

My opinion in manuscript essd-2020-296

Fuch et al., “

A spectral library for laser-induced fluorescence analysis as a tool for rare earth element identification”

General comments:

The search for REE elements using non-destructive methods is an important issue, also in the economic aspect. A quick and easy method of assessing the mineral content of REE in the drill core is desirable. The authors propose such a method. Therefore, undertaking such a research task is positive. I understand and approve need to obtain a quick and relatively easy answer to the question of whether there are REE in the natural sample, i.e., in a mineral or in a rock. I understand and approve the idea of creating a digitized base of the luminescence spectra of the ions of these elements. All luminescence researchers have some form of base. It also includes references, which the authors call "paper" ones. Among them are works – books (for example Blasse& Brabmair, Springer) or websites, easy to check.

I am glad to read an article promoting the possibilities of the luminescence method. You have to be very careful when interpreting the luminescence spectra. The authors of this work know this. However, I believe that they should make it clearer in the reviewed article that neither the base they created, nor the tables or charts of this work will make beginner researchers take measurements and interpret their results correctly.

I cannot define the target audience of this work. If the group of readers is to be wide - judging from the profile of the journal - then you need to be not only substantive, but also in addition to the advantages of this method, very clearly indicate its limitations. The recommendations in Figure 9 will not suffice. If this work is to assist a wide range of drill developers, those who have not had much experience with luminescence measurements, readers should also be alerted to how samples are prepared for measurement. I don't know if they will be separate grains or cuts. In the latter case - it would be a reflective measurement, i.e., different than for base materials. I do not know if such reflective luminescence spectra were made - you can only see absorption ones.

I also checked the functionality of the database. The compatibility of the database files with own files from measurements made on two different devices was checked. As might be expected, the main, sometimes big problem was to choose the right scale of the Y axis to check whether or not the emission line is overlapping. When superimposing several spectra from the base and several measurement spectra, the problem was very time-absorbing. It was hard for me to notice any clear advantage over the classical method. But - maybe it's a matter of the employee's age and habits.

Positive detailed comments

1. the authors know the commonly measured effect that the emission bands of 4f ions are often split into components and that the emission may come from several closely spaced energy levels (Pr³⁺);

2. the measurements that have been taken are summarized in the figures 3-7 and in Tables 1-4, in particular in Figure 9, is a summary for workers who are starting their research on lanthanide luminescence;
3. the spectra (files) are available through reference *Fuchs et al., 2020* – as .txt files, privately, I do not like such files, but they can be used. Used and compared with own data.
4. the reviewed study indicates to the future researcher many cases that require additional research - e.g. the presence of Sm(3+) beside to Eu(3+), and Pr(3+) beside to Sm(3+). It has rightly been noted that the 611nm -615nm line from Eu(3+) may be missed if Sm³⁺ is also present in the sample. However, the excitation spectra of the two ions differ, so it should be recommended to perform them;
5. the proposed set of measured spectra may be applicable and helpful, but be aware of its limitations.

Some critical remarks:

1. In my opinion, the material prepared as in the reviewed article cannot be called “the base”.
2. The Authors’ results allow only a fairly approximate verification of the presence of these ions in the tested sample.
3. Only 3+ ions were tested, but what about the ubiquitous Eu²⁺? between Ce(3+) and Eu(2+) there is often an energy transfer and the band from Eu(2+), very often in 415-460 nm range, is more intense than from Ce?
4. The photoluminescence spectrum of the tested sample will show the presence of the center, in this case the 4fⁿ ion, when it is excited to glow with the appropriate energy. In the case of this article - a laser line of the appropriate length. This is a basic and known fact. What is shown in Figures 3-8 and in Tables 2, 3, 4, is commonly known from the "paper" literature, the references that the authors of this work wish to escape from.
5. The measurements were made for standards of only one lanthanide phosphate. And yet, the presence of several lanthanide ion together in minerals, as is usual, may cause problems in their unambiguous identification. In my opinion, the automation of digitized measurements proposed by the authors may lead to numerous errors. It must be remembered that the 4f ions that appear next to each other can transmit the emitted energy (energy transfer effect), in a sense obscure each other. In this situation, it is of great help to perform excitation measurements for individual emission lines. This problem was mentioned in the reviewed work quite briefly, and it is very complex. Even the measurements shown in Fig. 8 show how much excitement measurements are needed. For this reason, the spectra in the earlier Figures 3-7 and Tables 2-4 cannot be considered sufficient for the correct / final identification of the 4f ions. Measurements made for excitation with 3 laser lines can actually be very helpful in checking the presence of some lanthanide ions in the tested sample, but in my opinion, they will not replace the full / fuller spectroscopic characteristics of the test object. Although the wavelength of emission lines of RE ions, apart from Eu(2+) and Ce(3+), weakly depend on the strength of the crystal field, their exact value sometimes changes depending on the matrix. An example is Yb (3+) - see literature and figure at the bottom of the review. One can therefore overlook one ion, especially when it is present in the sample in small amounts alongside another one with more intense luminescence. Moreover, the intensity of some Eu(3+) transitions depend on the site symmetry and could be very weak.

6. The luminescence efficiency of individual ions in the same matrix is different. Comparing the spectra on an arbitrary scale may introduce the (younger) researcher to erroneous conclusions. For example, for the excitation of 323 nm and 1: 1 proportion of Dy and Eu (0.1%) in the phosphate glass, the emission bands from Dy are much stronger than the Eu (3+) bands; actually, a very weak band at 611 nm is visible. Using only the 325 nm laser excitation, it cannot be concluded that Eu (3+) is present in the tested sample.
7. There is no indication of the detection limit of the ion; this can be checked in previously published (paper) articles, for example for phosphate glasses subsidized with 4f ions.
8. The results and “base” can certainly be treated as an auxiliary statement.
9. Of course, authors can only measure the available laser lines. Therefore, for precise identification tests, I will recommend other measurements, as in the reference Czaja et al., (2013) Journal of Mineralogical and Petrological Sciences, 108, 47-54, <https://doi.org/10.2456/jmps.111229>.

Some minor / detailed comments:

1. Line 170: I do not know the mineral for which Ce(3+) emission band has been measured at 540 nm . I purpose to delete this value. The Ce (3+) is of great economic importance. Perhaps it should be written a little more clearly that the position of the emission band of this may change depending on the material / mineral in which it occurs.
2. Line 250-255: Sm(2+) luminescence is measured ONLY at low temperature (see, for example Gaft et al., 2005 page 142)
3. The 4fⁿ ions often substitute for Ca (2+). However, Mn²⁺ is quite common in Ca minerals, so in the measured spectra gives an intense emission band, from about 600-700 nm. It often obscures emissions from Sm(3+), Eu(3+) and Pr(3+). So - how to get out of such a situation? In many minerals containing 4fⁿ ions, luminescence can be caused by other centers, not only Mn(2+), also anions of WO₄ MoO₄ CrO₄, TiO₆ complexes, defective oxygen and others. The emission from these ions may obscure the emission from the lanthanides.
4. The excitation band at 442 nm is favored primarily for Pr(3+), and to some extent also for Sm (3+). In order to distinguish between these ions, it is more advantageous to use different excitation wavelengths, also, by the way, not to lose Eu(3+). However, I am not sure if this line efficiently excites Er(3+) (Fig. 6 and Table 3). According to my (and other reference) data, the emission intensity of Er(3+) is more than 3 times weaker for this excitation, compared to the excitation of 377 nm.
5. Please explain why in figure 9 it is indicated that the distinct emission bands from Eu (3+) were measured at each of the 3 excitation lines? earlier figures/tables do not confirm this.
6. Fig. 11 - I believe that the bands marked in yellow and with a question mark are surely the bands from Sm³⁺; in my opinion, the question mark can be removed.

