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Effect of Sample Preparation Route on the Thermal Diffusivity of Nd_2O_3 - A Laser Induced Photoacoustic Study

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Abstract

Knowledge of thermal and optical properties of rare earth oxides is important in the context of optoelectronic component and device development. The method of preparation of a sample has profound effect on its physical as well as chemical properties. In the present work Nd_2O_3 is prepared by two different methods such as oxalate and hydroxide methods. The thermal diffusivity of these differently Nd_2O_3 samples are determined by laser induced photoacoustic technique. The method is standardised by determining the thermal diffusivity of copper. The effect of method of preparation on thermal diffusivity of Nd_2O_3 is studied.

Keywords: Photoacoustics; Thermal diffusivity; Hydroxide method; Oxalate method

Introduction

The photoacoustic (PA) effect has been revived as a very useful technique for measuring the optical [1-7] and thermal [8-10] properties of materials because of its high sensitivity and non destructive nature. The basic principle of photoacoustic effect is that a sample illuminated by periodically modulated (chopped) light undergoes optical absorption and gets heated by nonradiative transitions. Heat which is periodically deposited in the sample is transferred to the coupling medium by thermal conduction and this causes pressure oscillations in the coupling medium at the modulation frequency. These pressure variations are detected by a microphone and constitute the photoacoustic signal. In this energy conversion process (optical to acoustical) the thermal properties of the sample play a significant role. Hence photoacoustic effect can be used for the study of thermal properties of solids such as thermal diffusivity, phase transition etc. By studying the chopping frequency dependence of the acoustic signal generated in the coupling gas at a fixed optical wavelength, the thermal diffusivity of the sample can be evaluated [9].

The method of preparation of a sample has profound effect on its physical as well as chemical properties. A material prepared by two different methods shows slightly different surface as well as chemical properties. Kuo et al have shown [10] by mirage effect that the thermal diffusivities of differently prepared specimens of SiC differ. In the present paper the effect of method of preparation on thermal diffusivity of Nd_2O_3 has been determined by photoacoustic technique.

Materials and Methods

In the present study Nd_2O_3 has been prepared by (1) hydroxide method and Oxalate method as described below.

Hydroxide Method

The sulphate solution of the sample (250ml) containing 0.5g of Nd_2O_3 is heated to boiling and 1:1 ammonium hydroxide solution is added drop wise with stirring until the precipitation is complete. It is then allowed to digest on a steam bath until the precipitate is flocculated and settled. The precipitate is then filtered on a whatman No.41 filter paper and washed with small portion of an aqueous solution containing 2g ammonium chloride and 10ml of concentrated ammonium hydroxide in 100ml until the precipitate is free from cl. The precipitate is then kept in an air oven at 100 °C overnight and is ignited in a china dish at 300 -400 °C for two hours.

Oxalate Method

The chloride solution of Nd (250ml) is heated to boiling and 60ml of 12% oxalic acid solution is added slowly with constant stirring and allowed to stand overnight. The precipitate is filtered on whatman No.42 filter paper and washed with 2% oxalic acid in 1:99

HCl. The precipitate is then kept in an air oven at 100 °C for one day and then ignited in a china dish at 850 – 900 °C to constant weight. The weights obtained represent rare earth oxide present.

Photoacoustic Study

In the single beam photoacoustic (PA) spectrometer assembled for the present investigation, the 488nm line of Argon ion laser (LiCONIX 5300) has been used as the pump source. To generate acoustic signal in the PA cell, the pump beam is modulated using an electromechanical chopper (SR 540). The acoustic signal generated in the coupling medium is detected by small, highly sensitive (100μV/Pa) microphone is kept close to the sample compartment and its output is processed by means of a lock in amplifier (EG & G Model 5208). Block diagram of the experimental setup is shown in Figure 1.

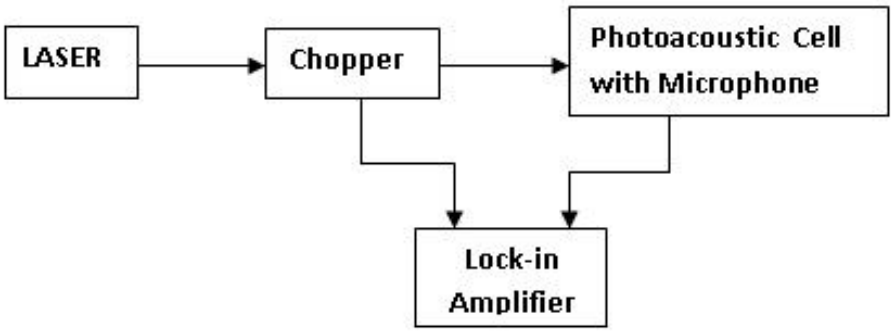
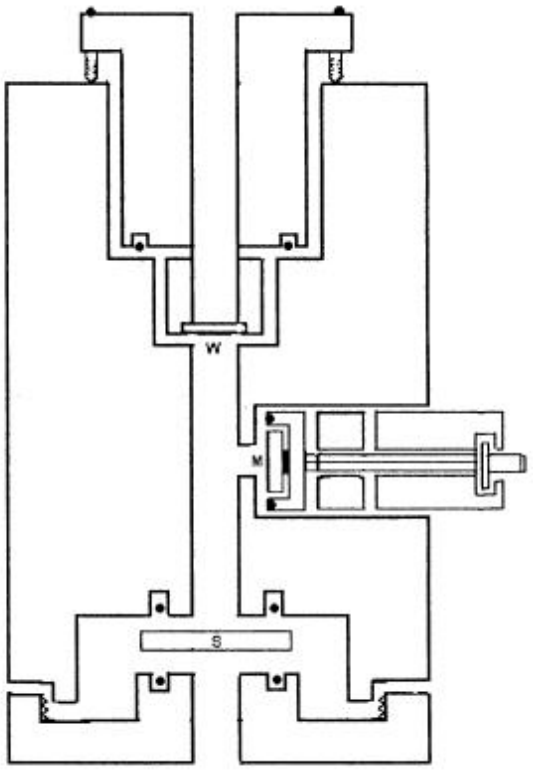


Figure 1: Single beam photoacoustic (PA) spectrometer

The PA cell is the most important part of any PA spectrometer. The description of the PA cell used for the room temperature measurement is given below. A small volume non-resonant cell for room temperature measurement is made out of aluminium is shown in Figure 2. The cell has axial bore of about 0.5 cm diameter. One side of the bore is closed by a glass window and to the other side the sample is placed and closed air tightly. The bore provided at the back side of the cell helps us to study the effects on rear side illumination. The acoustical isolation of the cell volume from outside is achieved by using 'O' rings on the window holders. The PA signal is detected using a microphone kept very close to the sample compartment in a separate port with provisions for electrical connections. A small size, high sensitive microphone has been used for the detection of the acoustic signal. The microphone output is fed to the lockin amplifier through a BNC connector.



M – Microphone; S – Sample; W – Quarts window
Figure 2: Cross sectional view of the Photoacoustic cell used

Thermal diffusivity can be evaluated from the chopping frequency dependence of the PA signal [9]. For a given sample thickness (l_s), one can have a transition from thermally thin regime to thermally thick regime by increasing the chopping frequency. The transition appears as a slope change at the characteristic frequency (f_c) in the log(amplitude) Vs log(frequency) plot. Knowing the actual thickness of the sample (l_s), the thermal diffusivity (α) can be calculated using the relation

$$\alpha = l_s^2 . f_c$$

To determine the thermal diffusivity, about 0.5g of the sample is pelletized under high pressure (6tons/cm^2). Keeping the sample in the PA cell the frequency dependence of the acoustic signal is studied. The variation of signal amplitude with frequency for copper (the sample used for standardization) is shown in Figure 3. Knowing the thickness (l_s) of the sample and characteristic frequency (f_c) from the log(amplitude) Vs log(frequency) plot, the thermal diffusivity can be calculated (Figure 4).

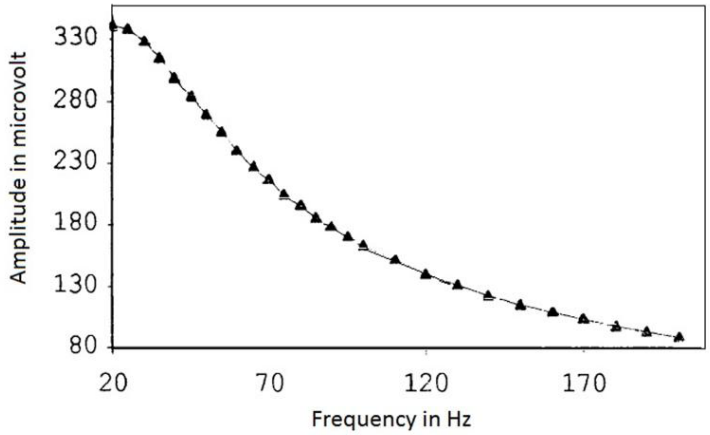


Figure 3: PA signal amplitude Vs Frequency plot for copper

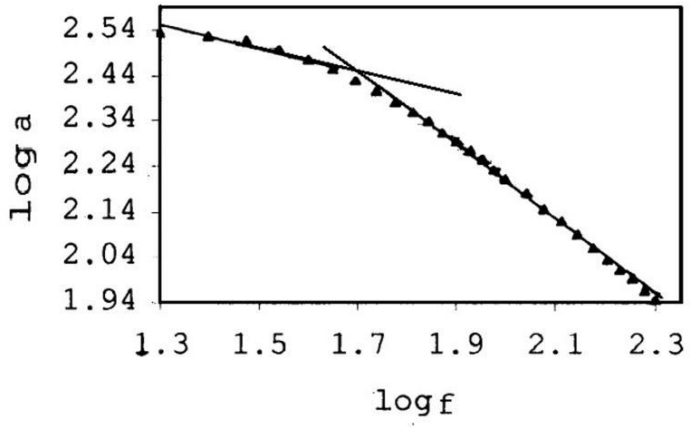


Figure 4: log(amplitude) Vs log(frequency) plot for copper

Result and Discussions

The thermal diffusivity of copper and aluminium were also determined to confirm the validity of the present experimental setup. The values obtained in the case of copper (α = 1.16 cm^2/s for l_s = 1.56 mm and f_c = 48.8 Hz) and aluminium (α = 0.979 cm^2/s for l_s = 1.28 mm and f_c = 59.8 Hz) agree with the reported values 1.16 and 0.98 cm^2/s respectively. The accuracy of the measurement depends on the determination of l_s and f_c. The values obtained are accurate up to third digit. The thermal diffusivities of pelletized samples of Nd_2O_3 prepared by oxalate method and hydroxide method are given in Table 2. The samples are then degassed at 500 °C. The thermal diffusivities are measured and are given in Table 2. The log(amplitude) Vs log(frequency) plot for Nd_2O_3 prepared by oxalate method is given in Figure 5. The difference in thermal diffusivity values may be attributed to the difference in the preparation method.

A search through literature reveals that oxides like Al_2O_3, Nd_2O_3 etc on exposure to water vapour (moist air) are terminated by a layer of hydroxyl groups at the surfaces [12,13]. The presence of hydroxyl groups at the surface has been shown by deuterium exchange and infrared (IR) spectroscopy and chemical methods [12-14]. The IR spectrum of the oxides show bands between 3300 cm^{-1} and 3800 cm^{-1}, typical of surface OH groups [15]. These surface hydroxyl groups get expelled as the sample is heated to higher temperature [16].

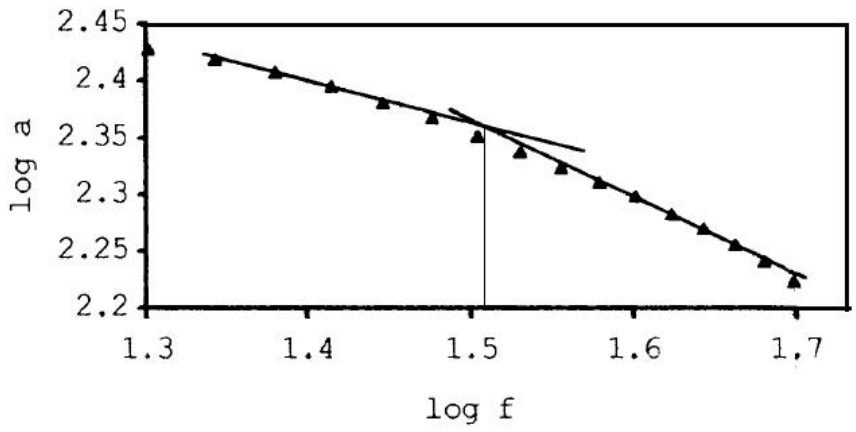


Figure 5: log(amplitude) Vs log(frequency) plot for copper

The IR spectrum of Nd_2O_3 prepared by the two methods is recorded. The transmittance values obtained from the spectrometer are given in Table 1. It shows more number of peaks between 3300 and 3800 cm^{-1} for the Nd_2O_3 prepared by oxalate method than the Nd_2O_3 prepared by hydroxide method. Peaks are observed at 3673.9, 3748.1 and 3819.5 cm^{-1} for the Nd_2O_3 prepared by hydroxide method and at 3606.4, 3612.1, 3671.9, 3676.8 and 3745.2 cm^{-1} for the Nd_2O_3 prepared by oxalate method. The increased number of peaks in the IR spectrum of Nd_2O_3 prepared by oxalate method is due to the greater number of surface hydroxyl groups. This may be due to the fact that method of preparation alters the surface properties.

Oxalate Method at 30 °C		Hydroxide Method at 30 °C	
Wave number (cm^{-1})	% Transmittance	Wave number (cm^{-1})	% Transmittance
3745.2	1.02	3668.7	6.86
3676.8	1.09	3852.3	6.8
3671.9	1.34	3819.5	6.97
3612.1	4.74	3748.1	7.33
3606.4	4.4	3673.9	6.96
2954.3	4.66	2854	1.2
2923.5	3.9	1699.5	11.91
2854	4.65	1652.2	9.94
1735.2	7.95	1575.1	7.56
1718.8	7.7	1568.3	7.09
1701.4	8.15	1563.5	7.03
1696.6	8.59	1557.7	5.45
1685	8.22	1553.8	5.78
1654.2	7.68	1549	5.3
1648.4	7.97	1538.4	3.44
1464.1	8.1	1532.6	3.46
1456.4	8.21	1520.1	2.56
1377.3	0.06	1516.2	2.75
1070.6	9.47	1505.6	2.14
673.2	0.35	1495	2.52
667.5	9.95	1436.2	2.3
443.7	3.94	1418.8	3.42
437.9	3.79	1081.2	9.55
430.2	3.51	816	8.61
418.6	1.89	726.3	5.37
		435	9.41
		420.5	8.4
		417.6	8.12

Table 1: IR spectral data for Nd_2O_3 prepared by oxalate method and hydroxide method

In the case of Υ- Al_2O_3, it has been reported that as the degassing temperature increases the thermal diffusivity decreases. The reason for which is attributed to the loss of surface OH groups [16].

Table 2 shows a decrease in thermal diffusivity with the increase of degassing temperature for both the samples. The variation in the thermal diffusivity is very small in comparison with that of Υ- Al_2O_3 [16]. This is due to the fact that the specific surface area and hence the number of surface hydroxyl groups is very much lower in Nd_2O_3 than that in Υ- Al_2O_3.

	Thermal diffusivity (cm^2/s)	
Preparation Method		
	At 30 °C	At 500 °C
Oxalate method	0.099 ± 0.001	0.095± 0.001
	(f_c=32.73 Hz)	(f_c=31.4 Hz)
Hydroxide method	0.119± 0.001	0.103± 0.001
	(f_c=39.34 Hz)	(f_c=34.05 Hz)

Table 2: Thermal diffusivity (α) of Nd_2O_3 (sample thickness l_s = 0.055 cm and the characteristic frequency f_c is given in the Table)

Conclusion

From the study it can be concluded that the surface hydroxyl groups play a role in the thermal diffusivity of Nd_2O_3 also. It is also found that that the same sample prepared in two different methods alters the number of surface hydroxyl groups and there by changes the thermal diffusivity. The values at 500 °C further confirm the above conclusion.

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