Magneto–optical effect of TEB30A liquid crystal doped with thulium oxides*

Liu Gui-Xiang(刘桂香)† and Jin Xiang(金 香)

Baotou Teachers College, Inner Mongolia University of Science and Technology, Baotou 014030, *China*

(Received 8 November 2013; revised manuscript received 23 December 2013; published online 20 March 2014)

The influences of an external magnetic field on the optical properties of the TEB30A nematic liquid crystal doped with thulium oxides (Gd_2O_3, Dy_2O_3, Nd_2O_3, Y_2O_3, and Sm_2O_3) are studied. It is shown that a magnetic field applied parallelly to the sample cell surface leads to the rotational orientation of mesogenes. All samples except for the sample doped with Sm_2O_3 nanoparticles undergo structural deformations. The behavior of the TEB30A/Sm_2O_3 differs from those of the TEB30A liquid crystal doped with other four nanoparticles. The presence of Sm_2O_3 nanoparticles in the TEB30A liquid crystal does not cause the structural deformation of the liquid crystal matrix. At the same time, the anchoring type of the liquid crystal molecules on the nanoparticle surface is different. The director $\boldsymbol{n}$ is parallel to the magnetic moment $\boldsymbol{\mu}$ in the TEB30A/Sm_2O_3, and inclined to the magnetic moment $\boldsymbol{\mu}$ in the TEB30A/Nd_2O_3, and perpendicular to the magnetic moment $\boldsymbol{\mu}$ in each of TEB30A/Gd_2O_3, TEB30A/Dy_2O_3, and TEB30A/Y_2O_3. Besides, the dependence of the structural deformation on the critical magnetic field for the TEB30A is obtained.

Keywords: magnetic field, TEB30A nematic liquid crystal, thulium oxides

PACS: 42.70.DF **DOI:** 10.1088/1674-1056/23/4/044216

1. Introduction

Magnetic nanoparticles suspended in the liquid have attracted wide interest in many areas of science, technology, and medicine.[1–3] Recently, magnetic nanoparticles-doped nematic liquid crystals become a new focus.[4–16] It is known that nematic liquid crystal with a weak anisotropy of diamagnetic susceptibility can undergo the rotational orientation of mesogenes under the action of an external magnetic field $\boldsymbol{H}$. The rotation takes place with or without being accompanied by structural transitions in the nematic liquid crystals.

The threshold field H_c of the structural transitions is about 10^4 Oe (1 Oe = 79.5775 A·m^{-1}) for the nematic liquid crystal (relatively large) since the diamagnetic susceptibility of the nematic liquid crystal is rather small (about 10^{-7}).[4] In order to reduce the value of the operated magnetic field, Brochard and de Gennes[4] have suggested the incorporation of magnetic grains into liquid-crystalline matrix. If the grains are fine in shape, elastic interactions give rise to their orientation in the liquid crystal matrix. Such a system is the so-called ferronematic or ferrocholesteric system. These systems have magnetic susceptibilities that are at least some orders of magnitude higher than a pure liquid crystal. They allow their structures to be controlled by relatively low magnetic fields. Therefore, the most essential characteristics of these systems are the orientational coupling between the magnetic nanoparticles and the liquid crystal matrix.

In this paper we study the optical properties of the TEB30A liquid crystal doped with thulium oxide nanoparticles (Gd_2O_3, Dy_2O_3, Nd_2O_3, Y_2O_3, and Sm_2O_3) in magnetic field parallel to the surface of the sample cell. The magnetic field ranges from 0 mT to 1200 mT. The size of thulium oxide nanoparticles is several hundred nanometers. It is shown that the anchoring type of the liquid crystal molecules on the particle surface is different, and the dependence of the structural deformation on critical magnetic field for the liquid crystal is found. In the case of the structural deformation, the value of the threshold field is strongly reduced if orientational coupling between the thulium oxide nanoparticles and the TEB30A nematic liquid crystal matrix is realized.

2. Experimental methods

About 1 mg of thulium oxides was dissolved in 6 ml of alcohol under 20-min ultrasonic irradiation. Then 0.1 ml of the TEB30A nematic liquid crystal was added into the thulium oxides alcohol solution, and stirred for 30 min. The quantity of thulium oxide nanoparticles in the TEB30A nematic liquid crystal was 10 mg/ml. The liquid crystal cell consisted of two identical glasses, the gap between which was filled with the mixture. The cell thickness value was 20 μm.

The thulium oxides were Gd_2O_3, Dy_2O_3, Nd_2O_3, Y_2O_3, and Sm_2O_3, respectively. And each of these thulium oxides had a purity of 99.99% and a size of several hundred nanometers. The birefringences of the TEB30A nematic liquid crystal were $n_e = 1.69$ and $n_o = 1.52$, at wavelength 532 nm.

*Project supported by the National Natural Science Foundation of China (Grant No. 50862007), the Natural Science Foundation of Inner Mongolia Autonomous Region, China (Grant No. 20080404MS0114), and the Inner Mongolia Autonomous Region Scientific Research Fund, China (Grant No. NJZY12203).

†Corresponding author. E-mail: gxliuemail@126.com

© 2014 Chinese Physical Society and IOP Publishing Ltd

The cell was placed in a steady constant magnetic field $\boldsymbol{H} \parallel x$, which enable to reorient the nematic director smoothly through 90° within the xz-plane in Fig. 1.

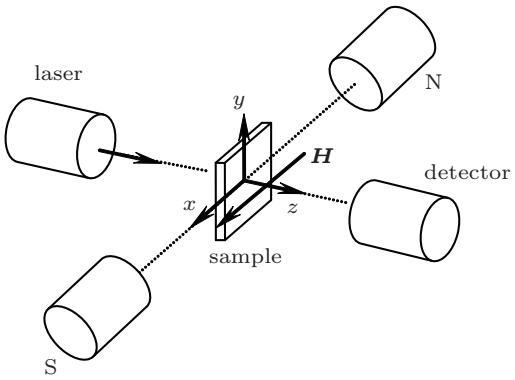


Fig. 1. Schematic illustration of experiment setup.

3. Results and discussion

Figure 2 shows that the dependences of transmission T on applied magnetic field $\boldsymbol{H}$ for the pure TEB30A and the TEB30A doped with thulium oxides (Gd_2O_3, Dy_2O_3, Nd_2O_3, Y_2O_3, and Sm_2O_3). It is clearly seen that the behaviors of the TEB30A doped with thulium oxides differ significantly from that of the neat liquid crystal, while the strong influence of magnetic nanoparticles is immediately noticeable.

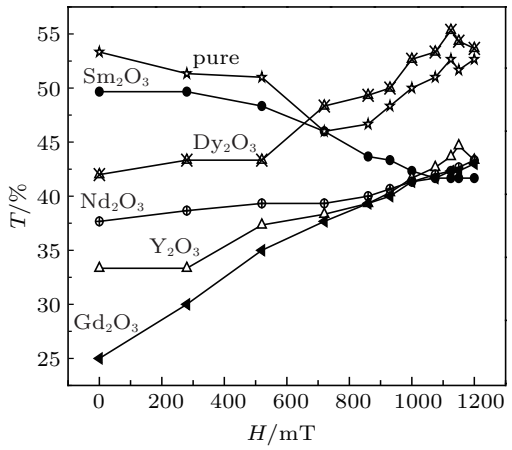


Fig. 2. Curves of transmission T of samples versus the applied magnetic field H.

In the case of the liquid crystals doped with the magnetic nanoparticles, the magnetic moments of the magnetic nanoparticles are oriented along the magnetic field direction, and the liquid crystal molecules anchored at the magnetic nanoparticle surfaces should follow their movements.[15] Therefore, covering the thulium oxide nanoparticles with the TEB30A nematic liquid crystal leads to orientational coupling between the magnetic moment and the local director $\boldsymbol{n}$, and causes the TEB30A liquid crystal matrix to deform. The structural transitions of the TEB30A depend on the magnetic intensity of the thulium oxide nanoparticles and the external magnetic field.

The relationship among the distortion amplitude l of the director $\boldsymbol{n}$ and the threshold H_c and the magnetic moment $\boldsymbol{\mu}$ may be described by the following equation[4]

$$H_c = \frac{kl}{\mu}, \tag{1}$$

where k is the average elastic constant of the nematic liquid crystal.

Equation (1) shows that the magnetic moment μ is larger and the threshold H_c is smaller in a certain distortion l of the director $\boldsymbol{n}$. Therefore, the threshold field H_c of the neat liquid crystal must be larger than that of the liquid crystal doped with thulium oxide nanoparticles. Figure 2 shows that the threshold field H_c of the neat TEB30A is about 720 mT, while the threshold field H_c of the TEB30A doped with thulium oxide nanoparticles is significantly lower than 720 mT. Meanwhile, figure 2 also shows that in the pure TEB30A when the magnetic field is below 720 mT, the structural transition does not appear, but the magneto–optical effect of the pure TEB30A still exists, for example, the transmittance of the pure TEB30A decreases from 53.33% to 46% with the increase of magnetic field. And the deformation occurs when the magnetic field is above 720 mT.

Both of magneto–optical characteristics and threshold field H_c are significantly different among the samples of the TEB30A nematic liquid crystal doped with different thulium oxide nanoparticles (Fig. 2). Accordingly, we discuss the influence of the magnetic moment of thulium oxide nanoparticles and the type of anchoring between the liquid crystal molecule and the particle surface on the optical properties of the TEB30A nematic liquid crystal.

The magnetic moment vector can be expressed as[17]

$$\boldsymbol{\mu} = -g\left(\frac{e}{2m}\right)\boldsymbol{J}, \tag{2}$$

where $\boldsymbol{J} = \boldsymbol{L} \pm \boldsymbol{S}$ is the total angular momentum vector, $\boldsymbol{L}$ is the orbital angular momentum vector, $\boldsymbol{S}$ is the spin angular momentum vector, and g is Land factor.

The magnetic moment modulus is given by

$$\mu = g\sqrt{J(J+1)}\mu_B, \tag{3}$$

where J is the total quantum number, and μ_B is the Bohr magneton.

Land factor g for trivalent thulium ions is given by

$$g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}, \tag{4}$$

where S is the spin quantum number, and L is the orbital angular momentum quantum number.

The Y^{3+} ion belongs to the transition element, and the orbital angular moment of material consisting of the transition

elements is frozen. Therefore, the magnetic moment of the Y_2O_3 thulium oxide is given by

$$\mu = 2\sqrt{S(S+1)}\mu_B. \quad (5)$$

Since the sum of the magnetic moments is zero for the full electronic shell, we only consider the contribution of the outer electrons to the total magnetic moments.[17] The magnetic moments of the thulium oxides can be shown in Table 1.

Table 1. Magnetic moments of thulium oxides.

Thulium oxides	L	S	J	μ/μ_B
Gd_2O_3	6	3/2	9/2	7.937254
Dy_2O_3	5	5/2	5/2	3.944043
Nd_2O_3	0	7/2	7/2	3.618137
Y_2O_3	0	1/2	1/2	1.732051
Sm_2O_3	5	5/2	15/2	0.084516

Table 1 shows that the magnetic moment of Gd_2O_3 nanoparticles is largest. Thus, as can be seen from Eq. (1), with the low field in the TEB30A/Gd_2O_3, it should be possible to align the grains completely. We have seen in particular that when the magnetic field increases from 0 mT to 280 mT, the sample transmittance obviously rises from 25% to 30%. When $H = 1200$ mT, its transmittance increases to 43%. This shows that the liquid crystal molecules are strongly anchored at the Gd_2O_3 particle surface, and the anchoring orientation $\boldsymbol{n}$ is perpendicular to the magnetic moment $\boldsymbol{\mu}$ of the Gd_2O_3 nanoparticles. So the sample responds to the applied magnetic field sensitively, and the critical magnetic field is significantly reduced, far below 300 mT.

As can be seen from Table 1, the magnetic moment of Dy_2O_3 nanoparticles is 3.944043 μ_B. It is the second largest. From Eq. (1), the threshold field H_c of the TEB30A/Dy_2O_3 is larger than that of the TEB30A/Gd_2O_3. Figure 2 shows that there are no magneto–optical characteristics in the TEB30A/Dy_2O_3 when the external magnetic field H is below 520 mT, but the transmittance significantly increases from 43.33% to 53.67% when H increases above 520 mT. It is indicated that the structural transition occurs above 520 mT in the TEB30A/Dy_2O_3. It is also shown that the liquid crystal molecules are strongly anchored at the Dy_2O_3 nanoparticle surfaces and the anchoring orientation $\boldsymbol{n}$ is perpendicular to the magnetic moment $\boldsymbol{\mu}$ of the Dy_2O_3 nanoparticles. Therefore, if the Dy_2O_3 nanoparticles rotate materially, the threshold field H_c must be above 520 mT. The value is more than the magnetic field H_c of the TEB30A/Gd_2O_3.

The magnetic moment of Nd_2O_3 nanoparticles is $3.618137\mu_B$. Based on Eq. (1), the threshold field H_c of the TEB30A/Nd_2O_3 is larger than that of the TEB30A/Dy_2O_3. Figure 2 shows that the threshold field H_c is below 720 mT. Compared with the neat TEB30A, when the magnetic field H is below 720 mT, the TEB30A/Nd_2O_3 has hardly any magneto–optical characteristics. And when H is above 720 mT, the TEB30A/Nd_2O_3 transmittance slightly increases from 39.33% up to 43.33%, while the neat TEB30A transmittance from 46% up to 52.67%. It is indicated that the liquid crystal molecules in the TEB30A/Nd_2O_3 are strongly anchored at the Nd_2O_3 nanoparticle surfaces, and the director $\boldsymbol{n}$ is inclined to the magnetic moment $\boldsymbol{\mu}$, and the angle between the director $\boldsymbol{n}$ and the magnetic moment $\boldsymbol{\mu}$ is very small.

The magnetic moment of Y_2O_3 nanoparticles is 1.732051 μ_B. Seeing Eq. (1), the threshold field H_c of the TEB30A/Y_2O_3 should be very large. But the result shows that the threshold H_c is only about 280 mT, and the transmittance obviously increases from 33.33% to 43.33% in a range from 280 mT to 1200 mT (Fig. 2). The theoretical value is inconsistent with the experimental result. There must be other factors contributing to the magnetic moment. It is suggested that the liquid crystal molecules are strongly anchored at the Y_2O_3 nanoparticle surfaces, and the anchoring orientation $\boldsymbol{n}$ is perpendicular to the magnetic moment $\boldsymbol{\mu}$ of the Y_2O_3 nanoparticles. So the TEB30A/Y_2O_3 responds to the applied magnetic field sensitively, and the critical magnetic field H_c is significantly reduced to less than 300 mT.

The magnetic moment of Sm_2O_3 nanoparticles is 0.084516. It is very small. From Eq. (1), the threshold field of the TEB30A/Sm_2O_3 is very large. Figure 2 shows that there is a significant magneto–optical effect rather than structural transition in the TEB30A/Sm_2O_3 in the whole range of magnetic field. For example, the transmittance obviously decreases from 49.67% to 41.67% with the increase of magnetic field. It is shown that the liquid crystal molecules are anchored at the Sm_2O_3 particle surfaces, and the anchoring orientation $\boldsymbol{n}$ is parallel to the magnetic moment $\boldsymbol{\mu}$ of the Sm_2O_3 nanoparticles. Therefore, the structural transition in the TEB30A/Sm_2O_3 could take place only when the threshold H_c of TEB30A/Sm_2O_3 is above 1200 mT.

The aim of this experiment is to confirm that thulium oxide nanoparticles can modulate the magnetic optical properties of the TEB30A. Owing to the presence of the bonded magnetic additives of the thulium oxides, a weak magnetic field can orient TEB30A/X_2O_3 (X denotes trivalent thulium ions) particles into its direction.

4. Conclusion

In this paper, it is found that in order to improve the magneto–optical properties of the TEB30A, the TEB30A liquid crystal should be doped with the magnetic nanoparticles. When the TEB30A liquid crystals doped with different thulium oxides expose to an external magnetic field, they can present different novel properties. The results show that these properties depend on the magnetic moments of these thulium oxide nanoparticles and the type of anchoring between the

TEB30A molecule and the thulium oxide particle surface. One of the aims of future work is to study the composite systems described here under the crossed polarizers, without and with magnetic field applied. It is also planned to characterize the anisotropic electrical properties by creating thin films with the oriented thulium oxide nanoparticles or embedding them in polymer matrices to form anisotropic nanocomposites.

References

[1] Kam N W S, O'Connell M and Wisdom J A 2005 *Proc. Natl. Acad. Sci. USA* **102** 11600-5
[2] Bradley K, Gabriel J P and Gruner G 2003 *Nano Lett.* **3** 1353
[3] Kuang Z, Kim S N and Crookes-Goodson W J 2010 *Nano.* **4** 452
[4] Brochard F and de Gennes P G 1970 *J. Phys.* **31** 691
[5] Kopčanský P 2008 *Phys. Rev. E* **78** 011702
[6] Kopčanský P, Koneracká M and Timko M 2006 *Phys. Status Solidi B* **243** 317
[7] Liu Y J, Xuan L and Hu L F 2005 *Acta Opt. Sin.* **25** 1682 (in Chinese)
[8] Ren G J, Yao J Q and Wang P 2007 *Acta Phys. Sin.* **56** 994 (in Chinese)
[9] Petriashvili G, Matranga M A and De Santo M P 2009 *Opt. Express* **17** 4553
[10] Zyryanov V Y, Myslivets S A and Gunyakov V A 2010 *Opt. Express* **18** 1283
[11] Podoliak N, Buchnev O, D'Alessandro G, Kaczmarek M and Sluckin T J 2010 *Phys. Rev. E* **82** 030701
[12] Challa P K, Curtiss O, Williams J C, Twieg R, Toth J, McGill S, Jákli A, Gleeson J T and Sprunt S N 2012 *Phys. Rev. E* **86** 011708
[13] Zhou S, Nastishin Y A and Omelchenko M M 2012 *Phys. Rev. Lett.* **109** 037801
[14] Francescangeli O, Vita F and Fauth F 2011 *Phys. Rev. Lett.* **107** 207801
[15] Mitróová Z, Tomašovicvá N L and Timko M 2011 *New J. Chem.* **35** 1260
[16] Zakhlevnykh A N and Sosnin P A 1995 *J. Magn. Magn. Mater.* **146** 103
[17] Liu G H 2005 *Thulium Materials and Application Technology* (Beijing: Chemical Industry Press) pp. 20–35 (in Chinese)