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Energy transfer processes in Pr^{3+}: $Be_2La_2O_5$ crystals

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Abstract

Up-converted blue emission has been generated in a 1 at.% Pr^{3+}:$Be_2La_2O_5$ crystal after orange and infra-red excitation. The responsible up-conversion mechanisms were investigated and shown to be energy transfer and excited state absorption, respectively. The dynamics of the involved excited states have been studied under pulsed laser excitation. These results are compared with those for Pr^{3+} ion in different laser crystals.

Keywords: Praseodymium; Pr^{3+}:$Be_2La_2O_5$; Luminescence; Up-conversion

1. Introduction

Lanthanum beryllate crystals $Be_2La_2O_5$ (BLO) doped by lanthanide ions have been recently investigated as potential laser systems. Neodymium doped BLO was shown to have a good lasing properties [1], holmium doped BLO was investigated as the potential 3-μm laser material [2] and polarized optical spectra and TR ESA have been measured in BLO:Pr [3]. In [4] we have reported the absorption, emission, excitation and fluorescence lifetime measurements for sample containing 1 at.% of Pr^{3+} ions. We presented also a Judd–Ofelt analysis of the Pr^{3+} ion oscillator strengths in BLO.

Trivalent praseodymium ion (Pr^{3+}) in various crystals is well known for having a very rich emission spectrum extending from the ultra-violet (UV) to the infra-red (IR) [5,6]. Because of the energy level structure, and suitable lifetimes of the excited states, Pr^{3+} systems are also attractive as short wavelength up-conversion laser materials [7]. Recently, simultaneous blue and orange wavelength lasing in Pr^{3+} doped YAG, YAP and YLF crystals has been studied [8] and observation of lasing at 486 nm in Pr^{3+}:GGG has been also reported [8].

This encouraged us to study possible up-conversion processes of Pr^{3+} ion in $Be_2La_2O_5$. In this work we analyze up-conversion processes leading to blue fluorescence from the excited $^3P_0$ state of the Pr^{3+} ion in $Be_2La_2O_5$ crystal. We report the IR-to-blue and orange-to-blue wavelength up-conversion.

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2. Experimental

The experimental apparatus used to investigate spectroscopic properties of Pr^{3+} ion in $Be_2La_2O_5$ has been described previously [9].

2.1. Orange-to-blue wavelength up-conversion

It was observed that excitation of the $^1D_2$ Stark levels results in an intense emission from the higher lying $^3P_0$ state. The excitation spectrum of this anti-Stokes up-converted emission in the $Be_2La_2O_5$ crystal, presented in Fig. 1, was recorded when collecting the $^3P_0$ fluorescence at 491 nm and tuning the laser frequency over the lowest Stark component of the $^1D_2$ manifold at 16 500 cm^{-1} (606 nm). For comparison the excitation spectrum of the $^1D_2$ emission, measured by monitoring the $^1D_2$ near IR fluorescence, is also displayed in the same figure. It is seen that differences between the shape of the excitation profiles exist. The temporal evolution of the $^3P_0$ Stokes and anti-Stokes emissions are presented in Fig. 2. It can be seen that the up-converted signal has a short rise time of 0.2 μs and decay is non-exponential, approaching at long time delays the decay time of 2 μs which is nearly equal to the $^3P_0$ fluorescence decay time measured under OP excitation conditions.

2.2. IR-to-blue wavelength up-conversion

Blue and several transitions in the visible part of the spectrum, characteristic for the $^3P_0$ emission of praseodymium has been observed between 10 and 300 K

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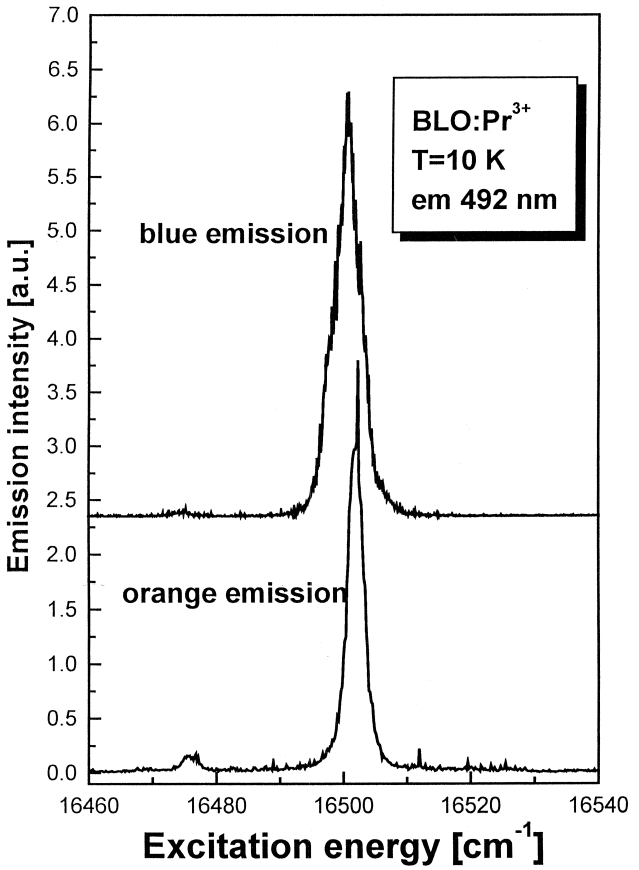

Fig. 1. Excitation spectra of the up-converted $^3P_0$ (492 nm) emission (upper curve) and $^1D_2$ emission (lower curve) in BLO:Pr^{3+} at $T=10$ K. The laser excitation energy was tuned around the $^3H_4$ (1)→$^1D_2$(1) absorption transition.

for several excitation wavelength in the 850–930 nm band. The excitation spectrum of this anti-Stokes fluorescence measured at 10 K in Pr^{3+}: $Be_2La_2O_5$ is presented in Fig. 3. The decay profile of the blue emission resulting from the IR excitation at 911 nm (10 977 cm^{-1}) is shown in Fig. 4. For comparison, directly, one-photon (OP) excited decay is also presented in the same figure. It can be seen that IR excited decay is exponential with a low-temperature lifetime of 2 μs and no observable rise-time, as after OP direct excitation. Finally, a square intensity dependence of the up-converted $^3P_0$ emission on IR excitation power was determined.

3. Discussion

3.1. Orange-to-blue wavelength up-conversion

The quadratic dependence of the blue up-converted emission on the incident orange pump intensity indicates a two-photon (TP) excitation process. TP absorption process could be ruled out because there is no energy state of Pr^{3+} with twice of the excitation photon energy of 16 500 cm^{-1}. In addition, the short rise time in the TP excited $^3P_0$ fluorescence dynamics is characteristic for an energy transfer up-conversion (ETU) process. The ETU process has been investigated in various praseodymium systems [9,10] and was related to the following quasi resonant mechanism;

$$^1D_2(1) + {}^1D_2(1) \rightarrow {}^1G_4(8) + {}^3P_2(2) + E_{\text{phonon}}$$

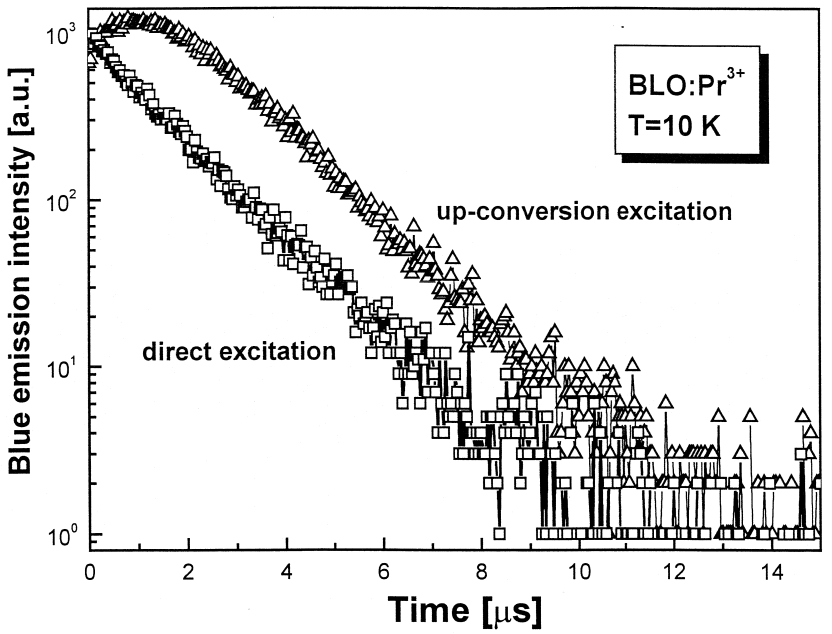

Fig. 2. Decay profile of the $^3P_0$→$^3H_4$ (492 nm) luminescence in BLO:Pr^{3+} resulting from up-conversion orange excitation at 16 500 cm^{-1} and direct one-photon excitation measured at 10 K.

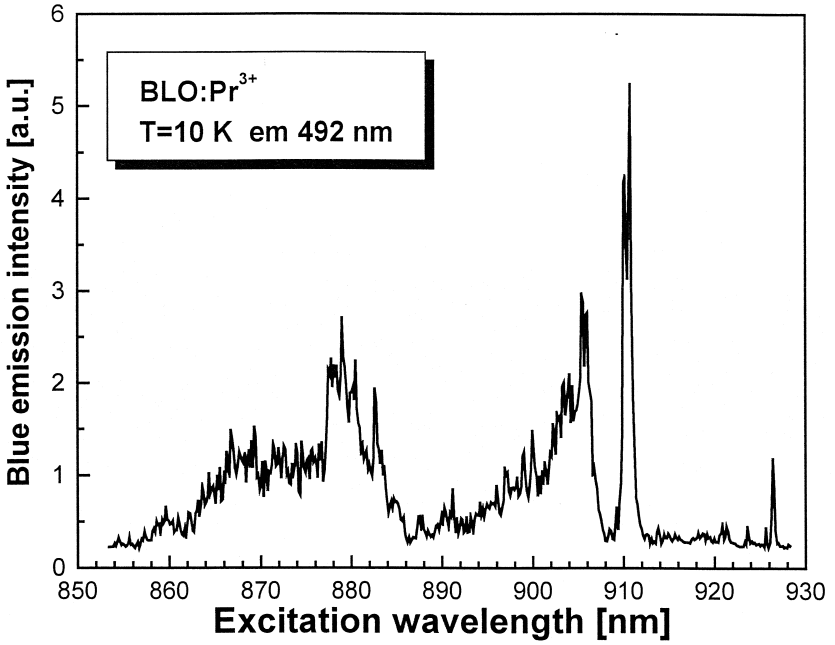

Fig. 3. IR excitation spectrum of the blue $^3P_0$ emission in BLO:Pr^{3+} at 10 K.

where in BLO the excess energy of 38 cm^{-1} is released.

The energy level scheme for BLO:Pr^{3+} [3] shows that there is also possibility of resonant ESA mechanism. After relaxation from the $^1D_2$ to $^3H_6$ state there is ESA from $^3H_6$ to $^3P_1$ which, after fast non-radiative decay, finally results in $^3P_0$ emission according to the scheme

$$^1D_2(1) \rightarrow {}^3H_6(1) + {}^1D_2(1) = {}^3P_1(1)$$

Thus, it is possible that two different up-conversion processes, ETU and ESA, are simultaneously active in the Pr^{3+}:$Be_2La_2O_5$ system.

3.2. IR-to-blue wavelength up-conversion

The TP character of the observed up-conversion process is confirmed by its square intensity dependence. The

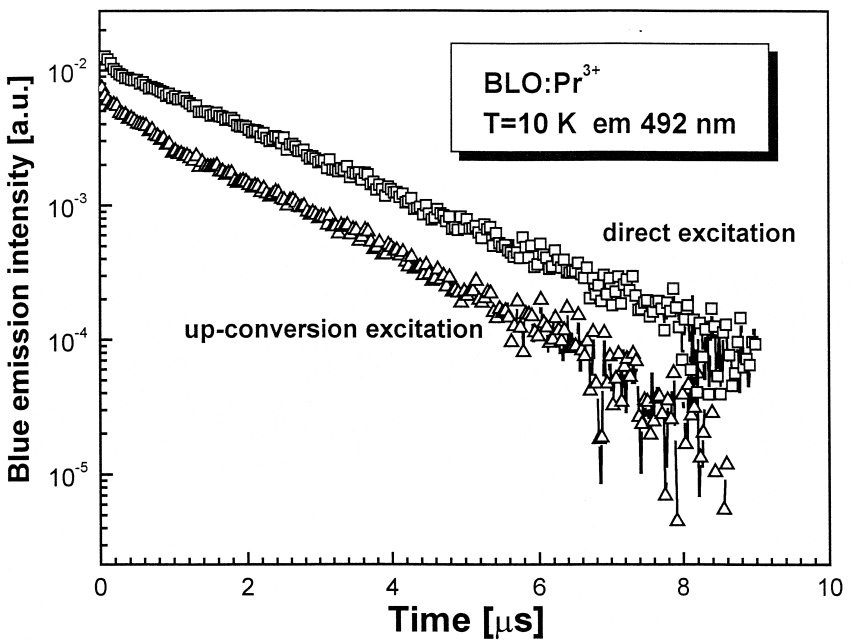

Fig. 4. Decay profiles of the blue $^3P_0 \rightarrow {}^3H_4$ (492 nm) luminescence in BLO:Pr^{3+} resulting from IR up-conversion excitation (911 nm) and direct one-photon excitation at 10 K.

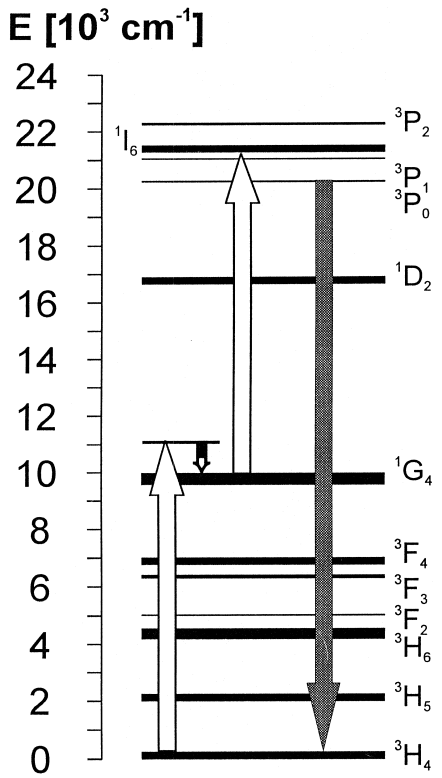

Fig. 5. Simplified energy level diagram for BLO:Pr^{3+} explaining the IR-to-blue wavelength up-conversion excitation process.

absence of rise time and lack of any lifetime changes with respect to OP excited decay is typical of an ESA process. As in the case of investigated earlier praseodymium activated YAG, YLF and YAP crystals [9,11] the only possible up-conversion mechanism, which results in the excitation of the blue emission with IR photons, is ESA from the $^1G_4$ state. Analysis of the collected data lead to the up-conversion mechanism as presented in the energy level diagram in Fig. 5. The spectrum in Fig. 3 corresponds to the second ESA step from the lowest $^1G_4$ Stark level to the levels of the $^3P_0 + {}^1I_6 + {}^3P_1$ manifolds. The first step is non-resonant absorption to the phonon band of the $^3H_4 \rightarrow {}^1G_4$ transition. After rapid non-resonant relaxation, the lowest $^1G_4$ Stark level is populated. In Fig. 6 comparison of the OP excitation and ESA spectra for BLO is shown, which allowed identification of lowest Stark component of the $^1G_4$ multiplet at 9719 cm^{-1}. It could be seen that ESA spectrum shows an enhanced weak structure around 20 800 cm^{-1} observed in OP excitation. Thus, spin allowed $^1G_4 \rightarrow {}^1I_6$ transitions provided us with better resolved spectra of the $^1I_6$ manifold that was observed for OP excitation spectra.

The fluorescence lifetime of the $^1G_4$ state is measured in $Be_2La_2O_5$ crystal to be very short, less than 0.2 μs, resulting in much lower than in YAG and YLF [11] efficiency of the Pr^{3+} up-conversion.

Finally, with the use of Judd–Ofelt intensity parameters

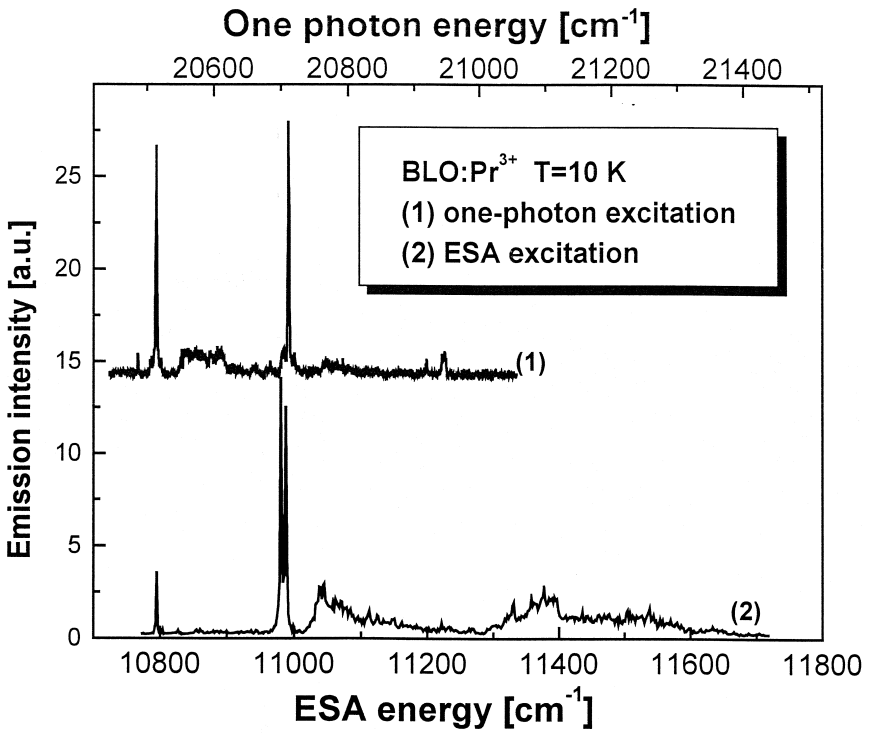

Fig. 6. Comparison of the excitation spectra of the $^3P_0$ (492 nm) emission obtained in BLO:Pr^{3+} after IR two-photon pumping (lower curve) and after blue one-photon pumping (upper curve), $T = 10$ K.

determined by us in [4] and ESA spectrum presented in Fig. 3, effective ESA cross section for the $^1G_4 \rightarrow {}^1I_6$ transition was calculated to be $\sigma_{ESA} = 3.55 \times 10^{-19}$ cm^2. In contrast to this strong ESA the first step GSA to the $^1G_4$ levels is extremely weak, of the order of 10^{-21} cm^2. Absorption cross sections for OP $^3H_4 \rightarrow {}^3P_J$ transitions were calculated to be 1×10^{-20} cm^2, 1.3×10^{-20} cm^2 and 1.8×10^{-20} cm^2, respectively for $J = 0$, 1 and 2.

4. Conclusion

In summary, two different mechanisms of up-conversion leading to blue $^3P_0$ emission have been studied in Pr^{3+}:BLO crystals; energy transfer between two ions in the $^1D_2$ state after orange-wavelength excitation and ESA via intermediate $^1G_4$ and $^3H_6$ manifolds after IR and orange excitation, respectively.

References

[1] L. Goldberg, M.K. Chun, Appl. Phys. Lett. 55 (1989) 218.
[2] S.A. Payne, L.K. Smith, W.F. Krupke, J. Appl. Phys 77 (1995) 4274.
[3] N.V. Kuleshov, A.S. Shinkevich, V.G. Shcherbitsky, V.P. Mikhailov, T. Danger, T. Sandrock, G. Huber, Optics Mater. 5 (1996) 11.
[4] R. Piramidowicz, M. Malinowski, W. Woliński, in: Proc. TSSL '96 Conference SPIE, 1996, p. 74.
[5] A.A. Kaminskii, Advanced Solid-State Lasers, New Orleans, MS1-3 February 1993, Vol. 15, A. Pinto, T.Y. Fan (Editors), OSA, Washington, DC, p. 266.
[6] A.A. Kaminskii, Phys. Stat. Sol. A 148 (1995) 9.
[7] D.M. Baney, G. Rankin, K. Chang, Optics Lett. 21 (1996) 1372.
[8] M. Malinowski, M.F. Joubert, R. Mahiou, B. Jacquier, J. Phys. IV (1994) C4–541.
[9] M. Malinowski, C. Garapon, M.F. Joubert, B. Jacquier, J. Phys.: Condens. Matter 7 (1995) 199.
[10] J.C. Vial, R. Buisson, F. Madeore, M. Poirier, J. Phys. 40 (1979) 913.
[11] M. Malinowski, M.F. Joubert, B. Jacquier, Phys. Rev. B 50 (1994) 12367.