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TITLE: **COMPARISON OF THE SPECTRA AND DYNAMICS OF $ER^{3+}:Y_{2-X}SC_XO3$ (X=0,1,2)**

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RE: LAUR-90-557 (Abstract)

COMPARISON OF THE SPECTRA AND DYNAMICS OF $Er^{3+}:Y_{2-x}Sc_xO_3$ (x=0,1,2)

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Abstract

We have studied the spectra and lifetimes of Er^{3+} in the isostructural series, Y_2O_3, $YScO_3$, and Sc_2O_3. Addition of Sc^{3+} to $Er^{3+}:Y_2O_3$ shifted the energy level positions, changed the inhomogeneous broadening and shortened the fluorescence lifetimes for Er^{3+} in the C_2 site. Going from $Er^{3+}:Y_2O_3$ to $Er^{3+}:Sc_2O_3$ increased the barycenter of the four lowest J-multiplets, decreased the barycenter of the ${}^4F_{9/2}$ and higher multiplets, and increased the crystal-field splitting within each J-multiplet. The inhomogeneous linewidths in the $Er^{3+}:YScO_3$ spectra were much larger than in $Er^{3+}:Y_2O_3$ or $Er^{3+}:Sc_2O_3$ due to random substitutional disorder in the mixed system. The random disorder in $Er^{3+}:YScO_3$ removed the inversion symmetry of the C_{3i} lattice site and allowed observation of transitions from Er^{3+} ions in this site. All fluorescence lifetimes decreased with addition of Sc^{3+} indicating an increase in the nonradiative relaxation.

Introduction

Y_2O_3, $YScO_3$, and Sc_2O_3 are isostructural with the cubic C (bixbyite) structure. The lattice constant decreases from a = 10.6 Å for Y_2O_3 to a = 9.8 Å for Sc_2O_3.[1] The structure has two inequivalent cation sites of C_2 and C_{3i} symmetry, which are present in a 3:1 ratio. Crystal-field analysis of the spectra of rare earth-doped Y_2O_3 shows that the observed transitions arise almost exclusively from rare earths in the C_2 lattice site.[2][3] The spectra of $Er^{3+}:Sc_2O_3$ are very similar to those of $Er^{3+}:Y_2O_3$ but are shifted and have larger crystal-field splittings.[4]

Weber has studied the fluorescence dynamics of rare earths in Y_2O_3, and some of his lifetime measurements in $Er^{3+}:Y_2O_3$ are listed in Table 1.[5] Other measurements of $^4S_{3/2}$ lifetimes in $Er^{3+}:Y_2O_3$ range from 100 to 300 μs.[5] Weber reported concentration quenching in 1% $Tm^{3+}:Y_2O_3$ and similar quenching may account for the range of lifetimes reported in $Er^{3+}:Y_2O_3$.

We observed $Er^{3+}:Y_2O_3$ to upconvert infrared light to green fluorescence with an efficiency comparable to that of Er^{3+}-:$YAlO_3$, which has been operated as an upconversion laser.[6] The strongest $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition terminates on the highest $^4I_{15/2}$ Stark level at 506 cm^{-1}, and is a possible laser transition. Sc^{3+} was added to $Er^{3+}:Y_2O_3$ to increase the crystal-field splitting of the $^4I_{15/2}$ multiplet thereby increasing the possibility of laser action at a relatively high temperature. Addition of Sc^{3+} in $Nd^{3+}:Y_{2-x}Sc_xO_3$ was reported to increase the crystal-field splitting within the J-multiplets.[7] The effect of Sc^{3+} on the fluorescence lifetimes and upconversion efficiency in $Er^{3+}:Y_{2-x}Sc_xO_3$ was also studied since no previous results of this type have been reported.

Experimental

The samples were ca. 0.4 mm dia. single-crystal fibers grown by the laser-heated pedestal growth method.[8] Starting materials were Y_2O_3 (99.999%), Sc_2O_3 (99.99%), and Er_2O_3 (99.99 %). The distribution coefficient of rare earths in Y_2O_3 is known to be 1,[9] but has not been reported for Sc_2O_3. The Er^{3+} concentration in the fibers are assumed to be the same as in the starting material (1 mol-%), although the true concentration in the $Er^{3+}:Sc_2O_3$ fiber may be less. The laser spectroscopy system consisted of a Nd^{3+}:YAG-pumped dye laser, closed-cycle refrigerator (12-300 K), monochromator, photomultiplier tube, and appropriate detection electronics for recording spectra or fluorescence transients.

Results and Discussion

Figure 1 shows the $^4I_{15/2} \rightarrow {}^4S_{3/2}$ excitation spectra monitoring Stoke's fluorescence of $1\%Er^{3+}:Y_{2-x}Sc_xO_3$, and Figure 2 shows the $^4I_{15/2} \rightarrow {}^4I_{9/2}$ excitation spectra monitoring green upconverted fluorescence. Both figures illustrate the changes in linewidths and shifts in Er^{3+} energy levels seen in all of the excitation and fluorescence spectra as the Sc^{3+} concentration increases in the $Er^{3+}:Y_{2-x}Sc_xO_3$ series. The line broadening and energy level shifts are similar to results in $Nd^{3+}:Y_{2-x}Sc_xO_3$.[7] The large inhomogeneous broadening in the spectra of $Er^{3+}:YScO_3$ is due to the random distribution of Y^{3+} and Sc^{3+} on the cation sites. The small increase in broadening in $Er^{3+}:Sc_2O_3$ compared to $Er^{3+}:Y_2O_3$ occurs because of the greater size mismatch between Er^{3+} and Sc^{3+} compared to Er^{3+} and Y^{3+}.

Figure 3 shows the energy level positions of selected J-multiplets. The similarity of the energy level structure confirms that the spectra in the Sc^{3+} containing samples arise from Er^{3+} ions in the C_2 site. The energy level measurements in the $Er^{3+}:Y_2O_3$ and $Er^{3+}:Sc_2O_3$ fibers agree with results in bulk crystals.[2][4] On going from $Er^{3+}:Y_2O_3$ to $Er^{3+}:Sc_2O_3$, the barycenter of the four lowest J-multiplets ($^4I_{15/2}$, $^4I_{13/2}$, $^4I_{11/2}$, and $^4I_{9/2}$) shift to higher energy while the barycenter of the $^4F_{9/2}$ and higher multiplets shift to lower energy. The crystal-field splitting within each J-multiplet increases with addition of Sc^{3+}. The highest $^4I_{15/2}$ Stark level increases from 506 cm^{-1} in $Er^{3+}:Y_2O_3$ to 538 and 602 cm^{-1} in $Er^{3+}:YScO_3$ and $Er^{3+}:Sc_2O_3$, respectively.

The dynamics of the Er^{3+} fluorescence were very different in the different hosts. Table 1 lists the measured fluorescence lifetimes at 14 K of the $^2H_{9/2}$, $^4S_{3/2}$, $^4F_{9/2}$, and $^4I_{11/2}$ levels. No fluorescence was observed from the $^4F_{7/2}$ level. All of ths lifetimes were measured after direct excitation, except for the $^4I_{11/2}$ level which was estimated from the upconverted $^4S_{3/2}$ fluorescence transient exciting $^4I_{15/2} \rightarrow {}^4I_{9/2}$. The approximation assumes the upconversion originates from $^4I_{11/2}$ and that the upconversion transfer rate is smaller than the decay rate from $^4I_{11/2}$. The fluorescence decay from $^4S_{3/2}$ then has a lifetime that is 1/2 of the $^4I_{11/2}$ lifetime.[10] All of the directly measured fluorescence transients were single exponentials except for the $^4S_{3/2}$ fluorescence in $Er^{3+}:Y_2O_3$, which was nonexponential at short times.

Our observed lifetimes for $1\%Er^{3+}:Y_2O_3$ are shorter than Weber's measurements for a $0.2\%Er^{3+}:Y_2O_3$ crystal. The differences are probably due to concentration quenching in the $1\%Er^{3+}:Y_2O_3$ sample. The $^4S_{3/2}$ fluorescence intensity has been reported to be concentration dependent, increasing linearly from 0.01 to 0.5 mol-% Er^{3+}, increasing slightly at 1 mol-% Er^{3+} and decreasing above 1 mol-% Er^{3+}.[11] The integrated intensity of $^4S_{3/2}$ fluorescence was less in $Er^{3+}:Sc_2O_3$ than in $Er^{3+}:Y_2O_3$.[4] The lower fluorescence yield and the decrease in lifetimes indicates that the nonradiative relaxation rate increases when Sc^{3+} is added to $Er^{3+}:Y_2O_3$.

The $^4S_{3/2}$ lifetimes of $Er^{3+}:Y_{2-x}Sc_xO_3$ as a function of temperature are listed in Table 2. The temperature behavior is the same in all three hosts with the lifetimes remaining relatively constant up to 200 K but decreasing at room temperature. The integrated Stoke's fluorescence efficiency in $Er^{3+}:Y_2O_3$ has been reported to decrease when the temperature is raised from 77 K to room temperature.[12] The decreases in lifetimes and fluorescence efficiency indicate that the nonradiative relaxation is temperature dependent above 200 K.

Upconversion was observed in all samples exciting the $^4I_{15/2} \rightarrow {}^4I_{9/2}$ (790-815 nm) or $^4I_{15/2} \rightarrow {}^4F_{9/2}$ (648-661 nm) transitions. In both cases the predominant upconverted fluorescence was from $^4S_{3/2}$. Upconverted fluorescence from higher levels ($^2P_{3/2}$ and $^2H_{9/2}$) was also seen exciting $^4I_{15/2} \rightarrow {}^4F_{9/2}$. The upconversion power dependence was quadratic (exponents of 2.1, 2.0, and 1.9 ± 0.1 for Y_2O_3, $YScO_3$, and Sc_2O_3, respectively) in all three samples for incident laser energies of 0.1 to 1 mJ.

$^4I_{9/2}$

The $^4S_{3/2}$ fluorescence transients after $^4I_{15/2} \rightarrow {}^4I_{9/2}$ excitation had nearly single exponential decays while $^4I_{15/2} \rightarrow {}^4F_{9/2}$ excitation produced biexponential decays. The decay lifetimes of the upconverted $^4S_{3/2}$ fluorescence are listed in Table 3. All of the transients had risetimes of 5 to 70 μs indicating that the upconversion mechanism was an energy transfer process rather than a sequential two-photon absorption.[13]

In all three hosts, either up~~conversion~~ excita~~tion pathway~~ pumping method gave upconverted $^4S_{3/2}$ decay times much longer than for direct excitation. The longer decay times reflect the involvement of long-lived intermediate states. For $^4I_{15/2} \rightarrow {}^4I_{9/2}$ excitation the most likely upconversion mechanism is energy transfer between two Er^{3+} ions in the $^4I_{11/2}$ level.[13] In all hosts there was good overlap between twice the $^4I_{11/2}$ energy and the $^4F_{7/2}$ level (see Figure 3). The shorter decay times for $^4I_{15/2} \rightarrow {}^4F_{9/2}$ versus $^4I_{15/2} \rightarrow {}^4I_{9/2}$ excitation indicate a different upconversion process, and the biexponential decays for $^4I_{15/2} \rightarrow {}^4F_{9/2}$ excitation indicate that two different mechanisms occur simultaneously.

The $^4I_{15/2} \rightarrow {}^4I_{9/2}$ excitation spectrum of Er^{3+}:$YScO_3$ contained additional lines besides those expected for the C_2 site. Exciting the strongest new transition at 812.5 nm (12304 cm^{-1}) gave an upconverted $^4S_{3/2}$ lifetime of 69 μs compared to 176 μs for the C_2 site. These new lines are attributed to Er^{3+} in the C_{3i} lattice site. The random disorder of Y^{3+} and Sc^{3+} on the cation sites removes the inversion symmetry of the C_{3i} site allowing transitions to be observed.

In summary, addition of Sc^{3+} to Er^{3+}:Y_2O_3 shifts the Er^{3+} energy levels and significantly changes the fluorescence dynamics. The random disorder of the cations in Er^{3+}:$YScO_3$ greatly broadened the linewidths and removed the inversion symmetry of the C_{3i} site allowing new transitions to be observed. These results demonstrate that in principle it should be possible to tailor the energy level positions, linewidths, and fluorescence dynamics to obtain luminescent materials with desired characteristics.

Fig. 1 $^4I_{15/2} \rightarrow {}^4S_{3/2}$ excitation spectra monitoring direct fluorescence at 14 K of (a) 1%Er^{3+}:Y_2O_3, (b) 1%Er^{3+}:$YScO_3$, and (c) 1%Er^{3+}:Sc_2O_3.

Figure 2. $^4I_{15/2} \rightarrow {}^4I_{9/2}$ excitation spectra monitoring green upconverted fluorescence at 14 K of (a) 1%Er^{3+}:Y_2O_3, (b) 1%Er^{3+}:$YScO_3$, and (c) 1%Er^{3+}:Sc_2O_3. A long delay (300 μs) was used in the gated detection for the 1%Er^{3+}:$YScO_3$ spectrum to discriminate against lines from the C_{3i} site.

Figure 3. Selected Er^{3+} energy level positions in 1%Er^{3+}:$Y_{2-x}Sc_xO_3$.

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Table 1. Fluorescence lifetimes at 14 K of 1%Er^{3+}:$Y_{2-x}Sc_xO_3$ (in μs).

	Y_2O_3[a]	Y_2O_3	$YScO_3$	Sc_2O_3
$^2H_{9/2}$	~5	1.9 ±0.2	0.6 ±0.1	0.2 ±0.1
$^4S_{3/2}$ ±1	155 ±10	95 ±20[b]	52 ±3	17±1
$^4F_{9/2}$	~30	21 ±1	6.3 ±0.3	1.5 ±0.1
$^4I_{11/2}$	3900 ±400	2500[c]±500	500[c]±100	190[c]±40

[a] 0.2%Er^{3+}:Y_2O_3 at 77 K from Weber.[5]

[b] The $^4S_{3/2}$ fluorescence transient of Er^{3+}:Y_2O_3 was not a single exponential at short time.

[c] Estimated from the upconverted $^4S_{3/2}$ fluorescence decay excited by $^4I_{15/2} \rightarrow {}^4I_{9/2}$. See ref. [10]. for method

Table 2. $^4S_{3/2}$ lifetimes of 1%Er^{3+}:$Y_{2-x}Sc_xO_3$ at different temperatures (in μs).

T(K)	Y_2O_3	$YScO_3$	Sc_2O_3
14	95 ± 5	52 ± 3	17 ± 1
100	92 ± 5	45 ± 2	17 ± 1
200	102 ±10	42 ± 4	17 ± 1
290	53 ±10	27 ± 2	12 ± 1

Table 3. Fluorescence lifetimes of the $^4S_{3/2}$ level after excitation via upconversion (in μs).

method pump	Y_2O_3	$YScO_3$	Sc_2O_3
$^4I_{15/2} \rightarrow {}^4F_{9/2}$ (short component)	320 ± 30	173 ± 18	56 ± 6
$^4I_{15/2} \rightarrow {}^4F_{9/2}$ (long component)	580 ± 60	436 ± 44	255 ± 26
$^4I_{15/2} \rightarrow {}^4I_{9/2}$	1230 ± 10	176 ± 15	96 ± 10

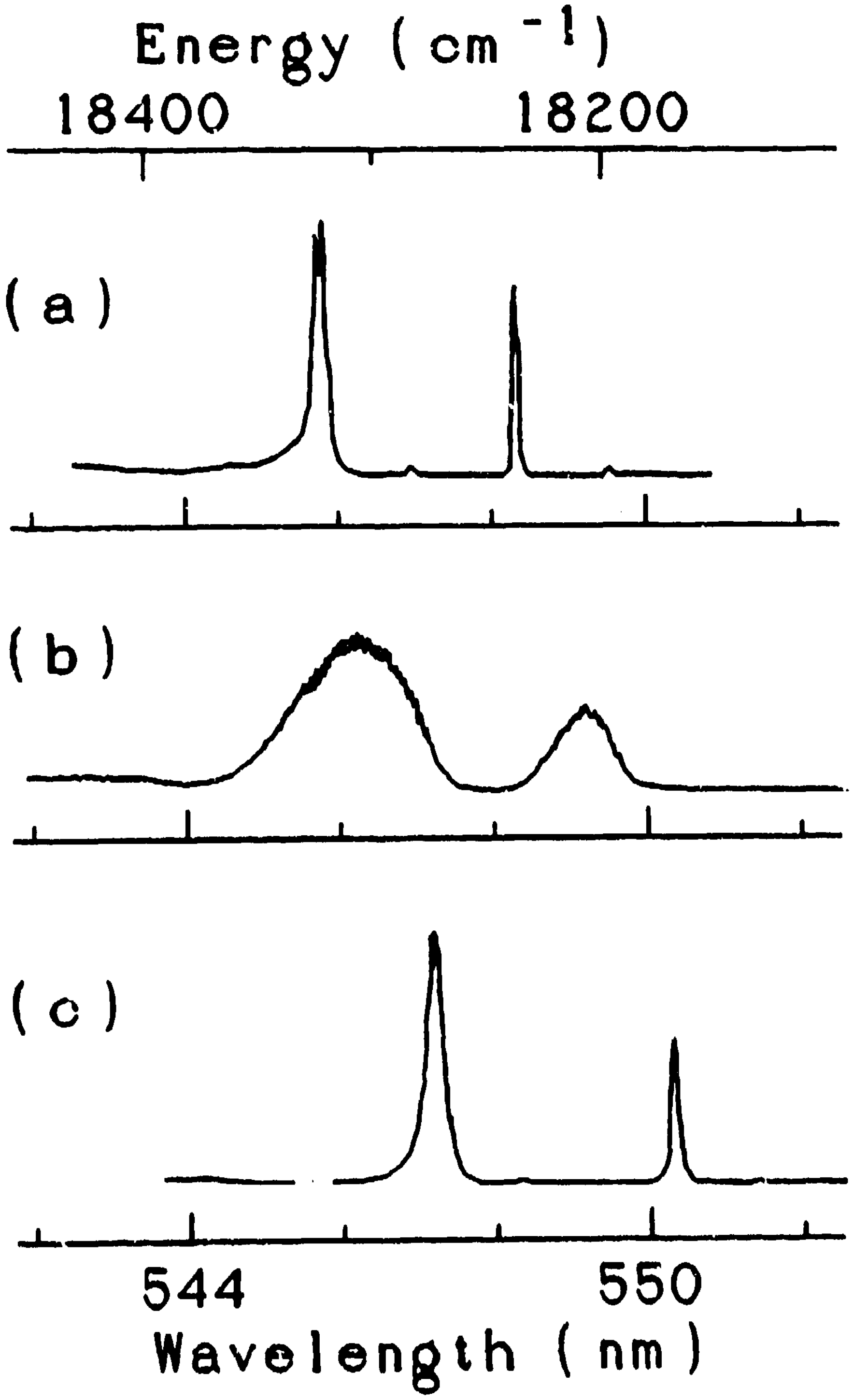


fig 1

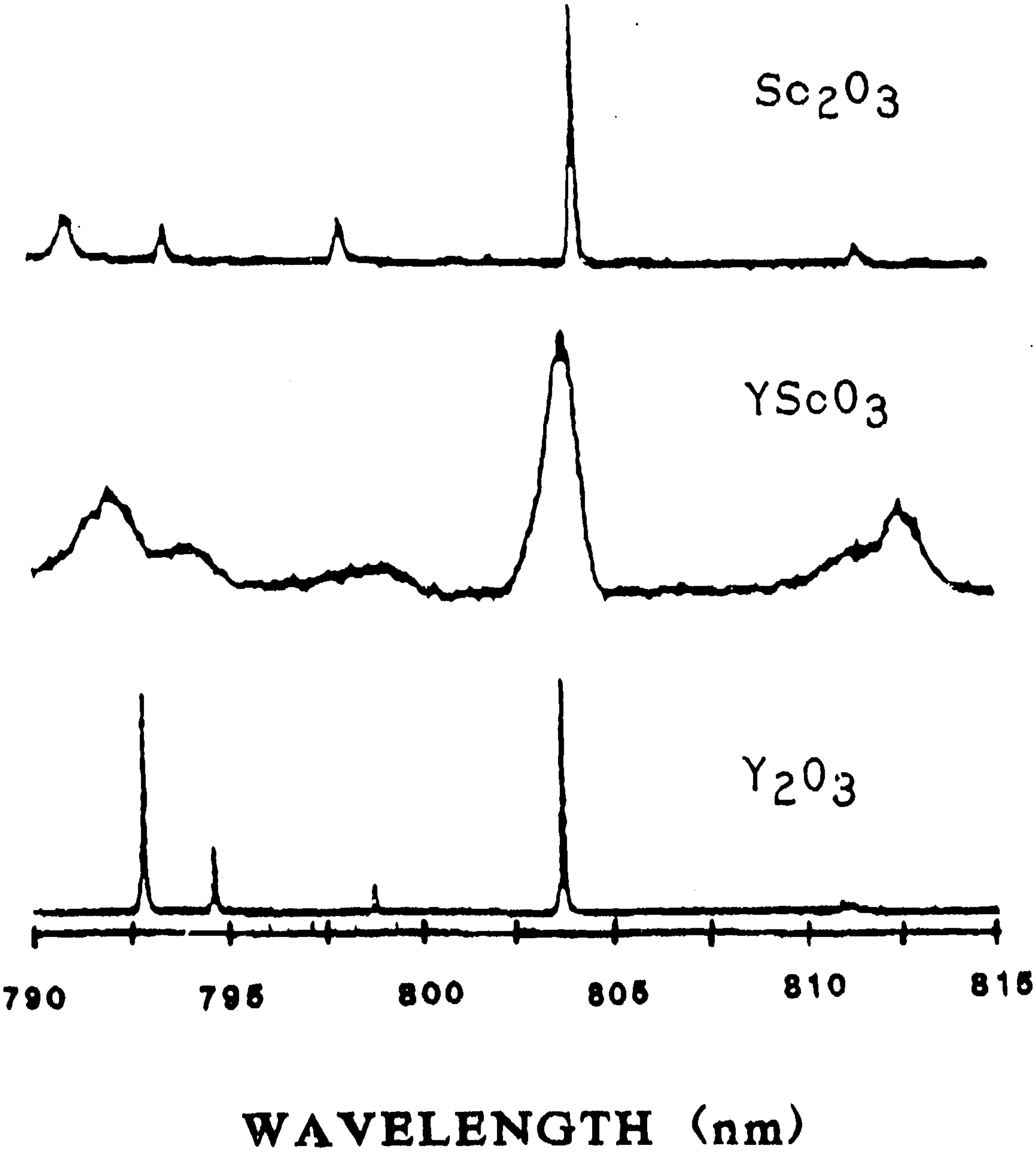
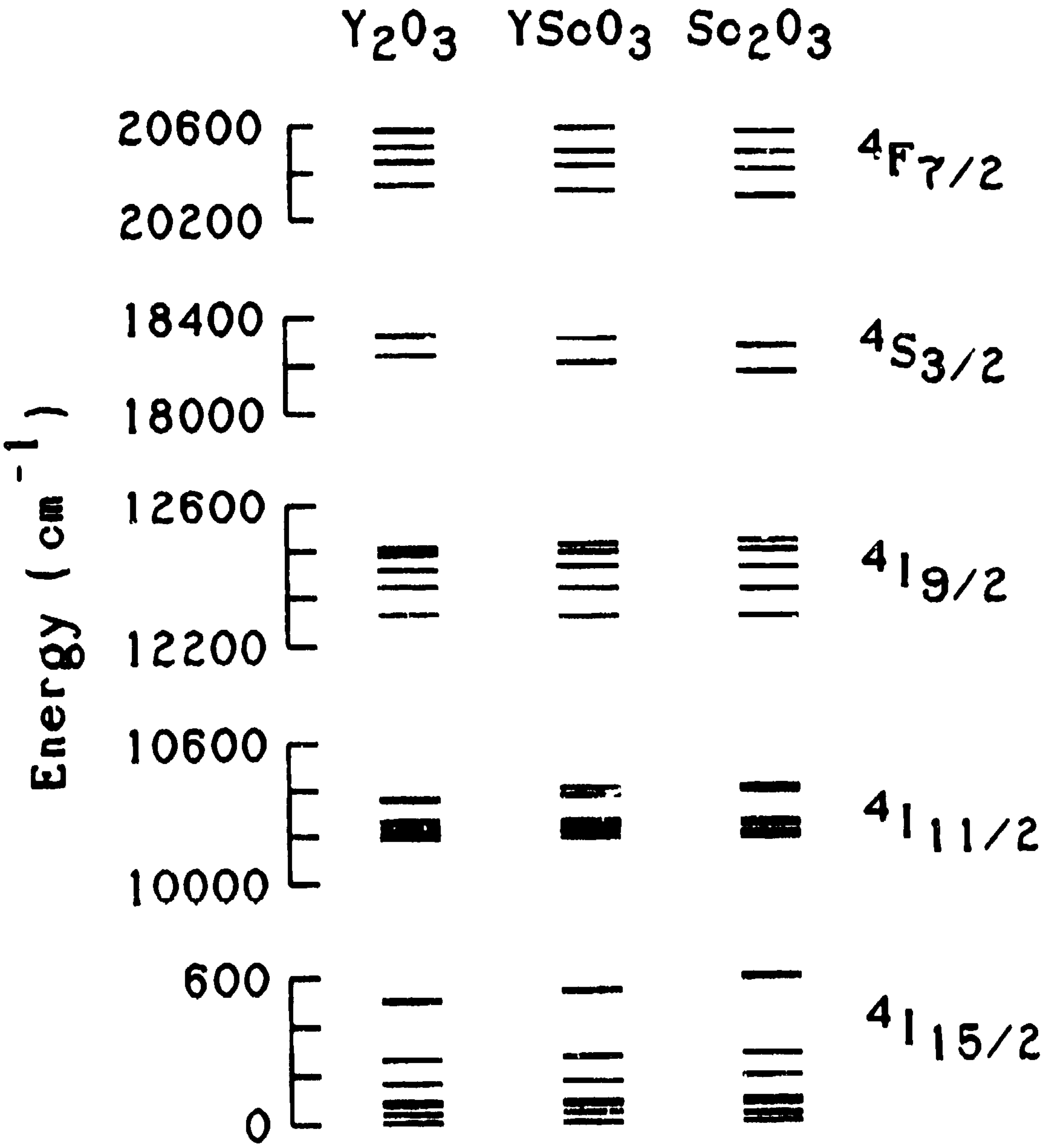


Fig 2



Y_2O_3
$YScO_3$
Sc_2O_3
Energy (cm^{-1})
20600
20200
18400
18000
12600
12200
10600
10000
600
0
$^4F_{7/2}$
$^4S_{3/2}$
$^4I_{9/2}$
$^4I_{11/2}$
$^4I_{15/2}$

Fig 3