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Optical properties of transparent Pr:YSAG ceramic

Tao Feng, Jianlin Shi [*], Danyu Jiang

Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Ding-Xi Road, Shanghai 200050, China

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Abstract

Pr-doped $Y_3Sc_xAl_{(5-x)}O_{12}$ (Pr:YSAG) powders were prepared with a chemical combustion method. Transparent Pr:YSAG ceramics with up to 40% scandium substitution for aluminum (Pr:$Y_3Sc_2Al_3O_{12}$) and 4 at.% of Pr doping were successfully fabricated by sintering the powder compact at 1800 °C under H_2 atmosphere. Optical properties of Pr:YSAG transparent ceramics were investigated in detail. It was found that by the scandium substitution for aluminum, the YSAG lattice expanded, which favored the formation of Pr:YSAG solid solution.

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Keywords: C. Optical properties; YSAG; Transparent ceramic

1. Introduction

Yttrium aluminum garnet $Y_3Al_5O_{12}$ (YAG) is a stable refractory material with good thermal–mechanical properties. It can resist high temperature and thermal-shock, and it is transparent over a wide spectral range which makes it a privileged host for luminescent application. YAG crystal has a cubic phase within the *Ia*-3*d* space group. The oxygen ions form a three-dimensional structure in which three kinds of sites exist: dodecahedral, octahedral and tetrahedral. Yttrium cations are located at dodecahedral, and aluminum cations are at octahedral and tetrahedral sites. After being incorporated into the lattice, lanthanide dopants will be located at dodecahedral site. Other small dopants are located at the octahedral and tetrahedral sites depending on the ionic radius of the doped cations. Lanthanide-doped YAG can be used as solid-state laser material.

Due to the useful laser transition of Pr^{3+} at both visible and infrared wavelength, many researchers have an on-going interest in identifying optimal host for it. Pr-doped YAG has been investigated as a potential amplifying medium at 1.3 μm (the $^1G_4 \rightarrow {}^3H_4$ transition) [1], a wavelength of interest in optical communication. Though it attracts a lot of attentions, there are still some difficulties in the fabrication of Pr-doped YAG single crystals.

Since the ionic radius of Pr^{3+} is larger than that of Nd^{3+} ions, Pr^{3+} is more difficult to be doped into a YAG single crystal than Nd^{3+}. Monchamp [2] has reported that the effective segregation coefficient of Pr^{3+} ions for a YAG single crystal fabricated by Czochralski method is near zero, which means that Pr^{3+} ions are very difficultly to dissolve into the lattice of YAG single crystals. There are some report on the successful fabrication of Pr:YAG single crystal, but the concentration of Pr in those single crystal is very low, usually at 0.08–0.12% [3–5].

Ikesue and Sato reported that they have fabricated Pr-doped YAG transparent ceramics, and the related optical properties were also given [6]. They stated that Pr ions can be doped into the ceramic lattice just because the difference in the structure relaxation between the ceramic and single crystal, or the dissolution of Si element into YAG lattice. An alternative approach to dope more Pr is to substitute for aluminum with elements of larger size in YAG without changing the crystal structure. The larger ionic size will lead to the lattice expansion, in this way more Pr^{3+} ions can be accommodated in the lattice, as Pr^{3+} is apparently larger than Y^{3+} for which Pr^{3+} substitutes. Sc^{3+} has larger size than Al^{3+}, and therefore is selected to replace Al^{3+} in YAG. Sc_2O_3 has been reported to form a cubic solid solution $Y_3Sc_xAl_{(5-x)}O_{12}$(YSAG). The former study shows that Cr^{4+}:$Y_3Sc_xAl_{(5-x)}O_{12}$ single crystals had much decreased quantum efficiency as compared with Cr^{4+}:$Y_3Al_5O_{12}$

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[*] Corresponding author. Tel.: +86 21 52412712; fax: +86 21 39986004.
E-mail address: jlshi@sunm.shcnc.ac.cn (J. Shi).

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[7,8]. The fabrication of Nd:YSAG ceramics has also been tried [9–11].

Here we report the successful fabrication of transparent Pr-doped yttrium aluminum (scandium) garnet (Pr:YSAG) ceramics with x value in Pr:$Y_3Sc_xAl_{(5-x)}O_{12}$ being 0, 0.5, 1, 1.5, and 2, respectively, by a chemical combustion route.

2. Experiment

2.1. Material preparation

Pr-doped YSAG powder was prepared with a chemical combustion method. $Y(NO_3)_3{\cdot}H_2O$ (99.99% purity), $Al(NO_3)_3{\cdot}9H_2O$ (99.99% purity), ammonium triacetic acid (NTA) (analysis grade purity), Sc_2O_3 and Pr_4O_{11} were used as raw materials. Solutions were obtained by dissolving $Y(NO_3)_3{\cdot}H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ in de-ionized water and Sc_2O_3 and Pr_4O_{11}(99.99% purity) in nitric acid. The mixed solutions containing Y^{3+}, Al^{3+}, Sc^{3+}, and Pr ions were prepared from the as-prepared solutions with appropriate volumes. A Pr:YSAG precursor solution with a molar ratio of (Y + Pr):(Al + Sc) = 3:5, in a glass beaker, was continuously stirred during heating at 85–90 °C on a hot plate, and an appropriate amount of NTA aqueous solution (NTA to metal ion ratio of 1) was added into the metal ion solution. The mixed solution slowly became viscous, and turned into gel, then was put into a furnace pre-heated at 500 °C for combustion. A tan-colored powder formed afterwards. The powder was then calcined at different temperatures for 2 h for XRD. The prepared powders were cold pressed into disks ≈20 mm in diameter at 70 MPa, then cold isostatically pressed at 200 MPa. Specimens were then pre-sintered at 1000 °C for 2 h in air to remove any residue organics introduced during molding operation. Finally specimens were sintered at 1800 °C for 6–12 h with a heating rate of 15 °C/min in dry H_2. The thermal etching process was conducted at 1400 °C for 20 min in air, then cooled down to room temperature in furnace. The detailed process was shown in references [10,11].

2.2. Characterization of specimens

XRD patterns of the samples were recorded on D/MAX-2550 V (Japan RIGAKU) with Cu $K\alpha_1$ radiation. Optical transmission spectra and absorption spectra were obtained on a UV 3101 PC spectrophotometer (Japan SHIMADZU) in the wavelength from 200 to 2600 nm. The emission spectra and fluorescence lifetime were obtained using FLUOROLOG-3 (Jobin Yvon American) with a HAMAMATSU R5509–72 (InP/InGaAs) detector (step = 1 nm, resolution = 0.5 nm), and the emission spectra were recorded from 1100 to 1500 nm (step = 1 nm, resolution = 0.5 nm).

3. Result and discussion

Fig. 1. A photograph showing transparent Pr(2 at.%):$Y_3Sc_{1.5}Al_{3.5}O_{12}$ pellet sintered under hydrogen atmosphere at 1800 °C for 6 h (unpolished; thickness = 1 mm).

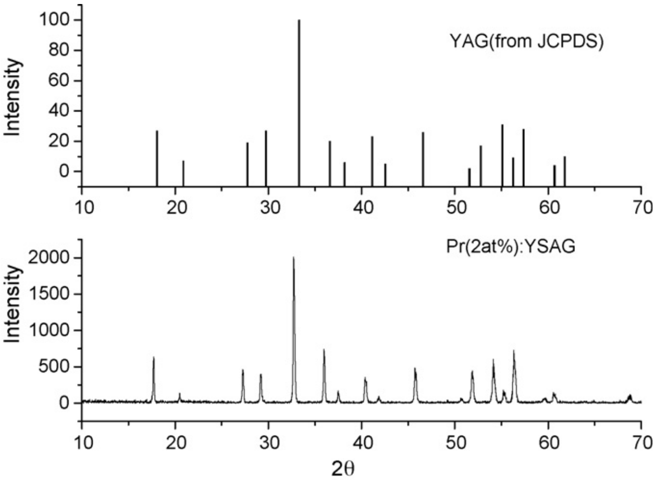

Fig. 2. XRD patterns of a standard YAG crystal and sintered Pr:$Y_3Sc_{1.5}Al_{3.5}O_{12}$ materials.

Fig. 1 is a photograph of the hydrogen-sintered Pr:$Y_3Sc_{1.5}Al_{3.5}O_{12}$ pellet doped with 3 at.% Pr. The sintered pellet is 10 mm in diameter and 1 mm in thickness. The Pr:YSAG powder produced in such a way is highly sintering active, and can be sintered to high transparency at 1800 °C without SiO_2 addition which was used as a sintering aid by Ikesue [6,9,12–14] Sintering in of H2 atmosphere is not only favorable for the pore removal, also help to reduce Pr^{4+} to Pr^{3+} ions which we needed. In one word, we have successfully fabricated transparent Pr^{3+}:YSAG ceramic by this method.

Fig. 2 is the XRD pattern of sintered sample. It is obvious that the sample has a pure cubic phase. The XRD pattern of

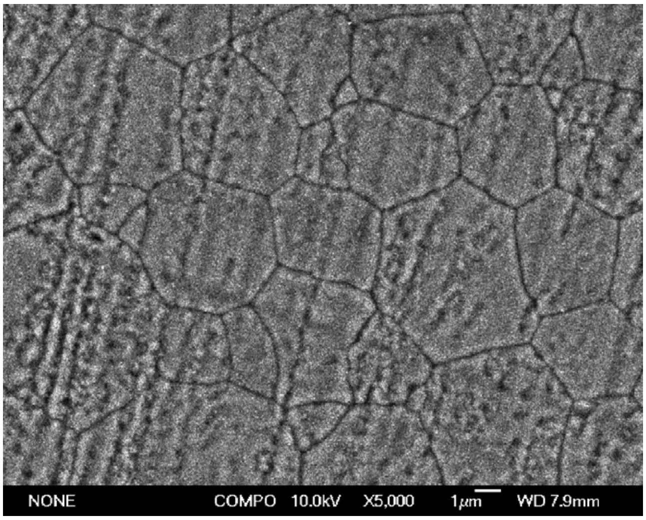

Fig. 3. SEM image of thermal-etched surface of Pr:$Y_3Sc_{1.5}Al_{3.5}O_{12}$ transparent ceramic (1400 °C, 10 min).

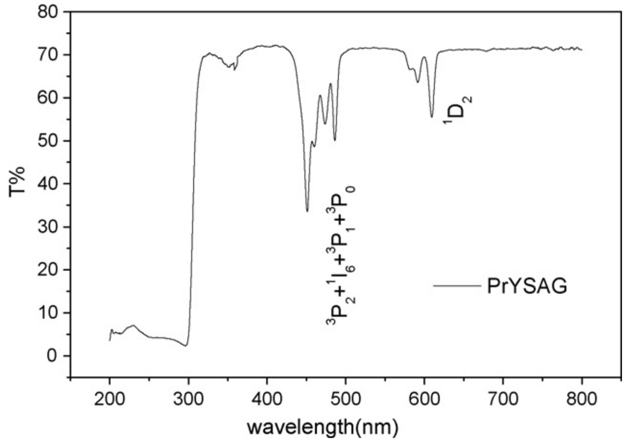

Fig. 4. Light transmission spectrum of $Pr:Y_3Sc_{1.5}Al_{3.5}O_{12}$ transparent ceramics.

$Pr:Y_3Sc_{1.5}Al_{3.5}O_{12}$ is almost identical to that of pure YAG with a little shift of the peak positions towards smaller 2θ values (larger lattice constants) due to the substitution of scandium for aluminum, which means that the Pr and Sc ions have dissolved into the crystalline lattice and do not exist as any separate phase.

Fig. 3 is the photograph of thermal etched surface of $Pr:Y_3Sc_{1.5}Al_{3.5}O_{12}$ transparent ceramics. The sample was thermal etched in air at 1400 °C for 20 min. In this figure, most of the grain size of Pr:YSAG transparent ceramics are below 10 μm and the grain boundary is very clear.

Fig. 4 illuminates the light transmission curve of transparent ceramic $Pr:Y_3Sc_{1.5}Al_{3.5}O_{12}$ doped with 3 at.% Pr (thickness = 1 mm) at visible range. From this figure, we can see that the transparent $Pr:Y_3Sc_{1.5}Al_{3.5}O_{12}$ ceramic has a very high light transmission higher than 70%. Higher transmittance would be expected if pore content in $Pr:Y_3Sc_{1.5}Al_{3.5}O_{12}$ transparent ceramics was lowered; it also shows the strong absorption bands near 450 and 600 nm by Pr^{3+} ions.

Fig. 5 is the absorption spectrum (thickness = 1 mm) of $Pr:Y_3Sc_{1.5}Al_{3.5}O_{12}$ in the range from 200 to 2600 nm. It is very similar with Pr:YAG absorption spectra measured by Ikesue [6]. The crystal field around Pr in $Y_3Sc_{1.5}Al_{3.5}O_{12}$ is the same as that in YAG. Strong absorption bands can be seen near 500, 1500 and 1900 nm.

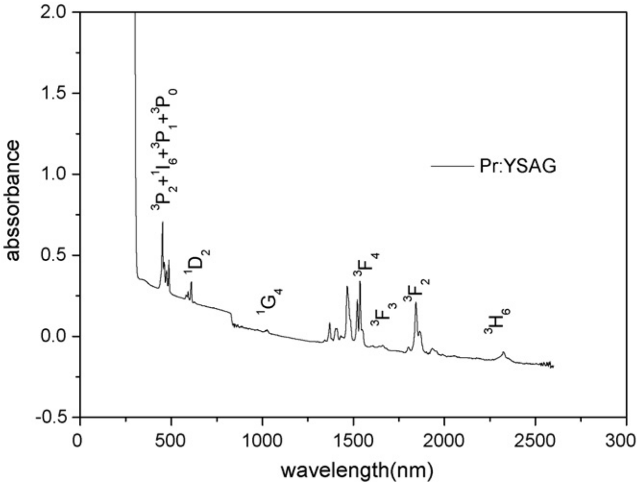

Fig. 5. Absorption spectrum of 3 at.% $Pr:Y_3Sc_{1.5}Al_{3.5}O_{12}$ ceramic.

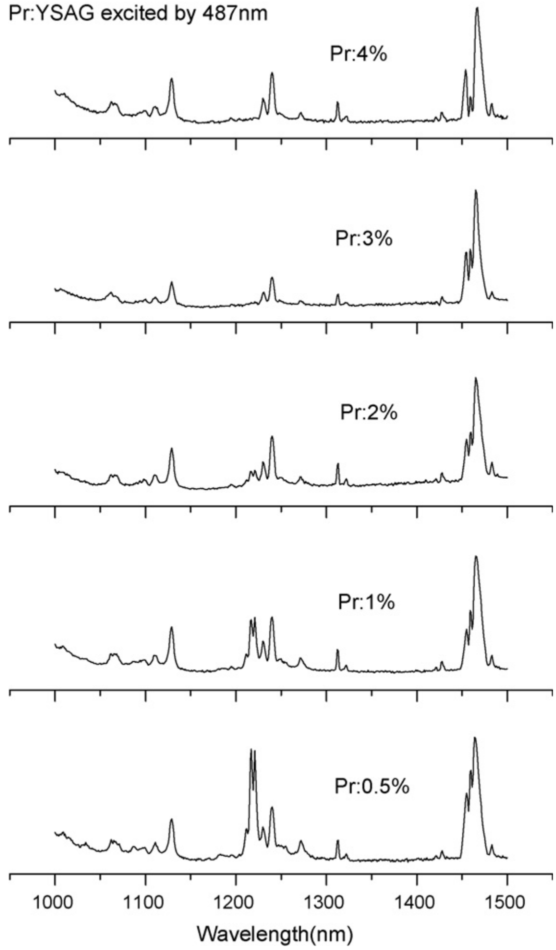

Fig. 6. Emission spectra of $Pr:Y_3Sc_{1.5}Al_{3.5}O_{12}$ with different Pr concentrations excited at 487 nm.

Fig. 6 shows the fluorescence spectra of $Pr:Y_3Sc_{1.5}Al_{3.5}O_{12}$ ceramics with different Pr concentrations excited by 487 nm beam of a xenon lamp. From this figure, we can see that there is an emission peak near the 1310 nm. In the absorption spectra there is an absorption peak around 1000 nm. The wavelength of the emission peak at 1310 nm fit the requirement for the amplifying medium of 1.3 μm. As the concentration of Pr increases, the emission peak around 1200 nm becomes weaker, that is, the relative emission intensity is changed.

Fig. 7 presents the emission spectra of $Pr:Y_3Sc_xAl_{5-x}O_{12}$ with different scandium contents excited by 487 nm beam of a xenon lamp. When the scandium content increases, the relative emission intensity between the emission peak of 1310 nm and that around 1200 nm also changes. The change of relative emission intensity of 1200 and 1310 nm is accompanied with concentrations of Sc and Pr. As the concentrations of Sc and Pr increased, the constant of crystal lattice is enlarged. May be this is the real reason for the change of relative emission intensity of 1200 and 1310 nm.

Fig. 8 is the fluorescence decay curve of Pr:Y(S)AG. It can be seen that as the Pr doping level increases, the decay time of

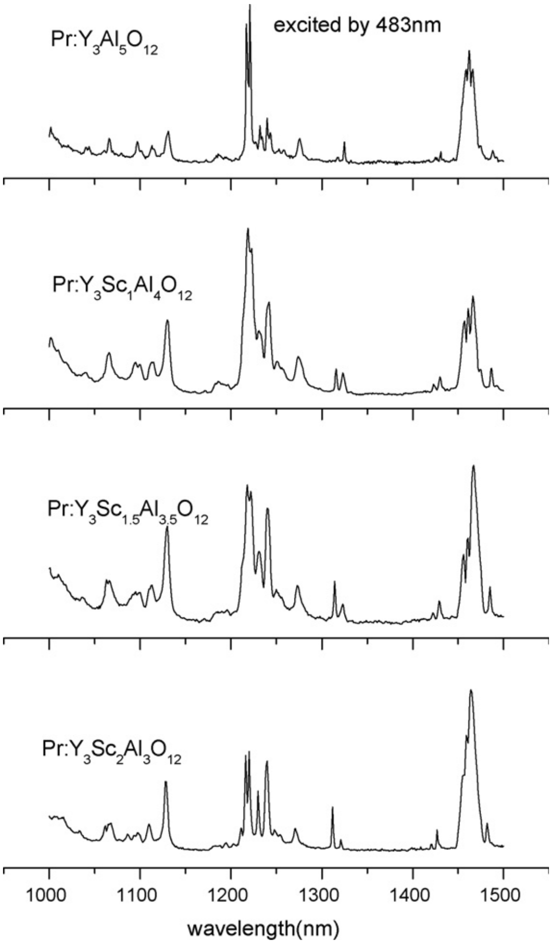

Fig. 7. Emission spectra of Pr(1 at.%):$Y_3Sc_xAl_{5-x}O_{12}$ ($x = 1$–2) doped with different contents of scandium excited at 487 nm.

the emission at 1310 nm became shorter in both $Y_3Sc_{1.5}Al_{3.5}O_{12}$ and YAG. The dependence of the decay time on doping is also displayed in Fig. 9. In Pr:YAG ceramics, the decay time decreases from 200 to 120 μs as the Pr concentration increases from 0.5 to 2 at.%; Similarly, it changes from 160 to 100 μs in Pr:$Y_3Sc_{1.5}Al_{3.5}O_{12}$ ceramics.

Just because the effective segregation coefficient of the Pr is close to zero, it is very difficult to fabricate Pr-doped YAG single crystal. This difficulty might be caused by the relatively large difference between the radius of Y^{3+}(0.102 nm) and Pr^{3+}(0.116 nm). However, in this work, we have fabricated transparent Pr:YSAG ceramic doped with up to 4 at.% Pr ions. When the scandium replaces aluminum ion in the YAG structure, due to the larger radius of Sc^{3+}(0.73 nm) than that of Al^{3+}(0.51 nm), such a replacement results in the lattice expansion which creates more space for the acceptance of large ions in the lattice. In this way we can fabricate transparent Pr high-doped YSAG ceramics without the appearance of second phase. The transparent Pr:YSAG ceramics obtained in this work was confirmed by XRD to have a pure YAG structure, by spectroscopy to have good optical transmittance. Both of those results proved that Pr^{3+} ions were homogeneously doped into the host material (YSAG ceramic). The substitution of scandium for aluminum contributes to the formation of Pr:YSAG solid solution of transparent YSAG ceramics.

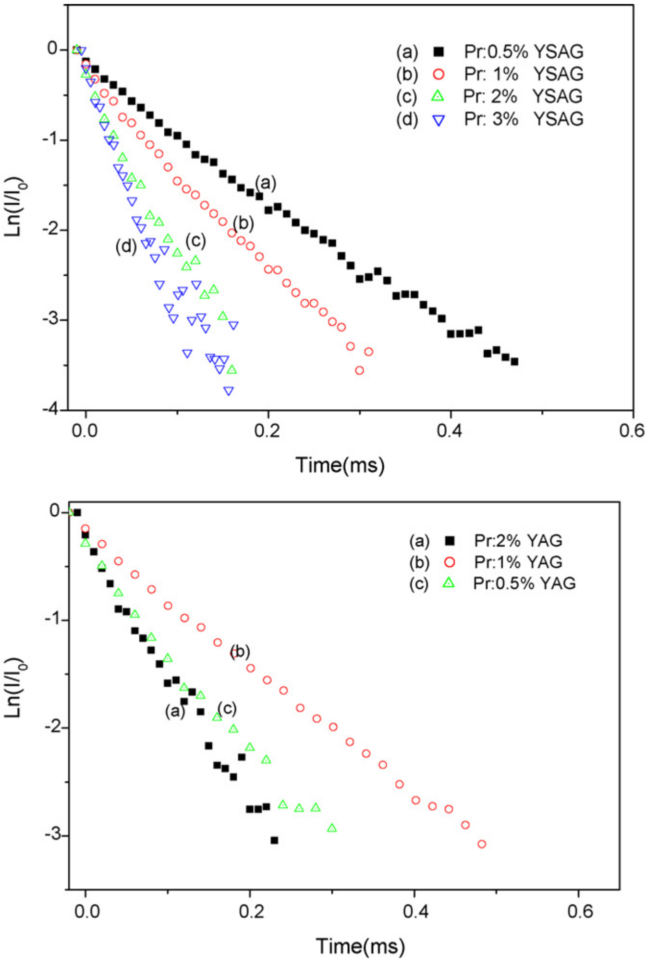

Fig. 8. Fluorescence decay curves of Pr:YSAG (the upper figure), and Pr:YAG (the bottom figure) doped with different contents of Pr ($\lambda_{em} = 1310$ nm).

These results indicate that Pr:YSAG exhibits suitable spectroscopic properties at 1.3 μm, which make the system interesting as laser gain media operating at this wavelength.

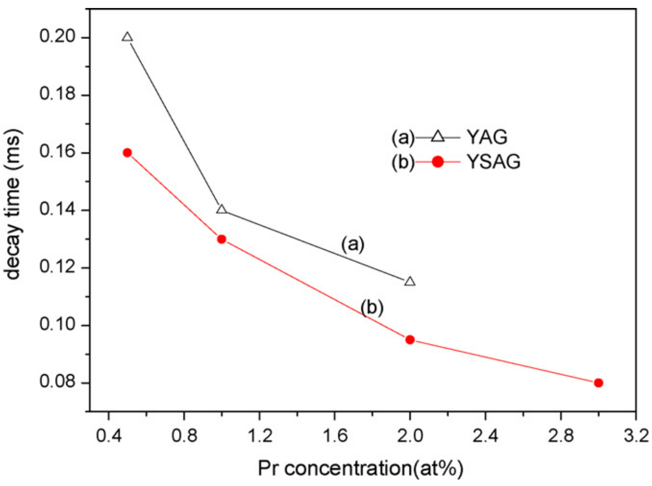

Fig. 9. Fluorescence lifetime of Pr:YAG and Pr:$Y_3Sc_{1.5}Al_{3.5}O_{12}$ ($\lambda_{em} = 1310$ nm).

4. Conclusion

We have successfully fabricated highly transparent Pr:YSAG ceramics by a chemical way (powder precursor by chemical combustion synthesis and sintering under H_2 atmosphere), which overcomes the difficulty in fabricating Pr:YAG single crystal. The doping concentration is up to 4 at.% Pr ions, which cannot be realized in single crystal. Pr:YSAG transparent ceramics is a suitable material for laser operating around 1.3 μm.

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