Dynamic local structural symmetries and luminescence properties of the yellow emitting phosphor Ce$^{3+}$-doped $Y_3Al_5O_{12}$

Yuan-Chih Lin
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Abstract

This thesis centers on investigations of the local structure and vibrational properties of the oxide garnet $Y_3Al_5O_{12}$ (YAG), which when substituted with a few percent of the activator ion Ce$^{3+}$ to replace Y$^{3+}$ ($Y_{3-x}Ce_xAl_5O_{12}$, YAG:Ce$^{3+}$) is one of the most important phosphors for solid state lighting. The study builds on a comprehensive analysis of the nature of the phonons and localized vibrational modes in YAG:Ce$^{3+}$ and how these depend on the Ce$^{3+}$ concentration and temperature and how they affect key optical properties, such as the intensity and frequency of the emitted light. The investigations have been carried out by using a combination of Raman, infrared, luminescence, and neutron spectroscopies, together with mode-selective vibrational excitation, and are further supported by computer modeling. The results show that the static and dynamic structure of YAG:Ce$^{3+}$ are dependent on both Ce$^{3+}$ concentration and temperature. The substitution of the heavier Ce$^{3+}$ ions compared to Y$^{3+}$ is found to lower the vibrational frequencies of most of the phonons and localized vibrational modes around the Ce$^{3+}$ ions, implying that they become more populated at a given temperature. As the temperature increases, vibrational modes of higher and higher frequency are activated, some of which induce significant dynamical tetragonal distortions around the Ce$^{3+}$ ions. These distortions are shown to lead to a red-shift of the frequency of the emitted light. In addition, some of the high-frequency phonons are shown to be notably related to non-radiative relaxation of the excited-state electrons of the Ce$^{3+}$ ions via electron-phonon coupling, which decreases the emission intensity when these phonons are activated. The reduction in emission intensity at elevated temperature is however a complicated process as it is found to relate also to thermal ionization of the excited-state electrons into the conduction band of the host crystal, which may be followed by charge trapping by defects.

Keywords: phosphor, garnet, luminescence, vibrational spectroscopy, neutron scattering, free electron laser, light emitting diode, thermal quenching.
List of publications

This thesis includes the following papers

I Inorganic Phosphor Materials for Lighting
Yuan-Chih Lin, Maths Karlsson, and Marco Bettinelli
*Topics in Current Chemistry, 374, 1–47, (2016)*

II Local structure and vibrational properties of the yellow-emitting phosphor \(Y_{3-x}Ce_xAl_5O_{12}\) (\(x = 0 - 0.09\))
Yuan-Chih Lin, Paul Erhart, Marco Bettinelli, Stewart F. Parker, and Maths Karlsson
In manuscript

III Mode-selective vibrational excitation and relationship to thermal quenching in the yellow-emitting phosphor \(\text{Ce}^{3+}\)-doped \(Y_3Al_5O_{12}\)
Yuan-Chih Lin, Marco Bettinelli, Suchinder Sharma, A. F. G. van der Meer, Britta Redlich, Adolfo Speghini, and Maths Karlsson
In manuscript

Other papers to which I have contributed but that are not part of this thesis

i Structural and Vibrational Properties of Silyl (\(\text{SiH}_3^–\)) Anions in \(\text{KSiH}_3\) and \(\text{RbSiH}_3\): New Insight into Si–H Interactions
Verina F. Kranak, Yuan-Chih Lin, Maths Karlsson, Janos Mink, Stefan T. Norberg, and Ulrich Häussermann
doi: 10.1021/ic502931e

ii Vibrational properties of \(\beta\)-\(\text{KSiH}_3\) and \(\beta\)-\(\text{RbSiH}_3\): a combined Raman and inelastic neutron scattering study
Janos Mink, Yuan-Chih Lin, Maths Karlsson, Carin Österberg, Terrence J. Udovic, Henrik Fahlquist, and Ulrich Häussermann
*Journal of Raman Spectroscopy, (2016)*
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In Press
# Contents

1 Introduction .......................................................... 1

2 Inorganic phosphors .................................................. 5
   2.1 General characteristics ......................................... 5
   2.2 Garnet type phosphors and YAG:Ce$^{3+}$ ......................... 6
      2.2.1 Crystal structure ......................................... 6
      2.2.2 Optical properties ....................................... 8
      2.2.3 Vibrational properties .................................. 11
   2.3 Thermal quenching .............................................. 12
      2.3.1 Electron-phonon coupling ................................ 12
      2.3.2 Thermal ionization ...................................... 15

3 Experimental ......................................................... 17
   3.1 Vibrational spectroscopy ...................................... 17
      3.1.1 Infrared spectroscopy .................................. 17
      3.1.2 Raman spectroscopy .................................... 18
      3.1.3 Inelastic neutron scattering ............................ 19
      3.1.4 Phonon assignment by symmetry coordinates .......... 20
   3.2 Luminescence .................................................. 22
      3.2.1 Photoluminescence ...................................... 22
      3.2.2 Thermoluminescence .................................... 23
   3.3 Free electron lasers .......................................... 24

4 Instruments .......................................................... 27
   4.1 The Bruker IFS 66v/s spectrometer .......................... 27
   4.2 The Dilor XY 800 spectrometer ............................... 28
   4.3 The TOSCA INS spectrometer ................................ 29
   4.4 Photoluminescence and thermoluminescence experiments .. 30
   4.5 The FELIX infrared free electron laser .................... 31

5 Summary of results .................................................. 33
6 Conclusions and outlook 35
Acknowledgments 37
Bibliography 39
Papers I–III 47
## Glossary

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>LEDs</td>
<td>Light emitting diodes</td>
</tr>
<tr>
<td>RGB</td>
<td>Red, green, and blue</td>
</tr>
<tr>
<td>CCT</td>
<td>Correlated color temperature</td>
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<tr>
<td>CRI</td>
<td>Color rendering index</td>
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<tr>
<td>pcWLEDs</td>
<td>Phosphor converted white light emitting diodes</td>
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<tr>
<td>QE</td>
<td>Quantum efficiency</td>
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<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray absorption fine structure</td>
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<tr>
<td>DOS</td>
<td>Density of states</td>
</tr>
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<td>CB</td>
<td>Conduction band</td>
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<td>VRBE</td>
<td>Vacuum referred binding energy</td>
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<td>IR</td>
<td>Infrared</td>
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<td>INS</td>
<td>Inelastic neutron scattering</td>
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<td>Electromagnetic</td>
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<td>Photoluminescence</td>
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<td>Thermoluminescence</td>
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<td>FEL</td>
<td>Free electron laser</td>
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<td>Radio frequency</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
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<tr>
<td>CCD</td>
<td>Charge coupled device</td>
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<tr>
<td>CW</td>
<td>Continuous wave</td>
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<tr>
<td>FELIX</td>
<td>Free Electron Laser for Infrared eXperiments</td>
</tr>
<tr>
<td>Linac</td>
<td>Linear accelerator</td>
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Chapter 1

Introduction

Lighting consumes as much as approximately one fifth of worldwide electricity [1, 2]. The enormous demand for lighting drives the rapid growth of the new and environment-friendly solid-state white lighting technologies that aim to replace the old and inefficient technologies that have been phased out (incandescent lamps) or are problematic from an environmental point of view (compact fluorescent lamps) [2]. The invention of bright-blue light emitting diodes (LEDs) [3, 4] in the mid-90s has led to the development of devices capable of producing white light in a reliable and efficient way, based on inorganic phosphors. These consist of a crystalline host lattice [e.g. $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG)] and a small concentration of activator ions (e.g. the lanthanide $\text{Ce}^{3+}$, $\text{Pr}^{3+}$, and so forth), which convert light from the LED into longer wavelengths. The admixture of different wavelengths results in white light emission. Most commonly, blue LEDs ($\sim 450–480$ nm) can be used to excite either a yellow phosphor or a green and a red phosphor, whilst UV LEDs ($\sim 380–410$ nm) are used to excite red (R), green (G) and blue (B) phosphors, to produce white light, see Figure 1.1.

The lighting characteristics are typically defined by the correlated color temperature (CCT) and the color rendering index (CRI). The CCT is a measure of the perceived color temperature of the emitted light compared to that of black-body radiation such as from the sun. The CRI is a parameter indicating the capability to reproduce colors of an object with respect to that as illuminated by a black-body radiation source. A low CCT ($< 4000–5000$ K) and a high CRI (close to 100) yield a warm, natural and comfortable white light emission spectrum, generally suited for, e.g., indoor lighting.

Currently, one of the most widely used phosphor converted white LEDs (pcWLEDs) on the market is the blue LED coated with the yellow-emitting phosphor $\text{Ce}^{3+}$-doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG:Ce$^{3+}$), which can emit bright white light with a relatively high efficiency (up to 85 %) [6]. However, a major
disadvantage of currently available devices is that the emitted white light has a strong blue component and hence is perceived as cold and unnatural. In comparison, UV LEDs coated with RGB phosphors produce a warmer white light, however these devices may suffer from technical complexity of mixing different phosphors onto LED chips, and low efficiency [7]. Furthermore, pcWLEDs generally suffer greatly from thermal quenching, *i.e.* a pronounced reduction in emission intensity or quantum efficiency (QE)\(^1\) of the phosphors, observed at elevated temperature, typically a few hundred degree centigrade. To conclude, the trade-off between different measures, such as CCT, CRI, QE, cost, fabrication and so forth, always presents and it is hardly satisfactory in all aspects [5,9].

In view of these materials challenges, which have hindered the development and widespread use of pcWLEDs, recent, promising research points toward that the lighting characteristics of inorganic phosphors can be modulated significantly by changing their short-range (local) crystal structure and vibrational characteristics [10]. In effect, this may provide a means to tune the light emission so that the emitted light is perceived as, *e.g.*, warmer and thus more suitable for indoor lighting, or so that the phosphor is more thermally stable. However, the correlation between optical properties, local structure, and vibrational dynamics of phosphors is not fully understood. For this reason, this thesis aims to clarify in detail how the local structure and dynamics of phosphors affect their optical properties, in particular in

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\(^1\)QE is divided into internal and external. Internal QE = the number of emitted photons / the number of absorbed photons; External QE = the number of emitted photons / the number of incident photons. [8]
relation to emission wavelength and thermal quenching. The studies are focused on the technologically very important yellow phosphor YAG:Ce^{3+}. The primary tools involve the use of infrared, Raman, luminescence, and neutron spectroscopies together with computer modeling based on density functional theory (DFT). Additionally, a new approach is used, that is the application of monochromatic infrared irradiation simultaneously with the electronic excitation of activator ions, for studying of how certain vibrational modes couple to luminescence.
CHAPTER 1. INTRODUCTION
Chapter 2

Inorganic phosphors

2.1 General characteristics

An inorganic phosphor consists of activator ions, which serve as luminescent centers, and a host lattice that accommodates the activator ions, see Figure 2.1(a). The activator ions convert light of a certain wavelength into light of a longer wavelength and heat. The energy conversion process involves transitions between electronic states as well as between vibrational states. This may be explained by a so called configurational coordinate diagram, as that shown in Figure 2.1(b). The electronic transition redistributes electrons from the ground state to the excited state. The excited-state electrons are often relaxed to lower vibrational states before returning to the electronic ground state, due to the much shorter lifetime of vibrational transitions (on the order of fs–ps) compared to electronic transitions (on the order of ns). The shapes and intensities of the absorption/excitation and emission spectra are determined by the square of the (vertical) overlap integrals of the vibrational wavefunctions of the ground and excited states. The overlap integrals are affected by the difference in nuclear coordinates between the ground- and excited-state parabolae, which depends on the difference in bonding forces between the ground and excited states. It can be concluded that the luminescence properties of inorganic phosphors depend on the electronic configuration of the activator ions, both in the ground and excited states, as well as on the vibrational properties of the activator ions and the host lattice in which they are incorporated.
2.2 Garnet type phosphors and YAG:Ce\(^{3+}\)

2.2.1 Crystal structure

Although the nature of the luminescent ion contributes to the optical properties of phosphors, the structure and dynamics of the host lattice is also critically important. Examples of host matrices for generating yellow light emission are oxynitrides, silicates, and aluminates [5]. The most important class of hosts of technological interest is, however, oxide garnets, particularly Ce\(^{3+}\)-doped ones [5]. For instance, the garnet families of aluminates (Y, Tb, Gd, Lu)\(_3\)Al\(_5\)O\(_{12}\) [6, 13–15], silicates Ca\(_3\)Sc\(_2\)Si\(_3\)O\(_{12}\) [16], and the more complex compositions, such as Y\(_3\)Mg\(_2\)Si\(_2\)O\(_{12}\) [17], Y\(_3\)Sc\(_2\)Ga\(_{3–x}\)Al\(_x\)O\(_{12}\) [18], Ca\(_2\)GdZr\(_2\)Al\(_5\)O\(_{12}\) [19], and Lu\(_2\)CaMg\(_2\)(Si,Ge)\(_3\)O\(_{12}\) [20] have been reported and their chemical formula can be generally expressed as \(A_3B_2(XO_4)_3\), where \(A\), \(B\) and \(X\) are cations located at distinct Wyckoff positions, and \(O\) is oxygen. Of specific concern for this thesis is the yttrium aluminium garnet, YAG. The YAG crystal structure is built up of tetrahedra (AlO\(_4\)), octahedra (AlO\(_6\)), and 8-fold coordinated Y cations, as illustrated in Figure 2.2. It crystallizes into the space group \(Ia\overline{3}d\) (O\(_h^{18}\)) [21], which is a body-centered cubic Bravais lattice, and its unit cell consists of 160 atoms. For the Ce\(^{3+}\)-doped equivalent, YAG:Ce\(^{3+}\), the Ce\(^{3+}\) ions substitute for the Y\(^{3+}\) ions.

The local environment of the Y\(^{3+}\) ions in YAG, or equivalently Ce\(^{3+}\) in YAG:Ce\(^{3+}\), is shown in Figure 2.3(a). Since Ce\(^{3+}\) is larger than Y\(^{3+}\), the substitution for Ce\(^{3+}\) results in a local lattice expansion. Results obtained
2.2. GARNET TYPE PHOSPHORS AND YAG:Ce$^{3+}$

Figure 2.2: The unit cell of the YAG crystal, where the Y, Al$^{VI}$ and Al$^{IV}$ cations are situated at the Wyckoff positions 12c, 8a and 12d, respectively, and are coordinated dodecahedrally, octahedrally and tetrahedrally to the neighboring O anions which occupy the Wyckoff position 48h.

from extended X-ray absorption fine structure (EXAFS) experiments have shown that the lattice environment around the Ce$^{3+}$ ions is expanded upon increasing Ce$^{3+}$ doping and that the expansion ratio becomes smaller at outer shells [22, 23], implying that the distortion is local. However, even the first-shell expansion, i.e. the Ce–O bonds, is smaller than one would expect from the difference in ionic radii between Ce$^{3+}$ and Y$^{3+}$. It implies that the YAG lattice appears to be a rigid structure against Ce$^{3+}$ doping [22]. In effect, the local structure around the Ce$^{3+}$ ions in YAG:Ce$^{3+}$ is somewhat compressed. In view of the averaged structure, the lattice expansion in YAG:Ce$^{3+}$ follows a linear relationship with increasing Ce$^{3+}$ concentration [22,24,25], see Figure 2.3(b).
2.2.2 Optical properties

The ground state electronic configuration of Ce\(^{3+}\) is \([\text{Xe}]4f^{1}5d^{0}\). Typically, the Ce\(^{3+}\) luminescence originates from electronic transitions between the \(4f^{1}5d^{0}\) and \(4f^{0}5d^{1}\) states, namely \(4f-5d\) transitions. The \(4f-5d\) transition energy of the free Ce\(^{3+}\) ions is in the range of UV light (\(\sim 6.12\) eV), but is shifted by 3.41 eV \([D(A)\text{ in Figure 2.4(a)}]\) to lower energies (in the range of visible light) when incorporated in the YAG crystal [26]. The local lattice environment mainly affects the outer shell of the Ce\(^{3+}\) ions, i.e. the 5\(d\) states, in terms of the covalency of the Ce–O bonds, and the ligand field [27].

The ligand field [28, 29] describes how the energies of the 5\(d\) orbitals of the Ce\(^{3+}\) ions are split due to the combined effects of the electrostatic (crystal) field created by the surrounding oxygens, and the interactions of the bonding orbitals. The Ce–O covalency effect, or equivalently the nephelauxetic effect results from the extensive overlap of the molecular orbitals of the Ce\(^{3+}\) ions and the coordinated O\(^{2-}\) ions, which increases the covalency of the Ce–O bonds and thereby gives rise to a large centroid shift \(\varepsilon_{cs}\), cf. Figure 2.4(a). Since the Ce\(^{3+}\) ions coordinate to eight O\(^{2-}\) ions in a cubic-like geometry, the centroid shifted 5\(d\) states are firstly split into the triplet states \(2T_{2g}\) with higher energy and the doublet states \(2E_{g}\) with lower energy. The energy difference between the \(2T_{2g}\) and \(2E_{g}\) states is \((8/9)\cdot10Dq\), where the coefficient \((8/9)\) is a coordination factor related to the cubal ligand field. The quantity of \(Dq\) can be approximated by the point charge model as,
2.2. GARNET TYPE PHOSPHORS AND YAG:CE$^{3+}$

Figure 2.4: (a) The 4f and 5d electronic states of the Ce$^{3+}$ ions in the free state as well as embedded in an oxide garnet, e.g. YAG, adapted from [26]. (b) Luminescence spectra of YAG:Ce$^{3+}$, adapted from [33].

$$Dq = \frac{Ze^2r^4}{6R^5},$$

(2.1)

where $Z$ is the charge or valence of the anion, $e$ is one electron charge, $r$ is the radius of the 5d-orbital wavefunction, and $R$ is the Ce–O bond length in YAG:Ce$^{3+}$ [30–32]. Subsequently, the $^2T_{2g}$ and $^2E_g$ states are further split into non-degenerate states because of the lowered symmetry (from the cubical to dodecahedral coordination) of CeO$_8$ in the garnet structure. The dodecahedral coordination results in a tetragonal ligand field. Since the Ce$^{3+}$ 4f–5d transition in YAG:Ce$^{3+}$ involves not only the Ce$^{3+}$ electronic states but also the vibrational states, the Ce$^{3+}$ 5d electrons relax to lower vibrational states by the Stokes shift $\Delta S$ of $\sim$ 2000–4000 cm$^{-1}$ before they radiatively return to the 4f ground state. $\Delta S$ may be evaluated by the difference between the peak positions of the excitation and emission spectra [33,34], see Figure 2.4(b). The Ce$^{3+}$ 4f states are primarily affected by the spin-orbit coupling, which leads to a splitting of the 4f states into the $^2F_{5/2}$ and $^2F_{7/2}$ states which are separated by $\sim$ 2000 cm$^{-1}$ in YAG:Ce$^{3+}$ [29,35]. The two emission bands corresponding to the $^2F_{5/2}$ and $^2F_{7/2}$ states have been observed in the low-temperature photoluminescence spectrum [Figure 2.4(b)].

2.2.2.1 Relationship between optical properties and tetragonal lattice distortions of the CeO$_8$ moieties

An important result from luminescence data of the garnet phosphors Ce$^{3+}$-doped (Gd, Y, Lu)$_3$(Al, Ga)$_5$O$_{12}$ is that the frequency of the emitted light
depends strongly on the strength of the tetragonal ligand field, that is the
degree of tetragonal distortion of the nearly cubic CeO$_8$ moieties. In ef-
fact, the splitting energy $\Delta_{12}$ is changed [26], cf. Figure 2.4(a). In order
to quantify/estimate the degree of tetragonal distortion, a distortion param-
eter has been defined by the ratio of the O–O distances between different
edges of a YO$_8$/CeO$_8$ moiety, $d_{88}/d_{81}$, as shown in Figure 2.5(a). For in-
stance, the substitution of the larger Ga for Al in the related garnet phos-
phors (Y, Gd)$_3$(Ga, Al)$_5$O$_{12}$:Ce$^{3+}$ enlarges the lattice dimension and the
local CeO$_8$ turns into more cubic-like symmetry which reduces $d_{88}/d_{81}$ as
well as $\Delta_{12}$ and gives a blue shifting effect of the emitted light [36–38]. A
similar blue shifting effect has been observed in another garnet phosphor,
Y$_3$Sc$_2$Ga$_{3-x}$Al$_x$O$_{12}$:Ce$^{3+}$, as the Ga$^{3+}$ content increases [18]. In contrast, a
red shifting effect is enhanced when larger cations replace the cation situated
at the D$_2$ site (equivalent to the Wyckoff position 12c) in the series of (Y,
Gd, Tb, Lu)$_3$Al$_5$O$_{12}$:Ce$^{3+}$ [13, 14, 25] whose local bonding distances show the
relation Gd–O > Tb–O > Y–O > Lu–O [39]. The counteracting effect on
$\Delta_{12}$ in terms of the lattice dimension is explained by that the CeO$_8$ mo-
eties tend to be more tetragonally distorted when the D$_2$ site is occupied by
larger cations. Similar results are also found in the Ce$^{3+}$ and Li$^+$ co-doped
(Ca$_{1-x}$Sr$_x$)$_3$RE$_2$Ge$_3$O$_{12}$ phosphors [10].

Intuitively, the elongation of the Ce–O bonds is expected to lead to a
decreased tetragonal ligand field and hence a blue-shifted emission spectrum.
The red-shift effect upon increasing Ce$^{3+}$ concentration in YAG:Ce$^{3+}$ [Figure
2.4(b)], is thought to relate to energy transfer from the Ce$^{3+}$ ions at higher
5$d$ vibronic states to the nearby ones at lower energy states, as well as to
enhanced ligand-field splitting of the Ce$^{3+}$ 5$d$ states due to the compressed
local environment around the Ce$^{3+}$ ions [22]. However, the observed red-
shift could also relate to the dynamical properties of the system, as certain
vibrational modes, such as symmetric compression and bending motions of
the CeO$_8$ moiety [40, 41] [cf. Figure 2.5(b–c)], induce dynamical tetragonal
distortions of the nearly cubic CeO$_8$. Whatever the case, the effects of the
local structural dynamics on the optical properties of YAG:Ce$^{3+}$ as well as
on other phosphors, are not fully understood. Their investigation lays at the
heart of this thesis.
2.2. **GARNET TYPE PHOSPHORS AND YAG:CE**

![Diagram](image)

Figure 2.5: (a) Schematic illustration of the distortion parameter $d_{88}/d_{81}$ at the $D_2$ site in YAG, adapted from [10]. (b–c) Schematic illustration of the local lattice distortions as induced by (b) symmetric stretching and (c) symmetric bending motions, respectively, adapted from [41].

### 2.2.3 Vibrational properties

Since the YAG primitive cell is half of the unit cell and thereby comprises 80 atoms, the three dimensional freedoms contributed from each atom lead to a total of 240 vibrational modes of the YAG structure. At the $\Gamma$–point in the Brillouin zone these modes can be denoted by their irreducible representation according to factor group analysis [42],

\[
\Gamma = 5A_{1u} + 3A_{1g} + 5A_{2u} + 5A_{2g} + 10E_u + 8E_g + 14T_{1g} + 18T_{1u} + 14T_{2g} + 16T_{2u}, \tag{2.2}
\]

where $3A_{1g} + 8E_g + 14T_{2g}$ and $17T_{1u}$ are the Raman- and IR-active vibrational species, respectively, $1T_{1u}$ is the acoustic motion, whereas the remaining species are optically silent modes. To correlate the vibrational species in Equation 2.2 with the site symmetries in the oxide garnets $A_3B_2(XO_4)_3$, the correlation method [43, 44] has been performed on the silicate garnets [45] and the result has assigned the vibrational species to the translatory motion of the cations $A$ and $B$, and all types of the vibrations (translatory, rotatory and intra-molecular motions) of the tetrahedral $XO_4$ moiety. More specifically, the studies [42, 46–48] on the vibrational properties of the rare-earth aluminate garnets $RE_3Al_5O_{12}$ have revealed that the lattice vibrations are predominantly related to RE motions and motions of octahedral $AlO_6$ and tetrahedral $AlO_4$ moieties in the spectral range of low frequency ($\lesssim 300$ cm$^{-1}$) and medium-to-high frequency ($\sim 300$–1000 cm$^{-1}$), respectively, as seen in the one phonon density of states (DOS) [Figure 2.6].
2.3 Thermal quenching

Thermal quenching, i.e. the pronounced reduction in QE of phosphors at elevated temperature (see Figure 2.7), is primarily thought to be the result of two different processes, electron-phonon coupling and/or thermal ionization. These processes are briefly described in the following.

2.3.1 Electron-phonon coupling

Thermal quenching via electron-phonon coupling refers to the phenomenon that may occur when the excited-state electrons interact with phonons in such a way that the excited-state electrons may return to the ground state without sending out light, i.e. in a non-radiative manner. This process may be described by a configurational coordinate diagram [49], see Figure 2.8(a). The two parabolae represent the 4f and 5d electronic levels of a Ce\(^{3+}\) ion, where the horizontal lines are the quantized vibrational states. Since when the electron in a Ce\(^{3+}\) ion is excited from the 4f to the 5d state and the electronic charge distribution of the Ce\(^{3+}\) ion becomes more attractive to the neighboring anions so that the luminescent center shrinks [50], the 5d parabola shifts in the nuclear coordinate by ∆R (< 0) with respect to the 4f parabola. ∆R is a critical measure of the strength of the electron-phonon coupling and can be estimated by the Huang-Rhys coupling constant \(S_{HR}\) [51] and further correlated to the Stokes shift [\(\Delta S\) in Figure 2.4(a)], according
2.3. THERMAL QUENCHING

Figure 2.7: Temperature dependence of the emission intensity and lifetime of YAG:3%Ce$^{3+}$, as measured in this thesis.

to [11, 32, 52]:

\[
S_{HR} = \frac{1}{2} \frac{M \omega^2}{\hbar \omega} \Delta R^2 \simeq \frac{\Delta S}{2 \hbar \omega}.
\]  

(2.3)

Here, \( M \) is the effective ionic mass and \( \omega \) is the vibrational frequency of the phonon or local vibrational mode to which the excited-state electron couples with. To induce non-radiative relaxation, the excited 5d electrons have to couple with vibrational modes of energy \( \geq \Delta E \), including higher-order transitions, cf. Figure 2.8(a). Besides, the symmetry and oscillating strength of the vibrations are decisive for the characteristics of non-radiative relaxation. As the requirements for 4f–5d crossover are fulfilled, the Ce$^{3+}$ 5d electrons return to the 4f ground state in a non-radiative way. The vibrational energy turns into heat dissipation in the lattice.

The rate of the non-radiative decay (\( R_{non}, \ s^{-1} \)) due to 4f–5d crossover is given by,

\[
R_{non} = A \cdot \exp^{-\Delta E/kT},
\]  

(2.4)

where \( A \) is a rate constant of the order of \( 10^{13} \, s^{-1} \), \( \Delta E \) is the activation energy from the relaxed 5d state to the 4f–5d crossing node, \( k \) is the Boltzmann constant and \( T \) is the temperature [53, 54]. Since the transition rate \( R = R_{rad} + R_{non} \) (where \( R_{rad} \) is the radiative rate, which is usually independent of temperature) and the emission lifetime \( \tau \) equals to \( 1/R \), the quantum efficiency (\( \eta \)) can be determined by the ratio \( \tau/\tau_0 \) [Equation 2.5]. \( \tau \) can be expressed as Equation 2.6.
Figure 2.8: (a) Schematic illustration of the non-radiative relaxation process for Ce$^{3+}$-doped phosphors, e.g. YAG:Ce$^{3+}$. (b) The phonon side band structure of YAG:Ce$^{3+}$, adapted from [35].

\[
\eta = \frac{\tau}{\tau_0} = \frac{1/(R_{\text{rad}} + R_{\text{non}})}{1/R_{\text{rad}}} = \frac{R_{\text{rad}}}{R_{\text{rad}} + A \cdot \exp^{-\Delta E/kT}} \quad (2.5)
\]

\[
\tau = \frac{1}{R_{\text{rad}} + A \cdot \exp^{-\Delta E/kT}} \quad (2.6)
\]

$\tau_0$ is the emission lifetime without any non-radiative relaxation involved. It follows that at a given $\Delta E$, $\eta$ and $\tau$ are enormously reduced when $T$ is higher than $T_Q$.

From Figure 2.8(a), it can be seen that the larger $\Delta R$ is, the lower $\Delta E$ or $T_Q$ one can expect and also the broader the luminescence bands are [53]. $\Delta R$ is comparatively large if the bonding force between the activator ion and the coordinated anions greatly changes when the activator ion is electronically excited. Therefore, $4f-5d$ transitions lead to a larger $\Delta R$, as compared to that for the intra-configurational $4f-4f$ transition. Although the $T_Q$ of YAG:Ce$^{3+}$ of the $4f-5d$ transition would have been low, the high rigidity of the YAG lattice reduces the population of the phonon modes at a given temperature and hence the $4f-5d$ crossover probability. Information about which particular phonon(s) that are actually at play may be indicated by the phonon side band structure in the luminescence spectra. The spectra in Figure 2.8(b) suggest that phonons of energies $\sim 200 \text{ cm}^{-1}$ may interact with the electrons of Ce$^{3+}$ ions during the absorption/excitation and emission processes [33,35].
2.3. THERMAL QUENCHING

2.3.2 Thermal ionization

Thermal ionization refers to the thermal promotion of electrons of the activator ions into the conduction band (CB) of the host crystal. This reduces the probability of radiative transitions, e.g. the $5d \rightarrow 4f$ transitions for Ce$^{3+}$ ions, and hence luminescence lifetime ($\tau$) and intensity. The occurrence of thermal ionization speeds up the transition rate $R (= \tau^{-1})$ of electrons by a non-radiative rate $R_{\text{ion}}$ so that $R = R_{\text{rad}} + R_{\text{ion}}$, where $R_{\text{ion}} = A_{\text{ion}} \cdot \exp(-\Delta E_{\text{ion}}/kT)$, and $\Delta E_{\text{ion}}$ and $A_{\text{ion}}$ are the activation energy and rate coefficient of thermal ionization, respectively [12]. Figure 2.9(a) shows, as an example, the situation of thermal ionization when electrons at the excited state ($e$) are thermally promoted into the CB (by providing an energy of $\Delta E_{\text{ion}}$), and then get trapped by a defect state. Defects in this sense can be, e.g., impurities, oxygen vacancies, bound excitons and antisite defects [11, 55, 56]. The trapped electrons might be thermally released and promoted back to the CB, while still having a low probability of emitting radiatively [Figure 2.9(a)]. Figure 2.9(b) shows, for comparison, the case when the electrons are excited from the ground state ($g$) to the excited state ($e$) situated in the CB, and the delocalized electrons recombine with holes at a recombination center. This process is known as photoionization, which leads to strong or even complete luminescence quench [11].

Information about thermal ionization in phosphors can be obtained from measurements of the temperature dependent photocurrent [57, 58] and thermoluminescence (TL) [59]. An increased photocurrent and TL as a function of increasing glow intensity are a sign of thermal ionization in the material, which has been seen for, e.g., Ce$^{3+}$-doped Y$_3$Al$_{5-x}$Ga$_x$O$_{12}$ (YAGG:Ce$^{3+}$). In particular, luminescence lifetime data [60, 61] and the so called vacuum referred binding energy (VRBE) scheme (i.e. binding energies relative to the vacuum energy) [26] of YAGG:Ce$^{3+}$, show that the higher the Ga substitution is, the probability for thermal ionization increases. However, thermal ionization has not yet been correlated to the reduction of luminescence lifetime on a quantitative scale or compared to other quenching mechanisms. Hence, the phenomenological existence of thermal ionization in inorganic phosphors needs to be further investigated to reflect on its importance in thermal quenching phenomena.
Figure 2.9: Schematic depiction of thermal ionization at the luminescent center $A$, for the cases when the electronic excited-state ($e$) is situated (a) below the CB (adapted from [57]), and (b) within the CB (adapted from [11]). $E_g$ is the energy of the bandgap, and ($g$) is the ground state of $A$. 
Chapter 3
Experimental

3.1 Vibrational spectroscopy

The vibrational spectra of materials can be investigated by infrared (IR) and Raman spectroscopies or by inelastic neutron scattering (INS), which each of them reveals the energy transitions between vibrational states. In the oversimplified case of a harmonic oscillator, the energy of the vibrational states of a specific mode may be expressed as $E_n \equiv (n + 1/2)h\nu$, where $n$ is the quantum number (0, 1, 2, ...), $\nu$ is the vibrational frequency of the mode, and $h$ is the Planck constant. The three techniques rely on different selection rules and, therefore, they are complementary to each other. For instance, vibrational modes that are inactive (silent) by photon excitation (i.e. by IR and Raman spectroscopies) may be observable in INS. Moreover, IR and Raman spectroscopies only measure zone-center (in the Brillouin zone) modes, whereas INS can probe vibrations at different wavevectors.

3.1.1 Infrared spectroscopy

IR spectroscopy measures the absorption of IR electromagnetic (EM) waves irradiated on a sample. The actual measurement may be performed in either of two different modes of operation, i.e. transmittance (absorbance) or reflectance. Figure 3.1(a) shows, as an example, the setup for a typical transmittance (absorbance) measurement, where $I_r$ and $I_s$ are the intensities of the IR light transmitting through the reference and sample, respectively, with a given IR frequency, $\nu_r$. Absorption occurs when the permanent electric dipole moment $\mu$ of a molecule, or vibrating moiety, oscillates at the identical frequency as that of the oscillating electric field of the incident IR light (i.e. at the resonance frequency, $\nu = \nu_r$), which leads to the vibrational transition from, e.g., $n = 0$ to $n = 1$, see Figure 3.1(b). An absorbance-like
3.1.2 Raman spectroscopy

Raman spectroscopy measures the light scattered by the sample as illuminated by monochromatic light of frequency $\nu_0$, see Figure 3.1(a). The oscillating electric field $\varepsilon = \varepsilon_0 \cdot \cos(2\pi \nu_0 t)$, where $\varepsilon_0$ is the maximum amplitude of the electric field, induces a dipole moment $\mu_{ind}$ (= $\alpha \varepsilon$, where $\alpha$ is the polarizability) in the sample. If $\alpha$ oscillates around the equilibrium polarizability $\alpha_0$ with the same frequency as that of a specific vibrational mode, i.e. $\alpha = \alpha_0 + \Delta \alpha \cdot \cos(2\pi \nu t)$ (where $\Delta \alpha$ is the maximum variation for $\alpha$), $\mu_{ind}$ can be re-formulated as [62]

$$\mu_{ind} = \alpha_0 \varepsilon_0 \cos(2\pi \nu_0 t) + \frac{1}{2} \Delta \alpha \varepsilon_0 \{\cos[2\pi(\nu_0 - \nu)t] + \cos[2\pi(\nu_0 + \nu)t]\}. \quad (3.1)$$

It can be seen that most light is scattered elastically with frequency $\nu_0$, cf. the first term in Equation 3.1. This is known as Rayleigh scattering. A small fraction of the light is scattered inelastically with frequency $\nu_0 - \nu$ (Stokes scattering) and $\nu_0 + \nu$ (anti-Stokes scattering), cf. the second and third terms in Equation 3.1, respectively. This is known as Raman scattering. The elastic and inelastic scattering occurs through the excitation to an intermediate virtual level, where the electronic wavefunctions are temporarily perturbed [44,63], cf. Figure 3.1(b).
3.1.3 Inelastic neutron scattering

Inelastic neutron scattering (INS) uses neutrons rather than photons for obtaining a vibrational spectrum. In comparison to IR and Raman spectroscopies, both transferred energy (\(\hbar\omega, \text{meV}\)) and momentum (\(Q, \text{\AA}^{-1}\)) are measured at the same time. The measured quantity is associated with the double differential scattering cross section, \(d^2\sigma/(d\Omega dE_f)\), where \(d\Omega\) is the solid angle \(= A_d/d^2_f\), as defined in Figure 3.2, and \(\sigma\) is the total scattering cross section \([64,65]\). In a crystal lattice, a local molecular motion (internal mode) is mostly probed by incoherent INS, whereas a collective lattice mode (external mode) is mostly measured by coherent INS \([66,67]\).

For one specific atom \((l)\), Equation 3.2 can be rewritten as

\[
\frac{d^2\sigma}{d\Omega dE_f} l = \frac{\sigma_{coh}}{k_i} \frac{1}{4\pi} \sum l \int_{-\infty}^{\infty} dt \langle e^{-iQ \cdot r_l(0)} e^{iQ \cdot r_l(t)} e^{-i\omega t} \rangle
\]

where \(\omega = (E_i - E_f)/\hbar\) for an incident neutron energy of \(E_i\) and a final neutron energy of \(E_f\), and \(\sigma_{coh}\) and \(\sigma_{inc}\) are the coherent and incoherent scattering cross sections, respectively \([64,65]\). Equation 3.3 can be further re-formulated in terms of the transition order \(n\) (0 for the elastic scattering; 1 for the fundamental transition; 2 for the first overtone, and so forth) and the atomic displacement \(u\) of the \(\nu\)-th vibrational mode, which is conventionally represented by \(S^*(Q, \omega_\nu)\) (related to the amplitude and cross section weighted density of states) in the spectrum as shown in Equation 3.4 \([66]\).

\[
S^*(Q, \omega_\nu)_l^n \propto \sigma_l \frac{[(Q \cdot u_{\nu,l})^2]_n}{n!} \exp[-(Q \cdot u_{\nu,l})^2]
\]

The observed intensity in the INS spectrum is proportional to the summation of \(S^*(Q, \omega_\nu)_l^n\) over all the atoms in the material.
Figure 3.2: A scattering process between neutrons and a substance. $\theta$ is the scattering angle, $k_i$ and $k_f$ are the wavevectors of the incident and scattered neutrons, respectively, and $Q$ is the transferred momentum (or the scattering vector), adapted from [66].

### 3.1.4 Phonon assignment by symmetry coordinates

For a crystal containing $N$ atoms in the primitive cell, there are $(3N-3)$ optical-mode and 3 acoustic-mode lattice vibrations. Generally, the total $3N$ vibrations can be represented by the normal coordinates $Q_i$, which give the vibrational frequency $\nu_i$ and phase $\delta_i$ for the $i$th mode ($i = 1, 2, ..., 3N$). The oscillation of all nuclei in a crystal can be expressed by $Q_i = Q_i^0 \sin(2\pi\nu_it + \delta_i)$, where $Q_i^0$ is the maximum amplitude of the vibration. Since the 3 acoustic modes exhibit translational motions of the primitive cell as a whole (i.e. the center of gravity is stationary), these modes are usually not considered as using $Q_i$. Therefore, for a crystal of $N$ atoms, $(3N-3)$ normal modes/vibrations may be represented by $Q_i$. The $Q_i$ can be transformed into the mass-weighed Cartesian coordinates $q_k$ as,

$$ q_k = \sum_i B_{ki} Q_i^0 \sin(2\pi\nu_i t + \delta_i), $$

(3.5)

where $B_{ki}$ is a coefficient for the coordination transformation. Physically $q_k = \sqrt{m_k} \Delta d_k$, where $m_k$ is the mass of the nucleus and $\Delta d_k$ is the displacement of the nucleus in one of the $x$-, $y$- and $z$-directions. The correlation between $q_k$ and $Q_i$ reveals that the motion of an nucleus is a superposition of all normal modes [44]. Equation 3.5 also indicates that if only a single normal mode ($i = j$) is considered, all nuclei vibrate in phase with the identical $\nu_j$ and $\delta_j$, as generalized by $q_{kj} = B_{kj} Q_j^0 \sin(2\pi\nu_j t + \delta_j) = B_{kj} Q_j$. Furthermore, the collective motions of $q_{kj}$ (the $j$th-mode phonon) can be correlated to the discrete vibrational levels $[E_{nj} = (n_j + 1/2)h\nu_j]$ in the quantum mechanics frame by plotting $E_{nj}$ in a potential parabola with respect to $Q_j$, namely...
the configurational coordinate diagram \([e.g.\ Figure\ 2.8(a)]\), and classically the quantum number \(n_j\) means the number of the \(j\)-th-mode phonon. In this thesis, the eigenvalues \((\nu_j)\) and eigenvectors \((q_{kj})\) are obtained by using density functional theory (DFT) calculations.

To assign the phonon in terms of local motions which are determined by the symmetries of the local molecules in the crystal, the displacing vectors \((q_{k}/\sqrt{m_k})\) of the local molecule are decomposed into a linear combination of the translational, rotational and intra-molecular motions. Since the translational and rotational motions only change the spatial position of the molecule with respect to the reference frame, the structural symmetry of the molecule does not vary with such motions. However, for the intra-molecular motions, the molecular bonds vibrate in different symmetries which are based on the irreducible representations of the point group of the molecule, and these molecular vibrations can be expressed by the symmetry coordinates \(S_l\) in terms of the internal coordinates \(\Delta s\) as

\[
S_a = \sum_R R \cdot \chi_a^R \cdot \Delta s, \tag{3.6}
\]

where \(a\) and \(R\) stand for the irreducible representations and the symmetry operations of the point group of the molecule, respectively, \(\chi_a^R\) is the character value for the irreducible representation \(a\) under the symmetry operation \(R\), and \(\Delta s\) is the internal coordinates defined by the bonding length \(r\) and angle \(\theta\) (corresponding to stretching and bending vibrations, respectively) \([62]\). To graphically illustrate this, Figure 3.3 shows the molecular vibrations of the \(A_{1g}\) stretching for the cubic \(\text{YO}_8\) moiety \([68]\), the doubly degenerate \(E_g\) stretching for the octahedral \(\text{AlO}_6\) moiety \([69]\), and the triply degenerate \(T_{2g}\) bending for the tetrahedral \(\text{AlO}_4\) moiety \([44]\). Their symmetry coordinates are shown in Equation 3.7.

Figure 3.3(a): \(A_{1g}'\) = \(\Delta(r_1 + r_2 + r_3 + r_4 + r_5 + r_6 + r_7 + r_8)\)

Figure 3.3(b): \(E_g'\) = \(\Delta(r_1 + r_2 - 2r_3 + r_4 - 2r_5 + r_6)\) \(\tag{3.7}\)

Figure 3.3(c): \(T_{2g}'\) = \(\Delta(\theta_{12} + \theta_{13} + \theta_{14} - \theta_{23} - \theta_{24} - \theta_{34})\)

It can be noted that the free-state molecules shown in Figure 3.3 are highly symmetric and their point groups are assigned by \(O_h\) for the cubic and octahedral molecules and by \(T_d\) for the tetrahedral molecule. However the structural symmetries of molecules generally become lowered when they are in the crystalline state and they are known as the site symmetries in crystals, \(e.g.\) in \(\text{YAG}\), the site symmetries of \(\text{YO}_8\), \(\text{AlO}_6\) and \(\text{AlO}_4\) molecules are \(D_2\), \(S_6\) and \(S_4\), respectively. Since lattice vibrations (phonons) are primarily
determined by the site symmetry and space group of a crystal, the phonon assignment with using the symmetry coordinates of free-state molecules is an approximate method for probing the local vibrational symmetries in a crystal lattice.

3.2 Luminescence

3.2.1 Photoluminescence

Photoluminescence (PL) of phosphor materials produces spontaneous emission of photons as light impinges on the phosphors. The excitation and emission processes may be described graphically by a configurational coordinate diagram, as depicted in Figure 2.1(b). The intensities of the two processes depend on the transition probability between vibronic levels, which leads to band-like distributions for the absorption and emission spectra, respectively. The frequencies of the absorbed and emitted light are mainly characterized by the electronic energy levels of the activator ions. In most cases, the emission spectrum is shifted to lower energies with respect to the excitation/absorption spectrum. The energy shift $\Delta (= h\nu_{\text{abs}} - h\nu_{\text{emi}}$, where $\nu_{\text{abs}}$ and $\nu_{\text{emi}}$ are the frequencies of the excited and emitted light, respectively) is a measure of the Stokes shift which in turn is correlated to the shift between the ground and excited electronic levels. An increased Stokes shift generally enhances electron-phonon coupling, which in turn broadens the spectral bands.

To investigate the time dependent photoluminescence of phosphors, a pulsed wave light is used as the excitation source. The light pulses promote
electrons of population density $N_0$ from the ground to excited states at the optical center. The population evolves with time, $t$, according to

$$N(t) = N_0 e^{-A_T t}, \quad (3.8)$$

where $A_T$ is the total decay rate, i.e. the summation of the radiative and non-radiative rates [70]. The radiation intensity $I(t)$, observed by a photon detector, is proportional to $dN(t)/dt$, i.e. $I(t) = I(0)e^{-A_T t}$. Therefore, the luminescence lifetime $\tau (= 1/A_T)$ can be estimated from the time-dependent emission decay curve.

### 3.2.2 Thermoluminescence

Thermoluminescence (TL) occurs via a recombination process of electron-hole pairs when a substance, that previously absorbs energy from light excitation, is thermally stimulated. Energy may be charged into trapping (defect) states by optical excitation. More specifically, light may ionize the substance so that electrons and holes are created respectively in the conduction and valence bands. The carriers (the delocalized electrons and holes) might then get trapped at trapping states within the band gap, see Figure 3.4. The trapping states can result from intrinsic defects, such as lattice imperfections, or extrinsic defects, such as impurity contamination.

Since the carrier trapping at defects is at a non-equilibrium state, which is energetically metastable, the metastable state leads to an attempt to return to an equilibrium state by the annihilation of the electron-hole pairs, resulting in so-called TL glow. For a typical annihilation process, the trapped electrons are firstly promoted from the defect levels to the conduction band by coupling with thermally activated phonons. Subsequently, the promoted electrons recombine with the trapped holes at the recombination center. However, the annihilation might not occur if the promoted electrons in the delocalized conduction band are re-trapped by the defects. Consequently, TL glow intensity, which depends on the annihilation rate, is primarily determined by the dynamical process of electron de-trapping, electron re-trapping and electron-hole recombination. The first-order kinetics for TL intensity assumes that the effect of electron re-trapping is negligible. The TL intensity can then be written as

$$I(t) = -\frac{dn}{dt} = n \cdot s \cdot \exp^{-E/kT} = n \cdot R_{de}, \quad (3.9)$$

where $n$ is the concentration of the trapped electrons, $s$ is the frequency factor in the order of phonon frequency ($\sim 10^{12} - 10^{14} \text{ s}^{-1}$), $E$ is the energy
Figure 3.4: Energy band diagram for the one-trap TL model with the steps i) optical excitation, ii) carrier trapping, iii) electron de-trapping, and iv) electron-hole recombination, adapted from [71]. D is the defect, and R is the recombination center.

difference between the CB minimum and the electron trapping level, \( k \) is the Boltzmann constant, \( T \) is the temperature, and \( R_{de} \) is the de-trapping rate for one electron [71]. As \( T \) is varied linearly by a constant heating rate \( \beta \), Equation 3.9 can be re-formulated as a function of temperature, see Equation 3.10 [71]. The maximum of TL intensity can be found at the temperature \( T_m \) with given \( s \), \( \beta \) and \( E \) via Equation 3.11 which is derived from the relation \( d \ln I(T)/dT = 0 \) [71]. However, in practice, Equation 3.11 is frequently used for evaluating \( E \) instead of \( T_m \).

\[
I(T) = -\frac{1}{\beta} \frac{dn}{dt} = n_0 \cdot s \cdot \frac{1}{\beta} \cdot \exp\left(-\frac{E}{kT} - \frac{s}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E}{kT'}\right) dT'\right),
\]

\[
\frac{\beta E}{kT_m^2} = s \cdot \exp\left(-\frac{E}{kT_m}\right),
\]

where \( n_0 \) and \( T_0 \) are \( n \) and \( T \) at \( t = 0 \), respectively.

### 3.3 Free electron lasers

In a free electron laser (FEL), electrons are accelerated by a radio frequency (RF) linear accelerator (linac) to a relativistic speed, i.e. close to the speed of light. The electrons are grouped into sub-bunches of ps duration with a repetition rate of the order of GHz, which in turn are encapsulated into bunches of \( \mu s \) duration separated by some hundreds of ms. The bunches are guided into a cavity comprising two high-reflectivity golden mirrors at the
two ends which contain in between an undulator, i.e. a series of pairs of permanent magnets with periodically alternating magnetic poles, cf. Figure 3.5. The undulator transversely accelerate electrons so that electrons propagate along the undulator in zigzag, which results in synchrotron radiation due to the radial acceleration of electrons. While the radiation propagates more forwardly by an integer number \( n \), so called harmonic number [72]) of the radiation wavelength with respect to the electrons, the electrons are in resonance with the radiation. The resonance condition results in a spontaneous emission, which is, however, incoherent radiation. The wavelength \( \lambda \) of the spontaneous emission can be expressed as

\[
\frac{n \lambda}{\gamma} = \frac{1}{2 \gamma} (1 + K^2) = \frac{\lambda_{un}(1 + K^2)}{2 \gamma^2},
\]

where \( \lambda_{un} \) is the periodic distance of the magnetic structure of the undulator, \( \gamma \) is the Lorentz factor \( (\gamma=1/\sqrt{1-\beta^2}) \), \( \beta \equiv v/c \), \( v \) is the electron velocity and \( c \) is the speed of light), and \( K \) is a dimensionless parameter which is proportional to the magnetic field \( B \) [73,74].

Since the electric field of the radiation interacts with the oscillating electrons, energy is exchanged between the radiation field and the electrons. The electrons propagate with a faster speed if energy is transferred from the radiation field to the electrons and vice versa. As a result, the forward-drifting electrons from the lagged electron group catch up with the backward-drifting electrons from the advancing electron group. The electrons bunch together periodically on the order of the wavelength of the radiation so that the radi-
CHAPTER 3. EXPERIMENTAL

...ation can be amplified by the coherent spontaneous emission radiated from the bunched electrons. To acquire an amplification gain, the initial electron velocity is for instance biased by a small forward velocity, which leads to an off-resonance condition, and in this condition the radiation averagely extracts a net energy from the bunched electrons. The off-resonance gain is called the small-signal gain, which enhances the radiation power gradually as the radiation wave cycles in the cavity until the power reaches saturation. To conclude, a FEL provides a powerful and fast-pulsed monochromatic source, which for example is useful for performing time-resolved experiments on vibrational dynamics in relation to luminescence properties of inorganic phosphors.
Chapter 4

Instruments

4.1 The Bruker IFS 66v/s spectrometer

For the IR spectroscopy measurements reported in this thesis, I used a Fourier transform infrared (FTIR) spectrometer of the model Bruker IFS 66v/s. A key component of a FTIR spectrometer is the interferometer, which contains four major optical elements, a collimating mirror, a beam splitter, a fixed mirror and a moving mirror [Figure 4.1(a)]. The collimating mirror is used to collimate the incoming IR light, which is then partially reflected and transmitted by the beam splitter. The reflected and transmitted IR beams propagate respectively toward the fixed and moving mirrors, which reflect the IR beams back to the beam splitter where they are recombined into one beam. Since the traveling distance is fixed for the beam propagating between the beam splitter and the fix mirror but not for the beam traveling to the moving mirror, the reflected and transmitted beams travel with an optical path difference, $\delta$. This results in an interference pattern, also known as an interferogram. The interferogram is manifested by a combination of constructive and destructive interference. The interference depends on $\delta$ and the wavelength ($\lambda$) of the IR light, and it is recorded as a function of $\delta$. Each $\lambda$ is transformed into a cosine wave with a Fourier frequency in real space. The Fourier frequency is correlated with the velocity of the moving mirror, and the $\lambda$ of the IR light [75]. The interferogram shows the summation of all such cosine waves. Therefore, any $\lambda$ absorption by a sample reduces the amplitude of the interferogram, which is recorded by a detector situated behind the sample. Then, the recorded interferogram is Fourier transformed into a transmittance spectrum [$I_r$ for the reference, or $I_s$ for the sample, as shown in Figure 4.1(b)]. The vibrational spectrum is usually presented as absorbance, i.e. $A = \log(I_r/I_s)$, see Figure 4.1(b).
Figure 4.1: (a) Schematic layout of the Bruker IFS 66v/s spectrometer. (b) An interferogram, the transmittance spectra of the reference and sample, and the vibrational spectrum.

4.2 The Dilor XY 800 spectrometer

For the Raman spectroscopy measurements performed in this thesis, I used a triple-grating Dilor XY 800 spectrometer. The Dilor XY 800 spectrometer is equipped with a tunable Ar$^+$/Kr$^+$ laser, which produces an intense light that is linearly polarized. The linearly polarized light enters a microscope, which focuses the incident beam onto a sample. The backscattered light is guided through the entrance slit, $S_1$, of the triple grating system, see Figure 4.2. From this point, the optical path depends on the setup of the spectrometer. In this thesis, the so called double subtractive mode was used. In this mode, the polychromatic light coming from the sample is dispersed by the first grating, $G_1$, and then led to propagate through the second slit, $S_2$. Here, $S_2$ acts as a bandpass filter, i.e. only light of specific wavelengths can enter the next stage, and thereby the width of $S_2$ determines the spectral range for detection. In the second stage, the light is merged by the second grating, $G_2$, and then focused onto the slit $S_3$, which rejects stray light. In the third stage, the polychromatic light is dispersed by the third grating $G_3$ and projected onto a charge-coupled device (CCD) detector cooled by liquid nitrogen. In short, the first and second stages work as a sharp bandpass filter, which significantly reduces stray radiation [76], and thus spectra can be measured close to the laser (Rayleigh) line. The third stage resolves the polychromatic light so that the dispersed light in a wide spectral range can be measured at once by an array detector, i.e. the scanning time for a desirable spectral window is shortened.
4.3. THE TOSCA INS SPECTROMETER

4.3 The TOSCA INS spectrometer

For the INS spectroscopy measurements performed in this thesis, I used the TOSCA spectrometer as located at the ISIS Pulsed Spallation Neutron Source at the Rutherford Appleton Laboratory in the U.K. On TOSCA, the sample and analyzer module are placed in a configuration so that the neutrons are inelastically backscattered by the sample through a constant angle of 45° or 135°, see Figure 4.3. The backscattered neutrons then strike on a graphite crystal analyzer which only allows one wavelength of the neutrons to be Bragg scattered with a given interplanar distance in the crystal [77]. Subsequently, the neutrons pass through a longpass beryllium filter and arrive at the detector. Only neutrons within a narrow energy range can be detected, meaning that the final energy of the neutrons is essentially constant. The difference in energy and momentum, as determined by time-of-flight, between the incoming and detected neutrons determines the vibrational energy $\omega\nu$ and the scattering vector $\mathbf{Q}$ (cf. Equation 3.4). Since the spectral intensity would be significantly reduced at high temperatures due to thermal motion, which is reflected by $\sum u$ shown in the exponential term (Debye-Waller factor) in Equation 3.4, the measurement is usually performed at $< 50$ K.
4.4 Photoluminescence and thermoluminescence experiments

For the photoluminescence (PL) and thermoluminescence (TL) measurements, I used a home-built optical setup. This is depicted in Figure 4.4(a). PL spectroscopy measurements rely on a continuous-wave (CW) source for excitation, whereas the measurements of PL decay curves need a pulsed source. To collect the emission spectrum, a commercial spectrometer (Ocean optics USB2000+) working in the ultraviolet and visible (UV-VIS) regions was utilized (with an optical filter). The most critical component of the spectrometer is the grating, which diffracts the light toward a focusing mirror that projects it onto a CCD detector [Figure 4.4(b)]. In contrast, the luminescence decay curve was measured by a fast photon detector (Hamamatsu H10721-20).

For the TL measurements, the sample was firstly illuminated by an excitation source at a charging temperature for a certain time period. Thereafter, it was rapidly (e.g. 100 K/min) cooled down to a low temperature (e.g. 300 K, which was the initial temperature before it increased to the charging temperature) to trap the charges at defect states. Upon increasing the temperature with a constant heating rate, the TL glow curve was measured by a photosensor (Hamamatsu H10721-20). The temperature was manipulated by a heating/cooling stage (Linkam THMS600).
4.5. THE FELIX INFRARED FREE ELECTRON LASER

For the experiments dealing with mode-selective vibrational excitation, I used the Free Electron Laser for Infrared eXperiment (FELIX) facility, as located in Nijmegen in the Netherlands. FELIX produces electron pulses of 1 GHz. The pulses are accelerated by linear accelerators (linac-1 and linac-2) to energies of 15–25 and 25–45/50 MeV [79, 80], as shown in Figure 4.5(a). The electrons accelerated by linac-1 and linac-2 are guided into two different cavities (FEL-1 and FEL-2), which comprise undulators and two golden mirrors placed at both ends of each cavity. The zig-zag propagation of electrons in the undulators results in spontaneous radiation, which becomes coherent due to energy exchange and stabilization between the radiation and electrons. The radiation is amplified by cycling it in undulators, which is then guided to the user stations.

The radiation wavelength can be modulated by varying the distance between the permanent magnets, i.e. adjusting the dimensionless $K$ parameter (the magnetic field $B$), cf. Equation 3.12. The IR pulses are tunable in the wavelength ranges of 30–150 $\mu$m (333–66 cm$^{-1}$) for FEL-1 and 3–45 $\mu$m (3333–222 cm$^{-1}$) for FEL-2 [80]. Figure 4.5(b) illustrates the FELIX pulse structure, which consists of macro pulses of 5–10 s length with a repetition rate of 10 Hz (i.e. a cycle period of 100 ms). Each macro pulse is built up of micropulses with a pulse length of ca. 1 ps and a repetition rate of 1 GHz, i.e. intervals of 1 ns. Each micropulse carries an energy of 1–20 $\mu$J, thus ca.

![Figure 4.5: Schematic layouts of (a) the optical setup as used for the PL and TL experiments and (b) the Ocean optics USB2000+ spectrometer, adapted from [78].](image)
100 mJ for each macropulse [80]. To investigate the mechanism of thermal quenching *via* electron-phonon coupling in the Ce$^{3+}$-doped phosphors, the sample is simultaneously excited by the FELIX beam (phonon excitation, in 250–1000 cm$^{-1}$) and a blue pulsed laser (electronic excitation) [see Figure 4.5(a)].

Figure 4.5: (a) Schematic layout of FELIX and the setup for the experiments of excitation by FELIX and a blue laser. (b) The pulse structure as generated by FELIX.
Chapter 5

Summary of results

The results in this thesis are reported in two papers, Paper II (Figure 5.1) and Paper III (Figure 5.2). Paper II reports on a comprehensive analysis of the vibrational properties of YAG and its relationship to luminescence of YAG:Ce$^{3+}$. A key result is the assignment of all vibrational modes, on the basis of symmetry coordinates, i.e. the symmetries and amplitudes of all (YO$_8$, AlO$_6$, and AlO$_4$) moieties in terms of stretching and bending vibrations, respectively. The dependence of vibrational properties on Ce$^{3+}$ concentration and temperature has also been elucidated. For example, we have shown that the vibrational motions of the CeO$_8$ moieties lead to pronounced tetragonal distortions that in turn induce a red-shifting effect on the Ce$^{3+}$ emission. However, at temperatures higher than the Debye temperature, a counteracting effect on the light emission is observed, which is attributed to the thermal lattice expansion that makes the distorted CeO$_8$ moieties more cubic-like. Building on these new results, we have, in Paper III, investigated how the activation of specific vibrational modes affect the lifetime and intensity of the luminescence. This has been done by employing, for the first time, mode-selective vibrational excitation combined with optical excitation. The results show that the activation of the high-frequency IR-active phonons indeed gives rise to an additional decrease in the emission lifetime and intensity. This suggests that the high-frequency phonons are coupled with the Ce$^{3+}$ excited electrons, which induce non-radiative relaxation via the 4f-5d crossover. But in addition, the TL glow curves of YAG:Ce$^{3+}$ reveal that the Ce$^{3+}$ excited electrons are thermally ionized and trapped by defect states. A lower activation energy obtained from the TL experiments, as compared to that shown in the VRBE scheme, suggests that the thermally-activated charge migration may be also involved in charge trapping. The contributions of electron-phonon coupling and thermal ionization to the reduction in the emission efficiency of YAG:Ce$^{3+}$ are dependent on temperature in an Arrhe-
nium manner. Based on their activation energies, electron-phonon coupling ($\Delta E_{4d-5d} \sim 0.24$ eV) has shown to be more dominant than thermal ionization together with thermally-activated charge migration ($\Delta E_{\text{ion}} \sim 0.38$ eV), at lower temperatures, and vice versa.

Figure 5.1: (a) Local structural environment of $Y^{3+}$ in YAG, and (b) the temperature dependent chromaticity coordinates of YAG:Ce$^{3+}$, adapted from Paper II.

Figure 5.2: (a) Schematic setup for the two pulsed laser excitation experiment as described in Paper III, and (b) the luminescence quenching through $4f$-$5d$ crossover in YAG:Ce$^{3+}$.
Chapter 6
Conclusions and outlook

To conclude, this thesis has established the relationship between local structure, vibrational dynamics, and optical properties, such as emission wavelength and thermal quenching, in the technologically very important phosphor YAG:Ce$^{3+}$. Our results have shown that the red-shifting effect of the emission spectra upon elevating temperature can be attributed to the activation of high-frequency phonons, related to symmetric stretching and symmetric bending motions of the CeO$_8$ moieties, which induce dynamical tetragonal distortions that strongly affect the optical properties of YAG:Ce$^{3+}$. Specifically, the pronounced tetragonal distortions with increasing temperature leads to a red-shift of the emitted light. However, the emission turns to be blue shifted as the temperature increases above the Debye temperature as an effect of that thermal lattice expansion becomes predominant and weakens the tetragonal distortions at high temperatures. Moreover, it has been shown that three of the highest-frequency IR-active vibrational modes at 698, 724, and 789 cm$^{-1}$, are coupled with the excited electrons of the Ce$^{3+}$ ions. This interaction between phonons and electrons induces non-radiative relaxation through 4f-5d crossover, thus, leading to thermal quenching. However, the pronounced reduction in emission intensity at elevated temperature is also found to be the result of thermal ionization. The co-existence of the two quenching mechanisms, electron-phonon coupling and thermal ionization, is qualitatively investigated, and both mechanisms are dependent on temperature in an Arrhenius manner. Based on their activation energies (0.24 and 0.38 eV for electron-phonon coupling and thermal ionization, respectively), electron-phonon coupling is shown to be more dominant than thermal ionization at low temperatures, and vice versa. Finally, a complete phonon assignment of the YAG crystal, based on symmetry coordinates, has been provided. Generally, the YAG phonon assignment is applicable to other garnets with the same site occupancy.
With a view to the future, I will investigate other oxide garnet phosphors, particularly Ce$^{3+}$-doped Y$_3$Al$_{5-x}$Ga$_x$O$_{12}$ (YAGG:Ce$^{3+}$), which show pronounced effects on the emission efficiency upon increasing Ga substitution. This leaves an intriguing question about the interplay between the structural variation caused by the Ga substitution and different quenching mechanisms, which will be further investigated based on our work at FE-LIX. Moreover, we will investigate the difference (if any) in the structure of the electronic ground and excited states in YAG:Ce$^{3+}$, by combining time-resolved optical excitation with time-resolved X-ray diffraction at the new beamline called FemtoMAX at the MAX IV laboratory in Lund, Sweden.
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