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Magneto-optic studies of rare earth containing sodium silicate glasses and semiconductor quantum dots in glass composites: Nonlinear effects

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ABSTRACT

Faraday rotation has been measured at room temperature and at magnetic field strengths up to 2.57 T for II–VI type semi-conductor nano-crystals (CdS and CdSe) in the form of quantum dots (QDs) and for rare earth containing sodium silicate glasses. The graph of Faraday rotation versus field strength for all quantum dots showed "kinks" (abrupt slope changes) which is evidence for a non-linear Faraday effect. Given the inverse linearity seen in dot size versus magnetic field, possible causes such as exciton coulomb interactions were considered as a mechanism for the enhanced Faraday rotation. The rare earth containing glasses also showed a non-linearity in the Faraday rotation as a function of magnetic field strength. However, a single crystal NaCl sample exhibited no kinks up to 2.57 T. Various mechanisms will be put forth and evaluated as to the feasibility of using these processes to explain the observed effects. We consider Landau levels, resonance effects, shape and piezo-electric effects, electron-spin correlation for the quantum dot composites; and intermediate range order (IRO) for the rare earth containing glass matrix itself and try to interpret how each of these mechanisms may or may not have an effect on the Faraday rotation behavior.

1. Introduction

Considerable interest always existed in the Faraday effect for semiconductors, metals and glasses, especially semiconductors in the form of quantum dots embedded in a glass matrix, for the information that such measurements may yield about electronic states, effective masses and for the information it may provide in understanding further the theory of solids in a magnetic field. Refs. [1–8] represent a few of the many papers that are concerned with semiconductors.

The step in proceeding from bulk materials to nanocrystals with respect to Faraday rotation measurement enhancement has been done by several authors [9–14]. Three dimensionally confined diluted magnetic semiconductor clusters of nano-crystalline size were synthesized inside a glass matrix. Nikitin et Al. [15] prepared $Cd_{1-x}Mn_xTe$ Nanocrystals embedded in an SiO_2 matrix and a study of the Faraday effect in this semi-magnetic semiconductor nano-crystal has revealed large enhancements of this effect, with respect to the bulk crystal. Faraday effect enhancement manifesting itself in strong nonlinear Faraday rotation, has been observed [16, 17].

We have studied paramagnetic and diamagnetic materials by Faraday rotation measurements [18]. In our work with paramagnetic rare earth ions in glasses, we find that Terbium oxide provides the strongest Faraday rotation, followed by Dysprosium oxide and Praseodymium oxide. The particular rare earth ion and its concentration determine the magnitude of the Faraday rotation, while the host glass is relatively unimportant. For applications requiring large Faraday rotation (large Verdet constants) dilute magnetic semiconductors become rather interesting. Faraday rotation studies on nano-crystalline CdS, CdSe and CdTe–glass composites have also been carried out and their Verdet constants are at least one order of magnitude larger than SiO_2 glass. With strong effects on the Faraday rotation being dependent on the individual quantum dot size and their distribution [19].

2. Theoretical background

Faraday rotation occurs when plane polarized light is passed through a sample parallel to the direction of an applied magnetic field. The linearly polarized light is a superposition of two circular polarizations, one rotating clockwise and the other counterclockwise when viewed along the direction of propagation. The application of a magnetic field removes the degeneracy of the resonant frequencies for the two circular polarizations. This results in a difference between their indices of refraction. As a result, one circular polarization will more rapidly pass through the material. When both polarizations emerge from the far end of the sample the recombined plane wave will have its plane of polarization rotated with respect to that of the incident light. More detailed explanations of Faraday rotation are given in the literature [20–29].

The classic equation for Faraday rotation is $\Theta = V\,l\,B$, where l is the length of the sample and B is the strength of the magnetic field. The constant of proportionality, V, is called the Verdet constant. For

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paramagnetic material the Verdet constant is given by the equation [30]

$$V_{para} = 4\pi^2\omega^2 \frac{\chi_m}{g\beta ch} \sum_{ij} \frac{C_{ij}}{\left(\omega^2 - \omega^2_{ij}\right)}$$

where g is the Lande` factor; β is the Bohr magneton; c the speed of light; h Planck's constant and ω the angular frequency of the light. The terms C_{ij} and ω_{ij} are measures of the transition probability and energy splitting between the ground state and excited states, respectively. The term χ_m is the d.c. magnetic susceptibility of the sample which is given by the Curie–Weiss law. For diamagnetic materials the frequency dependence of the Verdet constant derived from a quantum mechanical expression has the form [31]

$$V_{dia} = 4\ \pi\ N\omega^2 \sum_{ij} \frac{C_{ij}}{\left(\omega^2 - \omega^2_{ij}\right)^2}$$

where C_{ij} is a function of the transition moments between the ground state and excited states. ω is the light frequency; ω_{ij} is the frequency difference of the ground and excited states; and N is the number of atoms per unit volume. The Verdet constant of diamagnetic materials is usually temperature independent.

For the non-linear Faraday effects Yu and Osborn [32] extended the theory of the Faraday effect to treat non-linear terms in the electric field. A Verdet constant proportional to the light intensity was derived. Here, using a two energy level, the rotation of a non-uniform laser beam would be dependent on the beam intensity profile. Perlin [33] formulated the theory for non-linear optical polarization effects in quantum dot materials. He calculated the amplitude and dispersion relation of the cubic susceptibility tensor components and their combinations responsible for the Kerr and Faraday optical effects. It is shown that the susceptibilities increase smoothly in amplitude below the two-photon absorption threshold while remaining negative. Above the threshold, the susceptibilities exhibit sharp maxima associated with two-photon resonances. It is suggested to use the non-linear optical polarization effects in these materials to control high intensity light pulses.

3. Experimental techniques

A variety of samples were studied, in which glasses doped with rare earths were evaluated for Faraday rotation. These samples contained 33% rare-earth oxides in a sodium silicate glass. Optically these glasses all exhibited low Rayleigh scattering [34].

The quantum dot samples were prepared, using Schott-RG695 glass, which was bleached (struck) first, at 1100 °C and cooled to room temperature. The "striking" removes any nano-crystallites from the glass. Then these glasses are heat treated for varying lengths of time to obtain different sizes for the quantum dots. With sufficient time larger diameter dots grow at the expense of smaller dots. This occurs as smaller dots dissolve back into the glass matrix and larger dots grow at their expense. This base glass was a borosilicate glass with the primary constituents being SiO_2, B_2O_3 and minor constituents of Na_2O, CaO, K_2O and ZnO, all in the approximate ratios of 75:13.6:6.4:4.5:0.4, respectively. This base glass was doped with Cd and S, Se, or Te. Samples heat treated for longer periods of time had a higher degree of homogeneity than did the samples treated at higher temperatures for shorter periods of time, as determined from their absorption spectra peaks. More homogeneous CdSe samples were of greater sphericity, and varied in size approximately 7%, as opposed to 30% for the less homogeneous samples [35]. Sizes were measured by a technique involving low frequency Raman scattering and the analysis of the absorption spectra for various samples [36].

For the Magneto-optic studies the samples were placed in the gap of a "Magnion" electromagnet (NMR magnet with high field homogeneity, 1 part in 10^5) with field self-regulation and a maximum field up to 2.57 T. The light source consisted of either a helium–neon laser, at 633 nm (50 mw) or an Argon-ion laser at 488 nm (500 mw) passed through the long axis of the samples with the aid of a pair of mirrors placed at 45º from the angle of the incident beam to allow for the laser to be parallel with the applied magnetic field. The laser beam was collimated with two pinholes of the same diameter to assure that the light beam was always contained within the thinnest sample. The entire system was calibrated by using a standard sample of Corning 8463 glass and SiO_2 glass (homosil). A glan-laser prism was placed before and after the sample as a polarizer and analyzer, respectively. The beam intensity was read with a photo-detector and electrometer. The analyzer was set to 45º from the null point.

4. Results

A set of Faraday rotation measurements was done on samples consisting of CdS and CdSe quantum dots contained in a borosilicate–glass matrix. See Figs. 1, 2 and 3 where a striking effect is obvious that the Faraday optical rotation is not linear as a function of the applied field for all three figures. The onset of this inflection or "kink" in every case occurs at different applied field values and the sample with the smallest quantum dot size has this inflection at the lowest value of the external applied magnetic field. Note in the figures that the samples with the shortest heat treatment times will be those of the smallest quantum dot diameter. In Fig. 3, measurements of Faraday rotation versus applied field are also shown for a NBS-710 glass sample and the "kink" is absent up to the highest field value attained and its Verdet constant is considerably lower than any of the CdS or CdSe containing glasses. Another effect to be noted upon comparing the results from Figs. 1 and 2, both are CdSe quantum dots, but CdSe containing samples in Fig. 1 have a greater size variation (~30%) compared to CdSe samples in Fig. 2 which are of greater homogeneity (~7%) and have greater sphericity. The interesting effect here also shows that homogeneity of the particle size and sphericity (steric effects) affect the magnitude of the Faraday rotation. Comparing the magnitude of the Faraday rotation, for the smallest quantum dot size of the samples given in Figs. 1 and 2, there is about a seven-fold increase for the smallest quantum dot diameter with the higher homogeneity sample having the greater Faraday rotation. The samples heat treated for times longer than 8 h demonstrated little if any "kinks". Hence, optical rotation of homogeneous CdSe QDs demonstrates increased Verdet constants with increasing confinement

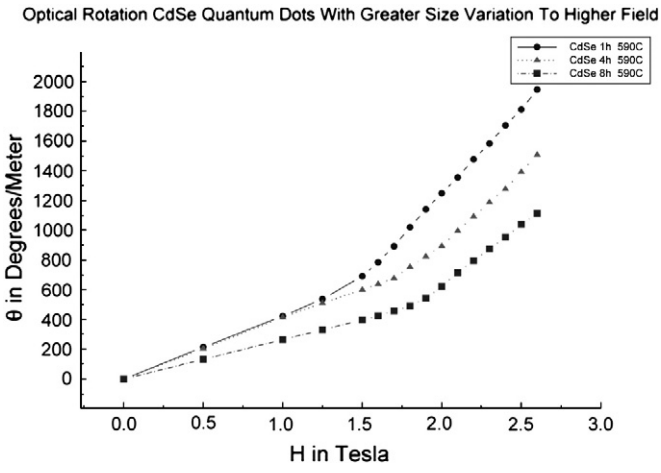

Fig. 1. Optical rotation of CdSe quantum dots with less homogeneity and greater size dispersion (~30%). (Estimated error from averaging a number of data runs is ±50 °/T-Meter).