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Publication Date

1985-12-01

Lawrence Berkeley Laboratory

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Materials & Molecular Research Division

Submitted to Optics Letters

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December 1985

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Resonance Electronic Raman Scattering in Erbium Phosphate Crystals

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Abstract:

Resonance enhancement factors of 10 to 100 have been observed for the electronic Raman scattering transitions in crystals of pure ErPO_4 and 1% Er^{3+} diluted in LuPO_4 . The resonances were excited by the 488.0 nm line of an argon-ion laser. This line is nearly coincident with the crystal field levels of the $^4F_{7/2}$ multiplet of Er^{3+} . The differences in relative intensities between the transitions in ErPO_4 and those in 1% Er^{3+} in LuPO_4 arise from shifts in the energy levels in the two systems and suggest that quantum-mechanical interference effects play an important role.

Electronic Raman scattering effects in rare-earth crystals have been the subject of numerous studies since the initial work of Hougen and Singh in 1963.^{1,2} Most of the experiments, however, were performed using a nonresonant experimental configuration, with the exciting line well removed in frequency from any electronic transition of the subject rare-earth ion. With the exception of the work of Koningstein³ and of Wadsack and Chang,⁴ there are few reports of resonance electronic Raman scattering in trivalent rare-earth doped crystals. In the resonance Raman studies noted above, enhancement factors that were on the order of 5 at most were reported. In the present work, we have observed resonance enhancement factors of 10-100 for electronic Raman transitions within the ground $^4I_{15/2}$ multiplet of Er^{3+} in concentrated and dilute erbium phosphate crystals. The resonance excitation occurs between the crystal field levels of the $^4F_{7/2}$ multiplet and the $^4I_{15/2}$ ground levels. To our knowledge, this represents the first time that such large enhancement effects have been observed. It should be noted, however, that somewhat similar resonance effects have been observed for other nonlinear optical processes in rare-earth crystals, such as four-wave mixing phenomena.⁵

The scattering amplitude for a Raman transition from a state n to a state k is given by:

$$(\alpha_{\rho\sigma})_{nk} = -\frac{1}{\hbar} \sum_r \left[\frac{\langle k | D_\rho | r \rangle \langle r | D_\sigma | n \rangle}{\nu_{rn} - \nu + i\Gamma_r} + \frac{\langle k | D_\sigma | r \rangle \langle r | D_\rho | n \rangle}{\nu_{rk} + \nu + i\Gamma_r} \right] \quad (1)$$

where D_ρ is the electric dipole operator, ρ and σ are Cartesian coordinates, $\hbar\nu_{rn}$ is the energy difference $E_r - E_n$ (E_r is the energy of

the intermediate state r), ν is the frequency of the incident radiation, and Γ_r is a damping factor that is inversely proportional to the lifetime of the intermediate state. For a $4f^N$ configuration, $4f^N \rightarrow 4f^N$ transitions are forced electric-dipole in nature with very small oscillator strengths⁶ so the intermediate states that dominate Eq. (1) arise from configurations of opposite parity to $4f^N$, namely $4f^{N-1}nd$ or $4f^{N-1}ng$. For Er^{3+} ($N=11$), the $4f^{10}5d$ configuration begins approximately $70,000\text{ cm}^{-1}$ above the ground state.⁷ The other opposite parity configurations lie at higher energies. Judd-Ofelt closure techniques can be used to perform the sum over intermediate states, and the results of such intensity calculations have been reported previously.^{8,9} The situation can be altered if the energy of the exciting radiation is very close to that of a $4f^N \rightarrow 4f^N$ transition. The energy denominator is then very small and this tends to compensate for the weakness of the $4f^N \rightarrow 4f^N$ matrix elements. Therefore, one may expect a noticeable change to occur in the electronic Raman intensity pattern with respect to the polarization of the incident and scattered photons.¹⁰ This situation occurs in the case of Er^{3+} as a result of a near coincidence in energy between the argon-ion laser excitation line at 488.0 nm and the transitions between the crystal field states of the ground $^4I_{15/2}$ multiplet and those of the excited $^4F_{7/2}$ multiplet.

The nonresonant electronic Raman spectrum of $ErPO_4$ and the experimental procedure employed in all of these studies, have been reported previously.⁸ In that work, the excitation sources were the 514.5 and 457.9 nm lines of an argon-ion laser, and the electronic Raman spectra produced by those two lines were identical. When the argon-ion

laser blue line at 488.0 nm ($20,486.7 \text{ cm}^{-1}$ in vacuum) is incident on the crystal, drastic changes occur in the Raman spectra. Figure 1 shows part of the energy level scheme of Er^{3+} in LuPO_4 and the positions of the relevant laser excitation lines. The widths of the multiplets result from crystal field splittings and range from 100 cm^{-1} to 300 cm^{-1} . A detailed study of the optical absorption and crystal-field levels of 1% Er in LuPO_4 has been reported previously.¹¹

The lines at 457.9 and 514.5 nm are at least 300 cm^{-1} away from the closest $\text{Er}^{3+} 4f^{11}$ excited levels, which precludes any significant role that these levels might play as intermediate states. For these two excitation frequencies, the dominant contributions to the electronic Raman amplitude are from the excited configurations $4f^{10}nd$ and $4f^{10}ng$.⁹ The line at 488.0 nm, however, is coincident with the ${}^4F_{7/2}$ multiplet which now contributes significantly to the electronic Raman intensities. Another favorable factor is that the oscillator strengths of the transitions between the ground multiplet and the ${}^4F_{7/2}$ excited multiplet are relatively large (on the order of 5×10^{-6} as determined by laser absorption measurements,¹² which classifies them as being among the strongest transitions of the Er^{3+} ion⁶).

Resonant and nonresonant Raman spectra were obtained for both pure ErPO_4 and 1% Er^{3+} in LuPO_4 . The nonresonant electronic Raman intensities for ErPO_4 were on the order of a few hundred counts per second for the existing experimental conditions. Using the identical experimental arrangement and similar laser input powers of about 50mW, resonant Raman signals as high as 10,000 counts per second were observed. Polarized spectra are shown in Figs. 2 and 3 for nonresonant

excitation at 514.5 nm and for resonant excitation at 488.0 nm. It should be noted that while the electronic Raman intensities have been strongly enhanced, the phonon intensities remain at about the same level. This effect is quite apparent for the E_g phonons at 134 cm^{-1} and 188 cm^{-1} .⁷ The fact that the phonons are not affected by the electronic resonance indicates that the coupling between the electronic states of Er^{3+} and the lattice vibrations is very weak.

Resonance Raman spectra were also obtained for 1% Er^{3+} in LuPO_4 . In this case, the signal level is much lower than that observed for pure ErPO_4 ; and, with nonresonant excitation at 514.5 nm, most of the electronic peaks cannot be observed. Table 1 lists the values determined for the crystal field levels of $^4I_{15/2}$ by the resonance and nonresonance Raman scattering experiments for both ErPO_4 and 1% Er^{3+} in LuPO_4 . Also listed in Table 1 are the calculated values from the crystal field fit, and the values determined from 77 K optical absorption measurements.¹¹

Several arguments can be made to demonstrate that the observed signal is, in fact, a Raman signal and not fluorescence. First, the 488.0 nm exciting laser line is not exactly in coincidence with one of the four crystal field levels of the $^4F_{7/2}$ multiplet (see Fig. 4). The four levels are labeled by the irreducible representations Γ_6 and Γ_7 of the point group D_{2d} which describes the Er^{3+} site symmetry. One would then expect to see differences of a few cm^{-1} between Raman and fluorescent peaks. For ErPO_4 , the transitions from the ground state to the excited levels e_1 , e_2 , e_3 , and e_4 are observed with both resonant and nonresonant excitation and no frequency shifts are found within an

accuracy of 1 cm^{-1} . Second, the fluorescence from the ${}^4\text{F}_{7/2}$ levels in ErPO_4 , excited by the higher-lying argon-ion laser line at 476.5 nm is quenched by energy transfer among the Er^{3+} ions and nonradiative decay to lower multiplets. In contrast, the resonant Raman peaks persist up to $T=100 \text{ K}$. They gradually decrease in intensity as the crystal field levels broaden significantly with temperature and begin to absorb both the incident laser radiation and the scattered Raman radiation. This latter absorption occurs when the higher-lying crystal field levels of the ${}^4\text{I}_{15/2}$ multiplet become populated.

Several other lines appear as the temperature is increased above $T=4.2 \text{ K}$. A Raman transition at 20 cm^{-1} that originates in the 33 cm^{-1} state and ends in the 53 cm^{-1} state increases in intensity with temperature as the first excited crystal field state e_1 becomes thermally populated. This peak is weakly observable with nonresonant excitation and is strongly enhanced by resonant excitation. As the temperature is raised, the Raman transition from the ground state to level e_1 initially drops in intensity more rapidly than the transition to level e_2 . This is due to the fact that the thermal population of level e_1 is significantly higher than that of e_2 at low temperatures. This permits the radiation with a 30 cm^{-1} Raman shift to be more strongly absorbed. The 20 cm^{-1} line also appears on the anti-Stokes side, along with a 33 cm^{-1} line that corresponds to the transition from the e_1 level to the ground state. Again, both are stronger than in the nonresonance case. The presence of the anti-Stokes peaks confirms that their corresponding Stokes peaks are Raman transitions.

An intriguing feature of the spectra for 1% Er^{3+} in LuPO_4 is that the relative intensities for the various resonant electronic Raman lines have changed relative to those observed for pure ErPO_4 . These relative intensities are very sensitive to the positions of the associated crystal field levels and these levels shift significantly in diluting pure ErPO_4 to 1% Er^{3+} in LuPO_4 (see Fig. 4). We may separate the expression for the Raman amplitude into a resonant part and a nonresonant part:

$$(\alpha_{\rho\sigma})_{nk} = -\frac{1}{\hbar} \sum_{4F_{7/2}} \frac{\langle j | D_{\rho} | r \rangle \langle r | D_{\sigma} | n \rangle}{E_{rn} - \hbar\nu + i\Gamma_r} + \text{non-resonant term} \quad (2)$$

For the resonant contribution, only the first term on the right-hand side of Eq. (1) was retained. This term contains the sum over the four crystal field levels of the $4F_{7/2}$ multiplet whereas the nonresonant term involves a sum over the excited $4f^{10}nd$ and $4f^{10}ng$ configurations. Thus quantum-mechanical interference effects between the various intermediate states can be observed. The shift in energy levels that occurs between ErPO_4 and 1% Er^{3+} in LuPO_4 significantly changes the relative amplitude that each of the $4F_{7/2}$ crystal field states contributes to the overall intensity.

Erbium phosphate systems are promising candidates for studies of resonance enhancements of other nonlinear optical processes. Since the electronic Raman intensities are greatly enhanced by the intermediate $4F_{7/2}$ resonance, two-photon absorption or four-wave mixing should also be significantly enhanced by the same intermediate resonance. The

quantum-mechanical expressions for the amplitudes of these last two processes involve terms similar to those that appear in the electronic Raman amplitude (see Eq. 2).

Acknowledgements

This work was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Oak Ridge National Laboratory is operated by Martin Marietta Energy Systems, Inc. for the U.S. Department of Energy under Contract No. DE-AC05-84OR21400.

References:

1. J.T. Hougen and S. Singh, Phys. Rev. Lett. 10, 406 (1963).
2. R.J.H. Clark and T.J. Dines, Advances in Infrared and Raman Spectroscopy, Vol. 9 (R.J.H. Clark and R.E. Hester, eds.), Heyden, London, 1982, p.282.
3. D. Nicollin and J.A. Koningstein, Chem. Phys. 49, 377 (1980).
4. R.L. Wadsack and R.K. Chang, Sol. St. Comm. 10, 45 (1972).
5. D.A. Ender, M.S. Otteson, R.L. Cone, and M.B. Ritter, Opt. Lett 7, 611 (1982).
6. B.R. Judd, Phys. Rev. 127, 750 (1962).
7. E. Loh, Phys. Rev. 147, 332 (1966).
8. P.C. Becker, N. Edelstein, G.M. Williams, J.J. Bucher, R.E. Russo, J.A. Koningstein, L.A. Boatner, and M.M. Abraham, Phys. Rev. B 31, 8102 (1985).
9. P.C. Becker, N.M. Edelstein, R.C. Leavitt, G.M.S. Lister, and B.R. Judd, J. Phys. C, 18, L1063 (1985).
10. P. Grunberg and J.A. Koningstein, J. Chem. Phys. 53, 4584 (1970).
11. T. Hayhurst, G. Shalimoff, N. Edelstein, L.A. Boatner, and M.M. Abraham, J. Chem. Phys. 74, 5449 (1981).
12. G.M. Williams, P.C. Becker, unpublished data.

Table 1. Crystal field energy levels of the $^4I_{15/2}$ ground multiplet of Er^{3+} , for both $ErPO_4$ and 1% Er in $LuPO_4$, from optical absorption measurements, resonance Raman measurements, and crystal field fits.^a

Level	Symmetry	Crystal	Optical	Resonance	Optical	Resonance	Non-resonance
		Field Fit	Absorption	Raman	Absorption	Raman	Raman
		for 1% Er	Measurements	Measurements	Measurements	Measurements	Measurements
		in $LuPO_4^b$	1% Er	1% Er	$ErPO_4$	$ErPO_4$	$ErPO_4$
			in $LuPO_4^b$	in $LuPO_4$			
e_0	Γ_7	0	0	0	0	0	0
e_1	Γ_6	36	36	35	33	33	33
e_2	Γ_7	50	53	52	53	53	53
e_3	Γ_7	101	98	c	105	105	105
e_4	Γ_6	133	c	151	145	145	145
e_5	Γ_6	230	c	c	232	234	c
e_6	Γ_7	247	c	c	244	246	c
e_7	Γ_6	287	c	c	c	269	c

^aenergy levels in cm^{-1} .

^bfrom reference 8.

^cnot observed.

Figure Captions

- Figure 1. Energy level structure of the $4f^{11}$ electronic levels of Er^{3+} in LuPO_4 in the $20,000 \text{ cm}^{-1}$ region. The laser lines used in the Raman experiments are indicated. The wavelengths are in air and the wavenumbers in vacuum. The width of the excited multiplets represents the total crystal field splitting of that multiplet.
- Figure 2. Polarized ErPO_4 Raman spectra at $T = 4.2 \text{ K}$, with both resonant and non-resonant excitation, in $Y(XZ)X$ and $Y(ZY)Y$ polarizations.
- Figure 3. Polarized ErPO_4 Raman spectra at $T = 4.2 \text{ K}$, with both resonant and non-resonant excitation, in $Y(XY)X$ and $Y(ZZ)X$ polarization.
- Figure 4. Crystal field energy levels of the ${}^4F_{7/2}$ multiplet of Er^{3+} (in cm^{-1}). The symmetry of the levels is indicated, as is the position of the 488.0 nm line of the argon-ion laser (all wavenumbers in vacuum).

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Figure 1

Excitation at $19,429.7\text{ cm}^{-1}$ (non-resonant)

Excitation at $20,486.7\text{ cm}^{-1}$ (resonant)

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Figure 2

Excitation at $19,429.7 \text{ cm}^{-1}$ (non-resonant)

Excitation at $20,486.7 \text{ cm}^{-1}$ (resonant)

XBL 859 3908

Figure 3

XBL 859-3914

Figure 4

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