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ARTICLE in JOURNAL OF POLYMER SCIENCE PART B POLYMER PHYSICS · JANUARY 1997

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Photoacoustic Spectroscopic Studies of Ho^{3+} , Er^{3+} , and Sm^{3+} Doped Polyvinyl Alcohol Films

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SYNOPSIS

Photoacoustic (PA) spectra of Ho^{3+} , Er^{3+} , and Sm^{3+} doped PVA films were obtained in 350–800 nm range. PA spectra were also obtained for the respective dopant oxides: Ho_2O_3 , Er_2O_3 , and Sm_2O_3 for comparison. It was found that in PVA the PA sensitivity has increased considerably compared to pure rare earth oxides. The relative intensities of absorption bands at 540 and 637 nm of Ho^{3+} : PVA have shown distinct enhancement, indicating the increase in nonradiative relaxation at these excitations. Furthermore, the PA signals at wavelengths for different PA absorption bands were monitored as a function of chopping frequency. These experiments have shown that PA signal varies ω^{-1} both for oxides and PVA samples, suggesting that they behave as thermally thin samples. © 1997 John Wiley & Sons, Inc.

Keywords: Photoacoustic spectroscopy • polyvinyl alcohol and rare earths

INTRODUCTION

Polyvinyl alcohol (PVA) films doped with rare earth ions are of current interest as the organic films are potential candidates for optical image storage and holography.¹ In such cases photo-induced electron transfer from an impurity ion/chemical bond plays the key role for image storage purposes. These properties can be investigated using photoacoustic and optothermal techniques.² Photoacoustic spectroscopy (PAS) is also used for measuring the molecular absorption spectrum of practically any material, solid, liquid, or gaseous for the purpose of determining its structure, composition, phase, color, concentration, thermal properties, or other molecular parameters. The PA spectrum is essentially similar to the electronic absorption, except for the relative intensities of lines. This is particularly useful for thin films in which conventional optical absorption gives weak signals. The magnitude of the PA signal and its phase relation with the excitation is expected to provide considerable information con-

cerning the optical and thermal properties of the sample. Using variable modulation frequencies it is possible to carry out depth profiling of any chromophore in a given sample. Monitoring of either the magnitude or phase of the PA signal as a function of modulation frequency can also provide measurement of thermal diffusivity of the sample.

In the present work PAS is used in the investigation of electronic absorption of Ho^{3+} , Er^{3+} , and Sm^{3+} in polyvinyl alcohol film. PA spectra were also obtained for oxide powder of these elements for comparison.

EXPERIMENTAL

Holmium, erbium, and samarium (10% by weight) doped in polyvinyl alcohol (PVA) films were grown by slow evaporation method at room temperature.³ PVA was dissolved in quartz double-distilled water and then heated on a hot plate for a few minutes. Subsequently the rare earth oxides dissolved in HCl were mixed with PVA solution. The solution was spread on a plain surface of glass. The films were peeled off from the glass surface after 48 h. These films were used for PAS investigations. The PAS spectra were obtained on

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a home built photoacoustic spectrometer operating in 350–800 nm range using 250 W tungsten-halogen (T-H) lamp as a source. The light beam is chopped at 33 Hz using a mechanical chopper unit which can also provide a reference voltage needed for lock-in amplifier. The chopped light beam after passing through 0.25 M Jarrell-Ash Ebert monochromator (model 82-410), focused on the sample in the PA cell. The acoustic signal was detected by an electric microphone (B&K 4155) with sensitivity 50 mV/pa. Finally this signal was synchronously detected using a lock-in amplifier (Unilock model-IE 1033) designed and fabricated at TPPED, Bhabha Atomic Research Centre (BARC). Further processing of the DC analogue signal generated at the lock-in amplifier, was made using a PC. The signal was digitized using ADC card PCL 207. Since the intensity distribution of the source is not uniform throughout the spectral region, the correction of the sample spectrum with respect to source intensity was made by obtaining the spectrum of carbon sample under identical conditions. The performance of the spectrometer was evaluated by recording the spectrum of standard Ho_2O_3 powder and it was in good agreement with the PA spectrum reported in the literature. This instrument has been coupled on-line to an IBM-PC. It has the facility to acquire the PAS data on-line with automatic scan of wavelength, and also the software has the facility to correct the spectrum for the variation in source intensity profile. The details of the instrument are described elsewhere.^{4–6}

RESULTS

Figures 1, 2, and 3 show the PA spectra obtained for rare earth oxides (Ho_2O_3 , Er_2O_3 , and Sm_2O_3) and corresponding rare earth ions in PVA matrix after correcting for the source (T-H lamp) intensity profile. With a view to obtaining information about thermal diffusivity, the PA spectra were obtained at different chopping frequencies (w). Figure 4a–c shows the typical behavior of PAS of Ho^{3+} oxide at different chopping frequencies. Similar investigations were carried out for Ho^{3+} : PVA. In both cases the PAS response was found to obey w^{-1} dependence.

DISCUSSION

Comparison of PA Spectra with Electronic Absorption and Assignment of Transitions

The energy level schemes of all the rare earth ions have been well documented by Dieke.⁷ This along with energy level schemes of free rare earth ions (+3) is given by Dieke.⁷ Ho^{3+} ion has an electronic configuration of $4f^{10}$ with Hund's rule ground state of 5I_8 . The PA spectrum obtained for Ho_2O_3 agreed quite favorably with that reported for the electronic absorption spectra of Ho^{3+} chloride and ethyl sulfate.⁸ Although PA spectra resemble electronic absorption, the relative intensities do not, in general, follow the same pattern. This is obviously due to the additional factors (e.g., thermal properties, nonradiative probability) present in PAS process. The transitions corresponding to different bands in PA spectra are assigned by comparing the PAS with electronic absorption as marked in Figure 1. In a similar way, the relevant transitions for Er^{3+} and Sm^{3+} spectra are also shown in Figures 2 and 3.

Comparison of PVA Film and Enhancement of Nonradiative Relaxation

In general it was observed that in PVA samples the PAS sensitivities are much larger compared to that in pure rare earth oxides. This becomes apparent by noting that rare earth concentration in PVA film is about three orders of magnitude smaller as compared to that in pure oxide samples. Furthermore, it may be noted from the PA spectrum of Ho^{3+} : PVA sample that the peaks at 540 nm (E group of lines) and 637 nm (D group of lines) have considerably higher relative intensity compared to the intense absorption at 445 nm (I group of lines). This clearly shows that D and E groups of excitations have enhanced nonradiative relaxation probability in PVA matrix. This reveals that in polymer matrix electronic–vibration interaction is much stronger than in ionic oxides.

Dependence of PAS on Chopping Frequency and Effect of Thermal Properties

The dependence of PA signal on chopping frequency contains important information on the thermal diffusivity properties of the sample. The PA signals at different wavelengths of Ho^{3+} in Ho_2O_3 and also Ho^{3+} : PVA were monitored at different chopping frequencies, w . They were all

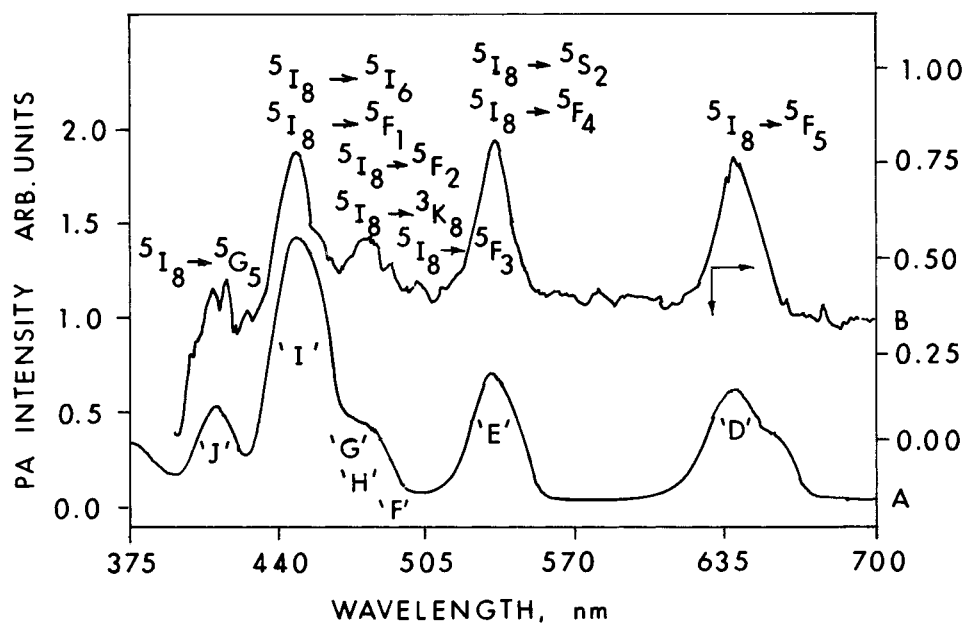


Figure 1. Normalized photoacoustic spectra of (A) holmium oxide and (B) holmium-doped PVA. The relative intensities of absorption bands at 540 and 637 nm of Ho^{3+} : PVA have shown enhancement compared to the intense absorption band 445 nm. The assignment of the PA spectra are shown in the figure.

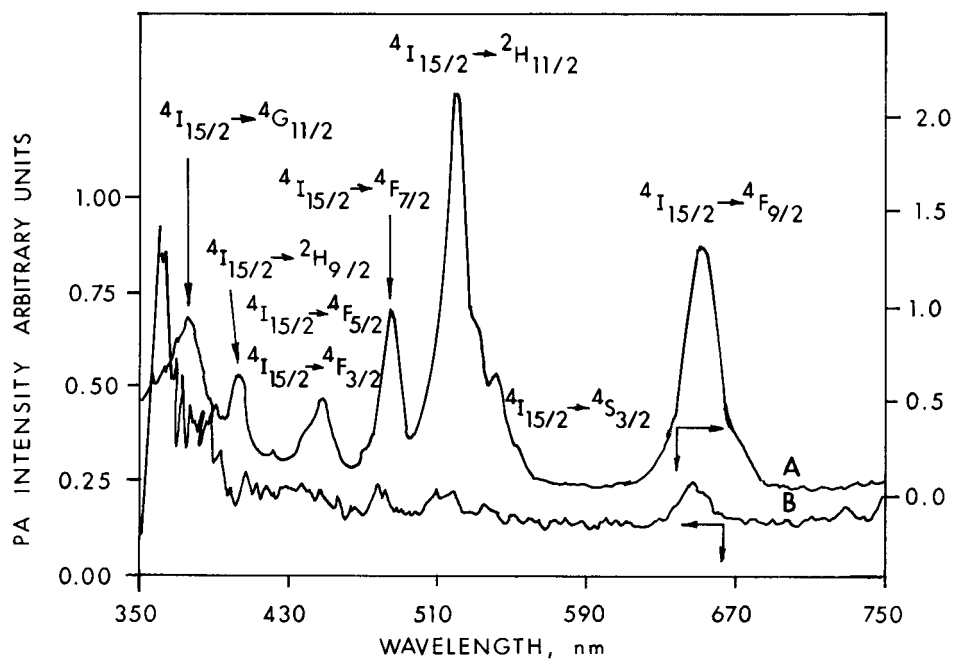


Figure 2. Normalized photoacoustic spectra of (A) erbium oxide and (B) erbium-doped PVA. Samples A and B show peaks corresponding to the energy level of the trivalent metal ions. The assignment of the transition corresponding PA spectra are shown.

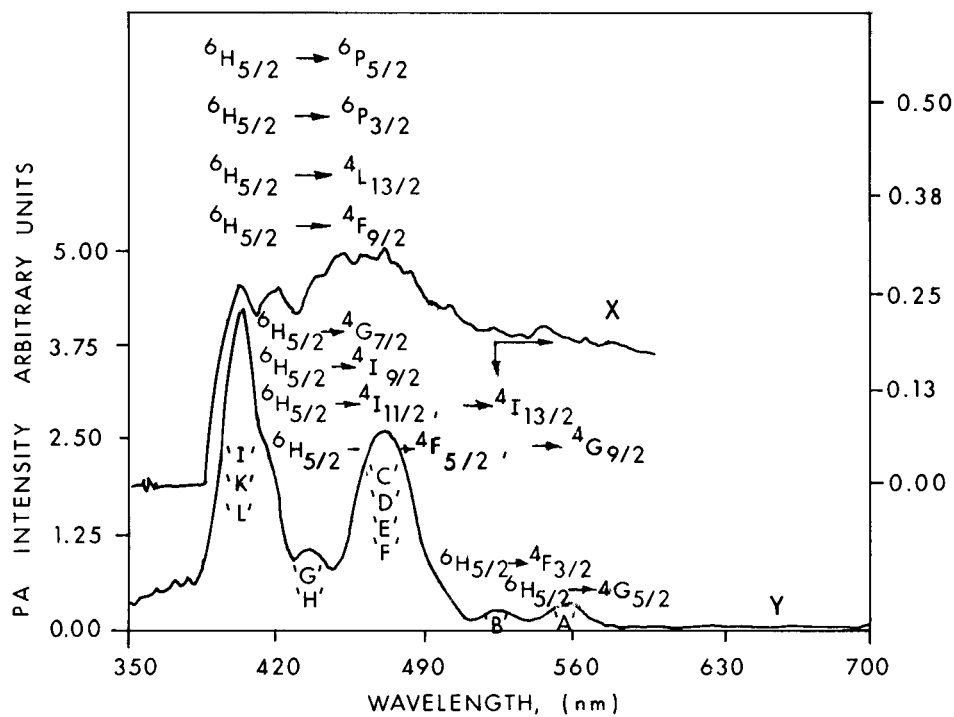


Figure 3. Normalized photoacoustic spectra of (X) samarium-doped PVA and (Y) samarium oxide. Samples X and Y show peaks corresponding to the energy level of the trivalent metal ions. The assignment of the transition corresponding PA spectra are shown.

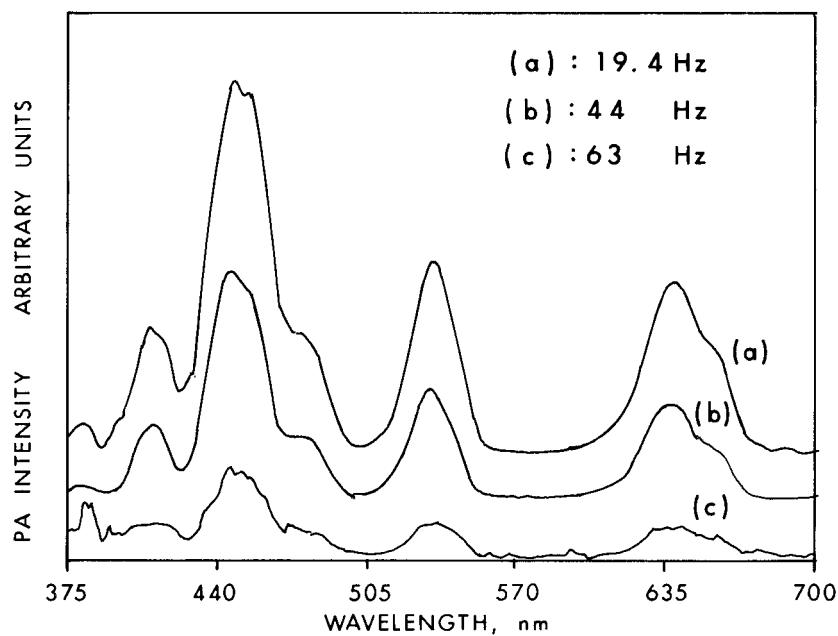


Figure 4. (a–c) Normalized spectra of holmium oxide at chopping frequencies of 19.4, 44, and 63 Hz. The intensities of absorption bands are decreased with higher chopping frequency.

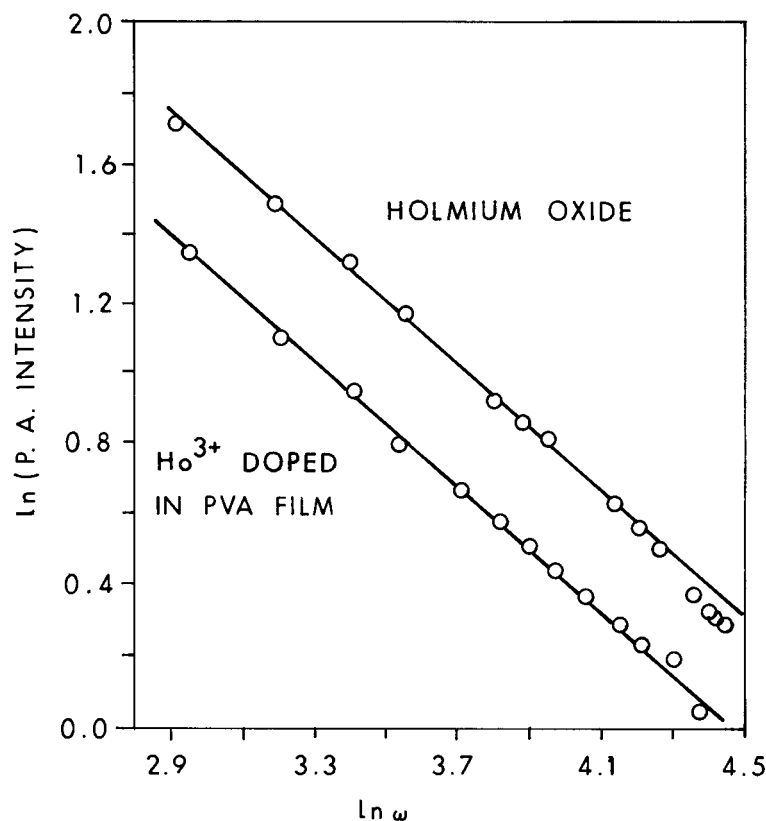


Figure 5. Dependence of photoacoustic intensity on chopping frequencies (ω). It may be seen that PA signal response is found to obey ω^{-1} dependence.

found to follow ω^{-1} dependence. Holmium samples are only typical representatives. The other samples also followed a similar behavior. Detailed work, however, was carried out only on Ho^{3+} samples in oxide form and in PVA matrix. Logarithm of PA signal intensity of D group of lines (at 637 nm) when plotted against that of ω gives a slope very close to -1 indicating ω^{-1} dependence of PA signal in both cases—pure oxide form as well as in PVA matrix. The results are shown in Figure 5.

In view of the relatively low optical absorption in $f \rightarrow f$ transition, rare earth solids can be classified as optically thin samples. The present experimental findings of ω^{-1} dependence in both oxides and PVA clearly show they are also thermally thin.⁸ This makes the comparison between relative intensities more meaningful in the sense that the only factor that decides the variation in PA intensity is the corresponding nonradiative transition probability. Therefore, the higher intensity of D and E groups in Ho^{3+} : PVA can definitely be associated with increased nonradiative probability in PVA matrix. This has relevance in under-

standing some of the optical nonlinear properties in PVA types of matrices. For example, it can be suggested that the formation of thermal gratings may be associated when a hologram is written at a wavelength corresponding to the absorption peak of rare earth dopant.

CONCLUSIONS

1. PA spectra of rare earth oxides and those doped in PVA film are similar to the respective optical absorption of these ions in solids.
2. The sensitivity of PAS is considerably enhanced when ions are incorporated with PVA film.
3. Both oxides and PVA films are found to be thermally thin samples.

The authors are grateful to Dr. R. H. Iyer, Head, Radiochemistry Division, BARC for encouragement during the course of this work.

REFERENCES AND NOTES

1. R. Changkakoti, G. Manivannan, A. Singh, and R. A. Lessard, *Opt. Eng.*, **32**(9), 2240 (1993).
2. A. Rosencwaig, in *Optoacoustic Spectroscopy and Detection*, P. Yoh-Han, Ed., Academic Press, New York, 1977, Chap. 8.
3. G. Manivannan, R. Changkakoti, and R. A. Lessard, *Opt. Eng.*, **32**, 671 (1993).
4. A. R. Dhobale and M. D. Sastry, *Solid-State Phys. (India)*, **32C**, 385 (1989).
5. A. R. Dhobale, M. Kumar, A. G. Page, and M. D. Sastry, BARC External Report BARC/93/E/0205.
6. A. R. Dhobale, T. P. Chaturvedy, S. Venkiteswarn, and M. D. Sastry, *Solid-State Phys. (India)*, **38C**, 455 (1995).
7. G. H. Dieke, *Spectra and Energy Levels of Rare Earth Ions in Crystals*, Interscience Publishers, New York, 1968, p. 279.
8. A. Rosencwaig, in *Optoacoustic Spectroscopy and Detection*, P. Yoh-Hon, Ed., Academic Press, New York, 1977, Chap. 8.

Received May 15, 1996

Accepted June 17, 1996