Concentration Dependent Thermal Diffusivity of Mn$_3$O$_4$ Nanoparticles Using Dual Beam Thermal Lens Technique

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Abstract. Concentration dependent thermal diffusivity measurement of Mn$_3$O$_4$ nanoparticles dispersed in ethylene glycol has been studied using dual beam mode mismatched thermal lens technique. The results reveal that the thermal diffusivity of the nanofluid depends on the concentration of Mn$_3$O$_4$ nanoparticles. The thermal diffusivity values were found to be greater than that of ethylene glycol for all sample concentrations. The samples with this high value of thermal diffusivity can be used as coolant for thermoelectric devices. The non-radiative decay process induced by defect states in the material, size and shape of nanoparticles etc. are the factors that control the thermal diffusivity of the nanoparticles dispersed in a solvent. The variation in thermal diffusivity of the Mn$_3$O$_4$ nanofluid is explained on the basis of changes in absorption and emission spectra with sample concentration. It is found that thermal diffusivity is inversely related with the emission intensity.

Keywords: Mn$_3$O$_4$ nanoparticles; thermal diffusivity; coolant.

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1 Introduction

Metal oxide nanoparticles are extremely exciting semiconducting materials which has wide range of application as energy storage material [1], semiconductor [2], insulator [3], catalyst [4], etc. Among the various metal oxide nanoparticles, Mn$_3$O$_4$ (trimanganese tetraoxide, hausmannite) is one of the most stable manganese oxides having spinel structure and special electronic configuration [5]. Compared to other forms of manganese oxide crystals, Mn$_3$O$_4$ has the advantage of low cost, non-toxicity and environmentally friendliness which find applications in various fields like biosensor, water treatment, cancer treatment, drug delivery, etc. [6–8].

The suitability of a material in various thermoelectric applications such as coolant, thermal insulators is determined by the thermal conductivity of the material. The various models proposed for the determination of thermal conductivity are Maxwell model, Hamilton- Crosser model, Yu-Choi model, Xue model, Strauss- Pober model, etc. [9–13]. In many of the proposed models, the experimental values are seen to be much deviated from the theoretical values. The measurement of thermal diffusivity ($D$) helps to determine thermal conductivity ($k$) as they are related by $D = \frac{k}{\rho C_p}$, where $\rho$ is the fluid density and $C_p$ is the specific heat capacity [14]. Thermal diffusivity is the ability of a material to respond to change in thermal environment. Material with large thermal diffusivity takes less time to reach a new equilibrium condition whereas those with smaller thermal diffusivity will react slowly to change in temperature. The concentration dependent thermal diffusivity behaviour of materials is particularly important in the nanoscale region as the large surface area of the nanoparticles particularly enhances the heat transfer capacity. In addition, these particles do not settle in fluid as compared to micro sized particles.

Several techniques such as laser flash, hot-wire, photoacoustic, thermal-wave cavity, temperature oscillation, etc. have been developed to measure the thermal diffusivity of materials [15–19]. The laser flash technique is a standard technique for the determination of thermal diffusivity of solid samples. However, the necessity of accurate sample geometric requirements is the main limitation of this technique [15]. The need for precise recording of the temperature rise of the wire is the limiting factor of hot wire method [16]. Sufficient photoacoustic signal can be obtained in photoacoustic
method only if the thickness of the sample is of the order of few tenth of millimetres [17]. In thermal wave cavity technique, measurement of thermal wavelength should be done at low modulation frequencies. Sensor sensitivity, noise, etc. limit the use of lower modulation frequencies in this technique [18]. The thermocouples should be located in isothermal planes in temperature oscillation technique to minimize the measurement uncertainty [19]. Compared to the above mentioned methods for thermal diffusivity measurement, thermal lens (TL) technique is an accurate and sensitive method for thermal diffusivity measurement. The determination of thermal nonlinearity of the Mn$_3$O$_4$ nanoparticles using dual beam thermal lens technique.

2 Theory

When laser beam passes through a sample, the atoms get excited to higher energy levels from where they come back to lower energy levels by two ways. One way is by emitting light of higher wavelength than the absorbed light and is called radiative relaxation. Other way is to dissipate the absorbed energy as heat called the non-radiative relaxation. The non-radiative relaxation process causes heating of the material. If the beam is Gaussian, maximum heating will be along the beam axis resulting in temperature and refractive index variation in the sample. The refractive index gradient is produced perpendicular to the axis of the beam depending on temperature gradient. The expansion of liquids on heating causes the refractive index gradient to be negative resulting in the formation of concave lens in the sample [26].

In thermal lens technique, the generated lensing effect by the pump beam is analysed by the passage of another beam called probe beam through the sample. The variation in the intensity of probe beam as a function of time is given by Ref. [27]:

\[
I(t) = I_0 \cdot \left[1 - \frac{\theta}{2} \tan^{-1} \left(\frac{2m^2}{(1+2m^2+V^2)(1+1+2m+V^2)}\right)\right]^2.
\]

\[
m = \left(\frac{\omega_{1p}}{\omega_e}\right)^2,
\]

\[
V = V' + \frac{Z_c}{Z_2}(V'^2 + 1),
\]

\[
V' = \frac{Z_1}{Z_c},
\]

\[
Z_c = \frac{\pi \omega_{1p}^2}{\lambda p},
\]

\[
\omega_{1p} = \omega_0 p^2(1 + V'^2),
\]

\[
\omega_e = \frac{\lambda_z}{D}.
\]

where $\omega_e$ and $\omega_{op}$ are the beam waist of the pump and probe beam respectively, $\omega_{1p}$ is the radius of probe beam in the sample. $Z_1, Z_2, Z_c$ are the distance between beam waist of the pump and probe beam, distance of the detector from the sample and rayleigh range of the probe beam respectively. $f$ is the focal length of the lens, and $D$ is the spot size of the laser beam.

The parameters $\theta$ and $t_c$ can be estimated by theoretically fitting Eq. (1) to the experimental data. $t_c$ is the characteristic thermal time constant associated with thermal diffusion in the sample. From the value of $t_c$, thermal diffusivity $D$ can be calculated using

\[
D = \frac{\omega_e^2}{4t_c}
\]
3 Preparation of Mn₃O₄ Nanoparticles

Potassium permanganate (KMnO₄) and L-cysteine are the precursors used for the preparation of Mn₃O₄ nanoparticles. 0.5 gm of KMnO₄ was dissolved in 60 mL of distilled water under constant stirring and 0.2 gm of L-cysteine was introduced into the above solution. After stirring at 60 ºC for 1 h, a brown precipitate was formed. The precipitate was collected and washed several times with distilled water in order to remove excess impurities. Finally, the residue is dried at 70 ºC for 12 h in a hot air oven [28].

4 Experimentation

The schematic diagram of the thermal lens setup is shown in Fig. 1. The sample is pumped using a Diode pumped Solid State laser (VORTRAN Stradus TM 405) operating at 403 nm with a maximum power of 100 mW. The detection of thermal lens signal is achieved by making use of a 4 mW CW He-Ne laser (JDS Uniphase) at 632.8 nm wavelength. Both pump and probe beams are aligned in a collinear configuration. The chopping frequency is fixed at 3 Hz for all measurements. As the unmodulated probe beam passes through the irradiated region, a diverging lens effect and thermal blooming occurs. The change in probe beam intensity is measured using a photo detector-DSO system. The morphology of Mn₃O₄ nanoparticles was investigated using TEM.

The structure of Mn₃O₄ nanoparticles was investigated using Bruker AXS D8 Advances X-ray diffraction (XRD) technique using Cu Kα radiation (λ = 1.54056 Å). The morphology of the nanoparticles was analysed using JEOL JEM-2100 transmission electron microscopy (TEM). Absorption and emission spectra were measured using JASCO V-770UV-vis-NIR spectrophotometer and Carry Eclipse Varian spectrophotometer respectively.

5 Results and Discussion

Fig. 2 shows the XRD pattern of the synthesized Mn₃O₄ nanoparticles. The formation of tetragonal Mn₃O₄ nanoparticles (hausmannite) was confirmed by indexing diffraction planes (101), (112), (200), (103), (211), (004), (220), (204), (105), (312), (303), (321), (224), (400), (305) and (413) (JCPDS file number 01-080-0382). No additional peaks of other phases had been detected in the XRD, indicating high purity and good crystallinity of Mn₃O₄ nanoparticles. The morphology of the synthesized nanoparticles analysed using TEM is shown in Fig. 3 which indicates the formation of Mn₃O₄ nanorods.

The optical absorption spectrum of Mn₃O₄ dispersed in ethylene glycol is shown in Fig. 4(a) and the emission spectrum is shown in Fig. 4(b). The electronic absorption spectrum of Mn₃O₄ is broad. Defects in the crystal structure create defect states to which electrons in the valance band can be excited to the conduction band [29]. The emissions peaks in the visible light region are due to the electronic transitions from the defects states in the crystal.

The calculated values of thermal diffusivity and the corresponding tc for all the samples are tabulated in Table 1.

Table 1 Thermal diffusivity of samples for 403 nm excitation.

<table>
<thead>
<tr>
<th>Sample concentration, (mg/ml)</th>
<th>tc, (s)</th>
<th>Dc, (×10⁻⁷ m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>0.0046</td>
<td>7.88</td>
</tr>
<tr>
<td>0.06</td>
<td>0.0113</td>
<td>3.24</td>
</tr>
<tr>
<td>0.09</td>
<td>0.0156</td>
<td>2.37</td>
</tr>
<tr>
<td>0.12</td>
<td>0.0217</td>
<td>1.70</td>
</tr>
<tr>
<td>0.18</td>
<td>0.0042</td>
<td>8.77</td>
</tr>
<tr>
<td>0.21</td>
<td>0.0022</td>
<td>16.5</td>
</tr>
</tbody>
</table>

Fig. 3 TEM images of the synthesized Mn₃O₄ nanoparticles with scale bars: (a) 20 nm, (b) 10 nm, (c) 5 nm, and (d) 2 nm.
Thermal diffusivity as a function of sample concentration is shown in Fig. 5. The thermal diffusivity decreases with increase in sample concentration and reaches a minimum value at 0.12 mg/ml. After the optimum concentration, thermal diffusivity increases with increase in sample concentration. For all concentrations, the thermal diffusivity of nanofluid is higher than that of base fluid. The reported value of thermal diffusivity of ethylene glycol is $0.938 \times 10^{-7} \text{ m}^2/\text{s}$ [30–32]. Thus the addition of Mn$_3$O$_4$ nanoparticles significantly enhances the thermal diffusivity of base fluid and it can be varied by adjusting the concentration of nanoparticles. The thermal response of the sample with concentration 0.03 mg/ml, 0.09 mg/ml, and 0.12 mg/ml is shown in Fig. 6. The dotted curve shows the experimental data and solid curve shows the experimental fit.

The incorporation of nanoparticles into a liquid results in the formation of nanolayers which increases the phonon scattering and thereby enhancing the thermal diffusivity. The increase in concentration increases the number of particles per unit volume thereby increasing the interaction between the particles and reducing the heat exchange between particles and surrounding medium. This causes the thermal diffusivity to decrease with increase in sample concentration [33–35]. The reduction in factors such as dispersion stability, Brownian velocity, convection velocity, etc. are the other factors contributing to the decrease in thermal diffusivity with increase sample concentration [36].

Thermal diffusivity is inversely related to specific heat capacity. The specific heat capacity of nanofluid is lower than that of base fluid as solids possesses lower specific heat capacity as compared to fluids [37]. Specific heat capacity is inversely related to sample concentration. The enhancement in thermal conductivity and reduction in specific heat capacity contribute to the enhancement of thermal diffusivity with sample concentration [38]. All the above mentioned factors dominate the factors decreasing the thermal diffusivity of the sample and cause the thermal diffusivity to increase after the optimum concentration.

Fig. 4 (a) Absorption spectra and (b) emission spectra of the Mn$_3$O$_4$ nanoparticles.

Fig. 5 Thermal diffusivity of Mn$_3$O$_4$ nanofluid with various concentrations.

Fig. 6 Thermal response of Mn$_3$O$_4$ nanofluid.
Fig. 7 Thermal diffusivity and PL intensity as a function of concentration.

The variation of thermal diffusivity and emission peak around 430 nm in the emission spectrum with sample concentration is shown in Fig. 7. It is a general fact that thermal diffusivity decreases with increase in emission intensity. This is due to the release of most of the absorbed energy in the form of radiative emission which reduces the non-radiative relaxation [36, 39]. Even though the dominant emission peak in the emission spectrum is around 530 nm, the relationship between thermal diffusivity and emission intensity is followed in the emission peak around 430 nm, the peak close to the excitation wavelength.

Thermophoretic motion, Brownian motion and osmophoretic motion are the most important mechanisms that affect the thermal conductivity of nanofluids [40]. The osmophoretic movement caused by the concentration difference is the main factor that controls the thermal diffusivity of samples at lower concentrations. Here, a decrease in the thermal diffusivity below 0.12 mg/ml results mainly from osmophoretic motion. After reaching an equilibrium state, Brownian motion plays an important role and increases the thermal diffusivity above 0.12 mg/ml [41].

6 Conclusion
The thermal diffusivity of Mn₃O₄ nanoparticles is measured using dual beam mode mismatched thermal lens technique. The thermal diffusivity is found to decrease with increase in sample concentration up to an optimum concentration and again increases with sample concentration. The correlation between the concentration and thermal diffusivity reveals that samples with desired thermal diffusivity for various applications can be obtained by adjusting the nanoparticles concentration. The obtained thermal diffusivity is higher than the thermal diffusivity of base fluid for all concentration. So the prepared nanoparticles can be used as coolant for thermoelectric devices.

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Disclosures
The authors declare no conflict of interest.

References


