmittance of narrow-gap TN-LCDs (cell gap of 3 μm) fabricated by NTN01 doped with and without γCyD-stabilized BaTiO$_3$ nanoparticles at 25°C and 0°C. The fast response time at 25°C was observed in the presence of γCyD-stabilized BaTiO$_3$ nanoparticles with the total improvement rate of response time (3.99%). Moreover, the total improvement rate of response time in the presence of γCyD-stabilized BaTiO$_3$ nanoparticles at 0°C (7.44%) was faster than that in the absence. This may suggest that doping nanoparticles may produce an effective rise in temperature. These results below 0°C are preliminary ones, so that we have to continue our research. Further studies will be described in detail elsewhere.

4. Conclusions

Barium titanate has been utilized extensively in various electroceramic areas, including the thermistors, electroluminescence, electro-optical devices, and multilayer ceramic capacitors, due to its ferroelectric response and high dielectric constant. We have succeeded in preparation of γCyD-stabilized BaTiO$_3$ nanoparticles by the ultrasonic/microwave method at 240°C in a tetraethylene glycol solution of barium (II) ethoxide, and titanium (IV) ethoxide in the presence of γCyD. The response of TN-LCDs in the presence of nanoparticles prepared by this method was faster than with nanoparticles prepared by the solvothermal method. The improvement rate of response time increased with decreasing particle size of γCyD-stabilized BaTiO$_3$ nanoparticles. Addition of γCyD-stabilized BaTiO$_3$ nanoparticles to liquid crystal materials could be a promising method to improve the response time without changing other components and systems in TN-LCDs. Fast response speed achieved by our present research may give a great impact to LCD industries such as digital signage, automobile display, and mobile phone.

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