New Light-Emitting Inorganic Materials

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Abstract. We are developing new inorganic light-emitting materials. In addition to the synthesis and crystal growth, our effort is devoted to an understanding of the relevant photophysical processes determining and limiting the light-emission properties. These can be influenced and tuned by chemical and structural variations. The working principles, typical results and conclusions are illustrated by a few selected examples.

1. Introduction

Making light has been a preoccupation of mankind from the earliest days. Inventions such as the candle, the incandescent lamp, fluorescent lamps and displays as well as the laser have been milestones in this development. The development is by no means finished, and materials research plays an increasingly important part. The principal aims in the lighting and display field are better quality and energy efficiency. In the laser field, the main research and development emphasis is on solid-state devices, with the main aims of higher efficiency and compactness as well as broader tuning ranges.

The activities of our research group are directed towards the development of new inorganic compounds with specific light-emitting properties. To this end we are synthesising new compounds containing transition-metal and rare-earth metal ions and study their optical spectroscopic properties in detail. We are aiming at identifying and characterising in detail the nonradiative and radiative processes taking place after a photoexcitation. Based on this knowledge, we are then hopefully in a position which allows the design of materials with very specific light-emitting properties.

For the present contribution we have chosen to illustrate our work in this area by presenting examples from two projects with very different objectives using very different classes of materials. New sharp-line and broad-band near-infrared (NIR) emitters based on 3d transition-metal ions are presented in *Sect. 2*. An example of a new NIR → VIS upconversion material containing Ho^{3+} as the active optical center is presented in *Sect. 3*.

2. Sharp-Line and Broad-Band Emitters in the NIR

Semiconductor diodes and the corresponding laser materials are the most efficient converters of electricity into light in the NIR. Between 600 nm and 1 μm, the wavelength of these sharp-line emitters can be tuned by the proper design and fabrication of the semiconductor nano- and microstructures. These materials are not the subject of the present contribution. They are, however, valuable excitation light sources for the materials described here.

A very large number of transition-metal and rare-earth metal-ion doped insulating materials exhibit spontaneous and stimulated emission in the NIR region between 700 nm and 1.6 μm. Al_2O_3:Ti^{3+}, which is the heart of the Ti:sapphire laser, is one of the most important laser materials [1]. It exhibits an exceptionally broad spectral tuning range from below 700 nm to *ca.* 1100 nm. It has to be pumped in the green using an Ar^+ ion laser or the second harmonic of a Nd^{3+} laser, which is a disadvantage. Nd^{3+} in a variety of host materials,
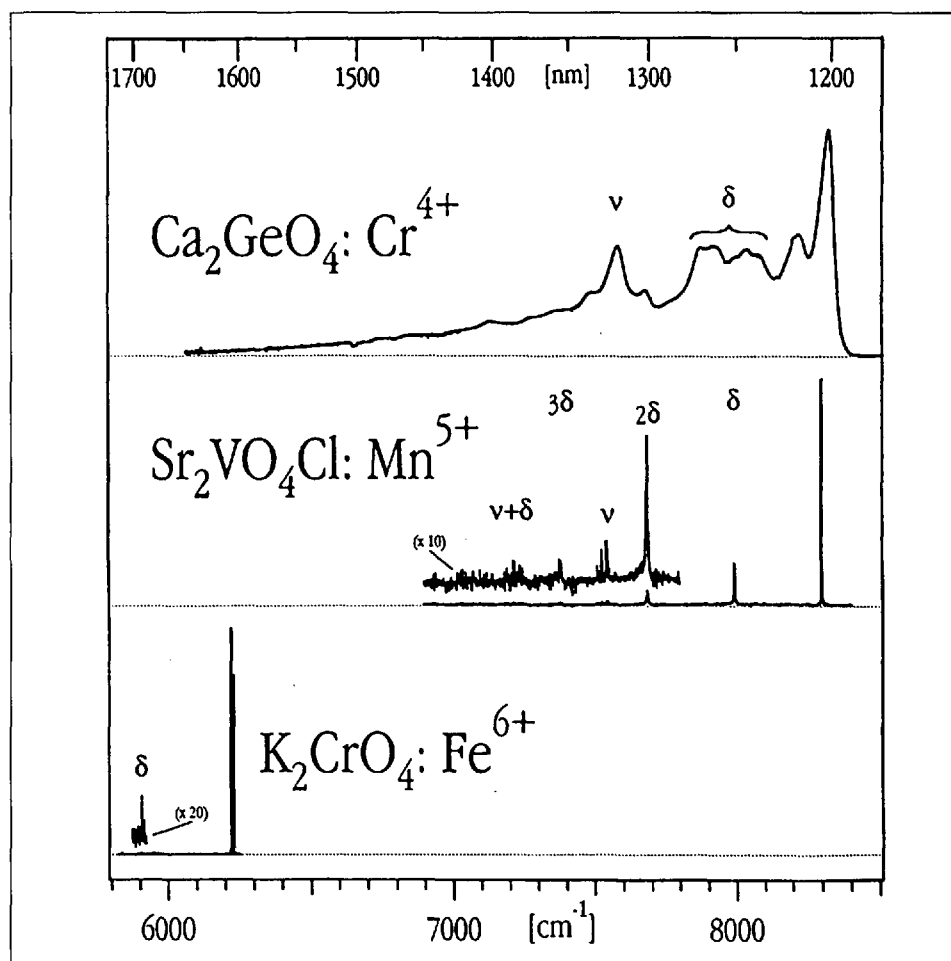
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Fig. 1. *NIR luminescence spectra of Ca$_2$GeO$_4$:Cr^{4+} (1%) at 9 K, Sr$_2$VO$_4$Cl:Mn^{5+} (0.1%) at 10 K and K$_2$CrO$_4$:Fe^{6+} (2%) at 15 K after photoexcitation in the visible.* The vibrational sidebands are assigned to bending (δ) and stretching (v) modes of the MO$_4$$^{n-}$ units (from [4]).

both crystalline and glassy, has a highly intense sharp emission around 1.06 µm, which can easily be doubled and tripled leading to a convenient and intense green and near UV laser light source [2]. An important laser wavelength in the NIR is around 1.54 µm. It is used in modern telecommunications. Er^{3+}-doped materials are used both for creating the laser

pulses and for their amplification along the line [3].

Our research in the past few years has centered on transition-metal ions with a $(3d)^1$ and $(3d)^2$ electron configuration in tetroxo coordination. The ions CrO_4^{3-}, MnO_4^{2-}, CrO_4^{4-}, MnO_4^{3-} and FeO_4^{2-} were incorporated in a variety of host lattices, and their NIR luminescence properties

were studied in depth [3–7]. *Fig. 1* shows 10-K luminescence spectra of the $(3d)^2$ ions CrO_4^{4-}, MnO_4^{3-} and FeO_4^{2-} in appropriate crystal hosts [4]. They all emit light in the NIR, and the spectra are characterised by sharp lines. In the case of MnO_4^{3-} and FeO_4^{2-}, the lines are exceedingly sharp. All the spectra are dominated by electronic origins, and the vibrational sidebands are readily assigned to O–M–O bending (δ) and M–O stretching (ν) vibrations. In the case of MnO_4^{3-} and FeO_4^{2-}, the luminescences are assigned to $^1E \rightarrow {}^3A_2$ spin-flip transitions. In CrO_4^{4-} the luminescence bandshape is broader, and the luminescence is due to a $^3T_2 \rightarrow {}^3A_2$ transition. *Fig. 2* shows the relevant part of the *Tanabe-Sugano* diagram for the three tetrahedral luminophors. CrO_4^{4-} lies to the left of the $^3T_2/^1E$ crossing point, while the other two lie to the right. The pronounced redshift of the FeO_4^{2-} luminescence down to about 1.6 µm is the result of increasing covalency along the series CrO_4^{4-}, MnO_4^{3-}, FeO_4^{2-}, thus decreasing electron repulsion and the $^1E \rightarrow {}^3A_2$ energy gap. In the FeO_4^{2-} ion, the reduction of this energy gap with respect to the free ion is more than 60%, indication a high degree of covalency. This is a rather neat example of tuning the light emission properties by chemical variation. The observed behaviour can be modelled with rather simple theoretical models, thus facilitating the design of new materials with very specific emission properties.

In going from the $(3d)^2$ to the $(3d)^1$ electron configuration and retaining the tetroxo coordination, we change the physical situation and thus the light emission properties completely. *Fig. 3* shows a 10-K luminescence spectrum of MnO_4^{2-} doped into Cs_2SO_4 [6]. It is an extremely rich spectrum, with a band originating around $11\,000$ cm^{-1} and extending out to *ca.* $7\,000$ cm^{-1}. Due to its high information content this band allows very detailed analysis. It is due to the d-d transition $^2T_2 \rightarrow {}^2E$, and its enormous width is mainly the result of a strong $T_2 \otimes e$ *Jahn-Teller* coupling involving a O–Mn–O bending vibration in the emitting state. Coupling to the totally symmetric breathing mode of MnO_4^{2-} is much weaker. This highly resolved spectrum of $Cs_2SO_4:MnO_4^{2-}$ is thus useful for an understanding of the fundamental excited-state distortions and the resulting photophysical processes [8]. As a potential laser material, however, it is useless. At room temperature the luminescence is quenched by nonradiative relaxation processes, and, in addition, Cs_2SO_4 is water-soluble. The situation is very different for $BaSO_4:MnO_4^{2-}$. In this chemically
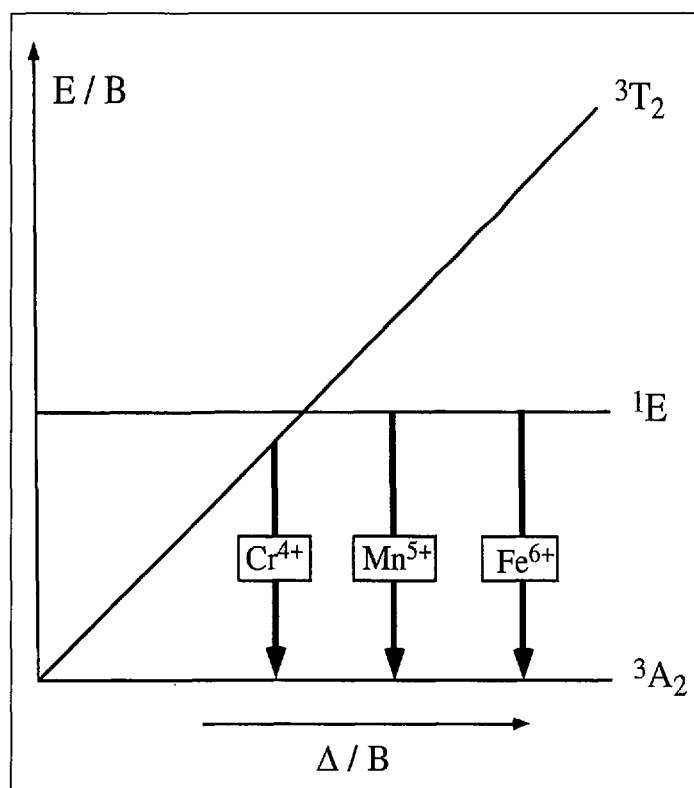
Fig. 2. *Relevant part of the* Tanabe-Sugano *diagram for (3d)² tetroxo ions.* The luminescence transitions are indicated.
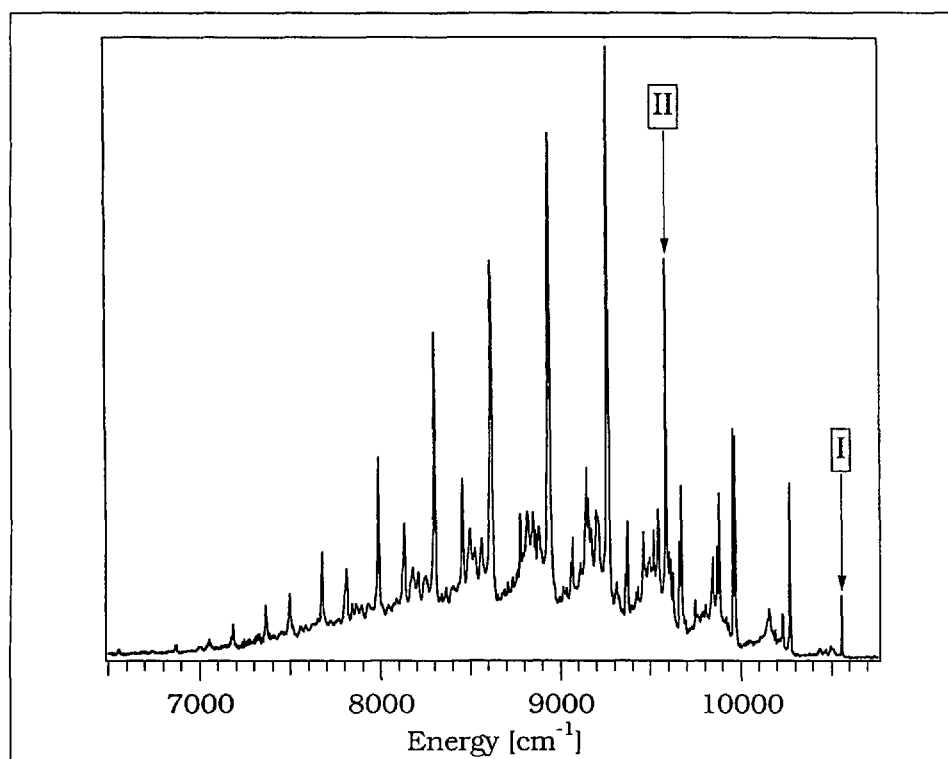
Fig. 3. *Spontaneous NIR emission spectrum of $Cs_2SO_4:Mn^{6+}$ (0.1%) at 15 K after visible photoexcitation* (from [6])

inert host, the MnO_4^{2-} luminescence has a quantum efficiency of 20% at room temperature. But, as illustrated in *Fig. 4*, we have a materials problem. Crystals grown under normal flux condition are contaminated by MnO_4^{3-}. Only by choosing a very special low-temperature flux, we were able to produce a material with pure MnO_4^{2-} luminescence.

We have tested the potential of $BaSO_4$:MnO_4^{2-} as a laser material at room temperature [9]. The results are very encouraging. The material is stable in air. In contrast to Ti:sapphire, excitation with a NIR diode laser is possible. The peak stimulated emission cross section is σ_{se} = 10^{-18} cm^2 at 9260 cm^{-1}, five times higher than in Cr^{4+}-doped forsterite, a tunable NIR laser material. Excited-state absorption is not detrimental. The potential tuning range is very large from *ca.* 900 nm to 1500 nm and covers a spectral region without any convenient broadly tunable lasers. The growth of optically perfect crystals is the main obstacle at present.

3. Near-Infrared to Visible Upconversion Materials

The search for new blue/green emitters is mainly driven by the need for more efficient and higher quality displays than presently available. Both in the phosphor and laser materials fields, a great research and development effort is devoted to higher light output and optimised wavelengths. A variety of technologies are being developed, and it is presently not foreseeable what part upconversion materials and processes will play in the future.

In this section we will discuss a physical situation which is fundamentally different from those encountered in *Sect. 2*: Materials and processes leading to visible emission after NIR excitation. This is a rather unusual situation, and it can only occur in materials in which multiphonon relaxation processes are not predominant, thus allowing more than one metastable excited state. In rare-earth compounds, the 4f or 5f electrons are efficiently shielded and thus not strongly involved in the metal-to-ligand bonding. As a consequence, electron-phonon coupling to f-f transitions is reduced, and multiphonon relaxation processes are less competitive. The phenomenon of upconversion is therefore most common and best studied in materials containing lanthanide ions. Several lasers based on upconversion processes have been reported [10][11]. There are only a few transition-metal ion systems exhibiting NIR-to-VIS upconversion.
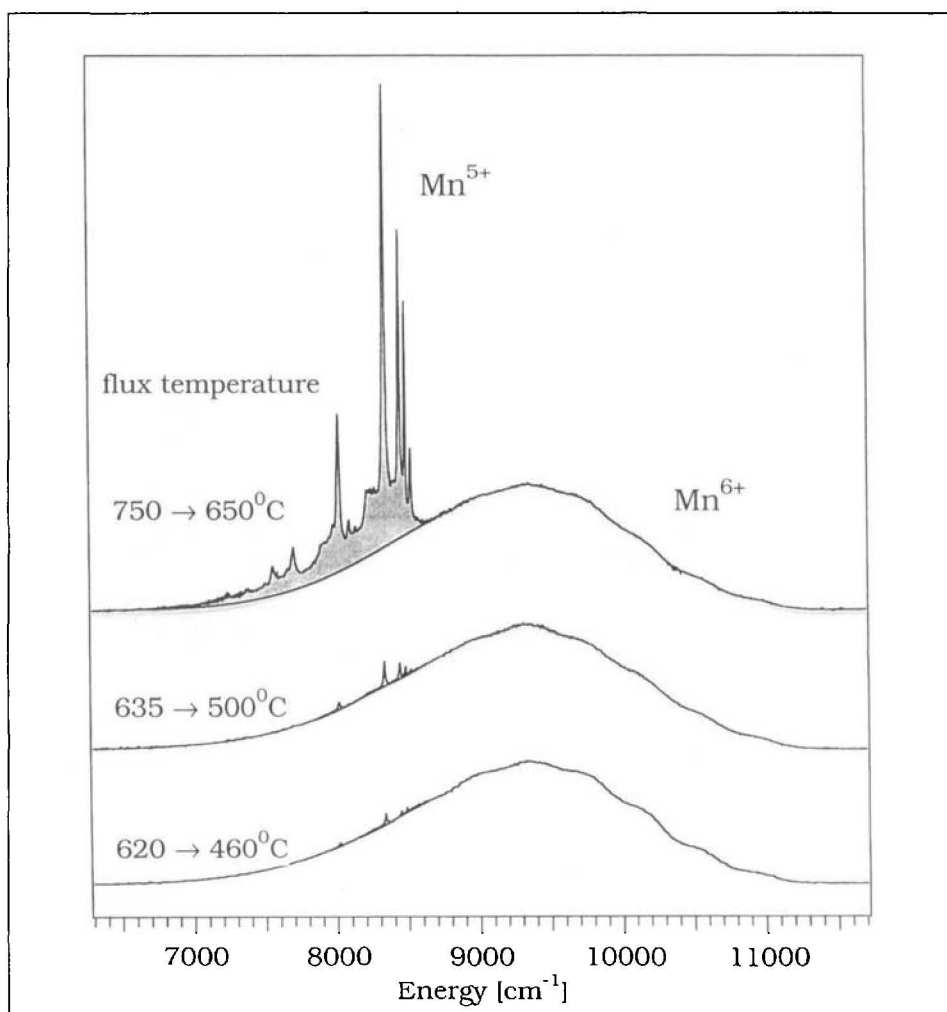

Fig. 4. *Room-temperature luminescence spectra of Mn-doped BaSO₄ crystals grown from alkalihalide fluxes at the given temperatures*
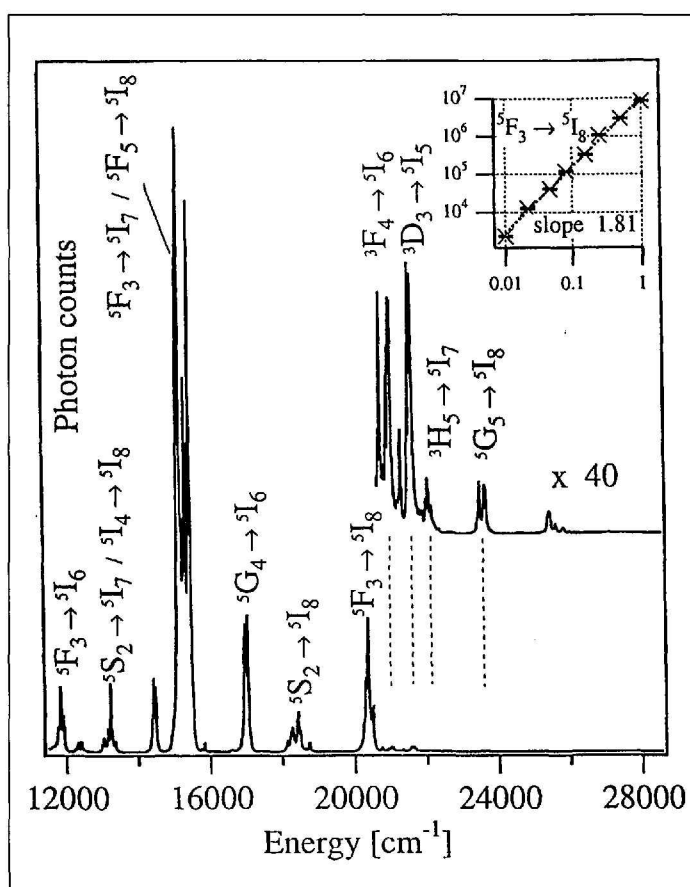

Fig. 5. *Room-temperature upconversion luminescence spectrum of CsCdBr₃:2.25% Ho³⁺ after ⁵I₅ excitation at 11060 cm⁻¹. The inset shows the power dependence on a logarithmic scale (from [17]).*

Ni^{2+} in a number of crystal lattices is the best documented example [12].

Our research in this area is governed by the principle of chemical and structural variation with the aim of finding new upconversion systems and tuning the upconversion properties. Both lanthanide and transition-metal ion systems are synthe-sised and spectroscopically characterised. As part of this project, we collaborate with the group of our colleague *J. Hulliger*, in which the techniques of crystal growth and synthesis are being developed and optimised [13].

The best studied upconversion materials are Er^{3+}-doped oxide and fluoride crys-tals or glasses [14]. Most of these show an intense green luminescence when excited around 980 nm or 810 nm. We have extended the chemical coordinate by including the heavier halides as well as other trivalent lanthanide ions [15][16]. *Fig. 5* shows the room-temperature upconversion luminescence spectrum of a CsCd-Br3:2.25% Ho^{3+} crystal excited at 11060 cm^{-1} [17], and *Fig. 6* shows the lowest energy levels of the (4f)^{10} electron configuration. The upconversion luminescence is intense and appears white to the naked eye. The initial excitation step around 11000 cm^{-1} is into $^5I_5$. This intermediate level has a long lifetime of 15 ms at 100 K in this host material. A second photon then excites the system up to the $^5F_3$ level, from which visible emission can take place. The inset in *Fig. 5* shows the power dependence of the VIS upconversion luminescence intensity. As expected, the dependence is close to quadratic, *i.e.*, we are dealing with a nonlinear process. The long lifetime of the intermediate $^5I_5$ level in the NIR is important in this upconversion process. This lifetime critically depends on the highest phonon energies of the crystal lattice. These are approximately 600 cm^{-1}, 400 cm^{-1}, 280 cm^{-1} and 180 cm^{-1} in oxides, fluorides, chlorides and bromides, respectively.

According to the energy-gap law, the multiphonon relaxation rate is given by

$$k_{mp} = \beta e^{-\alpha(\Delta E/\hbar\omega_{max})} \qquad (1)$$

where ΔE is the $^5I_5$–$^5I_6$ energy difference and $\hbar\omega_{max}$ the highest phonon energy of the crystal. Multiphonon relaxation across the $^5I_5$–$^5I_6$ energy gap of *ca.* 2400 cm^{-1} is clearly more competitive in the high-energy phonon oxides and fluorides than in CsCdBr$_3$:Ho^{3+}. By varying the composition of the host lattice towards the heavier halides, we decrease the multiphonon relaxation rates by many orders of magnitude and thus completely change the excited-state dynamics of the system and the steady-state populations of the various excited states under CW excitation. Similar considerations are also valid for the VIS emitting state $^5F_3$ and the $^5F_3/^5S_2$, $^5F_4$ energy gap.

The two most important upconversion mechanisms are schematically depicted in *Fig. 7* [18]. In the energy-transfer upconversion (ETU) mechanism, two neighbouring ions, which are both excited to the intermediate level, combine their excitation energy to create one highly excited state which can then luminesce. The excit-
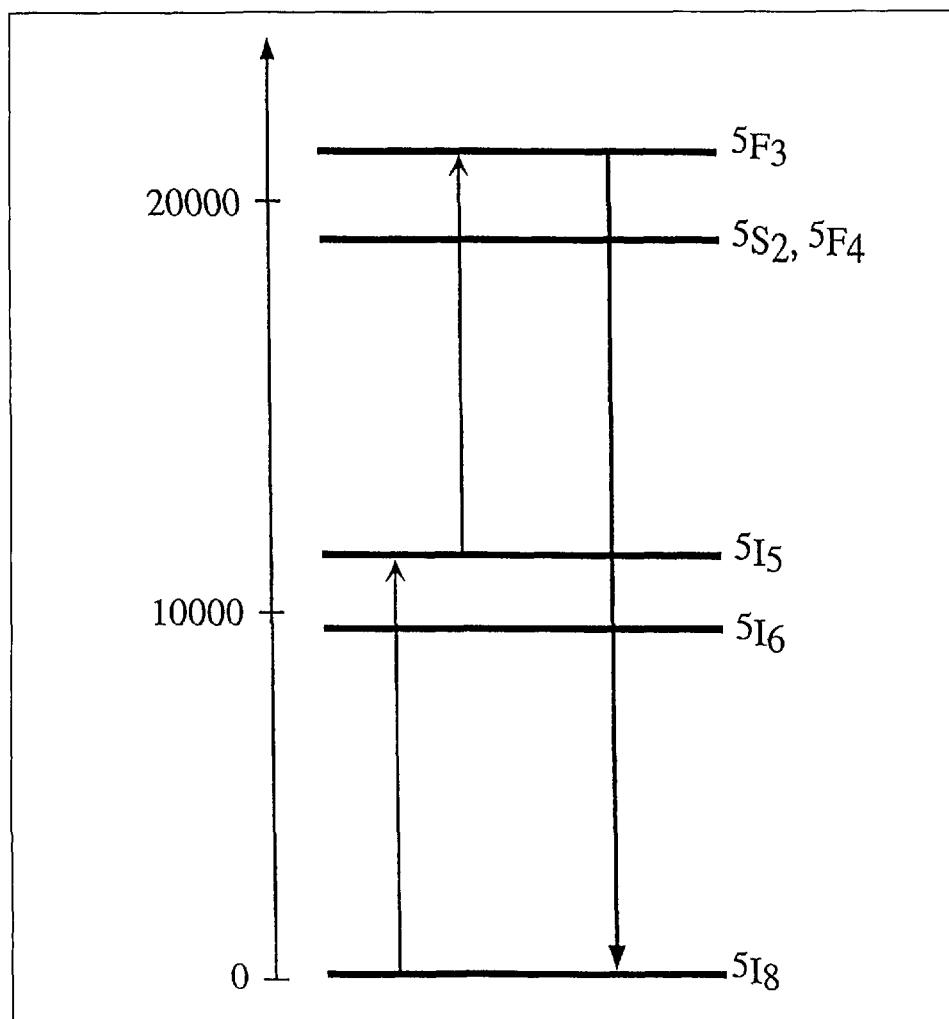
Fig. 6. *Relevant energy levels of Ho^{3+} with the upconversion excitation scheme employed in the present paper*
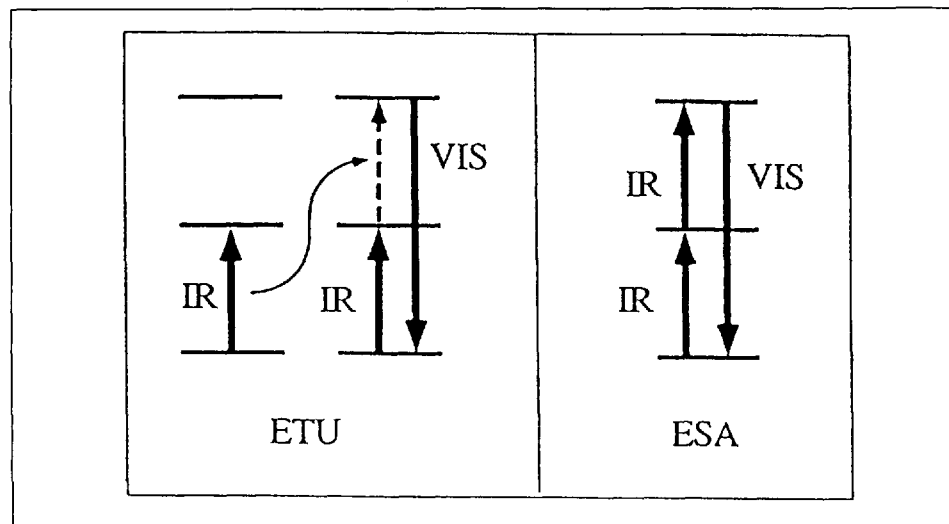
Fig. 7. *Energy transfer (ETU) and excited-state absorption (ESA) upconversion mechanisms*
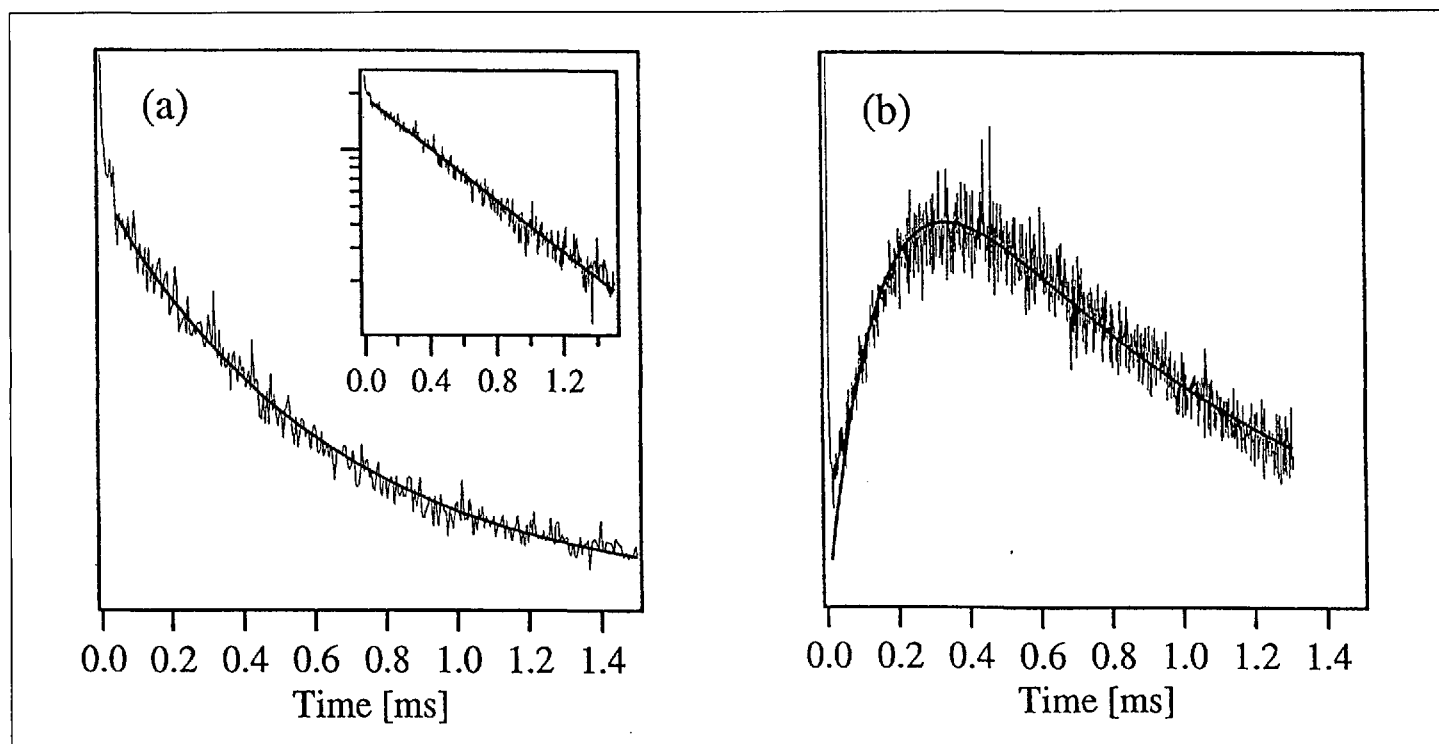
Fig. 8. *Time evolution of the $^5F_3$ upconversion luminescence at 100 K after excitation at 11028 cm^{-1} (a) and 11232 cm^{-1} (b), respectively* (from [17])

ed-state absorption (ESA) process can take place on one ion which is already excited to the intermediate level. We have developed fingerprinting techniques for the identification of the two types of mechanisms. One of them is based on the time evolution of the upconversion luminescence after an excitation pulse of 10 ns. In CsCdBr 3:2.25% Ho^{3+}, we observe both of them [17]. *Fig. 8* shows the transients of the $5F_3$ upconversion luminescence for two slightly different excitation energies around 900 nm. *Fig. 8, a* shows the typical time evolution of an ESA upconversion luminescence, in which the upconversion process has to take place within the 10 ns of the laser pulse. In *Fig. 8, b*, on the other hand, we see the typical signature of an ETU process. The transient has both a rise and a decay part, and from an analysis we derive $k_1 = 5815$ s^{-1} for the energy-transfer rate constant in $CsCdBr_3$:2.25% Ho^{3+}.

4. Conclusions

In the development of new inorganic materials for lasers and phosphors, the principle of chemical and structural variation is of great value. The relevant photophysical processes, which govern the light-emitting properties of a material, have to be thoroughly understood if a tuning of these properties is to be achieved. Besides a broad arsenal of synthetic and crystal growth techniques, this research requires rather sophisticated optical spectroscopic

and theoretical techniques. Questions ranging from chemistry and crystallography to solid-state physics and materials sciences requiring an interdisciplinary approach are important. For all those involved in these projects it is both a challenging and rewarding activity.

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