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Variable temperature optoacoustic studies of 4f-states of neodymium in oxide phases

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Abstract

High resolution optoacoustic studies on a wealky absorbing 4f electron manifold of Nd^{3+} in several samples of Nd_2O_3 of varying purity are reported using a tunable, pulsed laser as the excitation light source. In cases where nonlinear optoacoustic was observed, good agreement was found between the observed response and a simple nonlinear optical absorption model. To resolve differing spectral assignments for bands of Nd^{3+} in Nd_2O_3 observed by conventional and optoacoustic spectroscopy, this work was carried out at sample temperatures ranging from 4 K to 295 K in an apparatus designed for studies on air- or moisture-sensitive materials.

1. Introduction

An apparatus has been developed that enables detailed optoacoustic studies to be carried out at high sensitivity on strongly light scattering samples at variable temperature. Studies on an isolated and weakly absorbing 4f-electron state of Nd_2O_3 in several samples of Nd_2O_3 were carried out as a test of the sensitivity of the apparatus and to determine the influence of absorber concentration. In some cases, sublinear or supralinear optoacoustic response, as a function of incident laser energy, was observed. These non-linear responses are modelled using a simple non-linear optical absorption equation.

Many prior photoacoustic studies of lanthanide or actinide oxides have used an arc lamp as the excitation light source [1–5]. Higher spectral resolution has been achieved using a tunable laser as the excitation source but comparatively broad linewidths were reported [6–8] for lanthanide compounds due to the lack of sample cooling and thin sample layers were required to minimize problems arising from light scattering. Acoustic interference from scattered light is a particularly significant problem in studies of weakly absorbing powdered samples due to the high ratio of scattered to absorbed light [6,9,10].

Pulsed laser excitation is advantageous when studying weakly absorbing samples because acoustic waveform generation occurs in a time regime in which little ambient acoustic noise is present. The effect of scattered laser light can be minimized by use of an acoustic contact method that rejects light scattered from the sample and by employing time-gated detection following pulsed excitation [6,8]. The present apparatus exploits both of these methods so successfully that scattered laser light does not interfere with the observed photoacoustic signal. The acoustic sensitivity of our apparatus remains constant when sample temperature is varied widely because the transducer remains at ambient temperature. We have exploited these features of our apparatus to study the influence of absorber concentration on the observed photoacoustic spectra of 4f states of Nd^{3+} in Nd_2O_3.

2. Experimental details

In our apparatus, a solid fused silica rod provides acoustic contact, thermal isolation and sample support. Both ends of rod were polished flat to ensure good contact to an acoustic transducer and the sample, respectively. To prevent it from acting as a light pipe, a section of the rod was formed into a two turn coil whose surface was abraded by sand blasting with fine grit. A test in which a 2-mW 633-nm helium neon laser beam was directed into the rod resulted in barely discernible levels of light exiting from the opposite end of the rod, as detected by the dark-adapted eye of an

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observer. Our rod design is a more efficient three-dimensional variation on the two-dimensional sample holders used by Tam and Patel [6,8].

The acoustic contact rod was inserted into a vacuum-tight fused silica and borosilicate glass sample tube assembly. The glass sample tube assembly provided a means of controlling the atmosphere surrounding the sample and enabled recording photoacoustic spectra without interference from common atmospheric gases such as oxygen, water or carbon dioxide. The sample of interest (a solid pellet in the present work) was affixed to the acoustic contact rod with silicone vacuum grease. The sample tube assembly was evacuated and then back-filled with helium gas to provide thermal contact. The sample tube assembly was inserted into the heat exchange gas region of a cryostat (Oxford Instruments model CF-204) fitted with optical access windows.

The excitation source and electronics are much the same as those employed by Beitz and co-workers [11] for photoacoustic studies on liquid solutions. The excitation light source was a pulsed dye laser (LDS698 laser dye, 0.3 cm^{-1} spectral bandwidth) pumped by a pulsed Nd:YAG laser. In the present work, the acoustic transducer and a pre-amplifier (contained in a small aluminum box) were placed atop the acoustic contact rod. The acoustic signal was detected by a piezoelectric transducer (PZT). The PZT signal and a laser energy monitor signal were acquired using gated integrators whose outputs were recorded digitally. The photoacoustic spectra reported here have been normalized to the incident laser energy. The laser wavelength was corrected to vacuum and converted to wavenumbers. The dye laser wavelength was calibrated using the optogalvanic effect in a uranium hollow cathode discharge and the uranium wavelength tables of Palmer and co-workers [12].

Our investigations used powdered Nd_2O_3 from three different suppliers. The first two materials studied were specified to be 99% and 99.9% pure, respectively, on a rare earth oxide basis. The third material, from Johnson Mathey, was specified to be 99.99% pure on a metals basis with less than 50 ppm Y impurity. The 99% material was heated to 393 K to remove physically absorbed water. The 99.9% material had been heated to 1073 °C after receipt to ensure conversion to A-phase Nd_2O_3 [13]; the 99.99% Nd_2O_3 had been heated to 1320 K and then was allowed to cool in a nitrogen atmosphere dry box. Within the dry box, weighed amounts of the Nd_2O_3 material of interest and KBr (Mallinkrodt infrared grade), sufficient to give 10 wt.% Nd_2O_3 in KBr, were ground together. Serial dilution was used to make more dilute samples of Nd_2O_3 in KBr. The Nd_2O_3 in KBr mixtures were pressed into 1–2 mm thick pellets using a hand press in a dry box. The most concentrated pellet was light blue in color and opaque; the least concentrated pellet was a translucent white. A broad underlying optical absorption was observed from samples made using the 99% and 99.9% Nd_2O_3 material. Evidently due to d-transition metal impurities, this absorption was minimized by careful selection of the PZT gate delay. In some cases, as noted below, the residual part of this absorption was digitally subtracted to facilitate comparison of narrow 4f–4f transitions of Nd^{3+}.

3. Results and discussion

Within the spectral range investigated, the crystal field transitions expected [14] are those from the $^4I_{9/2}$ ground state of Nd^{3+} to its $^4F_{9/2}$ excited 4f state in A-type (hexagonal) Nd_2O_3. The $^4F_{9/2}$ state was chosen for study as it is relatively isolated but of sufficiently high J value to provide several bands in absorption. At 4 K, there is negligible thermal population of all but the lowest Stark component of the $^4I_{9/2}$ ground state. In consequence, within the spectral range investigated, only five purely electronic transitions are expected at 4 K, if the material is pure A-type Nd_2O_3. The observed photoacoustic spectrum of a 10 wt.% Nd_2O_3 in KBr sample (made using the 99% Nd_2O_3 material), recorded at a sample temperature of 4 K, showed 15 bands. Evidently, the 99% material contained significant amounts of phases other than A-type Nd_2O_3. The top three panels of Fig. 1 are the observed photoacoustic spectra of a 0.1 wt.% Nd_2O_3 in KBr sample made using 99.9% Nd_2O_3 material. The influence of temperature on the observed linewidths is evident as

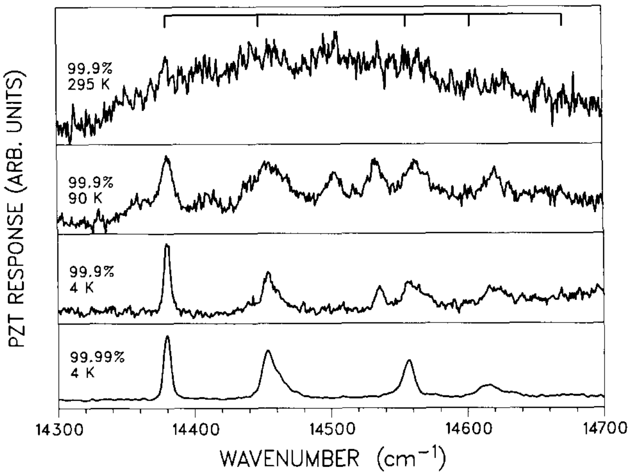

Fig. 1. Observed photoacoustic spectra from 0.1 wt.% Nd_2O_3 in KBr (made using 99.9% pure Nd_2O_3) as a function of temperature (top three panels) and the 4 K spectrum of 0.2 wt.% Nd_2O_3 in KBr (made using 99.99% pure Nd_2O_3). The reported [14] Stark components of the $^4F_{9/2}$ state of Nd^{3+} in A-type Nd_2O_3 are shown as vertical lines in the uppermost panel.

is the spectral simplification resulting from reduced thermal population of Stark components of the ground state. The positions of the Stark components of the $^4F_{9/2}$ state, as assigned by Caro and co-workers [14], are denoted by short vertical lines in the top panel of Fig. 1. The 4 K photoacoustic spectrum of a 0.2 wt.% Nd_2O_3 in KBr sample (made using 99.99% Nd_2O_3) is shown in the bottom panel of Fig. 1. In addition to the four peaks that are readily evident, a 5th peak at 14 669 cm^{-1} is discernible on expanding the ordinate of this spectrum. The energy of this peak was confirmed using a more concentrated sample. These five peaks from 99.99% Nd_2O_3 agree reasonable well (standard deviation = 6.5 cm^{-1}) with the energies assigned by Caro and co-workers [14] for the Stark components of the weakly absorbing $^4F_{9/2}$ state of Nd^{3+} in A-type Nd_2O_3. It is evident from peaks such as that at 14 536 cm^{-1} that the 99.9% Nd_2O_3 material contained phases other than A-type Nd_2O_3.

The influence of absorber concentration on the observed photoacoustic spectrum was investigated. The uppermost panel of Fig. 2 shows the 4 K photoacoustic spectrum of a 10 wt.% Nd_2O_3 in KBr sample (made using 99.9% Nd_2O_3) after subtracting out a broad, sloping baseline. This spectrum contains peaks not evident in the 4 K spectrum of a 0.1 wt.% Nd_2O_3 sample that had been made using the same source materials (see Fig. 1). In addition, those peaks that are present in both spectra are broader in the spectrum of the 10 wt.% Nd_2O_3 sample. These spectral differences largely arise from changes in the degree to which incident laser light was absorbed in the two samples.

In the absence of significant light scattering, the PZT voltage signal, V_{PZT}, is expected [8] to follow the relationship

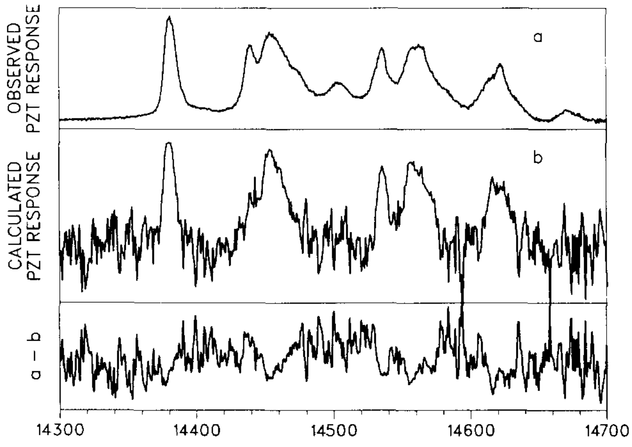

Fig. 2. Comparison of (a) the observed photoacoustic spectrum of 10 wt.% Nd_2O_3 in KBr at 4 K, (b) the calculated photoacoustic spectrum of 10 wt.% Nd_2O_3 at 4 K ($r = 4.5$, see text), and the spectrum resulting from subtracting (b) from (a).

$$V_{PZT} = cI - cI \exp(-\alpha l) \tag{1}$$

where c is an instrument constant, I is the incident laser pulse energy, α is the absorptivity of the sample at the laser wavelength, and l is the pathlength through the sample. For an optically "thin" sample (*i.e.* for $\alpha l \ll 1$), $V_{PZT} = cI\alpha l$. Evidently, the 0.1 wt.% sample was optically "thin" and the 10 wt.% sample was not. We can calculate the spectrum expected from a 10 wt.% sample in the absence of significant light scattering. Using primes to denote quantities associated with the 0.1 wt.% sample, we start by assuming that $\alpha' l' = V_{PZT}/cI$ and so can obtain $\alpha' l'$ values from the spectrum observed from the 0.1 wt.% sample (see Fig. 1). The calculated PZT voltage, V_{calc}, for the 10 wt.% sample is then obtained from

$$V_{calc} = cI - cI \exp(-r\alpha' l') \tag{2}$$

where $r = \alpha l / \alpha' l'$.

The absorption cross-section of Nd^{3+} in Nd_2O_3 is not known, but r, the ratio of the absorptivity-pathlength products, is available because we measured the dimensions and weight of our sample pellets. From those measurements, $r = 60$. However, using $r = 60$ results in a calculated spectrum with severely flattened and broadened peaks in comparison with the observed 4 K spectrum shown in Fig. 2. Allowing r to vary freely showed that a value of $r = (4.5 \pm 1)$ provides a good correspondence between the observed and calculated spectra for 10 wt.% Nd_2O_3 (see Fig. 2). This result is not unexpected as our samples are highly light scattering in comparison with their ability to absorb light in the wavelength range studied. In consequence, increasing Nd_2O_3 concentration is less effective (smaller r) in enhancing the observed pulsed photoacoustic signal than otherwise would be expected. Small peaks, such as that at 14 504 cm^{-1}, in the observed spectrum of 10 wt.% Nd_2O_3 in Fig. 2, evidently were too weak to be observable in the 0.1 wt.% Nd_2O_3 sample (see Fig. 1).

Non-linear photoacoustic response was observed in some cases. At 295 K, evidence for multiphoton absorption was obtained when using 689.45 nm excitation (Fig 3, filled symbols). These data are well fit (Fig. 3, solid line) by a relationship containing 1st and 2nd order light intensity terms,

$$V_{PZT} = aI + bI^2 \tag{3}$$

when $a = 19.4$ V/(mJ/pulse) and $b = 11.5$ V/(mJ/pulse)^2. Photoacoustic detection of multiphoton absorption has been reported previously [8] from organic liquids. At 4 K, evidence of optical saturation was obtained when incident laser energy was increased at 691.60 nm (Fig. 3, + symbols). Phenomenologically, the observed response was well fit (Fig. 3, solid line) by eqn. (3) when

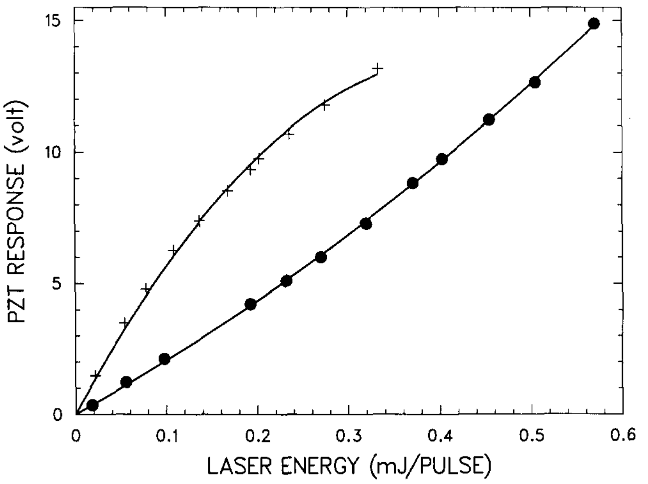

Fig. 3. Comparison of the observed (+) and modelled (solid line, eqn. (3)) photoacoustic response as a function of incident laser energy from 10 wt.% Nd_2O_3 in KBr at 4 K (+) with the observed (●) and modelled (solid line, eqn. (3)) response at 295 K.

$a = 64.1$ V/(mJ/pulse) and $b = -75.8$ V/(mJ/pulse)^2. Qualitatively, a negative second order term corresponds to optical saturation.

Both observed non-linear responses can be rationalized based on the 4f state energy level structure of Nd^{3+} in Nd_2O_3 and the influence of sample temperature. At 4 K, the non-radiative decay rate of Nd^{3+} ions in A-type Nd_2O_3 is about $1 \times 10^7\ s^{-1}$, based on a time-resolved fluorescence decay study [15]. Few initially excited Nd^{3+} ions return to the ground state during the 5-ns laser pulse; narrow transition linewidths reduce the probability that excited state absorption occurs. In consequence, as laser intensity is increased, ground state depletion occurs at 4 K. At 295 K, nearly continuous absorption is found across 4f state manifolds (see Fig. 1) due to increased transition linewidths, thermal population of Stark components of the ground state, and phonon side bands. As a result, the probability of excited state absorption during the laser pulse is increased. The supralinear response shown in Fig. 3 is attributed to excited state absorption.

Conventional optical absorption studies on single crystal Nd_2O_3 [16] and powdered A-type Nd_2O_3 [14] have been reported. From our study, we conclude that the photoacoustic spectrum of high purity Nd_2O_3 agrees well with the transition energies reported by Caro *et al.* [14] for 4f-4f transitions of Nd^{3+} in powdered A-type Nd_2O_3. In both conventional optical absorption studies, the spectrum of Nd^{3+} in Nd_2O_3 was reported to exhibit larger crystal field splitting, and be strongly displaced to lower energy, in comparison with that of Nd^{3+} in $LaCl_3$. It is surprising, therefore, that Narayanan and Thakur [7] assigned their ambient temperature photoacoustic spectrum of powdered Nd_2O_3 such that the Nd^{3+} ground state Stark components, and several components of $^2H_{11/2}$ occur at nearly the same energy as reported by Dieke [17] for Nd^{3+} in $LaCl_3$. For example, the total Nd^{3+} ground state splitting in Nd_2O_3 reported by Henderson *et al.* [16] is 496 cm^{-1}, that reported by Caro *et al.* [14] is 491 cm^{-1} , and that reported by Narayanan and Thakur [7] is 249 cm^{-1}.

Narayanan and Thakur reported a total of eight transitions of Nd^{3+} in Nd_2O_3 and assigned them all as purely electronic transitions. However, only six of their transitions occur close to the energies expected [14] for purely electronic transitions in A-type Nd_2O_3. It may be that the Nd_2O_3 studied by Narayanan and Thakur was not the A structure type. Rare earth sesquioxides can exist in several crystalline phases [18]; preparation of pure A structure type Nd_2O_3 requires holding a sample at an appropriate temperature for sufficient time [13]. Furthermore, Caro and co-workers [14] reported that minor traces of yttric or calcium impurities in Nd_2O_3 produce domains of the monoclinic B structure type that contain three crystallographic metal ion sites and found that many commercial samples of Nd_2O_3 exhibited supplementary absorption lines.

4. Conclusions

An apparatus for recording high sensitivity photoacoustic spectra from strongly light scattering samples has been constructed and tested at temperatures from 4 K to 295 K. The apparatus is suitable for use with air- or moisture-sensitive samples or radioactive samples requiring containment. Unlike an earlier [8] ambient temperature photoacoustic study on Nd_2O_3, the photoacoustic bands observed from high purity Nd_2O_3 in the present work agree well with the Stark components of 4f states of Nd^{3+} in A-type Nd_2O_3 as assigned by Caro *et al.* [14].

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