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Optical spectroscopy, 1.06 μm emission properties of Nd^{3+}-doped phosphate based glasses

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ABSTRACT

Neodymium doped phosphate based glasses with composition of ($P_2O_5 + K_2O + Al_2O_3 + CaF_2$) were prepared. The samples were analysed through differential thermal analysis (DTA), Fourier transform infrared (FTIR), absorption, emission and decay measurements. Judd-Ofelt parameters (Ω_λ) have been determined from the spectral intensities of absorption bands in order to calculate the radiative parameters like radiative transition probabilities (A_R), radiative lifetime (τ_R) and branching ratios (β_R) for the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ laser transition of Nd^{3+} ion. The effective emission bandwidths ($\Delta\lambda_{eff}$), experimental branching ratios (β_{exp}) and stimulated emission cross-sections (σ_e) have been determined from the emission spectrum. The decay curves of the $^4F_{3/2}$ level exhibited almost single exponential nature for all the Nd^{3+} ion concentrations.

1. Introduction

Rare-earth (RE) doped materials have been widely used in many fields of science and technology such as solid-state lasers, colour displays, optical communications owing to their structure of energy levels. Among them, the neodymium doped solid state laser materials have been widely investigated for various applications including optical amplifiers, atmosphere pollution monitoring, industry, military and remote sensing because the trivalent Nd^{3+} ion play a major role to exhibit 1.06 μm laser emission with high peak-powers [1–3]. The performance of Nd^{3+}-doped laser glasses depends on the high stimulated emission cross-section, narrow emission bandwidth, longer excited state lifetime and low threshold energy. For a good laser amplifier, the non-radiative decay rate caused by the multiphonon relaxation should be low to acquire high quantum yield [4–5]. As the physical and optical properties of Nd^{3+}-doped glasses depend on the host glass matrix, the metaphosphate based glasses are found to be more efficient, especially for high-energy peak-power outputs up to multi-kilojoules and multi-terawatts, which are highly useful for fusion energy research.

Typically, the phosphate glasses are more attractive due to their considerable applications in the field of optical transmission, detection, sensing and laser technologies [6]. Moreover, phosphate glasses possess unique characteristics such as higher solubility of RE^{3+} ions, low linear and nonlinear refractive indices, high transparency, low melting point, good thermal stability, low dispersion and high gain density [7]. Also the presence of fluorine in these glasses reacts with the OH group to form HF and strongly reduces OH absorption [8]. The addition, Al_2O_3 enhances the mechanical strength, chemical durability and lower coefficient of expansion, whereas the K_2O decreases the melting temperature to a convenient level [9,10].

The present work reports on the spectroscopic properties of Nd^{3+}-doped phosphate based laser glasses. The base glass composition has been composed from different chemical constituents used in the commercial Nd phosphate laser glass, LG-750 [2]. The Judd-Ofelt [11,12] intensity parameters Ω_λ ($\lambda = 2, 4$ & 6), have been evaluated from the oscillator strengths of the absorption bands of 1.0 mol% Nd^{3+}-doped PKAlCaFNd10 glass to calculate the laser characteristic properties of the $^4F_{3/2}$ excited level. Emission and decay measurements have been performed to understand the nature of radiative and non-radiative processes.

2. Experimental Details

2.1. Glass Preparation

Nd^{3+}-doped phosphate based glasses of molar composition: 44 P_2O_5 – 17 K_2O – 9 Al_2O_3 – (30 − x) CaF_2 – x Nd_2O_3, where x = 0.01, 0.05, 0.1, 0.5, 1.0 and 2.0 mol%

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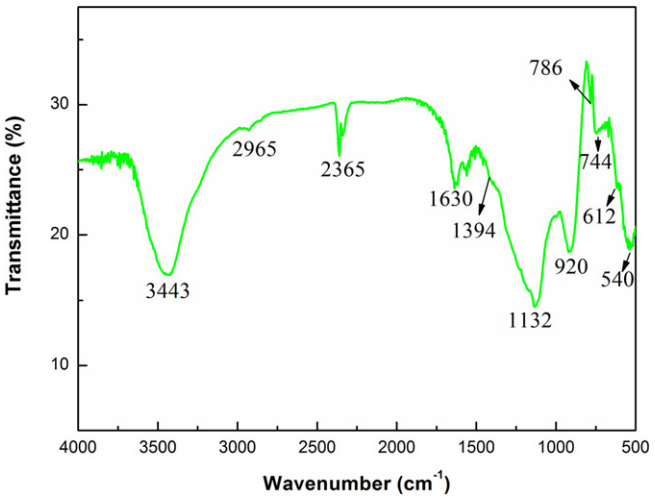

Fig. 1. FTIR spectrum of PKAlCaFNd10 glass.

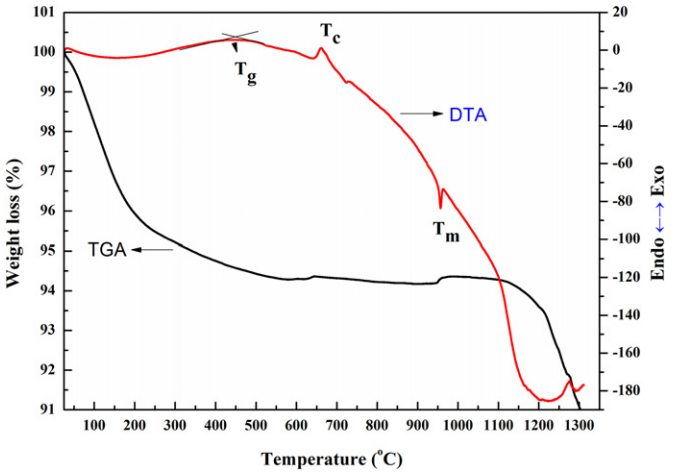

Fig. 2. DTA-TGA curves of PKAlCaF glass.

(here-after referred as PKAlCaFNd001, PKAlCaFNd005, PKAlCaFNd01, PKAlCaFNd05, PKAlCaFNd10 and PKAlCaFNd20, respectively) were prepared by the conventional melt quenching technique. About 20 g batch chemicals were mixed and crushed in an agate mortar and the mixture was transferred into a platinum crucible and melted at 1200 °C in an electric furnace for 1 h. The melt was then air quenched by pouring onto a preheated brass plate. The glass samples thus obtained were annealed at 380 °C to remove the thermal strain and polished carefully for optical measurements.

2.2. Experimental Methods

The physical parameters such as density (2.7132 g/cm^3) was determined by Archimedes' method using distilled water as an immersion liquid and refractive index (1.535) was measured using an ellipsometer (Woollam – M-2000) at sodium wavelength. The FTIR spectrum was measured with a resolution 1 cm^{-1} in the range 400–4000 cm^{-1} using Perkin- Elmer Paragon 500 FTIR Spectrometer. The DTA, TGA measurements were made using TA instrument Q600 from RT to 1300 °C at a heating rate of 10 °C/min. The optical absorption spectrum was recorded using a Perkin Elmer Lambda-950 UV–Vis–NIR spectrophotometer in the wavelength range of 300–950 nm. The photoluminescence spectra and the lifetime measurements were carried out in the NIR region (800–1500 nm) by exciting the sample at 808 nm using pulsed diode laser modulated with a function generator and the signal from the photodiode was collected by using a digital oscilloscope (Le Croy LS 140, 100 MHz).

Table 1
FTIR spectral bands and their assignments for PKAlCaFNd10 glass.

Wavenumber (cm^{-1})	Assignments	Reference
540, 612	Vibration of P—O bonds	[13]
744, 786	Symmetric stretching vibrations of P—O—P bonds	[13]
920	Asymmetric stretching vibrations of P—O—P bonds	[13]
1132, 1390	Asymmetric stretching vibrations of PO_3 and PO_2 bonds	[13]
1630, 2365, 2965	Stretching vibrations of P—O—H groups	[14]
3443	Symmetric stretching vibrations of O—H or H—O—H groups	[15–16]

3. Results and Discussion

3.1. FTIR Measurements

In order to estimate functional groups present in the PKAlCaFNd10 glass, the FTIR spectrum recorded in the region of 500–4000 cm^{-1} is shown in Fig. 1. The band positions are attributed to different vibrational modes [13–16] as listed in Table 1. From the FTIR spectrum, the OH content, N_{OH} (ions cm^{-3}) in the glass has been determined by the relation [17,18]

$$N_{OH} = \frac{N}{\varepsilon . L} \ln \frac{1}{T} \quad (1)$$

where N is the Avagadro's number, L the glass thickness (cm), T the transmittance, ε the molar absorptivity of the free OH groups (4.91×10^4 cm^2 mol^{-1}) in the glass. From the FTIR spectrum, the OH concentration (N_{OH}) responsible for the quenching of the $^4F_{3/2}$ excited state lifetimes of Nd^{3+} ions has been found to be 2.1×10^{19} ions cm^{-3} which is very much less than that of (5.82×10^{20} ions cm^{-3}) reported for zinc tellurite glass [18]. This clearly indicates that PKAlCaF glasses possess lower OH content (N_{OH}) and hence the quenching of Nd^{3+} ions luminescence is negligible.

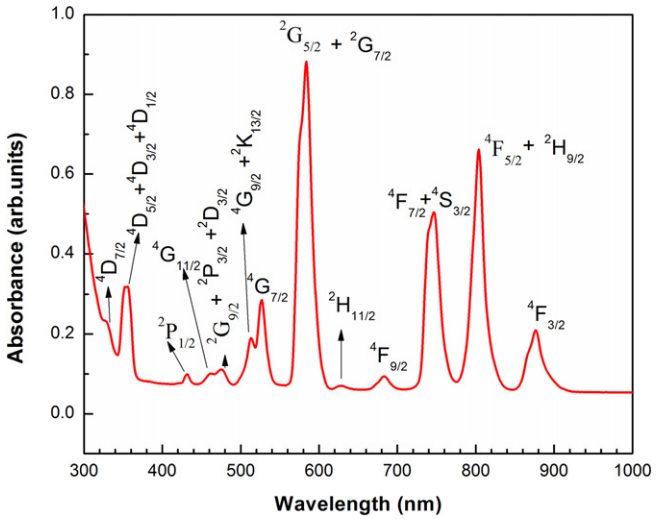

Fig. 3. Optical absorption spectrum of 1.0 mol% Nd^{3+} -doped PKAlCaF glass.