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Synthesis and emission spectra of $Ba_4In_{1.98}Nd_{0.02}O_7$ and $Ba_4In_{1.98}Er_{0.02}O_7$

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Abstract

The powder samples of $Ba_4In_{1.98}Nd_{0.02}O_7$ and $Ba_4In_{1.98}Er_{0.02}O_7$ were prepared from stoichiometric amounts of oxides by solid state reaction. The X ray examination confirmed the presence of a single phase with lattice parameters $a=4.164$ Å, $c=29.350$ Å. Luminescence spectra of Nd^{3+} and Er^{3+}recorded at room temperature and 5 K have been analysed. The energies of low-lying crystal field levels and splitting of several multiplets of Nd^{3+} and Er^{3+} ions have been estimated. Application of these compounds as potential luminescence materials was discussed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Luminescence; Powder compounds

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1. Introduction

Barium indate $Ba_4In_2O_7$ has been prepared for the first time by solid state reaction by Lalla and Müller-Buschbaum [1]. Investigation by X-ray has shown that the compound crystallises in a tetragonal system with space group $I4/_{mmm}$, $a=4.175$ Å, $c=29{,}483$ Å. In this structure two-dimensional slabs of $[InO_5]$-polyhedra are separated from each other by two $[BaO_2]$ layers along the c-axis.

The occurrence of $[InO_5]$ groups in this compound provides the possibility of the substitution the In^{3+} cations by other ions on the 3+ oxidation state. Er^{3+} and Nd^{3+} rare earth cations have been chosen as the first candidates to test these predictions. The ionic radii of Er^{3+} and Nd^{3+} are similar to that of the indium ion. Therefore the crystal structure of the compound is expected to be very weakly influenced by these dopants.

2. Experimental details

Powder samples of composition $Ba_4In_{1.98}Er_{0.02}O_7$ and $Ba_4In_{1.98}Nd_{0.02}O_7$ were prepared by solid state reaction from stoichiometric amounts of oxides: BaO_2, In_2O_3 and Er_2O_3 or Nd_2O_3. First the components were pulverised on an agate mortar, pressed into pellets and heated in air at 950°C for 20 h. Then the product was reground, again pressed into pellets and heated at 1050°C for 70 h. The obtained materials were analysed with a Stoe Powder diffractometer using CuKα radiation. Luminescence spectra were excited by Continuum Model OPO at 532 nm or 800 nm, dispersed with a 1 m double grating monochromator and detected with a photomultiplier having an S-1 spectral response. The resulting signal was analysed by a Stanford Model SRS 250 Boxcar integrator. For low temperature measurements, the samples were mounted in an Oxford Model CF 1204 continuous flow liquid helium cryostat.

3. Results and discussion

The X-ray examination of $Ba_4In_{1.98}Er_{0.02}O_7$ powder confirmed the presence of the single-phase but in the case of $Ba_4In_{1.98}Nd_{0.02}O_7$ the sample X-ray pattern contains an additional small intensity peak at $2\Theta=26.61°$ coming from an unidentified second phase. The lattice constants $a=4.164$ Å, $c=29.350$ Å determined for both systems are the same, but they are smaller than for the parent compound reported in [1]. In this structure one of three nonequivalent oxygen positions is occupied only by a half. There are two different Ba sites: Ba_I coordinates nine oxygen atoms whereas Ba_{II} has a six-fold coordination. The primitive cell contains two formula units i.e. two indium ions which coordinate O^{2-} forming InO_5 pyramids.

Trivalent rare earth ions can substitute indium ions, consequently optical absorption and emission spectra are expected to be consistent with a single, well-defined luminescence site.

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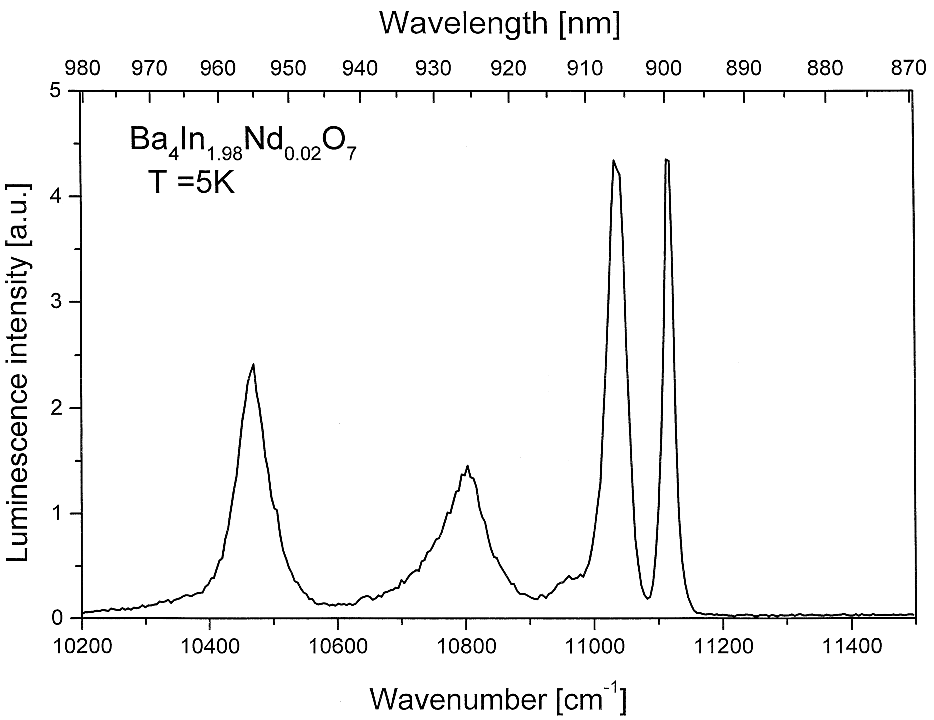

Fig. 1. Luminescence spectrum associated with $^4F_{3/2}$–$^4I_{9/2}$ transition of Nd^{3+} in $Ba_4In_{1.98}Nd_{0.02}O_7$ recorded at 5 K.

Luminescence spectra associated with the $^4F_{3/2}$–$^4I_{9/2}$ and $^4F_{3/2}$ –$^4I_{11/2}$ transitions recorded at 5 K are shown in Figs. 1 and 2 respectively. The transitions originate in the lowest component of the $^4F_{3/2}$ multiplet and crystal field components of the $^4I_{11/2}$ and $^4I_{9/2}$ multiplets may be located. Their energies and the overall multiplet splitting are given in Table 1.

Almost all intensity of the $^4F_{3/2}$– $^4I_{11/2}$ transition at 5 K is concentrated in two lines ending one of the lowest crystal field components of the terminal level. Only two of

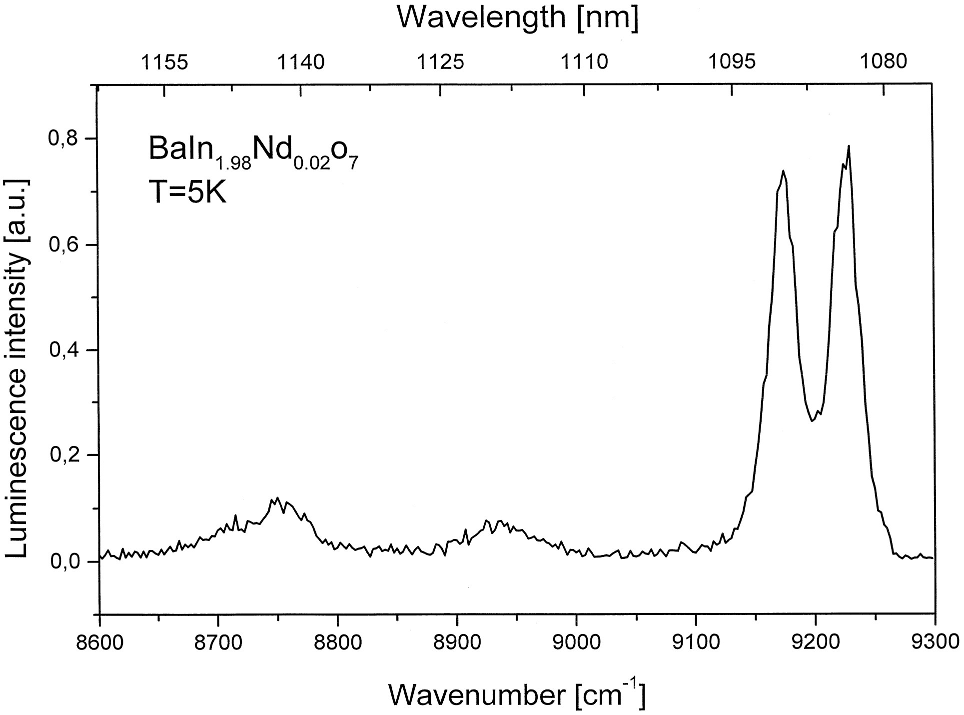

Fig. 2. Luminescence spectrum associated with $^4F_{3/2}$– $^4I_{11/2}$ transition of Nd^{3+} in $Ba_4In_{1.98}Nd_{0.02}O_7$ recorded at 5 K.

Table 1
Energies of crystal field levels and overall splitting of the $^4I_{9/2}$ and the $^4I_{11/2}$ multiplets of Nd^{3+} in $Ba_4In_{1.98}Nd_{0.02}O_7$

Multiplet	Stark level energy [cm^{-1}]	Number of components		Overall splitting [cm^{-1}]
		Theor.	Exper.	
$^4I_{9/2}$	0, 336, 485, 572, 650	5	5	650
$^4I_{11/2}$	1885, 1941, 2179, 2365	6	4	480
$^4F_{3/2}$	11 115			

the remaining four band components appear as weak and broad features in the spectrum. The 5 K emission spectrum associated with the $^4F_{3/2}$–$^4I_{9/2}$ transition is more informative: four band components appear as well as resolved lines and the remaining component has the form of a shoulder.

It can seen in Figs. 1 and 2 that the lines corresponding to transitions between individual crystals field levels are relatively broad. Their bandwidths are between 30 cm^{-1} to 10 cm^{-1} FWHM at 5 K indicating the importance of structural imperfections, which induce inhomogeneous line broadening. From low temperature emission spectrum the energy of the lowest component of the emitting $^4F_{3/2}$ level is found to be 11 115 cm^{-1}. To our knowledge it is the lowest reported energy for the $^4F_{3/2}$ level of Nd^{3+} in a crystal matrix.

Luminescence lifetime measurements revealed that the decay of the $^4F_{3/2}$ level is relatively fast. At room temperature the $^4F_{3/2}$ lifetime was 87 μs and it remained constant upon cooling the sample down to 77 K. At this stage of investigation the contribution of nonradiative relaxation to the decay cannot be determined precisely. Nevertheless, the multiphonon relaxation is not likely to be of significant importance. The crystal structure is built of heavy atoms, consequently the cut-off phonon energy should be low. We are not aware of published reports dealing with lattice vibrations of $Ba_4In_2O_7$, but IR spectra of other compounds of BaO–In_2O_3 system were reported [2]. The highest energy vibration at 595 cm^{-1} was recorded with a sample of $Ba_5In_2O_8$ compound, which is isostructural to $Ba_4In_2O_7$ with almost identical lattice constants. We suppose therefore that the luminescence lifetime measured indicates a high rate of radiative transitions of Nd^{3+} in this matrix.

The luminescence spectra for $Ba_4In_{1.98}Er_{0.02}O_7$ associated with the $^2H_{11/2}$, $^4S_{3/2}$–$^4I_{15/2}$ transition are presented in Fig. 3. At room temperature (dotted line) the $^2H_{11/2}$ and $^4S_{3/2}$ levels are thermally populated and transitions occur from $^2H_{11/2}$ and $^4S_{3/2}$, but at low temperature (solid line) only from the $^4S_{3/2}$ state. The luminescence lifetime of the

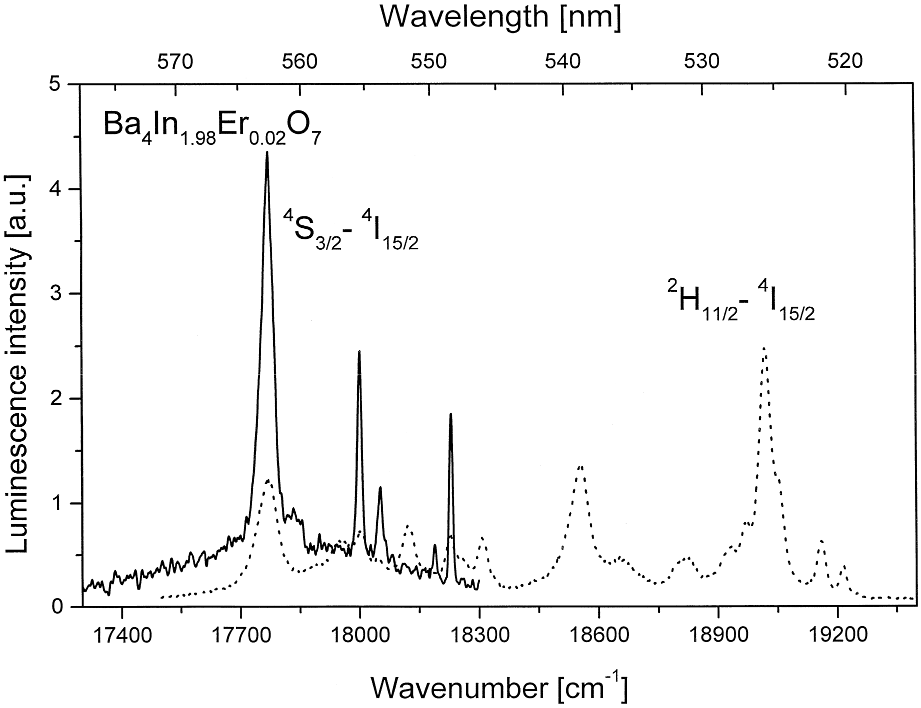

Fig. 3. Luminescence spectra associated with $^2H_{11/2}$, $^4S_{3/2}$ –$^4I_{15/2}$ transition of Er^{3+} in $Ba_4In_{1.98}Er_{0.02}O_7$ recorded at room temperature (dotted line) and 5 K (solid line).

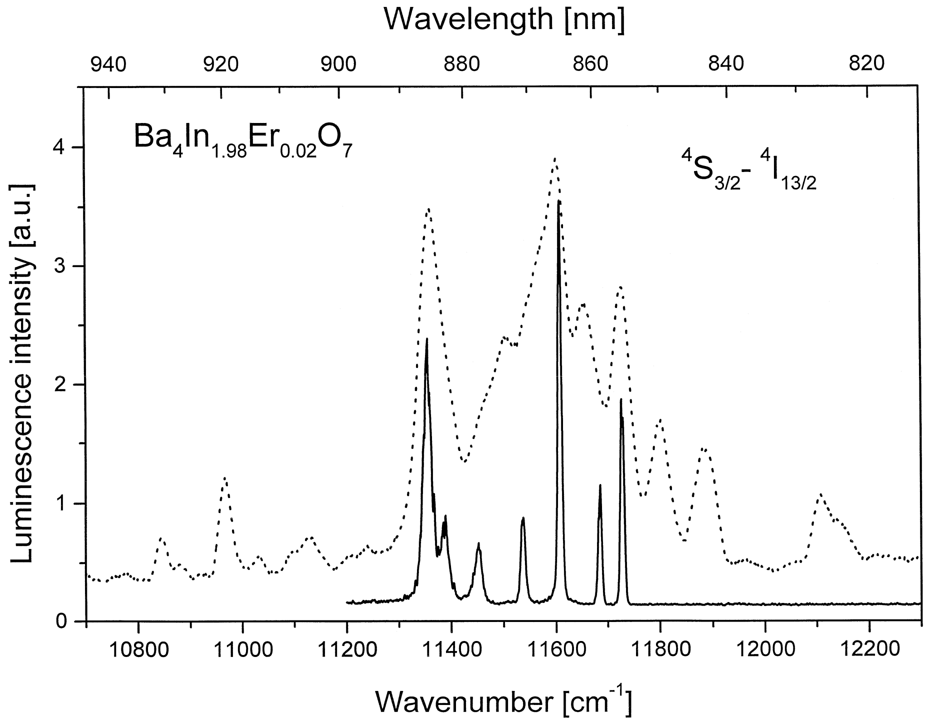

Fig. 4. Luminescence spectra associated with $^4S_{3/2}$–$^4I_{13/2}$ transition of Er^{3+} in $Ba_4In_{1.98}Er_{0.02}O_7$ recorded at room temperature (dotted line) and 5 K (solid line).

$^4S_{3/2}$ state measured at room temperature and at 5 K was found to be 14 μs and 69 μs respectively. In the highest temperatures, the additional relaxation channel is switched, on accelerating the decay of the $^4S_{3/2}$ state. The luminescence spectra associated with the $^4S_{3/2}$–$^4I_{13/2}$ transition recorded at room temperature and at 5 K are presented in Fig. 4.

The room temperature spectrum (dotted line) consists of

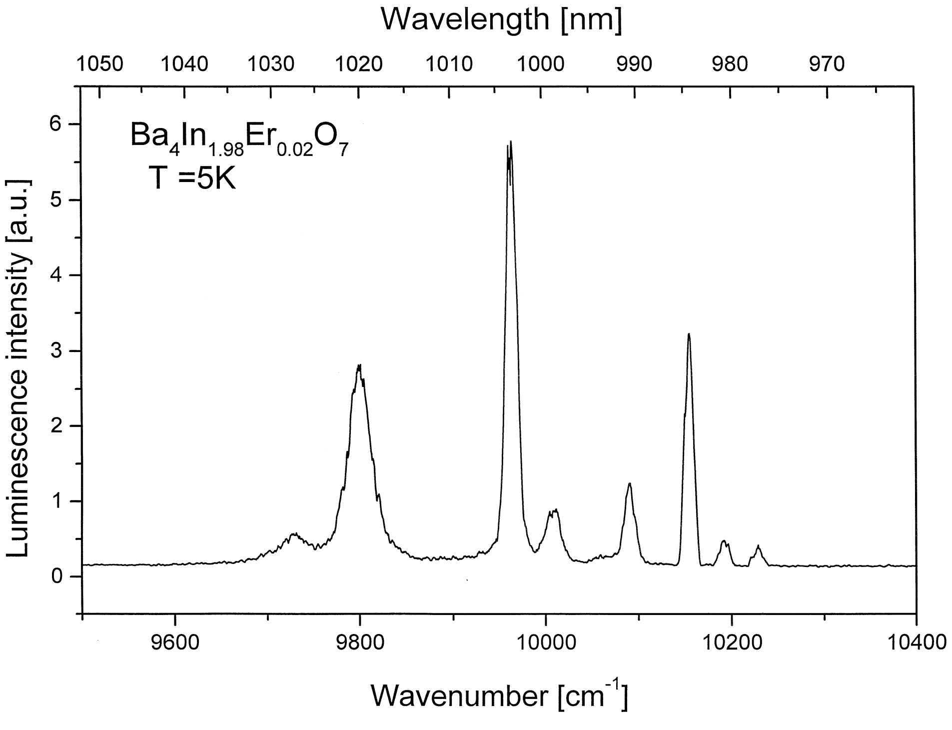

Fig. 5. Luminescence spectrum associated with $^4I_{11/2}$–$^4I_{15/2}$ transition of Er^{3+} in $Ba_4In_{1.98}Er_{0.02}O_7$ recorded at 5 K.

Table 2
Energies of crystal field levels and overall splitting of the $^4I_{15/2}$ and the $^4I_{13/2}$ multiplets of Er^{3+} in $Ba_4In_{1.98}Er_{0.02}O_7$

Multiplet	Stark level energy [cm^{-1}]	Overall splitting [cm^{-1}]
$^4I_{15/2}$	0, 72, 195, 279, 361, 427, 464, 501	501
$^4I_{13/2}$	6403, 6492, 6544, 6623, 6694, 6777, 6876	473
$^4F_{9/2}$	1506	
$^4S_{3/2}$	18 230	

poorly resolved bands which are formed by overlapping transitions between individual crystal field levels of initial and terminal multiplets. In the low temperature spectrum, the transition originates in the lowest component of the $^4S_{3/2}$ multiplet, and all crystal field components of $^4I_{13/2}$ may be located. The emission spectrum corresponding to the $^4I_{11/2}$–$^4I_{15/2}$ transition recorded at 5 K is presented in Fig. 5. All crystal field components of the ground state of Er^{3+} may be estimated from this spectrum. The luminescence lifetime of the $^4I_{11/2}$ state measured at 5 K was found to be 950 μs. Energies of crystal field levels and overall splitting of the $^4I_{15/2}$ and $^4I_{13/2}$, as well as energies of the lowest component of the multiplets $^4F_{9/2}$ and $^4S_{3/2}$ estimated from low temperature spectra are presented in Table 2.

4. Conclusions

Nd^{3+} and Er^{3+} ions substitute In^{3+} ions in $Ba_4In_2O_7$ and occupy well defined sites with six-fold coordination in the crystalline lattice. Results of luminescence lifetime measurements indicate that radiative transition rates for Nd^{3+} and Er^{3+} are high in this matrix. The energy of the $^4F_{3/2}$ luminescent level of Nd^{3+} is one of the lowest reported for neodymium doped compounds and consequently the Nd emission bands are shifted towards longer wavelengths.

References

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