Site Selective Spectroscopy on Erbium Ions in Stoichiometric Lithium Tantalate

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Abstract. Ferroelectric materials such as lithium niobate (LiNbO$_3$) and the isostructural lithium tantalate (LiTaO$_3$) play an important role in integrated optics since they allow the possibility to combine their favourable electro-optical, acousto-optical, and nonlinear properties with the ability to add additional functional groups by doping. Examples are rare earth ions that act as active centres for laser and optical amplifier applications. We present our site-selective spectroscopic studies on Er$^{3+}$ doped nearly stoichiometric LiTaO$_3$ that include results about the assignment of excitation and emission peaks to different sites, symmetry properties of these sites, energy transfer among major sites, and up-conversion efficiencies. We compare the results in LiTiO$_3$ with the corresponding ones in the much better studied LiNbO$_3$ host and find that the type of centres and their spectral feature are very similar.

1. Introduction The first section in your paper

Ferroelectric materials such as lithium niobate (LiNbO$_3$) and the isostructural lithium tantalate (LiTaO$_3$) play an important role in integrated optics since they allow the possibility to combine their favorable electro-optical, acousto-optical, and nonlinear properties with the ability to add additional functional groups by doping. Examples are rare earth ions that act as active centres for laser and optical amplifier applications. For this reason, extensive studies of the spectroscopic properties of many rare earth ions have been performed for the LiNbO$_3$ host material [1-5].

However, much less is known for lithium tantalite (LiTaO$_3$), although it offers better resistance against optical damage making it a more favourable host for high-power lasers in the visible spectral region. We present our site-selective spectroscopic studies on Er$^{3+}$ doped, nearly stoichiometric LiTaO$_3$ samples. While the Er$^{3+}$ ion is well known for its highly efficient emission in the telecommunication window around 1.5 µm, it offers also emission in the visible at around 550 nm and 650 nm that can be excited through up-conversion with widely available powerful semiconductor lasers around 980 nm. To this end, we focus on the excitation around 980 nm and address the following questions:
- What are the Er$^{3+}$ incorporation sites and how do they compare with the ones found in LiNbO$_3$?
- How do the different sites participate in the up-conversion processes?
- How does the defect distribution change under thermal annealing?

2. Experimental Technique

We address these questions using combined excitation emission spectroscopy in which we record a large number of emission spectra while continuously varying the excitation wavelength. Details of this technique and its potential are described in Ref [3, 6]. In our study, we use a tunable semiconductor laser with an external cavity that can be tuned smoothly from 965 nm to 990 nm. This allows us to excite the $^4I_{15/2}$ to $^4I_{11/2}$ transition and observe the emission at 1.5 µm ($^4I_{11/2}$ to $^4I_{13/2}$). Moreover, the laser has sufficient power (approx 10 mW) that allows the observation of emission at 550 nm that is excited through up-conversion processes. The relevant transitions for this work are indicated with the expected symmetry properties for C$_{3v}$ symmetry in Fig. 1. The emission spectra are recorded in reflection mode such that the propagation of excitation and emission is counter-propagating and parallel to the normal of the selected sample surface. Hence, for z-cut samples, the polarization of the emission and
excitation are perpendicular to the c-axis of LiTaO$_3$ allowing only $\sigma$-type transitions for Er$^{3+}$ ions in $C_{3v}$ symmetry.

**Figure 1.** Energy level scheme of Er$^{3+}$ in LiTaO$_3$. The transitions relevant for this work are indicated including the expected polarization properties for $C_{3v}$ point symmetry. In particular, two excitation transitions are highlighted that are not expected to appear for our reflection mode detection for a z-cut sample

3. Results and Discussion

3.1. Identification of Sites

For identification of the energy levels belonging to different incorporation environments in the crystal, we use 980nm excitation and detect the emission at around 1.5$\mu$m. From an inspection of the energy level scheme, we see that 6 excitation transitions and 8 emission transitions are expected. Although we limit our emission detection range to 5 transitions, we are still dealing with 30 transition pairs for a single site. In identifying these pairs, we make use of the CEES data (shown in a combined contour/image plot in Fig. 2 for 4 excitation/emission transition pairs) and exploit the property that the same emission transitions are expected for all seven excitation transitions and vice versa. As a consequence, pairs of excitation/emission transitions must lie on corners of square such as those drawn in Fig. 2. Through careful inspection of the whole data-set we are able to identify at least 7 different sites labeled (A…G). The corresponding transition energies are determined and listed in Table 1. Using these transitions, the crystal field splitting of the ground state $^4I_{15/2}$ and the excited $^4I_{11/2}$ state can be determined by simple subtraction of the transitions energies between the two respective lowest levels in each multiplet. The results are listed in Table 2. The ground state splitting can be calculated from all measured emission transitions and the same results have to be obtained. For our data this is fulfilled within $\pm0.1$meV.
Figure 2. Image plot of CEES data for two excitation (#1, #3) and two emission (#1, #2) transitions. Excitation/Emission peaks that belong to the same sites are identified using squares and are labeled.

Figure 3. Selectively excited emission spectra. The indicated splitting of the levels #3 and #4 are used to compare the sites with the corresponding ones in LiNbO$_3$. 
Table 1: Emission and Excitation energies of Er$^{3+}$ in LiTaO$_3$ for transitions in the IR and green. Several different sites are listed and the labels related to the ones used in publications on LiNbO$_3$.

| Site | A | B | C | D | E | H1 | H2 |
|------|---|---|---|---|---|----|----|
| Label In Ref [1] | 5 | 9 | 2 | 7 |    |    |    |
| Label in Ref [2] | A1 | A3 | B0 |    |    | A2 |    |
| Excitation | 1.2658 | 1.2663 | 1.2661 | 1.2659 | 1.2661 | 1.2662 | 1.2670 | 1.26708 |
| Energies for $^4I_{15/2}$ to $^4I_{11/2}$ transition | 1.2718 | 1.2735 | 1.2713 | 1.27225 | 1.2718 | 1.27208 | 1.27205 |
| Up conversion only | 1.2792 | 1.2818 | 1.2787 | 1.2794 |    |    |    |
| Emission energy for $^4I_{13/2}$ to $^4I_{15/2}$ transition | 0.8014 | 0.8103 | 0.811 | 0.81031 | 0.8107 | 0.81018 | 0.8105 |
| Emission energy for $^4S_{3/2}$ to $^4I_{15/2}$ transition | 2.2493 | 2.2501 | 2.2512 |    |    |    |    |

In the studies on LiNbO$_3$, it was noted that the splitting of the emission peaks to the 3rd and 4th ground state level (which corresponds to the splitting between them) is a good signature for the grouping of the sites into type 0,1,2,3, see Ref. [3]. In Fig. 3, we depict the emission spectra excited selectively for different sites. We note that again the splitting is characteristically different for the different sites. Through comparison of these splittings, we connect the sites A…G identified for LiTaO$_3$ with those in LiNbO$_3$. The assignments are included in Table 1. We find good correspondance and similarities in the relative strength and hence abundance amongst corresponding sites. However, as apposed to LiNbO$_3$, the relative strengths of the emission lines from different sites remain virtually unchanged after 5h annealing at 200°C. Only a narrowing of the emission lines can be observed indicating that just the intrinsic defects are ordering under these conditions while the Er$^{3+}$-related defects remain stable.
Table 2: Crystal field splitting of the $^{4}I_{11/2}$ and $^{4}I_{15/2}$ state.

| Site | A   | B   | C   | D   | E   | F   | G   |
|------|-----|-----|-----|-----|-----|-----|-----|
|      | 0   | 0   | 0   | 0   | *   | 0   |     |
| Splitting of $^{4}I_{11/2}$ state in meV | 4.8 | 5.4 | 4.4 | 5   | 4.7 | 0   | 4.6 |
|      | 6   | 7.2 | 5.2 | 6.35| 5.7 | 1.18| 5.85|
|      | 12.2| 13.6| 10.9|     |     |     |     |
|      | 13.4| 15.5| 12.6| 13.3|     |     |     |
|      | 0   | 0   | 0   | 0   | 0   | 0   |     |
| Splitting of $^{4}I_{15/2}$ state [meV] | 6.7 | 7.7 | 5.8 | 6.9 | 6.4 | 6.9 | 6.8 |
|      | 16  | 16.1| 14.8| 15.8| 15.7| 15.7| 16.0|
|      | 17.2| 20.1| 17.5| 18.0| 17.5| 17.7| 18.0|
|      | 24.5| 25.1| 25.5| 24.5| 25.1| 24.4| 24.7|
|      | 39.2| 42.2| 37  |     |     |     |     |
|      | 43.7| 46.8| 42  |     |     |     |     |
|      | 50.0| 53.4| 49.7|     |     |     |     |

* lowest level unknown; splitting calculated relative 2nd level

3.2. Local symmetry of defects

To further compare the sites between the two host materials, we compare their emission properties in terms of local point symmetry. In our observation geometry, we do not expect to see $\pi$-type transition for a z-cut sample while these transitions should appear for x-cut. For the latter crystal cut, both $\sigma$ and $\pi$ type transitions are expected depending on the polarization of the pump laser and the emission detection. In Fig. 4, we compare excitation spectra for the 3 major sites for excitation onto the z and x-surfaces. These excitation spectra can conveniently by extracted from our CEES data by taking vertical cross sections at emission wavelengths that are characteristic for a particular site.

We find for site A that the 2nd and 5th emission transition are essentially absent for the z-cut sample, indicating that we are dealing with a site with $C_{3v}$ symmetry. Site B and C show all six excitation transitions and most hence be connected with incorporation with lower site symmetry suggesting charge compensating defects that are off the c-axis. The situation was analogous for LiNbO₃.

3.3. Energy transfer

Close inspection of the CEES data reveal that emissions for Site A can always be observed for any excitation energy of site B. The relative strength of site A to site B is 20%. We can interpret this behavior by assuming an energy transfer from Site B to Site A. The branching ratio of such a transfer vs. emission within site B would be approximately 1:5 in our sample. The reverse transfer can be observed as well with a branching ration of 1:20. It is reasonable that the energy transfer occurs while the ions are in the lowest level of the excited $^{4}I_{13/2}$ state, which has a long radiative lifetime (approx ms). As can be seen by the emission data, the energy levels of the two sites are almost identical making energy transfer likely in both directions. The asymmetry in the branching ratio may be attributed to the difference in the relative abundance of site A (majority site) and site B.
Figure 4. Selected Excitation spectra for the three major sites obtained by exciting along the z- and x axis. The data were obtained as vertical cross sections of the CEES data

3.4. Up-conversion

The presence of a rather efficient energy transfer among the different sites suggest that up-conversion through energy transfer is possible by which an already excited ion receives energy from a near-by ion that in turn relaxes to the ground state. Unlike the energy transfer considered above, this process mostly occurs in the $^4I_{11/2}$ state, which still has a reasonably long lifetime. In Fig. 5, we present the CEES data that were obtained under 980nm-range excitation but emission detection this time at 550nm. The data reveals again excitation peaks that can be associated with the major sites that we identified above. This is indicated for site A, B, and C. However, a large number of additional sites with quite different energy levels can be found as well. These sites that are absent in the direct excitation scheme are most likely associated with rare earth ions clusters.

Turning the attention back to the up-conversion behavior of the majority sites we depict the excitation spectrum for the up-conversion emission (Fig. 6) and we notice that up-conversion of site A and B can also be achieved through excitation of the respective other site in the initial step. Apparently energy transfer can occur in the $^4I_{11/2}$ state as well, despite the smaller lifetime and the somewhat larger energy mismatch. Moreover, efficient up-conversion can be achieved even for excitation energies that do not correspond to levels of the $^4I_{13/2}$ state. In this case, the first step of the up-conversion excitation will invoke transitions that involve the weakly coupled phonons or local vibrations. For site B the energy difference (17.5meV or 141cm$^{-1}$) from the lowest lying level to the phonon assisted excitation peak corresponds closely to the lowest energy E(LO) or E(LO) mode [7]. For site A, however, the corresponding energy difference is smaller (15.3meV or 123cm$^{-1}$) and does coincide with a known phonon mode. We suspect that this difference corresponds to localized mode caused by the Er$^{3+}$ dopant itself.

Overall, the behavior of Er$^{3+}$ ions in LiTaO$_3$ in terms of up-conversion resembles again very closely the results for LiNbO$_3$[3]. This result does not come unexpected due to the similarities in the incorporation of the ion, the energy levels, and the phonon spectrum of the two host materials.
Figure 5. Image plot of CEES data obtained under excitation around 980nm and emission detection around 550nm. The dotted lines indicate the excitation position of the major sites. T=10K

Figure 5. Excitation spectrum for up-conversion (green) and regular IR emission. The spectra are obtained from the data in Fig. 2 and Fig 5 as vertical cross sections. The dotted vertical lines indicate the spectral positions for which energy transfer from A to B and from B to A take place. The energy difference between lowest and highest energy band is indicated.
4. Summary and Conclusions

Using the technique of combined excitation emission spectroscopy, we determined the energy levels of a large variety of sites. We find a strong resemblance with the sites in LiNbO$_3$ and hence assume that their nature is very similar. The large number of sites is due to the required charge compensation that lead to sites with local point symmetry lower than C$_{3V}$. The majority site in the host has almost perfect C$_{3V}$ symmetry and may be attributed to rare earth ions without a local compensation or with compensation that is arranged along the c-axis. Based on the analogy with LiNbO$_3$ for which the lattice location has been determined experimentally [8,9] we find no evidence for defect pairs with Er$^{3+}$ ions on adjacent Li and Nb sites such as proposed for LiNbO$_3$ by Jackson et al[10]. In such a pair, strong energy transfer would be expected. Sites A and B that are exhibiting a weak energy transfer have different local symmetries and hence cannot be such a pair for which C$_{3V}$ symmetry is expected for both ions.

Energy up-conversion takes place for modest excitation levels in ways that resemble LiNbO$_3$, including the involvement of local modes and bulk phonons.

Overall, the Er$^{3+}$ ion in LiTaO$_3$ shows a very similar behavior to Er$^{3+}$ in LiNbO$_3$. From this result we suspect that the ion can be used as an efficient probe for perturbation and variation in materials such as it has been demonstrated in LiNbO$_3$ for the imaging of waveguides [11] and domain walls [12].

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