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Spectroscopic Properties of Pr^{3+} Doped Transparent Oxyfluoride Glass Ceramic

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Abstract: In this paper, we reported the spectroscopic properties of praseodymium ions (Pr^{3+}) doped transparent oxyfluoride glass ceramic excited with different laser lines, such as 532, 514.5 and 476.5 nm. and the spectroscopic features of Pr^{3+} ions in LaF_3 nanocrystals (NCs) and in oxide glass were presented. It was found that the population on $^3P_0$ state of Pr^{3+} ion in NCs and in glass can be achieved by multi-phonon assistance process when excited by 514.5 nm laser lines. As a comparison, 476.5 nm laser line which is mainly resonant with the $^3H_4$ to $^3P_0$ transition of Pr^{3+} ions in NCs is used as the excitation source, transitions from $^3P_0$ state to many lower states, such as $^3H_5$, $^3H_6$, $^3F_2$ manifolds were observed and it showed significant difference from those excited by 532 nm and 514.5 nm laser lines in which only transition from $^3P_0$ to $^3H_5$ exists. We attribute those different spectroscopic features as selectively excitation of Pr^{3+} ions in different environments where exist strong/weak electron-phonon coupling in the $^3P_{0,1}$ states of Pr^{3+} ion in NCs and in glass. Crystallization behavior and vibrational properties of transparent glass ceramic were also studied by Raman spectroscopy excited by 532 nm and 514.5 nm laser lines.

Key words: transparent oxyfluoride glass ceramic; praseodymium; nanocrystals
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1 Introduction

RE ions have a long history in optical applications. Among RE ions, praseodymium ion (Pr^{3+}) is an attractive optical activator with many meta-stable states such as $^3P_0$, $^1D_2$, $^1G_4$ that provide stimulated emission from infrared to blue[1]. In the course of laser studies many fluorescence characteristics of Pr^{3+} ions in different hosts were investigated, such as $LiYF_4$[2], PrF_3[3], $LiKY_{1-x}Pr_xF_5$[4], $YAlO_3$, $Y_3Al_5O_{12}$[5]. Among those matrices, LaF_3 is well known laser material because of its wide band-gap, extensive RE solubility[6~8] and low phonon energy (350 cm^{-1})[9]. A large amount of research has been carried out to study the spectroscopic properties and laser behaviors of LaF_3 crystals doped with Pr^{3+} ions such as: stimulated emission from Pr^{3+} ions in LaF_3 crystals[10]; up-converted emission from $^3P_0$ state upon resonant excitation of $^1D_2$ manifold which is capable of achieving blue photon emission by red

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photon excitation[11]; ultraviolet emissions from $^1S_0$ state achieved either by upon resonant excitation of $^3P_0$ manifold[12] or upon resonant excitation of $^1D_2$ manifold[13]; two photon excitation Pr^{3+} ions and interconfigurational energy transfer from Pr^{3+} ions to other RE ions such as Gd^{3+} ions[14], Nd^{3+}[15] ions in LaF_3 crystals which are important for further development of tunable ultraviolet lasers.

In resent decade, much more attention has been paid to a new kind of material, the transparent oxyfluoride glass ceramic because of their improved fluorescence properties. Such materials provide a desirable fluoride environment for RE ions due to its low phonon energy, while maintaining good mechanical and chemical properties of oxide glass[16]. Transparent oxyfluoride glass ceramics based on LaF_3 crystals in an aluminosilicate glass were firstly produced in 1998[17]. LaF_3 NCs based on glass ceramics doped with RE ions are of major interest in resent years because of their characteristically spectroscopic properties which can be used in fiber amplifiers, up-convertion lasers and displays. Anti-Stokes blue emission from $^3P_0$ state upon resonant excitation of $^1D_2$ manifold (591.6 nm at 15 K)[18] and resonant excitation $^3P_0$ state of Pr^{3+} ions in NCs (478.4 nm at 11 K) and in glass (483 nm at 11 K) have been investigated[19] in LaF_3 NCs based glass ceramic.

In order to perceive more understanding about the photoluminescence properties of Pr^{3+} ions doped transparent oxyfluoride glass ceramics as well as the distribution of Pr^{3+} ions in LaF_3 NCs based glass ceramic, herein, we used several laser sources, such as 532, 514.5 and 476.5 nm laser lines, to study the spectroscopic properties of glass ceramic with various Pr^{3+} ions concentrations (0.005% 0.05%, and 0.5%, in mol fraction). When excited by 532 nm and 514.5 nm laser lines, a relatively strong green fluorescence (transition from $^3P_0$ to $^3H_5$ of Pr^{3+} ions in NCs) as well as red fluorescence (transition from $^1D_2$ to $^3H_4$ and $^3P_0$ to $^3H_6$ of Pr^{3+} ions in glasses) were observed. Population on $^3P_0$ state of Pr^{3+} ions in NCs and glass was achieved by multi-phonon assistance process. Pr^{3+} ions in certain environments with strong electron-phonon coupling in the $^3P_0$ state are believed to present these spectroscopic characteristics. As a comparison, directly resonant excitation transition from $^3H_4$ (ground state) to $^3P_0$ state of Pr^{3+} ions in NCs and in glass by using 476.5 nm laser line was performed, and this emission behavior of Pr^{3+} ions was monitored which is clearly different from those obtained by 532 nm and 514.5 nm laser line excitation. Using 476.5 nm laser line as the excitation source, Pr^{3+} ions in certain environments, where population on $^3P_0$ state can be directly achieved, clearly show different photoluminescence features. Fluorescence quenching was also observed for Pr^{3+} ions in NCs when excited by different wavelengths.

2 Experiments

Transparent oxyfluoride glass ceramic samples were fabricated by Corning Inc, by melting the appropriate batch of materials[8]. LaF_3 NCs were formed in glass with a size of ~20 nm after annealing process[8]. There are two different types of Pr^{3+} ions, those in LaF_3 NCs and those in the glass host. In the annealing process, Pr^{3+} ions enriched into the LaF_3 NCs, causes the concentration of Pr^{3+} ions in NCs to be several times higher than that in glass. The photoluminescence was measured by Renishaw in Via Raman system (532 nm excitation) and Jobin-Yvon T64000 Raman system (476.5 nm and 514.5 nm excitation) with a spectrum resolution of 0.1 nm.

3 Results and Discussion

In our experiments, a DPSSL 532 nm laser line is resonant with the excited state transition $^3H_5$-$^3P_0$ of Pr^{3+} ions in NCs and in glass with multi-phonon assistance process. Fig. 1 shows the emission spectrum of glass ceramic with different Pr^{3+} ions concentration (0.005%, 0.05%, 0.5% in mol fraction) and precursor glass at room temperature. Red fluorescence (broad peak) located at 610 nm are the emissions from Pr^{3+} ions in glass ($^1D_2$ to $^3H_4$ and $^3P_0$ to $^3H_6$)[19]. When $^3P_0$ state of Pr^{3+} ion in glass is populated, the relaxation of $^3P_0$ state is dominated

by multi-phonon process to $^1D_2$ state because of high phonon energy of oxide glass (1 100 cm^{-1})[19]. Sharp peaks centered at 540 nm arise from $^3P_0$ to $^3H_5$ state of Pr^{3+} ions in NCs[19], compared with emission spectrum of precursor glass, it can be further verified those transitions are from Pr^{3+} ions in NCs. It is interesting if we pay attention to the transition behavior of Pr^{3+} ions in NCs and in glass. It can be obviously seen that, when the concentration of Pr^{3+} ions increases, the fluorescence intensity of Pr^{3+} ions in NCs decreases. While for transition from Pr^{3+} ions in glass (red fluorescence centered at 610 nm), the intensity of transition shows an increase as the concentration of Pr^{3+} ions increases. This opposite emission behaviors of Pr^{3+} ions in NCs and in glass can be understood in terms of the different concentration distribution of Pr^{3+} ions in NCs and in glass. In the annealing process, Pr^{3+} ions partition in the LaF_3 NCs causes the concentration of Pr^{3+} ions in NCs to be 5 ~ 10 times higher than that in glass[20]. Thus, it is more easily for concentration quenching phenomenon to occur for Pr^{3+} ions in NCs.

From Fig. 1, it can be seen that when $^3P_0$ state of Pr^{3+} ion in NCs is populated, only transition from $^3P_0$ to $^3H_5$ state exists and we attribute that spectroscopic properties as the characteristic of Pr^{3+} ion in certain environment with strong electron-phonon coupling in the $^3P_0$ state because of this kind of excitation process must need multi-phonon assistance. As a comparison, another way to achieve population on

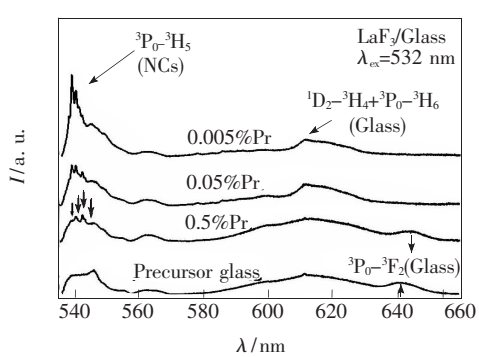

Fig. 1 Emission spectrum of the glass ceramic with different Pr^{3+} ions concentration (0.005%, 0.05%, 0.5% in mol fraction) and precursor glass at room temperature excited by 532 nm

$^3P_0$ state of Pr^{3+} ion in NCs without the help of phonon assistance excited by 476.5 nm is discussed which clearly show different fluorescence characteristics.

In order to get information about crystallization behavior and vibrational properties of transparent glass ceramics, we study the Raman spectrum of this kind of glass ceramics. Fig. 2 shows the Raman spectrum of oxyfluoride glass ceramics with different Pr^{3+} ions concentration excited by 532 nm laser line. Sharp peaks showed by solid arrows are the $^3P_0$-$^3H_5$ transition of Pr^{3+} ions in NCs and it clearly shows that when the concentration of Pr^{3+} ions increases, the emission intensity decreases. When the concentration of Pr^{3+} ions is 0.5%, only Raman peaks of LaF_3 NCs exist (289, 307, 362, 383 cm^{-1})[9], fluorescence from Pr^{3+} ions in NCs has been completely quenched by cross relaxation among neighboring Pr^{3+} ions[21]. Raman spectrum appears to be very sensitive to structural change of the glass network, thus, according to the Raman spectrum, we can tell after the heat treatment process, LaF_3 NCs are formed in the glass hosts.

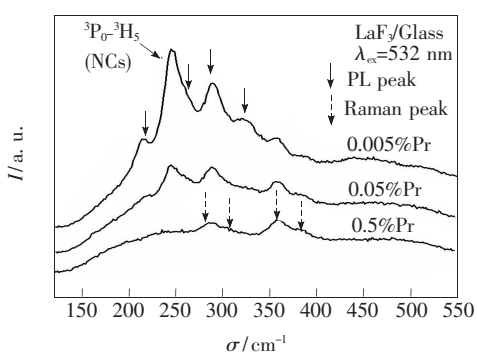

Fig. 2 Raman spectrum of the glass ceramic with Pr^{3+} ions concentration of 0.005%, 0.05%, 0.5% in mol fraction excited by 532 nm at room temperature.

In order to achieve more understanding about the photoluminescence properties of Pr^{3+} ions in NCs and in glass, directly resonant excitation involving transition from $^3H_4$ to $^3P_0$ state of Pr^{3+} ions in NCs by using 476.5 nm laser line (The $^3P_0$ state of Pr^{3+} ions in NCs is 478.7 nm at 11 K)[19] was performed. Fig. 3 shows emission spectrum excited by 476.5 nm line of an Ar^+ laser with different Pr^{3+}

ions concentration (0.5%, 0.05%, and 0.005% in mol fraction) at room temperature. Red fluorescence (broad peaks) centered at 610 nm ($^1D_2$-$^3H_4$, $^3P_0$-$^3H_6$), 643 nm ($^3P_0$-$^3F_2$) are the emissions from Pr^{3+} ions in glass[19]. Transition from $^3P_0$ state of Pr^{3+} ions in NCs to many lower states (sharp peaks), such as $^3H_5$, $^3H_6$, $^3F_2$ manifolds is observed[19]. That is clearly different from 532 nm emission spectrum in which only the transition from $^3P_0$ to $^3H_5$ of Pr^{3+} ions in NCs exists. As mentioned above, we attribute those different spectroscopic features excited by different laser lines as the contribution of Pr^{3+} ion in different environments. When excited by 532 nm laser line, multi-phonon assistance is needed to achieve population on $^3P_0$ state of Pr^{3+} ions in NCs and in glass, thus, Pr^{3+} ion in certain environments where with strong electron-phonon coupling contribute those photoluminescence features. When excited by 476.5 nm laser line, Pr^{3+} ions in certain environments where electron can be directly excited to $^3P_0$ state show different spectroscopy properties.

It is interesting if we pay attention to the concentration quenching phenomenon of Pr^{3+} ions in NCs when excited by 476.5 nm and 532 nm laser lines which clearly show different quenching concentration. From Fig. 3, it can be seen that when concentration of Pr^{3+} ions is 0.5%, the emission intensity from Pr^{3+} ions in NCs has began to quench due to cross relaxation among neighboring Pr^{3+} ions[21]. If we pay attention to emission spectrum excited by 532 nm, it shows different quenching concentration which is happening at the concentration of 0.05%. This phenomenon can be understood by the distribution of Pr^{3+} ions in NCs. As mentioned above, when excited by 532 nm, Pr^{3+} ions in certain environments where with strong electron-phonon coupling in the $^3P_0$ state contribute characteristic photoluminescence features. And concentration quenching phenomenon is easily happening for Pr^{3+} ions in such environment which indicates there have higher Pr^{3+} ions concentration. When excited with 476.5 nm, quenching concentration of Pr^{3+} ions is higher, begins at 0.5%, which clearly indicates that the concentration of Pr^{3+} ions in this environment is lower. According to above discussion, we could know that the distribution of Pr^{3+} ions in NCs is non-uniformly. When excited by different laser lines, Pr^{3+} ions in different environments contribute to different photoluminescence features.

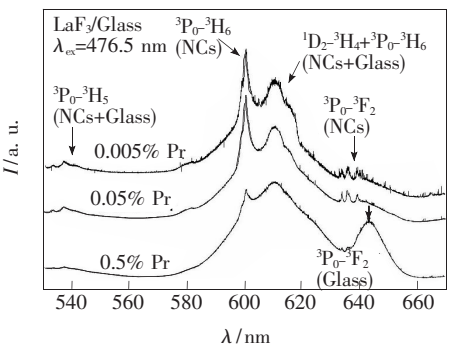

Fig. 3 Emission spectra of the glass ceramics with different Pr^{3+} ions concentration (0.005%, 0.05%, 0.5% in mol fraction) at room temperature excited by 476.5 nm when light mainly resonant with the $^3H_4$-$^3P_0$ transition of Pr^{3+} ions in NCs

When another wavelength 514.5 nm was also used to excite Pr^{3+} ions selectively, the photoluminescence features of Pr^{3+} ions were monitored. Fig. 4 presents the emission spectra of glass ceramics with different Pr^{3+} ions concentration (0.005%, 0.05%, and 0.5%, in mol fraction) excited by 514.5 nm line of an Ar^+ laser at room temperature. Red fluorescence (inset in Fig. 4) centered at 610 nm ($^3P_0$-$^3H_6$, $^1D_2$-$^3H_4$) is transition from Pr^{3+} ions in glasses. Multiphonon decay from $^3P_0$ state to $^1D_2$ state dominates for the relaxation of $^3P_0$ state of Pr^{3+} ions in glasses[19]. As the concentration of Pr^{3+} ions increases, the red fluorescence intensity increases. A relatively intense green fluorescence located at 540 nm arising from $^3P_0$ to $^3H_5$ of Pr^{3+} ions in NCs[19] is observed in Fig. 4, and this green fluorescence shows a decrease when the concentration of Pr^{3+} ions increases. When the concentration of Pr^{3+} ions is 0.5%, green fluorescence from Pr^{3+} ions in NCs has been completely quenched which is similar as 532 nm emission spectrum. In the whole spectral range, only transition from $^3P_0$ to $^3H_5$ exists which is definitely different from transition from $^3P_0$ state ex-

cited by 476.5 nm in which transition from $^3P_0$ state to many lower states such as $^3H_5$, $^3H_6$, $^3F_2$ manifolds is observed. These spectroscopic features can be understood by contribution of Pr^{3+} ions in certain environments where strong electron-phonon coupling in the $^3P_0$,1 state of Pr^{3+} ion in NCs. We believe the mechanism behind 532 nm emission spectrum and 514.5nm emission spectrum is the same. When excited by 532 nm and 514.5 nm, Pr^{3+} ions in certain environments where with strong electron-phonon coupling in the $^3P_0$,1 state contribute characteristic photoluminescence features such as when $^3P_0$ state is populated, only transition from $^3P_0$ to $^3H_5$ exists.

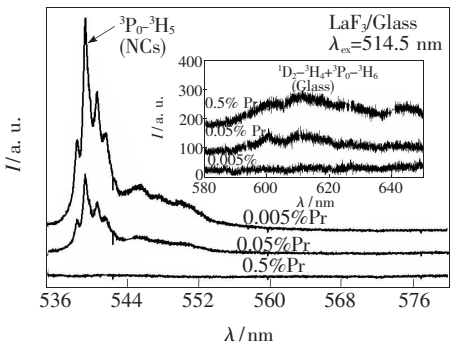

Fig. 4 Emission spectrum of the glass ceramic with different Pr^{3+} ions concentration (0.005% 0.05%, 0.5%, in mol fraction) at room temperature excited at 514.5 nm. Inset: red fluorescence from Pr^{3+} ions in glass excited by 514.5 nm

Fig. 5 shows the Raman spectrum of glass ceramic doped with different Pr^{3+} ions concentration excited by 514.5 nm laser lines. As we mentioned above, population on $^3P_1$ state of Pr^{3+} ions in NCs can be obtained with the help of multi-phonon assistance process, thus, transition from $^3P_1$ state of Pr^{3+} ions in NCs is observed. Sharp peaks located at 129.2 cm^{-1} (517.4 nm), 176.7 cm^{-1} (518.7 nm), 477.6 cm^{-1} (526.9 nm), 524.6 cm^{-1} (528.2 nm) are transition from $^3P_1$ to $^3H_5$ state of Pr^{3+} ion in NCs. For transition from Pr^{3+} ions in NCs, when the concentration increases, the emission intensity decreases. When the concentration of Pr^{3+} ions is 0.5%, the emission from Pr^{3+} ions in NCs has been completely quenched and only Raman peaks of LaF_3 NCs existing (289, 307, 362, 383 cm^{-1}[9]). This kind of transparent glass ceramic

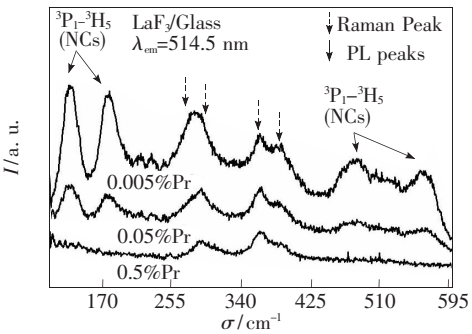

Fig. 5 Raman spectra of the glass ceramic with Pr^{3+} ions concentration of 0.005%, 0.05%, 0.5% in mol fraction excited by 514.5 nm at room temperature.

with different Pr^{3+} ions concentration clearly shows similar Raman features indicating the concentration effect of Pr^{3+} ions in the formation process of LaF_3 NCs is small.

4 Conclusion

In summary, spectroscopic properties of transparent oxyfluoride glass ceramic doped with Pr^{3+} ions with different concentrations were investigated by using excitation wavelengths of 532, 514.5 and 476.5 nm, respectively. Different spectroscopic features were observed, which can be understood as a consequence of Pr^{3+} ion in different environments. When excited by 532 nm and 514.5 nm laser lines, Pr^{3+} ions in certain environments where strong electron-phonon coupling in the $^3P_0$ state of Pr^{3+} ions in NCs and in glass contribute to certain characteristic fluorescence features, such as when $^3P_0$ state is populated, only transition from $^3P_0$ to $^3H_5$ exists. While excited by 476.5 nm, Pr^{3+} ions in certain environments where directly population on $^3P_0$ state of Pr^{3+} ions in NCs and in glass can be achieved which clearly show other fluorescence features, such as when $^3P_0$ state is populated, transition from $^3P_0$ to many other lower energy levels $^3H_5$, $^3H_6$, $^3F_2$ manifolds is observed. Above phenomenon can be understood as the contribution of Pr^{3+} ions in different environments. Firstly, according to the results of M. J. Dejneka[8], fluorides can come out of solution during cooling of the glass with the result that a fine crystalline precipitate is formed in glass. The TEM images of glass ceramics show those LaF_3 spherulites

up to 300 nm across and separations on the order of 500 nm. Reheating the glass to a temperature within or just above the annealing range permits atomic rearrangement to occur so that the crystalline fluoride nuclei formed. After the heat treatment process, ~20 nm LaF_3 NCs had grown in between them. Thus, the size of NCs may not evenly distribute in glass host. Secondly, the distribution of Pr^{3+} ions in NCs and in glass may be non-uniformly. At the surface of the NCs, there are many defects, vacancy, dangling bands which may cause the concentration of Pr^{3+} ions on the surface of NCs is much higher than inside the NCs. The RE ions surrounding in some cases could be determined from the change of electron transition probability. Thirdly, the optical properties of Pr^{3+} ions depend on the distribution of the Pr^{3+} ions in the NCs: whether it interstitial, or replaces a host ion, and whether it is at the surface of a NCs or segregate as oxides. The large contribution in the NCs luminescence could be from defects located close to the surface. According to above consideration, we believe when excited by different wavelengths, Pr^{3+} ions in different environments contribute different fluorescent features.

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Pr^{3+} 掺杂透明氟氧化物玻璃陶瓷的光谱特性

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摘要: 用不同的激发波长 532,514.5,476.5 nm,研究稀土 Pr^{3+} 掺杂的透明氟氧化物玻璃陶瓷中 Pr^{3+} 在 LaF_3 微晶环境和玻璃环境中的不同的荧光行为。对于微晶中的 Pr^{3+} 离子,当用 532 nm 和 514.5 nm 激发玻璃陶瓷时,观察到从 $^3P_0$ 能级到 $^3H_5$ 能级的发射,和 $^1D_2$ 能级到基态 $^3H_4$ 能级,$^3P_0$ 能级到 $^3H_6$ 能级的发射。我们认为微晶中 Pr^{3+} 离子的 $^3P_0$ 能级上的电子布局是依靠电声子耦合-多声子辅助来实现的。为了进行比较,用 476.5 nm 共振激发玻璃及微晶中 Pr^{3+} 离子的 $^3P_0$ 能级,观察到 $^3P_0$ 能级到很多低能级如:$^3H_5$、$^3H_6$、$^3F_2$ 的跃迁。而当在 532 nm 和 514.5 nm 非选择激发时,只有 $^3P_0$ 能级到 $^3H_5$ 能级的发射存在。我们认为这是由于不同的激光波长选择激发了不同环境中的 Pr^{3+} 离子,532 nm 和 514.5 nm 激发线选择激发了电声子耦合环境强中 Pr^{3+} 离子。不同 Pr^{3+} 离子掺杂摩尔分数分别为 0.005%,0.05%,0.5% 的发射光谱的研究还表明,这些电声子耦合环境强中的 Pr^{3+} 离子浓度很高,很容易发生浓度猝灭现象。最后,用拉曼光谱研究了这类玻璃陶瓷的结晶性为和振动特性。

关 键 词: 透明氟氧化物玻璃陶瓷; 镨离子; 纳米晶

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