Spectroscopy and energy level location of the trivalent lanthanides in $\text{LiYP}_4\text{O}_{12}$

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The excitation and emission properties of the lanthanides Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Tb^{3+} , Er^{3+} , Tm^{3+} , and Yb^{3+} in $\text{LiYP}_4\text{O}_{12}$ were studied by vacuum ultra violet spectroscopy at 10K. It provides information on the energies of 4f-5d excitation and emission bands. In the case of Er^{3+} spin forbidden emission was observed. Charge transfer excitation bands were identified for Eu^{3+} , Sm^{3+} , Tm^{3+} , and Yb^{3+} , and in the case of Yb^{3+} charge transfer luminescence is observed. All data appears to be consistent with each other and have been used to construct a level scheme showing the location of the energy levels of all trivalent and divalent lanthanides in $\text{LiYP}_4\text{O}_{12}$.

I. INTRODUCTION

The compounds $\text{AREP}_4\text{O}_{12}$ ($\text{A}=\text{Cs}$, Rb , K , Na , Li and $\text{RE}=\text{La}$, Pr , Gd , Y) form a family of related polyphosphate compounds, and luminescence properties of various lanthanide dopants in these compounds have been reported. Most studies deal with the luminescence of Ce^{3+} and Pr^{3+} . Ce^{3+} luminescence in $\text{LiLaP}_4\text{O}_{12}$ was studied by Blasse and Dirksen [1], in $\text{AGdP}_4\text{O}_{12}$ ($\text{A}=\text{Cs}$, K , Na , Li) by Zhong *et al.* [2], and recently we studied Ce^{3+} luminescence in $\text{LiYP}_4\text{O}_{12}$ [3] and $\text{LiGdP}_4\text{O}_{12}$ [4]. Srivastava *et al.* studied the photon cascade emission (PCE) of Pr^{3+} in $\text{LiLaP}_4\text{O}_{12}$ [5]. PCE emission is also observed in stoichiometric $\text{LiPrP}_4\text{O}_{12}$ [17]. Tb^{3+} in $\text{NaGdP}_4\text{O}_{12}$ was studied by Zhong *et al.* [6], and stoichiometric $\text{KTbP}_4\text{O}_{12}$ by Kim *et al.* [7]. A few luminescence studies involving Eu^{3+} have appeared, i.e., Eu^{3+} in $\text{LiLaP}_4\text{O}_{12}$ [1] and $\text{KEuP}_4\text{O}_{12}$ [8]. Charge transfer luminescence was reported for Yb^{3+} in $\text{LiYP}_4\text{O}_{12}$ [9].

When we analyze the existing data it turns out that the redshift of the lowest 5d state, i.e., its lowering in energy relative to its energy in the free lanthanide ion due to the crystal field, tends to decrease with smaller size of the alkaline (from Cs , to Rb , ..., to Li) and with larger size of the rare earth (from Y , Gd to Pr , La). Therefore the redshift is smallest in $\text{LiLaP}_4\text{O}_{12}$ and, although experimental data is not yet available, it is expected to be largest in $\text{CsYP}_4\text{O}_{12}$.

The entire family of $\text{AREP}_4\text{O}_{12}$ compounds forms a nice study material because one may tune the redshift by selecting an appropriate combination of A and RE . Although not much data is available we expect that the bandgap changes in a regular fashion with the size of A and RE too. It is of interest to study all the lanthanides in one and the same compound, and to establish where the lanthanide energy levels are located with respect to the valence and the conduction band. The spectroscopic information and the level scheme of that compound may then form a benchmark for the entire family of $\text{AREP}_4\text{O}_{12}$ compounds. Since Y^{3+} can be substituted by each trivalent lanthanide we decided to use $\text{LiYP}_4\text{O}_{12}$ as such potential benchmark and studied the spectroscopy of Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Tb^{3+} ,

Er^{3+} , Tm^{3+} , and Yb^{3+} under vacuum ultra violet excitation. We will identify the 4f-5d transitions and the electron transfer bands in excitation spectra that enables us to place the energy levels of all the lanthanides within the band gap of $\text{LiYP}_4\text{O}_{12}$. We will show that the spectroscopy and the scheme resembles very much that of the well studied system YPO_4 doped with trivalent lanthanides but that subtle differences can have large consequences for the luminescence and charge storage properties.

II. EXPERIMENTAL

The studies in this work were performed on powder samples of $\text{LiY}_{1-x}\text{Ln}_x\text{P}_4\text{O}_{12}$ ($\text{Ln}=\text{Ce}$, Pr , Nd , Sm , Tb , Er , Tm , Yb) polyphosphates synthesized using the melt-solution technique. For the synthesis, Li_2CO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, Y_2O_3 and an amount $x=0.1$ of oxides of lanthanides were used as starting materials. These reagents were mixed and fired in quartz crucibles at 700°C for two hours. After cooling down to RT, the samples were washed with 0.1 molar HNO_3 acid water and drained. The average size of the microcrystals was $5\mu\text{m}$, and the concentration of Ln^{3+} impurity in the final product was estimated to be in the 1-5mol% range. Analysis of XRD patterns of the studied powder samples confirms that they crystallize in the $\text{LiNdP}_4\text{O}_{12}$ structure type with C2/c space group [10], and their crystallographic data are in agreement with those reported for $\text{LiYP}_4\text{O}_{12}$ in [11].

Measurements of luminescence excitation and emission spectra were performed at Deutsches Elektronen Synchrotron (DESY, Hamburg) using synchrotron radiation from the DORIS III storage ring employing the SUPERLUMI experimental facility of HASYLAB [12]. A Helium flow-type cryostat was used to stabilize the temperature at $T=10\text{K}$. The emission in the UV-visible range was recorded with a spectral resolution of 0.3-5.0nm using a 0.3m ARC SpectraPro308 monochromator-spectrograph in Czerny-Turner mounting equipped with 1200 or 300groves/mm gratings and a Princeton Instruments CCD detector (1100×300 pixels)

or a HAMAMATSU R6358P photomultiplier. The VUV emission spectra were recorded with 2nm resolution using a 0.5m Pouey-type monochromator equipped with a solar blind Hamamatsu R6836 photomultiplier. Luminescence excitation spectra were scanned within the 3.7-10eV range with resolution of 0.32-0.06nm using the primary 2m monochromator in 15degrees McPherson mounting (equipped with a Jobin Yvon holographic concave grating with Al+MgF₂ coating and 1200grooves/mm). The primary monochromator was calibrated with 0.005nm accuracy using the $^1S_0 \rightarrow ^3P_j$ absorption of atomic xenon and krypton gases as a reference. Luminescence excitation spectra were corrected for the incident photon flux by using Na-salicylate as a reference.

III. RESULTS

The excitation and emission spectra of pure LiYP₄O₁₂ were reported already in Ref. [3, 9]. The excitation maximum of the phosphate groups E^{ex} is at 10 K at 8.62 eV (144 nm). Upon excitation in this band at low temperature, a 0.78 eV broad self trapped exciton (STE) emission band peaking at 2.86 eV is observed. In the excitation spectra of lanthanide luminescence in LiYP₄O₁₂ presented below, we can often recognize this phosphate group excitation. For some lanthanides it enhances the emission but for others it reduces emission intensity. It provides information on whether or not energy transfer from the excited phosphate groups to the lanthanide ion is efficient. Using the rule of thumb that the mobility edge is located approximately at 1.08 times the energy of exciton creation [13], we estimate the mobility edge in LiYP₄O₁₂ at $E_{VC} = 9.3$ eV which is practically the same as for YPO₄ [14].

A. Ce coping

The 10K excitation and emission spectrum is shown in Fig. 1 where the five 4f-5d excitation bands are clearly resolved at 4.18, 5.14, 5.40, 5.63, and 6.56 eV. The emission is the characteristic Ce doublet peaking at 3.98 eV and 3.72 eV. The separation of 0.26 eV is the expected spin orbit splitting between the $^2F_{5/2}$ and $^2F_{7/2}$ states. The Stokes shift of the emission to the ground state is 0.2 eV which is relatively small for Ce³⁺ in compounds. We studied Ce³⁺ in LiYP₄O₁₂ in a preceding paper where we showed that the so-called centroid shift and the total crystal field splitting of the 5d-configuration agrees with predictions from empirical relationships [3]. In Fig. 1 the peak due to the phosphate group excitations at 8.6 eV is weak which indicates that the transfer efficiency of excitation energy to Ce³⁺ is rather poor. Between E^{ex} and E_{VC} the excitation efficiency of Ce emission is very low and above 9.3 eV it starts to increase. Apparently unbound electrons and holes in the conduction band and valence band transfer excitation energy more efficiently

to Ce than excitons do.

In [3] we presented a first tentative scheme with the energy levels of Ce³⁺ placed with respect to the top of the valence and the bottom of the conduction band of LiYP₄O₁₂. From an Arrhenius plot of the 5d-4f decay time as function of the temperature we estimated that the first 5d state is located 0.75 eV below the mobility edge. This implies that the 4f ground state is at 4.35 eV above the top of the valence band and that all four higher 5d states are within the conduction band. Later in this work we will see that such placement is consistent with other data.

B. Pr doping

Figure 2 shows the excitation and emission spectra of Pr³⁺ in LiYP₄O₁₂. It is well established that the energy of the main 4f-5d excitation bands for Pr³⁺ can be predicted from the corresponding energies observed for Ce³⁺ by simply adding 1.51 ± 0.09 eV energy [16]. In Fig. 2 we therefore also show the Ce³⁺ excitation spectrum from Fig. 1 but shifted to higher energy. A value of 1.57 eV appears to provide a good match. One may recognize the main excitation bands, particularly the ones to 5d₁, 5d₂, and 5d₅ of Ce³⁺ within the excitation spectrum for Pr³⁺ emission. However, each main Pr³⁺ excitation band is accompanied by satellite bands at higher energy. For example the 5d₁ Pr³⁺ excitation band at 5.74 eV is accompanied by two satellite bands at 5.98 eV and 6.27 eV. These satellite bands are due to the coupling between the electron in the 5d orbital with the electron remaining in the 4f orbital. The same was observed for Pr³⁺ in YPO₄ by van Pieterse *et al.* [18, 19] where also a theoretical explanation can be found. The excitations to 5d₂, 5d₃, and 5d₄ build the broad structure between 6.45 eV and 7.75 eV. The emission bands at 5.48 eV, 5.22 eV, 4.89 eV, and 4.71 eV are identified as emissions from the lowest 4f5d state to the 3H_4 , 3H_5 , [3H_6 and 3F_2], and [3F_3 and 3F_4] states of Pr³⁺, respectively. The Stokes shift for the emission to the ground state is 0.26 eV.

The excitation of the $4f^2[^1S_0]$ state of Pr³⁺ is, as usually for Pr³⁺ in compounds, expected around 5.79 eV (214 nm). The relaxed lowest energy 4f5d state is located below this $4f^2[^1S_0]$ state, and photon cascade emission (PCE) from that $4f^2[^1S_0]$ state is not possible. The situation for PCE is more favorable in LiPrP₄O₁₂ and LiLaP₄O₁₂ [5, 17]. Because the ionic radius of Pr³⁺ and La³⁺ is larger than that of Y³⁺, the crystal field interaction with the 5d electron is somewhat smaller; just enough to locate the lowest 5d state above the 1S_0 state and PCE can occur.

C. Nd doping

Figure 3 shows the excitation and emission spectra for Nd³⁺ in LiYP₄O₁₂. Usually the lowest 5d state of Nd³⁺

is at about 2.80 eV higher energy than that for Ce^{3+} [20]. Therefore in Fig. 3 we have shown the first four Ce^{3+} excitation bands shifted by 2.77 eV in energy. Only the first band in the Nd exciton spectrum at 6.95 eV can be identified as the transition to the lowest energy $5d_1$ state. The two electrons that are still in the 4f-orbital may occupy different energy states that couple with the electron in 5d. This makes interpretation of the Nd excitation spectrum at higher energies very complicated. The emission to the $4f^3[{}^4I_{9/2}]$ ground state is observed as a clear band at 6.75 eV nm yielding a Stokes shift of 0.2 eV; similar to that for Ce^{3+} . The emission to the $4f^3[{}^4I_{11/2}]$ state is observed as a clear band at 6.51 eV. The emission to the ${}^4I_{13/2}$ and ${}^4I_{15/2}$ states, that are predicted at 6.26 eV and 6.02 eV, are not observed as resolved emission bands. The bands around 5.32 eV and 4.66 eV are due to transition to higher energy $4f^3$ states. Like for Ce^{3+} and Pr^{3+} the excitation efficiency is negligible near the mobility edge at 9.3 eV.

D. Sm doping

Figure 4 shows the excitation and emission spectra for Sm^{3+} in $\text{LiYP}_4\text{O}_{12}$. Sm^{3+} has never been observed to show 5d-4f emission in compounds because of rapid relaxation from the lowest $4f^45d_1$ state to lower energy $4f^5$ states. The sharp emission lines at 2.212 eV, 2.066 eV, and 1.913 eV in Fig. 4 are attributed to $4f^5$ - $4f^5$ transitions starting from the ${}^4G_{5/2}$ and ending at the ${}^6H_{5/2}$ ground state and higher energy ${}^6H_{7/2}$, and ${}^6H_{9/2}$ states, respectively. The first $4f^5 \rightarrow 4f^45d$ excitation of Sm^{3+} is always at 3.22 eV higher energy than that of Ce^{3+} and is then predicted at 7.38 eV. We therefore assign the band at 7.43 eV in Fig. 4 to that excitation. The relatively narrow band is located on top of a much broader excitation band that we attribute to the charge transfer (CT) band, i.e., electron transfer from the top of the valence band to Sm^{3+} . The maximum of this CT band is estimated around 7.35 eV. The $4f5d$ excitation features on top of a broad underlying CT band are very similar as in [18] for Sm^{3+} in YPO_4 . A main difference is that the CT band in $\text{LiYP}_4\text{O}_{12}$ is at somewhat higher energy than in YPO_4 and shifted more underneath the $4f5d$ bands. Note that the excitation intensity starts to drop steeply above 8.6 eV where the phosphate groups are being excited.

E. Eu doping

Figure 5 shows the excitation and emission spectra for Eu^{3+} in $\text{LiYP}_4\text{O}_{12}$. Like for Sm^{3+} , 5d-4f emission is never observed with Eu^{3+} and the emission spectrum shows only $4f^6$ - $4f^6$ emission lines at 2.103 eV, 2.032 eV, 1.912 eV (weak), 1.780 eV due to the ${}^5D_0 \rightarrow {}^7F_J$ ($J=1, 2, 3$, and 4) $4f^6$ - $4f^6$ transitions. The excitation band to the lowest energy $4f^55d$ state is expected at 4.38 eV higher energy than that for Ce^{3+} yielding a predicted value of

8.55 eV. This is at slightly lower energy than the phosphate excitation band at 8.62 eV. Figure 5 reveals a clear excitation band at 8.50 eV that we attribute to the first $4f5d$ excitation band of Eu^{3+} . Like for the Sm^{3+} excitation, the intensity drops steeply the moment phosphate groups are being excited, i.e. above 8.6 eV. The strong and broad excitation starting at 5.2 eV is like for Sm^{3+} attributed to the CT band, i.e., an electron is excited from the top of the valence band to Eu^{3+} . The maximum of the CT-band is located at 6.20 eV. This is at relatively high energy for Eu^{3+} in an oxide compound. One reason is the strong binding of the oxygen ligands in the polyphosphate compound. Another reason is the relatively small yttrium site size. For example in $\text{KEuP}_4\text{O}_{12}$ with the larger Eu rare earth the CT band peaks at 5.44 eV [8], and in $\text{LiLaP}_4\text{O}_{12}$ with the even larger La rare earth the CT band was reported to be located at 4.68 eV [1]. Similar observations as function of rare earth site size were reported for other families of related compounds [13, 21].

It is well established that once the energy of CT to Eu^{3+} is known the energy of CT to any other trivalent lanthanide can be predicted [22]. That for Sm^{3+} is always at 1.25 eV higher energy than that for Eu^{3+} [20]. To demonstrate this we have shifted the excitation spectrum for Eu^{3+} upward by 1.20 eV and drawn it in Fig. 4. It provides an impression of the contribution from the Sm CT band to the excitation spectrum.

F. Tb doping

Tb^{3+} has eight electrons in the 4f orbital and upon excitation of one electron to the 5d orbital the seven remaining electrons in 4f will occupy the lowest energy ${}^8S_{7/2}$ state with seven aligned electron spins. The electron in 5d can like for Ce^{3+} occupy the five crystal field split 5d states. The splitting is expected to be very similar as for Ce^{3+} in $\text{LiYP}_4\text{O}_{12}$. In addition, the 5d electron may orient its spin parallel or anti-parallel to the total spin of the ${}^8S_{7/2}$ state. One then expects two sets of five excitation bands. A lower energy set due to weak spin-forbidden transitions to the so-called high spin [HS] states, and a higher energy set due to the spin allowed transition to the low spin [LS] states.

Figure 6 shows the excitation and emission spectra of Tb^{3+} . The emission is very characteristic Tb^{3+} emission originating from the $4f^8[{}^5D_3]$ and $4f^8[{}^5D_4]$ states and terminating at 7F_J multiples. The spin-allowed transition to the [LS]5d₁ state is always found at 1.66 ± 0.12 eV higher energy than that for Ce^{3+} [16]. The corresponding excitation band for Tb^{3+} is then predicted at 5.82 eV which perfectly agrees with Fig. 6. The weak excitation band at 0.96 eV lower energy, at 4.86 eV, must then be attributed to the first spin-forbidden transition to the [HS]5d₁ state.

The dashed curve 1) in Fig. 6 shows the Ce^{3+} excitation spectrum shifted in energy by 1.64 eV. Note that

the locations of the first four excitation bands then agree very well with observed bands for Tb^{3+} . The fifth excitation band of Tb^{3+} at 8.10 eV is at 0.12 eV lower energy than predicted from the Ce^{3+} excitation spectrum. It suggests that the total crystal field splitting for Tb^{3+} is 0.12 eV smaller than that observed for Ce^{3+} and Pr^{3+} . Slight changes in crystal field splitting when going from Ce^{3+} towards Yb^{3+} are possible due to the lanthanide contraction. Together with the $[\text{LS}]5d_1$ excitation band at 5.82 eV, we observe at least two satellite bands at 5.93 and 6.15 eV. They are at about 1 eV lower energy than the spin allowed transitions to $[\text{LS}]5d_3$ and $[\text{LS}]5d_4$, and are therefore attributed to spin forbidden transitions to the $[\text{HS}]5d_3$ and $[\text{HS}]5d_4$ states. The spin forbidden transition to $[\text{HS}]5d_2$ is predicted to coincide with the transition to $[\text{LS}]5d_1$. To illustrate this further we have drawn in Fig. 6 the excitation spectrum of Ce^{3+} shifted by 0.64 eV. The excitation bands for Ce^{3+} then approximately reproduce the energies for the transitions to the $[\text{HS}]5d_i$ states of Tb^{3+} .

G. Er doping

Er^{3+} has 11 electrons in the 4f orbital, and upon excitation of one of the electrons to the 5d orbital the remaining 10 electrons may find themselves in one of the $4f^{10}$ excited states. The first spin allowed 4f-5d transition to the $[\text{LS}]5d_1$ state of Er^{3+} is on average at 3.74 eV higher energy than for Ce^{3+} and we therefore predict the Er^{3+} transition at 7.92 eV. The Er^{3+} excitation spectrum shown in Fig. 7 has its main maximum at 7.98 eV that we attribute to the transition to the $[\text{LS}]5d_1$ state. Like for Tb^{3+} the spin forbidden transition to the $[\text{HS}]5d_1$ state is at lower energy. The emission lines in Fig. 7 can all be assigned to spin forbidden transitions from this $[\text{HS}]5d_1$ state to states of the $4f^{11}$ configuration. Then, by adding the energy of the Stokes shift observed for Ce, Pr, and Nd (on average 0.22 eV) to the 7.20 eV energy of the emission to the ground state we obtain a pretty good estimate of 7.42 eV for the excitation band energy belonging to $[\text{HS}]5d_1$. This value coincides with the shoulder band observed in the excitation spectrum of Er^{3+} . The energy difference between the $[\text{LS}]$ and $[\text{HS}]$ state is therefore 0.66 eV.

H. Tm doping

The excitation and emission spectra of Tm^{3+} are shown in Fig. 8. The first spin forbidden and spin allowed transitions to the $[\text{HS}]5d_1$ and $[\text{LS}]5d_1$ states are at 7.52 eV and 7.89 eV. The exchange splitting between the $[\text{LS}]$ and $[\text{HS}]$ states is therefore 0.37 eV. Usually the CT to Tm^{3+} is at 1.72 eV higher energy than the CT to Eu^{3+} , and the CT band of Tm is therefore predicted at 7.92 eV. The situation is similar as for Sm^{3+} in Fig. 4 where the broad CT band is also underneath the nar-

rower 4f5d excitation bands. The predicted location of 7.92 eV is consistent with the Tm^{3+} excitation spectrum. Like for Sm^{3+} and Eu^{3+} , the excitation intensity drops sharply the moment phosphate groups are being excited, i.e., above $E^{ex}=8.62$ eV. To illustrate what the CT-band of Tm^{3+} would look like, we have drawn in Fig. 8 the energy shifted CT-band observed for Yb^{3+} in Fig. 9. The Yb^{3+} excitation spectrum was shifted by 1.29 eV, i.e., the average energy difference between the CT band energy for Tm as compared to Yb [20]. 5d-4f emission is not observed for Tm^{3+} ; most likely because it is quenched via the CT state. Instead only $4f^{12}$ - $4f^2$ emissions are excited.

I. Yb doping

The excitation and emission spectra of Yb^{3+} are shown in Fig. 9. The excitation spectrum is dominated by a 1.4 eV broad (FWHM) charge transfer band peaking at 6.59 eV. The Yb^{3+} CT band in compounds is on average found 0.43 eV higher in energy than the Eu^{3+} CT band [20, 22]. The observed position of the Yb^{3+} CT-band is therefore in excellent agreement with that of Eu^{3+} in $\text{LiYP}_4\text{O}_{12}$. The first 4f-5d excitation band in Yb^{3+} is expected at energies higher than the band gap and is not observed in Fig. 9. A faint peak due to excitation of the phosphate group is present at 8.6 eV. The emission spectrum is attributed to charge transfer luminescence. The transition to the Yb^{3+} $^2F_{7/2}$ ground state gives the emission band a 3.59 eV, and therefore the Stokes shift is 3 eV large. The second emission band with a maximum near 2.57 eV must be attributed to the transition to the $^2F_{5/2}$ excited state of Yb^{3+} . The about four times lower intensity of $^2F_{5/2}$ emission as compared to $^2F_{7/2}$ emission is commonly observed for CT luminescence involving Yb^{3+} . One reason for the lower intensity is the scaling of radiative lifetime, and therewith intensity, with the third power of the emission wavelength. This already accounts for a factor of 2.8 intensity difference.

Yb^{3+} doped $\text{LiYP}_4\text{O}_{12}$ was also studied in [9] where the two CT-luminescence bands at 2.8 eV and 4.04 eV and the excitation band peaked at 5.99 eV were observed. These values are significantly different from what we find in Fig. 9. Both the CT-emission and the CT-excitation spectra appear similar in position and shape as spectra presented by Nakazawa [23] on Yb^{3+} doped YPO_4 . It suggest that the sample studied in Ref. [9] contained an YPO_4 impurity phase that dominated the luminescence and excitation spectra.

IV. DISCUSSION

With the value for the first 4f-5d excitation band of Ce^{3+} in $\text{LiYP}_4\text{O}_{12}$, the first 4f-5d excitation band for all other trivalent lanthanides in $\text{LiYP}_4\text{O}_{12}$ can be predicted by using the (parameter) values for the first 4f-5d transitions of the free (gaseous) lanthanide ions. In column 4

of Table I we have compiled those predicted values using the most recent parameter values from [20]. Column 3 compiles the observed energies and the agreement is evident. For the heavy lanthanides Tb^{3+} , Er^{3+} , and Tm^{3+} also the energy of the first spin allowed transitions is compiled (shown within brackets). The CT band energies of all lanthanides in a specific compound can be predicted once that of Eu^{3+} in that compound is known. By using the parameter values and the method outlined in [20] best estimates are made and they are compiled in column 6 of Table I. The energies of the observed CT-bands for Sm^{3+} , Eu^{3+} , Tm^{3+} , and Yb^{3+} are compiled in column 5 and all agree well with expectation.

We have now sufficient information to place all the lanthanide levels with respect to the valence and conduction band of $\text{LiYP}_4\text{O}_{12}$. The results are shown in Fig. 10. The dashed line at $E^{ex}=8.62$ eV denotes the energy of excitation of the phosphate group. The bottom of the conduction band is estimated at 1.08×8.62 or 9.3 eV above the top of the valence band. The observed and predicted CT energies in Table I provide us with the location of the ground state of the divalent lanthanide ions in $\text{LiYP}_4\text{O}_{12}$. The curve labeled 4f(2+) connects the predicted CT energies from column 6 of Table I. The ground state energy of Ce^{3+} was estimated in [3] at 4.3 eV above the top of the valence band, and from that the ground state energies of all other trivalent lanthanides are known as well by using the parameters compiled in [20]. The curve labeled 4f(3+) connects those energies. We can now add the Dieke diagram to place all the excited 4f states in the scheme; these are the horizontal bars in Fig. 10. The curve labeled 5d(3+) connects the energies of the first 5d states of the trivalent lanthanides. For Ce^{3+} we have also drawn all five excited 5d energies and for Tb^{3+} , Er^{3+} , and Tm^{3+} the energies of the first low spin 5d states are shown.

For comparison we show in Fig. 11 the level scheme for YPO_4 as presented in [14]. In YPO_4 the lanthanide ion will like in $\text{LiYP}_4\text{O}_{12}$ substitute for an yttrium cation. The anion coordination around yttrium is like in $\text{LiYP}_4\text{O}_{12}$ eight-fold in the form of a dodecahedron. The average Y-O bond length is 234 pm which is quite close to that (239 pm) of $\text{LiYP}_4\text{O}_{12}$. The point symmetry is different, i.e. D_{2d} for YPO_4 and C_2 for $\text{LiYP}_4\text{O}_{12}$. At first sight both schemes appear very similar but there are subtle differences. The bandgap of $\text{LiYP}_4\text{O}_{14}$ is slightly (0.1 eV) larger. The energy for the CT-bands are almost 0.5 eV higher in $\text{LiYP}_4\text{O}_{12}$ and this brings the ground state energies of the divalent lanthanides 0.4 eV closer to the mobility edge than in YPO_4 . This would imply that trivalent lanthanides in $\text{LiYP}_4\text{O}_{12}$ trap electrons 0.4 eV less deep than in YPO_4 . Note that the ground state energy of Ce^{3+} in $\text{LiYP}_4\text{O}_{12}$ is about 0.3 V higher above the valence band than in YPO_4 . This together with a large 4f-5d difference in $\text{LiYP}_4\text{O}_{12}$ brings the lowest energy 5d states 0.7 eV closer to the mobility edge than in YPO_4 . As a consequence the 5d-4f emission of Ce^{3+} is expected to be less temperature stable than in YPO_4 . A param-

eter of importance for the level scheme is the energy differences between the 4f(2+) and 4f(3+) curves. For Eu that energy difference was found 7.0 eV in YPO_4 . In the scheme for $\text{LiYP}_4\text{O}_{12}$ the value is 7.1 eV. For other compounds like SrAl_2O_4 , LaBr_3 , CaGa_2S_4 , and GaN similar type of schemes were published [24–27]. Although a different parameter set than in [20] was used, the method of construction was the same as in this work for $\text{LiYP}_4\text{O}_{12}$ and YPO_4 . The collection of level schemes provides an impression how the level energies and properties of materials may change with type of anion in the compound. Energy level schemes based on X-ray photoelectron spectroscopy and ultra violet spectroscopy experiments on lanthanide doped LaF_3 and $\text{Y}_3\text{Al}_5\text{O}_{12}$ have been published in [28].

In this work we have obtained the values ΔE^{ex} of the exchange splitting between the [LS]5d₁ and [HS]5d₁ states of Tb^{3+} , Er^{3+} , and Tm^{3+} . The size of this splitting depends both on the type of compounds and on the type of lanthanide ion. This was analyzed in detail in [16]. Among the four lanthanides, the splitting is largest for Tb^{3+} (0.97 eV in $\text{LiYP}_4\text{O}_{12}$) because the spin of the 5d electron interacts with seven aligned spins in the 4f orbital. In the case of Er^{3+} the interaction is with four aligned spins and for Tm^{3+} with 3 aligned spins. The exchange splitting decreases to 0.56 eV for Er and 0.37 eV for Tm. Figure 12 is reproduced from [16] and shows that the exchange splitting scales linearly with the so-called spectroscopic polarizability α_{calc} . This is a parameter that can be obtained with a simple calculation from the electronegativity of the cations present in the compound [16]. The data point for Tb^{3+} in $\text{LiYP}_4\text{O}_{12}$ falls nicely within this empirically found behavior. In Fig. 12 we have also marked the data points for GdAlO_3 and Lu_2O_3 . These compounds have lower electronegative cations than the phosphates, the binding of the oxygen ligands is then smaller. It does not only decrease the exchange splitting but also the band gap, and it increased the centroid shift of the 5d configuration. The polyphosphates $\text{AREP}_4\text{O}_{12}$ contain a large fraction of strongly bonding phosphate atoms, and that is the reason that the exchange splitting and bandgap are amongst the largest, and the centroid shift amongst the smallest of the entire oxide family. Only fluorides like LiYF_4 show more extreme values.

V. CONCLUDING REMARKS

In this work we have studied the spectroscopy of Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Tb^{3+} , Er^{3+} , Tm^{3+} , and Yb^{3+} in $\text{LiYP}_4\text{O}_{12}$. The found energies for 4f5d excitation bands and CT-bands appear fully consistent with each other. Once we know the 4f-5d excitation energy for Ce^{3+} that of all other lanthanides can be predicted and predictions agree with experiment. The same applies for the predicted CT-band energies. A level scheme with all the divalent and trivalent lanthanide energy levels has been

constructed. The scheme appears very similar to that of YPO_4 nevertheless differences of the order of few tenths of an eV are present. This may seem small on the scale of the band gap energy but few 0.1 eV energy difference may be very important for the performance of the material as a luminescence or a charge carrier storage material.

In principle, knowledge on the energy of the phosphate group excitation, the redshift for the Ce^{3+} 5d-state, and the CT energy for Eu^{3+} in a $\text{AREP}_4\text{O}_{12}$ compound is already sufficient to draw all lanthanide level in a scheme like in Fig. 10. For the entire family of $\text{AREP}_4\text{O}_{12}$ polyphosphate compounds one may expect a quite similar level scheme as for $\text{LiYP}_4\text{O}_{12}$, but also then subtle differences may have large consequences for the spectroscopic and charge storage properties. The bandgap may

change few tenths of an eV within this family. That also applies to the redshift of the lowest 5d state. The largest changes are to be expected in the energy of charge transfer.

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TABLES

TABLE I: Observed and predicted energies for the first 4f-5d transition E_{fd} and for the CT-band energy E^{CT} . Values within brackets are for the first spin allowed 4f-5d transition. All energies are in eV.

Ln^{3+}	n	$E_{fd}(\text{obs})$	$E_{fd}(\text{pred})$	$\Delta E^{CT}(\text{obs})$	$E^{CT}(\text{pred})$
La	0	—	—	—	11.8
Ce	1	4.13	4.13	—	10.3
Pr	2	5.74	5.64	—	9.07
Nd	3	6.95	6.93	—	8.63
Pm	4	—	7.25	—	8.54
Sm	5	7.43	7.35	7.35	7.45
Eu	6	8.50	8.51	6.20	6.2
Gd	7	—	9.81	—	10.8
Tb	8	4.86 (5.82)	4.91	—	9.41
Dy	9	—	6.61	—	8.47
Ho	10	—	7.66	—	8.60
Er	11	7.42 (7.98)	7.56	—	8.78
Tm	12	7.52 (7.89)	7.51	≈ 7.9	7.92
Yb	13	—	8.71	6.59	6.63
Lu	14	—	10.01	—	—

FIGURES

FIG. 1: The excitation spectrum of 3.71 eV emission and the emission spectrum under 5.17 eV excitation of Ce^{3+} in $\text{LiYP}_4\text{O}_{12}$ at 10 K.

FIG. 2: The excitation spectrum of 4.96 eV emission and the emission spectrum under 6.89 eV excitation of Pr^{3+} in $\text{LiYP}_4\text{O}_{12}$ at 10K. The dashed curve is the excitation spectrum of Ce^{3+} emission shifted with 1.57 eV to higher energy.

FIG. 3: The excitation spectrum of 6.49 eV emission and the emission spectrum under 7.70 eV excitation of Nd^{3+} in $\text{LiYP}_4\text{O}_{12}$ at 10K. The dashed curve is part of the excitation spectrum of Ce^{3+} emission shifted with 2.77 eV to higher energy.

FIG. 4: The excitation spectrum of 2.07 eV emission and the emission spectrum under 7.13 eV excitation of Sm^{3+} in $\text{LiYP}_4\text{O}_{12}$ at 10 K. The dashed curve is part of the excitation spectrum of Eu^{3+} emission shifted with 1.20 eV to higher energy.

FIG. 5: The excitation spectrum of 2.11 eV emission and the emission spectrum under 7.09 eV excitation of Eu^{3+} in $\text{LiYP}_4\text{O}_{12}$ at 10 K.

FIG. 6: The excitation spectrum of 2.27 eV emission and the emission spectrum under 6.89 eV excitation of Tb^{3+} in $\text{LiYP}_4\text{O}_{12}$ at 10K. The dashed curve 1) and the dotted curve 2) are relevant parts of the excitation spectrum of Ce^{3+} emission shifted with 1.64 eV and 0.64 to higher energy, respectively.

FIG. 7: The excitation spectrum of 7.13 eV emission and the emission spectrum under 7.90 eV excitation of Er^{3+} in $\text{LiYP}_4\text{O}_{12}$ at 10K.

FIG. 8: The excitation spectrum of 3.60 eV emission and the emission spectrum under 7.13 eV excitation of Tm^{3+} in $\text{LiYP}_4\text{O}_{12}$ at 10K. The dashed curve is part of the excitation spectrum of Yb^{3+} emission shifted with 1.29 eV to higher energy.

FIG. 9: The excitation spectrum of 3.75 eV emission and the emission spectrum under 6.49 eV excitation of Yb^{3+} in $\text{LiYP}_4\text{O}_{12}$ at 10K.

FIG. 10: Lanthanide energy levels scheme for $\text{LiYP}_4\text{O}_{12}$.

FIG. 11: Lanthanide energy levels scheme for YPO_4 .

FIG. 12: Exchange splitting ΔE^{ex} between the [LS] and [HS] states of Tb^{3+} in compounds displayed against the calculated spectroscopic polarizability α_{calc} of those compounds.