Conf-950101--6

UCRL-JC-118195
PREPRINT

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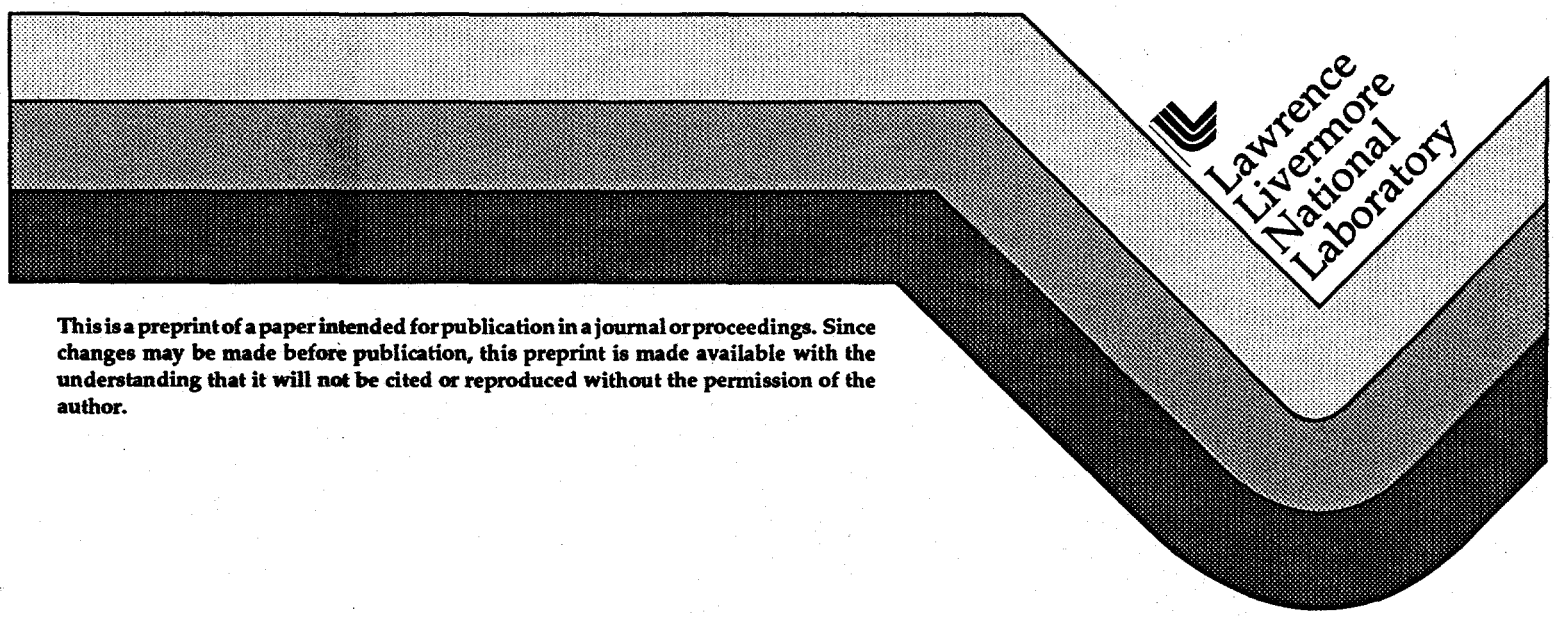
This paper was prepared for submittal to the
Advanced Solid State Lasers 10th Topical Meeting
Memphis, Tennessee
January 30-February 2, 1995

March 9, 1995



Spectroscopy and Decay Kinetics of Pr^{3+}-doped Chloride Crystals for 1300-nm Optical Amplifiers

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Abstract

Several Pr^{3+}-doped chloride crystals have been tested spectroscopically for suitability as 1300-nm optical amplifiers operating on the $^1G_4$ - $^3H_5$ transition. $^1G_4$ lifetimes are much longer than in fluoride hosts, ranging up to 1300 μsec and suggesting a near-unity luminescence quantum yield. Emission spectra are typically broad (FWHM ~ 70 nm) and include the 1310-nm zero-dispersion wavelength of standard telecommunications fiber.

Introduction

The recent development of fiber-optic amplifiers, with their high gain, extreme bandwidth, low distortion and noise, low cost, and "transparency" to modulation format, is revolutionizing the communications industry. Qualitatively, the optical amplifiers are simply linear systems which do not sense the transmitted information in any way; in other words, they are not "intelligent." On the other hand, the traditional repeater or regenerative amplifier [1] includes a detector for conversion of the optical signal to a digital electronic bit stream and a transmitter to turn the electronic signal back into a lightwave. The detector responds (without wavelength selectivity) to the total optical field present, and the amplifier package cannot preserve the input optical spectrum. Sandwiched between the detect/re-transmit portions of the amplifier is circuitry that cleans up the bit stream by re-shaping and re-timing its pulses. This function involves synchronizing a master clock to the incoming signal, and requires some standardization of bit rate and modulation format. So, such amplifiers inherently lack flexibility. Successful deployment of optical amplifiers, already in progress in the 1550-nm fiber system, will eliminate the need for many complex and costly electronic repeaters, and will allow for WDM (Wavelength Division Multiplexing) techniques that will enhance utilization of the inherently-high information-carrying capacity of optical communications systems. [2]

Several manufacturers supply compact, field-ready, diode-pumped Er^{3+}-doped fiber amplifiers for 1550-nm use. Er^{3+} amplifiers are especially worthwhile because the luminescent yield of the Er^{3+} 1550-nm transition is near unity in silica fibers, aiding facile integration of doped fibers into standard lightwave systems. The high quantum yield results in a high "specific gain" ranging up to almost 10 dB per mW of absorbed pump power, [3] allowing the amplifiers to be pumped with reliable, low-power diodes.

Presently, there is no such efficient, integratable amplifier for the 1310-nm systems which constitute most of the installed fiber throughout the world. The 1310-nm region is especially tantalizing since it includes the "zero-dispersion" wavelength of single-mode silica fiber. Also, it is the wavelength in use for some CATV systems, for which preamplifiers would be useful and where "fan-out" amplifiers will be needed as the networks branch out and the number of channels increases. Thus, the search is on for a good amplifier material working at 1300 nm. Preferably, a finished amplifier would show 30 dB gain over a >30 nm bandwidth centered at 1310 nm, and provide a saturated output above 10 mW for a pump power below 100 mW. Some of these requirements are codified in the SONET (Synchronous Optical Network) specification, [4] but the last one is mainly a matter of reliability, since powerful laser diodes tend to die young.

Luminescent transitions around 1300 nm have been observed in several host-dopant systems; candidate amplifier ions include Pr^{3+}, Nd^{3+}, Dy^{3+}, and Cr^{4+}. [5 - 8] Each has serious drawbacks that compromise amplifier performance, but so far, Pr^{3+} has been developed furthest, with its $^1G_4$ - $^3H_5$ transition (Fig 1) providing the gain. Low quantum yield is nevertheless quite a serious problem in this amplifier because of nonradiative decay from MPE (Multi-Phonon Emission) to lower energy levels. MPE tends to drain the ions out of the $^1G_4$ level, reducing the inversion and hence, the gain. Good quantum yields are obtained when the MPE rate is much smaller than the radiative rate, so that the observed energy storage lifetime of the $^1G_4$ level approximates its natural lifetime of ~2000 μsec.

Figure 1. Energy level scheme of Pr^{3+}, showing pump and gain transitions. Nonradiative decay from $^1G_4$ - $^3F_4$ multiphonon emission potentially reduces the $^1G_4$ lifetime and amplifier quantum yield.

The MPE rate has been cataloged for a wide range of level spacings and host phonon frequencies, [9] resulting in formulation of the "energy gap law." According to this law, the nonradiative rate K_{nr} scales roughly as

$$K_{nr} \sim A\exp[-b(\Delta E_{gap} / h\nu_{eff})],$$

where ΔE_{gap} is the spacing to the excitation sink and $h\nu_{eff}$ is a characteristic host phonon frequency. A and b are material-dependent constants. Although not explicitly shown here, K_{nr} increases with temperature, as one would expect for a phonon-activated process.

In Pr^{3+}, the small ($\Delta E_{gap} \sim 2500$ cm^{-1}) $^1G_4$ - $^3F_4$ gap causes rapid relaxation, and 1300-nm luminescence is rendered undetectable except in low-phonon-frequency hosts. Thus silica is out of the question, and heavy-metal-fluoride (e.g. ZBLAN) and other more exotic glasses (chalcogenides[6] and InF_3 derivatives[10, 11]) have been engineered to serve as host media. Even in ZBLAN, the ~100 μsec observed $^1G_4$ lifetime *vs* the estimated radiative value of ~2000 μsec indicates a quantum yield of only ~5%. Compensation by high-power (over 100 mW) pumping of the $^1G_4$ - $^3F_4$ transition provides adequate amplifier gain, but stringent constraints on reliability and electrical power consumption make it less practical as a solution in field installations. A recently-developed laboratory instrument [12] is pumped by a 1W-class Nd:YLF laser.

Experimental

Improvements in quantum efficiency could be expected if the host phonon frequencies were reduced by changing from fluoride compounds to chlorides. Also, some materials advantages may accompany the growth of crystals as opposed to glasses; for example, $PbCl_2$ is a non-hygroscopic crystal. We used the zone-melting and Czochralski techniques to grow Pr^{3+}-doped samples of $BaCl_2$, $SrCl_2$, $LaCl_3$, KPb_2Cl_5, $CsPbCl_3$, and several other crystals in the $K_xSr_yCl_z$ family. We found that La^{3+}-codoping improved the radiative properties of the $SrCl_2$ crystals, presumably by altering the clustering behavior of Pr^{3+} ions.[13] Pr normally constituted ~1 wt% of the starting material for crystal growth. Also on hand from previous studies were Pr^{3+}-doped fluoride crystals of several types, including LaF_3, SrF_2, KY_3F_{10}, BaF_2, $LiBiF_4$, $LiGdF_4$, $LiYF_4$, and $K_5Li_2LaF_{10}$.

Our experiments on the Pr-doped crystals gave us three data sets: absorption spectra, emission spectra, and $^1G_4$ lifetimes. To obtain the latter two, we excited the samples at wavelengths around 1020 nm with the Raman-shifted output of a Nd:YAG-pumped dye laser. Lifetimes were measured with a transient digitizer and cooled InAs detector whose risetime was ~10 μsec. Long-pass and interference filters were used to block stray pump light and selectively detect the 1300-nm transition. Given sufficient emission intensity, a 1300-nm emission spectrum was recorded with a 1m monochromator and cooled GE detector. A slit setting of 2 mm gave a resolution of ~3 nm.

Heights of Pr^{3+} peaks in absorption spectra gave a crude measure of the ease of doping the various hosts. In general, doping became more difficult as the cations varied from La^{3+} to Sr^{2+} to Ba^{2+} to Pb^{2+}. This behavior can be rationalized on the basis of charge compensation requirements and ionic radius mismatch. As is well known, La^{3+} sites can easily be substituted with trivalent rare earth ions, [14] and we suppose that the full Pr charge was incorporated as Pr^{3+} in the $LaCl_3$ crystals. Substitution of divalent host cations is

expected to be less favorable, and tables of ionic radii show that, depending on coordination number, the sizes increase in the order Pr^{3+} - Sr^{2+} - Pb^{2+} - Ba^{2+}. According to the trend mentioned above, Pb^{2+} is out of place, but we do not expect to explain all details of doping with such a simple argument.

Figure 2. Pr^{3+} $^1G_4$ lifetimes in several fluoride and chloride-crystal hosts. Chloride hosts have lower phonon frequencies, reducing the MPE rate and allowing radiation to dominate.

Figure 2 gives a dramatic display of the order-of-magnitude increase in $^1G_4$ lifetime obtained with the chloride crystals with respect to the fluorides. The Li-containing fluorides can safely be assumed to have the highest phonon frequencies and hence, highest MPE rates and lowest $^1G_4$ lifetimes, which we measured at ~15 - 20 μsec. Displayed chloride lifetimes (omitting $CsPbCl_3$, whose non-exponential decay precluded simple characterization) range from ~500 μsec for $LaCl_3$ to ~1300 μsec for $BaCl_2$. The latter was observed to be temperature-independent in the 50 - 375 K range. Since temperature changes did not sensibly affect the MPE rate's contribution to the overall decay rate, we believe 1300 μsec is essentially the radiative value. The shortened radiative lifetime (compared with ~2000 μsec for fluorides) is evidence that the "forced" electric-dipole transitions are somewhat stronger in the chlorides, further helping radiation compete with MPE. We also conclude that the radiative yield is virtually 100% at room temperature. Another check of the quantum efficiency was done by comparison of 1300-nm signal levels in the $SrCl_2$:$La_{0.1}Pr_{0.01}$ sample and a well-characterized Nd^{3+}:glass "standard" sample. Again, we concluded that the $^1G_4$ decay is predominantly radiative. Chloride hosts appear to solve the problem of low $^1G_4$ emission quantum yield.

Figure 3. Pr^{3+} emission spectra in the 1300 nm region, for several chloride-crystal hosts. The SONET OC-48 protocol 1280 - 1335 nm region is indicated, along with the 1310 nm zero-dispersion wavelength of standard single-mode silica fiber. Emission bands tend to be ~70 nm wide, and to have a substantial overlap with the desired window.

1300-nm emission spectra for a few chloride crystals are presented in Figure 3. The nominal 1310-nm "zero-dispersion" wavelength and 1280 - 1335 nm OC-48 band of the SONET protocol are also indicated

on each panel for comparison. Varying amounts of Stark structure are present. Most of the emission bands are ~70 nm wide, and significantly overlap the wavelength region of interest, which is quite a fortuitous accident of nature. Interestingly, the La-codoped $SrCl_2$ spectrum is nearly identical in shape to (but more intense than) a spectrum of $SrCl_2$:Pr we obtained. If indeed the La co-dopant were providing a clustering partner for the Pr^{3+} ions, we might have expected to see some small spectral changes. [15] $LaCl_3$ has the narrowest peak (as a consequence of small vibronic interactions [14]) and presumably the highest peak cross section. Incidentally, the recent demonstration of a 5-μm $LaCl_3:Pr^{3+}$ laser [16] constitutes further evidence of the potential of chloride-crystal hosts.

Conclusion

The high quantum yields and well-placed emission bands of the crystals we studied indicate that there is promise for the use of Pr^{3+}-doped chlorides as 1300-nm optical amplifiers. However, many other practical issues must be addressed, including pumping efficiency, optical quality, and development of suitable waveguide structures.

Acknowledgment

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

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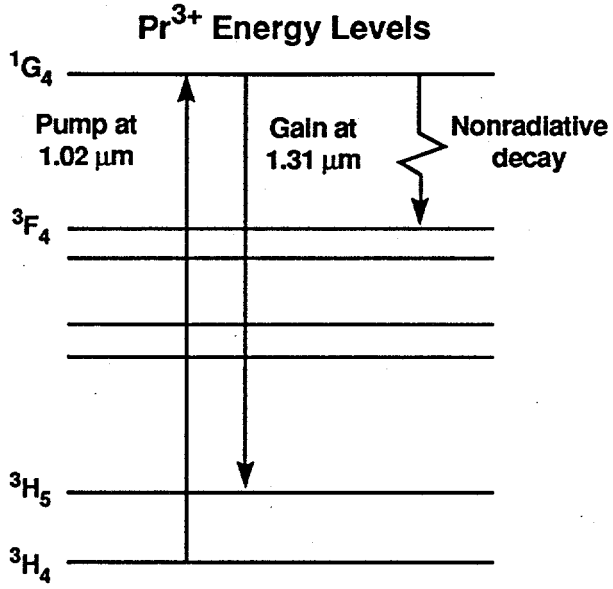

Figure 1.

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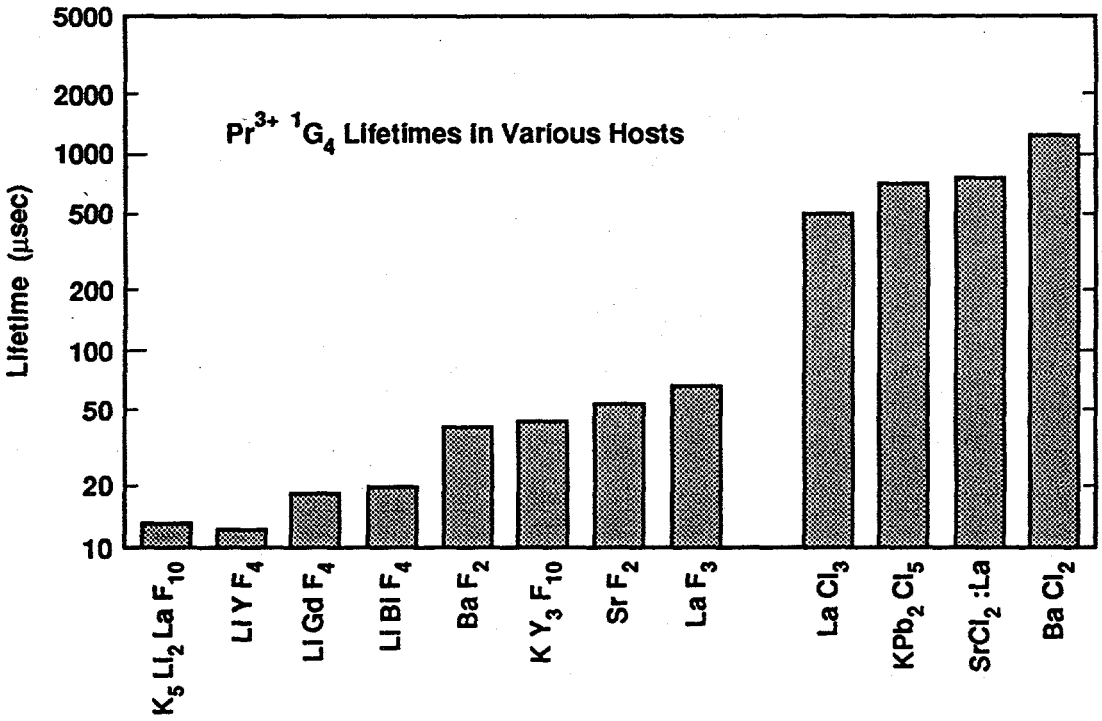

Figure 2.

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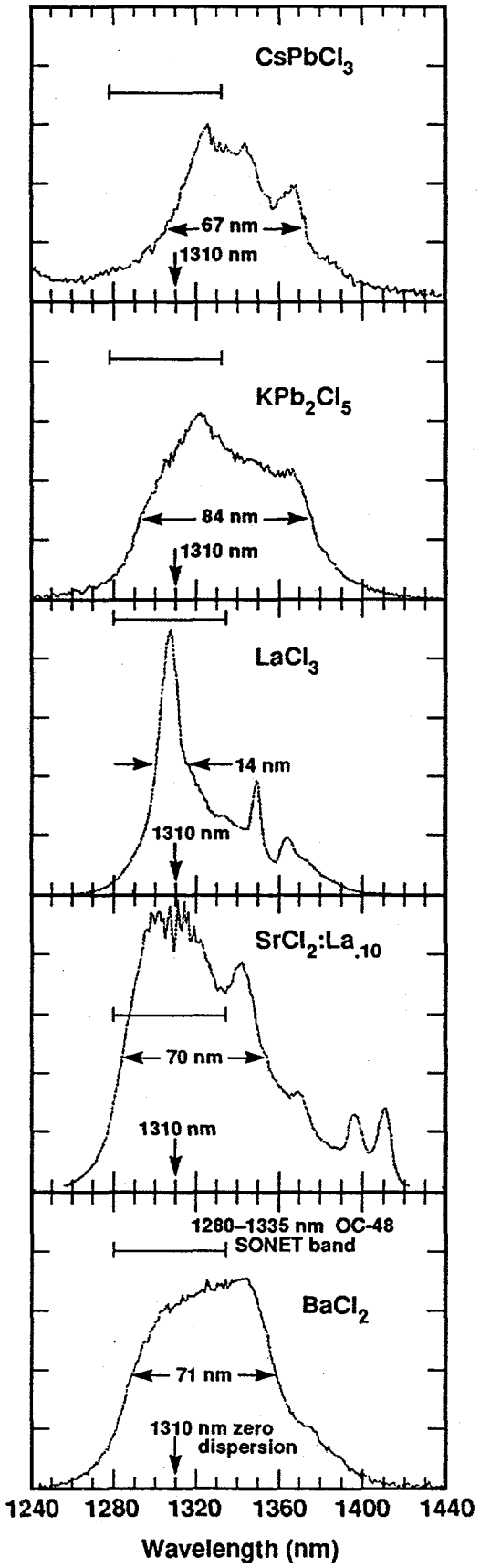

Figure 3.

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