

**Radiative and Non-Radiative Properties of  
Praseodymium Doped Glasses**

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**Abstract**

We report on the application of low phonon-energy glasses doped with praseodymium. Radiative and non-radiative properties, as determined by experimental and theoretical techniques are presented, along with absorption and fluorescence spectra, and measured lifetimes.

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The optical properties of praseodymium-doped glasses have attracted considerable attention recently for their potential application as a 1.3 micron optical amplifier. As a result, novel glass compositions are being developed and assessed. We have previously reported the properties of a series of novel  $\text{Pr}^{3+}$  glass compositions<sup>(1)</sup> for application in the second telecommunications window. The purpose of this work is to provide a complete evaluation of the radiative and non-radiative properties of  $\text{Pr}^{3+}$  in these materials, considering all radiative transitions, for other possible applications. Efforts are concentrated on novel heavy-halide glasses, namely, hafnium fluoride, indium fluoride, and cadmium fluorides and chlorides for which new transitions and improved quantum efficiencies are expected.

A large number of rare earth hosts, all based on multicomponent heavy metal halides

*and have been and will be employed. The basic optical and material*

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the  $^3P_0$  level, and then analyzing the emission. By chopping the signal and detecting the decay of the fluorescence, the lifetime of these levels could be determined. In undoped samples, Raman spectroscopy revealed the maximum phonon energy, from which the rate of multiphonon decay can be calculated<sup>(2)</sup>. Absorption in the UV to near IR was measured with a double grating spectrometer, and into the far infrared using FTIR. Also, from the absorption spectra data of doped samples, a Judd-Ofelt analysis was performed which yielded the radiative rates<sup>(3)</sup>.

Typical results are summarized in Table 2. Here the complete set of non-radiative and radiative rates for each energy level of the  $\text{InF}_3$ -based glass are tabulated. Differences between the measured and theoretical lifetimes are attributed to impurities in the glasses, and in particular  $\text{OH}^-$  in the  $\text{CdCl}_2$  containing glass. This analysis shows that radiative transitions originating from the  $^3H_5$ ,  $^3H_6$ ,  $^1G_4$ ,  $^1D_2$  and  $^3P_0$  are all possible without non-radiative decay dominating. This provides an opportunity for applications as diverse as visible or upconversion lasers and infrared sources.

Experimental measurement of the fluorescence in the visible and infrared regimes and lifetimes of the lasing levels completes the analysis of the optical properties. Figure 1 shows the fluorescence obtained by argon pumping of the  $^3P_1$  level for all the glasses. Significant differences in the branching ratios for the visible emission are observed as a function of glass host. This will have implications in the application of these glasses to upconversion lasers, providing sources at new wavelengths and with efficiencies which are

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not possible with conventional host materials such as ZBLAN.

In summary, through application of a series of experimental and theoretical techniques, the radiative and non-radiative properties of a series of low phonon energy glasses have been obtained. These results detail the properties of promising glass hosts for new transitions and applications.

### **References**

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Table 1. Glass compositions and basic properties of the low phonon energy glasses.

| Glass                               | Composition | n<br>(1.3 $\mu$ m) | d<br>(g/cm <sup>3</sup> ) | CTE<br>( $^{\circ}$ C <sup>-1</sup><br>$\times 10^5$ ) | Tg<br>( $^{\circ}$ C) | Tx<br>( $^{\circ}$ C) | Tm<br>( $^{\circ}$ C) |
|-------------------------------------|-------------|--------------------|---------------------------|--|-----------------------|-----------------------|-----------------------|
| CdCl <sub>2</sub> -CdF <sub>2</sub> | CNBKL-FC    | 2.31               | 4.0                       | 2.2  | 126                   | 228                   | 296                   |
| CdF <sub>2</sub>                    | CBN         | 1.51               | -                         | 2.6  | 134                   | 217                   | 305                   |
| InF <sub>3</sub>                    | IZnSBCN     | 1.49               | 4.9                       | 1.9  | 289                   | 390                   | 401                   |
| HfF <sub>4</sub>                    |             | 1.51               | 5.9                       | 1.7  | 332                   | 416                   | 577                   |

where n is the refractive index, d is the density, CTE is the coefficient of thermal expansion, and Tg, Tx and Tm are the glass transition temperature, temperature for the onset of crystallization and the melting temperature, respectively.

Table 2. Radiative and Non-Radiative Lifetimes for the entire set of energy levels of Pr<sup>3+</sup> doped InF<sub>3</sub> based Glass.

| Energy Level                | Energy<br>(cm <sup>-1</sup> ) | Radiative<br>Lifetime <sup>(a)</sup><br>( $\mu$ sec) | Non<br>Radiative<br>Lifetime<br>( $\mu$ sec) | Total<br>Lifetime<br>( $\mu$ sec) | Measured<br>Lifetime <sup>(a)</sup><br>( $\mu$ sec) |
|-----------------------------|-------------------------------|--|--|-----------------------------------|---|
| <sup>3</sup> H <sub>5</sub> | 2167                          | 163200   | 4.6  | 4.6                               | -   |
| <sup>3</sup> H <sub>6</sub> | 4310                          | 81500  | 4.0  | 4.0                               | -   |
| <sup>3</sup> F <sub>2</sub> | 5149                          | 8080   | 0.0  | 0.0                               | -   |
| <sup>3</sup> F <sub>3</sub> | 6500                          | 3210   | 0.1  | 0.1                               | -   |
| <sup>3</sup> F <sub>4</sub> | 6932                          | 4540   | 0.0  | 0.0                               | -   |
| <sup>1</sup> G <sub>4</sub> | 9901                          | 4720   | 266  | 252                               | 216   |
| <sup>1</sup> D <sub>2</sub> | 17007                         | 998  | $\infty$                                     | 998                               | 400   |
| <sup>3</sup> P <sub>0</sub> | 20899                         | 69   | 35360  | 69                                | 48  |
| <sup>3</sup> P <sub>1</sub> | 21459                         | 62   | 0.0  | 0.0                               | -   |
| <sup>1</sup> I <sub>6</sub> | 21460                         | 304  | 0.0  | 0.0                               | -   |
| <sup>3</sup> P <sub>2</sub> | 22676                         | 65   | 0.0  | 0.0                               | -   |

(a)  $\pm$  20% uncertainty in lifetimes

**Figure Caption**

Figure 1. Fluorescence spectrum in the visible in the  $\text{HfF}_4$ ,  $\text{InF}_3$  and  $\text{CdF}_3$  based glasses.

