Transition Metal Ion Lasers Other Than Cr

Stephen A. Payne
Published online on: 24 Jun 2021

CRC Press
Accessed on: 28 Dec 2023
3

Transition Metal Ion Lasers Other Than Cr\textsuperscript{3+}

Stephen A. Payne

CONTENTS

3.1 Introduction ........................................................................................................... 25
3.2 Survey of Transition Metal Lasers ........................................................................ 25
  3.2.1 Ti\textsuperscript{3+} Lasers .................................................................................. 25
  3.2.2 Transition Metal Lasers: V\textsuperscript{2+}, Co\textsuperscript{2+} and Ni\textsuperscript{2+} Ions in Octahedral Sites .................................................. 25
  3.2.3 Transition Metal Lasers: Cr\textsuperscript{4+}, Cr\textsuperscript{2+}, Fe\textsuperscript{2+} and Mn\textsuperscript{2+} Ions in Tetrahedral Sites ..................... 26
  3.2.4 Tabulation of Transition Metal Lasers ......................................................... 26
3.3 Physics and Engineering Issues ........................................................................... 26
  3.3.1 Electronic Structure .................................................................................... 26
  3.3.2 Absorption and Emission ......................................................................... 27
  3.3.3 Excited-State Absorption .......................................................................... 29
  3.3.4 Radiative Rates and Non-Radiative Losses ............................................. 30
  3.3.5 Optical Loss ............................................................................................. 30
  3.3.6 Laser Gain and Oscillation ........................................................................ 31
  3.3.7 Host Properties ......................................................................................... 31
3.4 Summary ............................................................................................................. 32
References .................................................................................................................. 32

3.1 Introduction

In this chapter, the background and status of transition-metal-based solid-state lasers are discussed [1,2]. The transition metal ions that have been demonstrated to lase include Ti\textsuperscript{3+}, V\textsuperscript{2+}, Cr\textsuperscript{2+}, Cr\textsuperscript{4+}, Cr\textsuperscript{2+}, Mn\textsuperscript{2+}, Fe\textsuperscript{2+}, and Ni\textsuperscript{2+}. All of these ions will be discussed in this chapter with the exception of Cr\textsuperscript{2+}. These transition metal ions have been demonstrated to laser oscillate in a cavity, by serving as the activators in various host media including oxide, fluoride, sulphide and selenide crystals. Laser oscillation has never been reported for any transition-metal-doped glass: all known laser systems are based on crystalline host media. They are incorporated onto sites of either fourfold or sixfold coordination, referred to as tetrahedral and octahedral sites, respectively. In terms of their practical use, Ti\textsuperscript{3+} in sapphire (Ti:Al\textsubscript{2}O\textsubscript{3}) is, by a wide margin, the most common transition metal laser. The next most common transition metal lasers include the Cr\textsuperscript{3+} lasers, alexandrite and Cr:LiSAF, forsterite (Cr\textsuperscript{4+} in Mg\textsubscript{2}SiO\textsubscript{4}) and Co:MgF\textsubscript{2}. Several other materials are still being explored. Lasers based on V\textsuperscript{2+} and Ni\textsuperscript{2+} do not seem to have taken hold significantly, in spite of the many years that have elapsed since the initial demonstration of their lasing capability. Some ions have been reported to exhibit gain but an ability to oscillate has not yet been demonstrated, for example Rh\textsuperscript{2+} [3] and Cu\textsuperscript{+} [4], as discussed later.

3.2 Survey of Transition Metal Lasers

3.2.1 Ti\textsuperscript{3+} Lasers

The Ti:sapphire laser is, undoubtedly, the most ubiquitous solid-state laser based on a transition metal ion dopant [5]. In a way, its emergence may be construed as the confluence of two essential discoveries: that of vibronic (broadband emitter) lasers and the ruby laser. By replacing the chromium ion in ruby with titanium (i.e. changing Cr\textsuperscript{3+}:Al\textsubscript{2}O\textsubscript{3} to Ti\textsuperscript{3+}:Al\textsubscript{2}O\textsubscript{3}), broadband laser operation becomes possible while the favourable thermo-mechanical properties of the sapphire host can simultaneously be exploited. Ti:sapphire can be a continuous wave (cw) pumped by powerful Ar ion lasers with 488 and 514 nm output lines, as well as with doubled Nd:YAG lasers. In fact, with the commercialization of high-power diode-pumped Nd:YAG and Nd:YVO\textsubscript{4} lasers, all-solid-state versions of these laser systems are now available. Ti\textsuperscript{3+} has also been shown to lase in chrysoberyl, or BeAl\textsubscript{2}O\textsubscript{4}, although inadequate information is available to assess the true potential of this material [6,7].

Another critical discovery ensued, which was the discovery that Kerr lens mode-locking provided a simple, robust means of generating femtosecond pulses with Ti:sapphire [8–10]. The Kerr lens mode-locked oscillator inspired a fresh realization that transition-metal-doped solid-state lasers could be unique.
as well as practical. Since then, Ti:sapphire has served as the workhorse of short-pulse lasers, often arranged with several stages of amplification to operate at average powers of more than 10 W [11].

The tuning range was found to be extraordinary, reaching beyond 0.66–1.18 μm, encompassing the 1.05 μm wavelength typical of Nd:glass lasers and permitting their use in hybrid systems (Ti:sapphire master oscillator with Nd:glass power amplifiers). The material properties of sapphire are outstanding, in light of its high thermal conductivity and high fracture toughness. Ti:sapphire lasers are most commonly pumped by argon ion and doubled Nd:YAG lasers, although other approaches such as flashlamps have been explored with some success. It is conceivable that Ti:sapphire may one day be pumped by nitride-based semiconductor lasers, if their brightness can be increased considerably beyond their current value.

3.2.2 Transition Metal Lasers: V²⁺, Co²⁺ and Ni²⁺ ions in Octahedral Sites

The V²⁺ ion [12,13] has only been lased in fluoride hosts, including V:MgF₂, KMgF₃ and CsCaF₃, primarily because of the difficulty in stabilizing the divalent oxidation state of vanadium in oxide media. The efficiencies have generally been found to be quite low, however, because of the presence of excited-state absorption (ESA) losses. Vanadium lasers operate in the range of 1.1–1.3 μm.

Ni:MgF₂ has been demonstrated to lase [14–16] in several hosts including KMgF₃, MgF₂ and Ca₂Mg₃Ge₃O₁₂, although the sub-ambient temperatures together with the low efficiencies (due to low luminescent efficiencies and ESA losses) have limited their practical utility. Nickel lasers operate in the range of 1.4–1.8 μm.

The most common Co²⁺ laser [17–19] is, undoubtedly, Co:MgF₂, which has been effectively pumped by a 1.31 μm Nd:YAG laser on a time scale shorter than the room temperature storage time of the medium (~37 μs). The tuning range for Co:MgF₂ is impressive, being 1.5–2.5 μm. The broad tuning range has enabled Nd:YAG-pumped Co:MgF₂ lasers to service a niche scientific market. Low-temperature operation of Co:KZnF₃ has also been reported [20,21].

3.2.3 Transition Metal Lasers: Cr⁴⁺, Cr²⁺, Fe²⁺ and Mn⁵⁺ ions in Tetrahedral Sites

It is interesting that, following much activity leading to the identification of over a dozen Cr³⁺ lasers, further exploratory work found that both Cr²⁺ and Cr⁴⁺ ions were also interesting and practical lasers. While Cr³⁺ is exclusively found in sixfold coordinat ed sites, the new valent and tetravalent species appear only in fourfold sites. Cr⁴⁺ has been found to lase in the 2.1–2.9 μm range in ZnS, ZnSe, CdSe and Cd₀.₅Mn₀.₅Se₀.₄ hosts [22–28]. Cr²⁺ lasers are actively being explored and developed and these have been pumped by Tm lasers, Co:MgF₂ and by 1.7 μm laser diodes. Fe²⁺ has been discovered to lase in ZnSe in the 4.0–4.5 μm region below about 200 K [29], although the first report of laser action dates back to 1983 [30], for Fe in the semiconductor InP and for 2 K (pumping above the bandgap).

Cr⁴⁺ lasers operate in the near-infrared at 1.2–1.6 μm and have been reported in such hosts as Mg₃SiO₄, Ca₂GeO₃, Y₃SiO₅ and Y₃Al₅O₁₂ [31–39]. These lasers can be conveniently pumped with a 1.06 μm Nd:YAG laser. The original material representing this new class of gain media is known as forsterite (Cr:Mg₃SiO₄). Several watts of power are presently available from this class of materials and both Cr:YAG and forsterite have been mode-locked [40–43].

Mn⁵⁺ lasers operate as the so-called three-level lasers, similar to the original ruby laser, where the laser transition at 1.18 μm terminates near the ground state of the ion. Mn⁵⁺ has been studied in the Ba₃(VO₄)₂ host crystal thus far, where a scientific observation of laser action has been reported [44].

3.2.4 Tabulation of Transition Metal Lasers

A summary of the known laser materials based on transition metals other than Cr³⁺ appears in Table 3.1. It should be noted that there is a diversity of host materials and ions and that there are certainly more media yet to be discovered.

3.3 Physics and Engineering Issues

3.3.1 Electronic Structure

Transition metals occupy three rows of the periodic table of the elements. Thus far, only the ‘first-row’ elements have demonstrated the ability to lase as an oscillator, although gain has been reported for Rh²⁺ [3] (second-row ion). The treatment of the electronic structure begins with the atomic species, which is described as 3dⁿ for the first row. Because the atomic interactions are the strongest, including the nuclear, repulsive and exchange interactions, the atomic states are the starting point of consideration [45].

For a 3dⁿ ion such as Ti³⁺, the only electronic state that arises from this configuration is the 3D state. The upper left superscript is the multiplicity (or degeneracy) of the spin, given as 2S+1, while the ‘D’ stands for the L = 2 orbital angular momentum. Since there is only a single electron (with spin 1/2), 2S+1 = 2, which is known as a doublet. If we now consider the Cu²⁺ ion, which has a 3d⁹ configuration, we may regard this as being one electron short of the 3d¹⁰ fully symmetric closed shell. Therefore, the 3d⁹ structure is characterized as having one hole and also yields the 3D atomic state. For more complicated transition metal ions, for example, those with the 3d⁵ configuration, numerous states result including the 5S, 5P and 5D states, where certain singlet and triplet states are excluded by the requirement of antisymmetrization for the overall electronic wavefunction. Again, d⁶ ions give rise to these same states as a consequence of the electron–hole symmetry noted earlier.

Once the atomic state is specified, the crystal field in which the ion is situated must be accounted for. The crystalline environment of transition metal ions is simplified however, since they occur mainly in fourfold or sixfold coordinated sites, referred to as tetrahedral or octahedral sites, respectively, see Figure 3.1. Furthermore, it is often the case that the sites do not deviate far from perfect sites (metal ion at the centre of the
TABLE 3.1

Laser Properties of Transitional Metal Lasers Other Than Cr\(^{3+}\)

<table>
<thead>
<tr>
<th>Laser ion</th>
<th>Laser Crystal</th>
<th>Electronic Transition</th>
<th>Wavelength, µm (temp., if &lt; (R_\text{T}))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(^{2+})</td>
<td>Al(_2)O(_3)</td>
<td>(^3)E(\rightarrow)T(_2)</td>
<td>0.66–1.18</td>
<td>[5]</td>
</tr>
<tr>
<td>V(^{2+})</td>
<td>CsCaF(_3)</td>
<td>(^4)T(_2)(\rightarrow)T(_2)</td>
<td>1.24–1.33 (80 K)</td>
<td>[12]</td>
</tr>
<tr>
<td>Cr(^{4+})</td>
<td>Mg(_2)SiO(_4)</td>
<td>(^3)T(_2)(\rightarrow)T(_2)</td>
<td>1.17–1.35</td>
<td>[31–33]</td>
</tr>
<tr>
<td>Cr(^{2+})</td>
<td>ZnS</td>
<td>(^3)E(\rightarrow)T(_2)</td>
<td>2.35</td>
<td>[23]</td>
</tr>
<tr>
<td>Cr(^{2+})</td>
<td>ZnSe</td>
<td>(^3)E(\rightarrow)T(_2)</td>
<td>2.1–2.8</td>
<td>[22,23,26]</td>
</tr>
<tr>
<td></td>
<td>Cd(<em>{1.5})Mn(</em>{0.5})Se(_2)</td>
<td></td>
<td>2.3–2.66</td>
<td>[24,25]</td>
</tr>
<tr>
<td></td>
<td>CdSe</td>
<td></td>
<td>2.3–2.9</td>
<td>[27]</td>
</tr>
<tr>
<td>Mn(^{3+})</td>
<td>Ba(_2)(VO(_4))</td>
<td>(^3)E(\rightarrow)A(_2)</td>
<td>1.81</td>
<td>[44]</td>
</tr>
<tr>
<td>Fe(^{2+})</td>
<td>(n)-InP</td>
<td>(^5)T(_2)(\rightarrow)E</td>
<td>3.53 (2 K)</td>
<td>[30]</td>
</tr>
<tr>
<td></td>
<td>ZnSe</td>
<td></td>
<td>3.98–4.54</td>
<td>[29]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(20–170 K)</td>
<td></td>
</tr>
<tr>
<td>Co(^{2+})</td>
<td>Mg(_2)F(_2)</td>
<td>(^3)T(_2)(\rightarrow)A(_2)</td>
<td>1.5–2.5</td>
<td>[17–19]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(80–300 K)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>KZnF(_3)</td>
<td></td>
<td>1.63–2.08</td>
<td>[20,21]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(25–150 K)</td>
<td></td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>KMgF(_3)</td>
<td>(^3)T(_2)(\rightarrow)A(_2)</td>
<td>1.59 (80 K)</td>
<td>[15]</td>
</tr>
<tr>
<td></td>
<td>Mg(_2)F(_2)</td>
<td></td>
<td>1.63, 1.73–1.75</td>
<td>[14]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(20–200 K)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ca(_2)Y(_2)Mg(_2)Ge(<em>3)O(</em>{12})</td>
<td></td>
<td>1.46 (80 K)</td>
<td>[16]</td>
</tr>
</tbody>
</table>

Octahedral Coordination  Tetrahedral Coordination

FIGURE 3.1 Depiction of a transitional metal ion in octahedral and tetrahedral sites in a crystalline lattice.

As an example of the result of this procedure, the d\(^8\) configuration of Ni\(^{2+}\) in an octahedral coordination appears in Figure 3.2. The abscissa of the Tanabe–Sugano diagram represents the magnitude of the crystal field, so at the furthest left-hand position, the energy levels are simply the atomic states. As a final note, it should be mentioned that a sign reversal in crystal field splitting occurs in two situations: incorporating the ion into a tetrahedral as opposed to an octahedral site and considering electrons instead of holes. In other words, the diagram in Figure 3.2 also represents a d\(^2\) ion in a tetrahedral environment.

3.3.2 Absorption and Emission

As an example of the type of absorption and emission spectra exhibited by all of the ions of interest in this chapter, the data for Cr\(^{2+}\):ZnSe are plotted in Figure 3.3. One of the features of the spectra is the approximate ‘mirror image’ quality of the absorption and emission spectra, where they appear to be roughly symmetrically disposed about a line of reflection. In principle, the material can be pumped anywhere within the wavelength range of the absorption band and the material may then be expected to emit photons according to the emission spectrum. Nearly all of the transition metal lasers operate in the vibronic mode by emitting vibrations during the emission process, with the exceptions of Mn\(^{3+}\) and high-field Cr\(^{3+}\).
Handbook of Laser Technology and Applications

(As in for the ruby laser). As a consequence, we will focus on broad-band vibronic emitters in this section.

A ‘configuration coordinate’ diagram description of absorption and emission is sketched in Figure 3.4. The essence of this conceptual diagram is that the Gaussian distribution of interatomic distances in the initial state is unchanged in the course of the electronic transition to the other state, so the distribution is mapped via the vertical intersection with the other curve (up for absorption, down for emission) and then to the energy axis. The shape of the potential energy surfaces is regarded as approximately harmonic in nature, given as \[ V = \frac{1}{2} k_{\text{gnd}} Q^2 \] for the ground state and as \[ V = \frac{1}{2} k_{\text{ex}} (Q - \Delta Q)^2 \] for the displaced excited state. \( Q \) is regarded as the embodiment of the generalized configuration coordinate representing the internuclear separation between the transition metal and the host anion and \( \Delta Q \) is the displacement between the two electronic states. If, for simplicity, we assume that the ground and excited states have the same shape (i.e. \( k_{\text{gnd}} = k_{\text{ex}} \)), then the ‘Stokes shift’ between the absorption and emission peaks is given as \( 2S h \nu_{\text{ph}} \), where \( S \) is known as the Huang–Rhys factor and \( h \nu_{\text{ph}} \) is the characteristic phonon energy of the host material. At low temperature, the spectral width of the absorption or emission feature is given as \( \Delta = S^{1/2} h \nu_{\text{ph}} \), so a greater \( \Delta Q \) shift between the ground and excited potential energy surfaces leads to broader spectral features. To a higher degree of specificity, the lineshape can be described by a Pekarian function:

\[
L_{\text{ph}}(p) = S^p \exp(-S)/p!
\]  

where \( p \) is the number of phonons, which are converted to photon energy via the relationship \( E = p h \nu_{\text{ph}} + E_{\text{ZPL}} \) by including the energy of the zero-phonon line (ZPL).

The emission bandshape is a critical aspect of the laser properties of the system since it determines the possible tuning range and has a major consequence on the magnitude of the emission cross section, which is given by [5]

\[
\sigma_{\text{em}} = \lambda^2 / (8 \pi n^2 \tau_{\text{rad}} \Delta \nu_{\text{em}})
\]  

where \( \lambda \) is the wavelength, \( n \) is the refractive index, \( \tau_{\text{rad}} \) is the radiative lifetime and \( \Delta \nu_{\text{em}} \) is the spectral width of the transition in \( s^{-1} \). It is, therefore, easy to see that, with other factors held constant, the emission cross section must necessarily be
reduced to capture the advantage of greater tuning range for the laser. In addition, the potential to generate short pulses also requires the availability of bandwidth, in that the shortest achievable pulselength is limited by the uncertainty principle

\[ \tau_{\text{lase}} > 0.3/\Delta \nu_{\text{lase}} \]  

(3.5)

and the laser pulselength must naturally be less than that of the emission band \( \Delta \nu_{\text{lase}} \ll \Delta \nu_{\text{em}} \). For the case of an amplifier having gain G, the bandwidth is given by

\[ \Delta \nu_{\text{lase}} = \Delta \nu_{\text{em}} / \left( \ln G \right)^{1/2} \]  

(3.6)

For example, if a multi-pass regenerative amplifier is operating with \( G = 10^6 \), then the gain-narrowing factor is 3.7, indicating an attainable pulselength of 12 fs. Work with Ti:sapphire oscillators has yielded a pulselength of ~5 fs [10] (close to the limit imposed by the emission bandwidth of \( \Delta \nu_{\text{em}} \approx 3 \) fs).

### 3.3.3 Excited-State Absorption

ESA is one of the more subtle aspects of laser materials that needs to be understood to determine whether it can offer net gain at the laser wavelength. The ESA cross section is directly subtracted from the emission cross section of Equation (2.4) to yield the net gain cross section:

\[ \sigma_{\text{gain}} = \sigma_{\text{em}} - \sigma_{\text{ESA}} \]  

(3.7)

In other words, the light passing through the gain medium can either experience stimulated emission, pump-induced loss or both, depending on whether the ion undergoes a transition from the excited state to a lower-lying level or to a higher level, respectively. For some ions such as Ti3+, there is no ESA, simply because there are no accessible excited states above the metastable pumped energy level of the ion. Other ways to avoid the negative impact of ESA for ions include situations where the ESA is either wavelength-shifted from the emission band such that it does not significantly overlap it or for cases where it possesses a significantly weaker cross section. We can consider several examples to compare these cases:

- no relevant higher-lying excited states—Ti:sapphire (octahedral site);
- weak ESA that is spin-forbidden—Cr2+ in ZnSe (tetrahedral site) and
- strong ESA which reduces the laser efficiency—Ni2+ and V2+ ions (octahedral site) and Cr4+ (tetrahedral site) in certain crystals.

The energy levels for each of these cases are shown in Figure 2.5. Ti3+ is the simplest case because the valence electronic configuration consists only of a single 3d electron. Then, we can imagine that the octahedral crystal field surrounding the ion splits the orbitals into two types: \( t_{2g} \) and \( e_g \) (\( t_{2g} \) orbitals ‘point’ between the oxygens, while the \( e_g \) orbitals point at them and, therefore, have higher energy). So, since there is a single electron, the states become the \( 2T_{2g} \) ground state and the \( 2E_g \) excited state, and the laser transition is the transition between them as pictured in Figure 3.5.

Cr2+ also does not suffer from extensive ESA losses [23], even though there are a great many excited states above the pumped metastable level. Cr2+ has four 3d electrons, so we can imagine that it is one 3d electron short of a half-filled shell—describable as a 3d hole. So with a 3d hole, the two lowest electronic states again become the \( T_{2g} \) and \( E_g \) states with a spin multiplicity of \( 2S+1 = 5 \). The laser transition occurs between the \( 3T_{2g} \) and \( 3E_g \) states. It is coincidentally the same orbital transition as for Ti3+ due to two inversions of its nature: because it is a hole rather than an electron and because it is a tetrahedral rather than an octahedral arrangement of host anions. The important point relevant to ESA is that all of the other excited states (of which there are many) must necessarily be either spin triplets or singlets and are, therefore, spin-forbidden from the excited state. For this reason, Cr2+ ions in a tetrahedral coordination experience little ESA loss. In contrast, Mn2+ and Fe3+ (d5) in octahedral sites do not lase because the ESA transitions are spin-allowed while the emission is forbidden—the opposite of the favourable condition that exists for Cr2+ in tetrahedral sites.

For the 3d8 Ni2+ laser ion situated in an octahedral environment [47,48] or the 3d2 Cr4+ ion in a tetrahedral site, the emission transition \( (T_{2g}^{-1}A_{2g}) \) may be expected to have roughly the same transition strength as the ESA transition \( (T_{2g}^{-3}T_{1g}) \). Similar considerations apply to V2+ although the electronic states are spin quartets rather than triplets [49,50]. In both cases, because the transitions are spin-allowed they derive their transition strength from vibrational interactions with odd-parity phonons that break the symmetry. (While there is sometimes a magnetic dipole contribution to the strength of d–d transitions, the vibrational component normally dominates.) It turns out that the \( \sigma_{\text{em}} \) and \( \sigma_{\text{ESA}} \) values are approximately comparable for these three systems, although, by serendipity, the emission cross section can sometimes be somewhat larger leading to efficient laser performance. For example, for forsterite \( (Cr^{4+}:Mg_2SiO_4) \), the emission cross section turns out to be significantly larger than that of the ESA for one of
three polarizations. In contrast, Cr\(^{4+}\)\(-\)LiAlO\(_2\) \([51]\) does not exhibit any net gain since the crystal is isotropic and it appears that \(\sigma_{\text{ESA}} > \sigma_{\text{em}}\). Another way in which the emission ‘beats’ the ESA is by reducing the temperature below ambient. This effect is apparent for Ni\(^{2+}\)\(-\)MgO where the emission features sharpen up and thereby rise above the ESA. The efficiency of V\(^{3+}\) lasers is also negatively impacted by ESA.

### 3.3.4 Radiative Rates and Non-Radiative Losses

The emission rate experienced by a metal ion doped into a host medium is the sum of the radiative and non-radiative rates. The basic equation governing the radiative rate is known as Fermi’s Golden Rule \([2]\):

\[
W_{\text{rad}} = \left(8\pi^3/\hbar^2\right)\left|\langle F|\mathcal{H}_\text{ph}\rangle\right|^2 f(v) (3.8)
\]

where the initial and final states, \(I\) and \(F\), are linked via the photon field, \(\mathcal{H}_\text{ph}\), and \(f(v)\) is the lineshape function in units of \(s\). For transition metal ions, the relevant electronic states are all derived from the 3d\(^{n}\) electronic shell, so the transitions are nominally symmetry-forbidden on the atomic basis. That is to say that the electronic states are both of even parity and, together in consideration of the odd parity of the photon operator, the overall integral is identically zero. However, for the case where the crystalline field is tetrahedral, the inversion symmetry of the ion is destroyed and the 3d–3d transition becomes allowed. This is the nature of the radiative transitions for Cr\(^{3+}\), Cr\(^{2+}\), Fe\(^{2+}\) and Mn\(^{2+}\) ions, all of which lase when they occupy the tetrahedral sites of certain host media. For Cr\(^{3+}\), Cr\(^{2+}\) and Fe\(^{2+}\), the radiative lifetimes are of the order of 1–100 \(\mu s\) for their spin-allowed laser transitions, while it is longer (about 1 ms) for Mn\(^{2+}\) because the laser transition is also spin-forbidden. In referring back to Equation (2.8), we see that the radiative rate can be seen as arising from the admixture of opposite parity states into the initial and final states, as a consequence of the crystal field.

For transition metals doped into an octahedral crystal field, the radiative rate can arise from the small residual acentric component of the crystal field and the dynamically induced transition strength resulting from the vibrations that destroy the centre of inversion. Magnetically induced dipole strength can also play a role as in the \(^{2}T_2 \rightarrow ^{4}A_{2}\) emission transition of V\(^{3+}\). Ti:sapphire is an example of the first case, since the sixfold coordinated site of Al\(_2\)O\(_3\) has a significant asymmetric component. The dynamic component of the radiative rate is more important for materials where the transition metal site is most purely octahedral such as for KMgF\(_3\).

Non-radiative decay is generally described as a thermally activated process for transition metal ions, where the excited state is thermally promoted to a very high vibrational level of the lower ground state and then subsequently decays to the ground state. At this point, the excitation energy is deactivated into vibrational energy and then heat. The competition between radiative and non-radiative decay can be described by

\[
k_{\text{em}} = k_{\text{rad}} + k_{\text{nur}} (3.9)
\]

where the non-radiative component is usually given by \(k_{\text{nur}} = A_{\text{nur}} \exp(\text{E}_{\text{nur}}/kT)\). The main issue is the magnitude of the ‘quenching temperature’, \(T_q\), where the radiative and non-radiative rates become comparable. As an example of this type of data, the emission lifetimes of Cr\(^{3+}\)\(-\)ZnSe and Fe\(^{2+}\)\(-\)ZnSe are plotted in Figure 3.6. \(T_q\) is about 170 and 380 K for these two materials \([23]\). For comparison, it is 500 \([52]\), 300 \([12]\) and 370 K \([53]\) for Ni\(^{2+}\)\(-\)MgO, V\(^{3+}\)\(-\)CsCaF\(_3\) and Ti\(^{2+}\)\(-\)Al\(_2\)O\(_3\), respectively.

The Cr\(^{4+}\) ion offers some insight into how it can sometimes be difficult to have both favourable emission efficiency and low ESA in a single material. The ion–host combination, Cr\(^{4+}\)\(-\)LiAlO\(_2\), proved to be >30% radiative at room temperature \([51]\) (while the standard forsterite laser material Cr\(^{4+}\)\(-\)Mg\(_2\)SiO\(_4\) is only about 13% efficient) \([31–33]\). As a result, there was initially much excitement based on the hope that a more efficient Cr\(^{4+}\) laser was about to emerge. In spite of the enhanced emission, researchers were unable to lase Cr\(^{4+}\)\(-\)LiAlO\(_2\). It was eventually recognized that ESA was more prominent in LiAlO\(_2\), because it did not have the advantage of a strong polarization dependence which can favour low ESA in a particular polarization.

### 3.3.5 Optical Loss

Optical loss in laser crystals can be due to crystal imperfections and the presence of impurities that absorb at the laser wavelength. In addition, absorption can arise from the differing oxidation states of the doped laser ion. Finally, poor optical quality of the gain element can, in effect, lead to diffraction of the light out of cavity mode so that it is registered as a loss (or a reduction in the beam quality of the oscillator or amplifier). Reducing the optical loss to \(\sim 0.1\% \text{ cm}^{-1}\) often requires several years of crystal growth development and, therefore, must be warranted on the basis of the anticipated properties of the laser material. Such was the case, for example, for Ti:sapphire, where eventually Ti\(^{4+}\) was eliminated using carefully controlled growth conditions, which reduced the losses to a favourable level. Some host materials such as Y\(_3\)Al\(_5\)O\(_12\), MgF\(_2\) and ZnSe had been developed partly for other reasons and are available as high-quality optical materials.

![FIGURE 3.6 Emission lifetimes of Cr\(^{3+}\) and Fe\(^{2+}\) in ZnSe. The precipitous drop in the lifetime is due to the onset of non-radiative decay.](image-url)
3.3.6 Laser Gain and Oscillation

Laser materials can naturally be arranged to operate in a wide variety of configurations, although we will consider the simple case of a cw longitudinally pumped material. The gain afforded by a laser material can be written as

$$G = T_{\text{surf}} \exp \left[ (\sigma_{\text{gain}} N_{\text{ex}} - \alpha_{\text{loss}}) d \right]$$

(3.10)

where $N_{\text{ex}}$ is the excited-state population, $\alpha_{\text{loss}}$ is the distributed loss in the material, $d$ is the pathlength of the light in the material and $T_{\text{surf}}$ is the surface transmission factor. The excited-state population is given as

$$N_{\text{ex}} = \alpha_{\text{abs}} I_{\text{pump}} \tau_{\text{em}} / h \nu_{\text{pump}}$$

(3.11)

where $\alpha_{\text{abs}}$ is the pump absorption coefficient, $I_{\text{pump}}$ is the pump intensity, $h \nu_{\text{pump}}$ is the energy of the pump photon and $\tau_{\text{em}}$ is the emission lifetime of the excited state. By employing equations (2.10) and (2.11) and allowing for the gain to just equal the loss in an oscillator, the threshold condition can be derived:

$$P_{\text{th}} = \pi \omega^2 h \nu_{\text{pump}} (T_{\text{OC}} + T_{\text{loss}}) / 4 \sigma_{\text{gain}} \tau_{\text{em}}$$

(3.12)

where $P_{\text{th}}$ is the minimum threshold pump power for the oscillator, $\omega$ is the pump laser radius, $T_{\text{OC}}$ is the output coupling, $T_{\text{loss}}$ is the total double-pass transmission of the gain medium, which accounts for the passive losses, and the emission lifetime accounts for the negative impact of non-radiative decay since $\tau_{\text{em}} = \tau_{\text{rad}} + \tau_{\text{nr}}$. Thus, Equation (2.9) reveals that losses, ESA (recall $\sigma_{\text{gain}} = \sigma_{\text{em}} - \sigma_{\text{ESA}}$) and non-radiative decay all lead to an increase in the laser threshold of the oscillator, by attenuating the light intensity, reducing the gain and reducing the inversion density, respectively.

3.3.7 Host Properties

Solid-state lasers operating in an ‘average power’ mode must appropriately manage the repercussions of the thermal gradients existing in the medium, which lead to thermal aberrations (sometimes mainly a spherical lens) and the potential to fracture the gain element. Assuming that the thermal gradients are fully developed in time (i.e. in equilibrium), then the allowed thermal flux that can safely be removed from the surface of a symmetrical thin slab without fracture is [54]

$$Q_{\text{th}} = 6 b R f / d$$

(3.13)

where $d$ is the thickness of the slab and $b$ is the safety factor (usually taken as 20%). An overall measure of a material’s ability to resist fracture is quantified with the parameter:

$$R f = \kappa (1 - \nu) K_{fc} / \alpha E$$

(3.14)

where $\kappa$ is the thermal conductivity, $\nu$ is Poisson’s ratio (0.2–0.3 for most materials), $K_{fc}$ is related to the material’s propensity to resist crack propagation, $\alpha$ is the expansion coefficient and E is Young’s modulus. Finally, $R_f$, the fracture toughness, is given by

$$R_f = R_f^0 / a^{1/2}$$

(3.15)

where $a$ is the radius of the surface flaws, which is usually taken to be $a = 25 \mu m$. Some typical values of $R_f^0$ and $\kappa$ are listed in Table 3.2 [54,55].

Another important impact of the thermal gradients within the optical material is the introduction of a thermal lens. This effect arises from the stresses, strains and temperature rise within the material. For simplicity, we can consider the case of an unstressed optical element, where the pathlength due to temperature variation of $\Delta T$ is given by

$$\Delta p = \left[ \alpha (n - 1) d n / d T \right] L \Delta T.$$  

(3.16)

The magnitude of the change in refractive index with temperature $dn / dT$ is an important parameter in determining the amount of thermal lensing exhibited by the material. From the data in Table 3.2, it should be noted that MgF$_2$, for example, has a much lower $dn / dT$ than ZnSe. The thermal gradient that occurs in the material generally gives rise to a large spherical wavefront distortion, which can be partially mitigated with additional optics.

Lastly, the magnitudes of several non-linear refractive indices are listed in Table 3.2 [56]. The $n_2$ becomes important for pulsewidths of the order of nanoseconds or less, since it leads to an intensity-dependent refractive index and lensing effect. The non-linear index, $n_2$, is defined by

$$n = n_0 + n_2 \langle E^2 \rangle$$

(3.17)

where $E$ is the electric field of the laser beam. The non-linear indices generally follow the rule of fluorides < oxides < selenides.

### TABLE 3.2

Thermal, Mechanical and Optical Properties of Host Media

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Thermal Conductivity, $\kappa$ (W m K$^{-1}$)</th>
<th>Fracture Toughness, $R_f$ (W m$^{-1}$)$^{1/2}$</th>
<th>Index Change $dn / dT$ ($10^4$ K$^{-1}$)</th>
<th>Non-linear Index $n_2$ ($10^{-11}$ esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>28</td>
<td>22</td>
<td>12</td>
<td>1.2</td>
</tr>
<tr>
<td>Y$_2$Al$_2$O$_12$</td>
<td>10</td>
<td>4.6</td>
<td>9</td>
<td>2.7</td>
</tr>
<tr>
<td>Y$_2$SiO$_4$</td>
<td>4.5</td>
<td>1.9</td>
<td>6, 7, 9</td>
<td>3.7</td>
</tr>
<tr>
<td>Mg$_2$SiO$_4$</td>
<td>8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MgF$_2$</td>
<td>21</td>
<td>7.6</td>
<td>0.3, 0.9</td>
<td>0.3</td>
</tr>
<tr>
<td>ZnSe</td>
<td>18</td>
<td>5.3</td>
<td>70</td>
<td>170</td>
</tr>
</tbody>
</table>

(a)isotropic)
FIGURE 3.7 Summary of tuning ranges offered by known laser ions.

The non-linear index is also responsible for Kerr lens mode-locking by virtue of the slight difference in the oscillator stability that arises from the intensity-dependent focusing power, causing the mode-locked state to be preferred over cw output.

3.4 Summary

In this chapter, the nature and scope of transition metal ion lasers (excluding Cr3+) have been summarized, as they are embodied in today’s solid-state laser systems. Ti:sapphire is by far the most common transition-metal-based solid-state laser, and it has led to many new opportunities for short-pulse lasers. Co2+:MgF2 lasers are commercially available and Cr4+ and Cr2+ lasers are growing in importance. Research in transition metal lasers is continuing, as the vibronic laser Fe3+:ZnSe was first reported to lase in 1999 and many of the second- and third-row ions are yet to be explored in depth. The electronic structure, absorption and emission spectra, ESA, radiative properties, optical gain/loss and host properties have been described. The tuning ranges encompassed by the known transition metal ions are pictured in Figure 3.7.

Work is done under the auspices of the US Department of Energy by the University of California Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

REFERENCES