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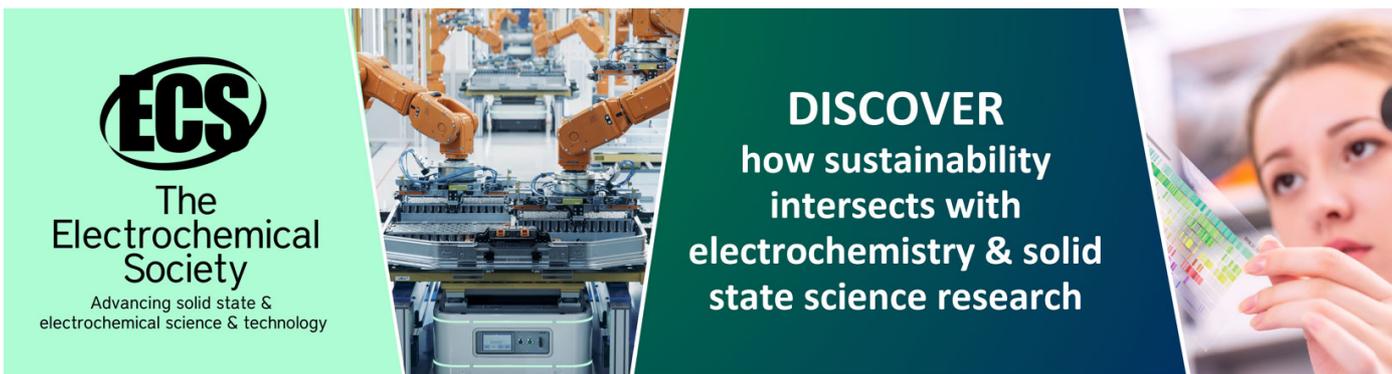
## Preparation of Er-doped $\text{Yb}_3(\text{Al}, \text{Fe})_5\text{O}_{12}$ garnets

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## Preparation of Er-doped $\text{Yb}_3(\text{Al}, \text{Fe})_5\text{O}_{12}$ garnets

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**Abstract.** This work focuses on mixed YbAG/YbIG garnet in a progressive substitution Al/Fe, where aluminium and iron occupy the tetrahedral or octahedral cation sites. In addition to it, the prepared garnet samples were doped with erbium that can profit from ytterbium-based matrix increasing so its absorption cross section. Bulk samples of Er-doped ytterbium–aluminium garnet ( $\text{Yb}_{2.94}\text{Er}_{0.06}\text{Al}_{5-x}\text{Fe}_x\text{O}_{12}$ ;  $x = 0-5$ ) were prepared by a sol-gel method based on Pechini process with citric acid and ethyleneglycol as polyesterification agents. The annealing had to be carried out in oxygen atmosphere in order to stabilize  $\text{Fe}^{\text{III}}$  in the phase equilibrium. Photoluminescence in the range of 1450–1650 nm was measured and the influence of iron doping on erbium luminescence properties was established.

### 1. Introduction

Rare earth iron garnets, variably doped with another rare earth ion, are frequently investigated for use in photonic integrated circuits. These magneto-optical oxides, such as  $\text{Ce}:\text{Y}_3\text{Fe}_5\text{O}_{12}$  or  $\text{Bi}:\text{Y}_3\text{Fe}_5\text{O}_{12}$ , possess high Faraday rotation and low optical loss, thereby making them applicable as optical insulators in photonic waveguides for telecommunications [1].

Iron garnets are part of a large family of mixed oxide ceramics with a cubic crystal structure (space group Ia-3d). Their general formula is  $\text{A}_3^{\text{III}}\text{Fe}_5^{\text{III}}\text{O}_{12}$ , where  $\text{A} = \text{Y}, \text{Bi}$  or a rare earth metal [2]. Yttrium-iron garnets ( $\text{Y}_3\text{Fe}_5\text{O}_{12}$  or YIG) were discovered in 1957 [3], since which time iron garnets have been widely studied for their magnetic or electrical properties (ferrimagnetism, high electrical resistivity and thermal conductivity, etc.) [4]. The substitution of other metals at the Fe site in the YIG structure led to a change in the magnetic and electrical properties of the material; for instance, the partial substitution of aluminium for iron was found to decrease the Curie temperature [5]. While  $\text{Y}_3\text{Fe}_5\text{O}_{12}$  remains the most extensively studied iron garnet, with substitutions being performed at both yttrium and iron sites, papers published on other members of the iron garnet family (e.g.  $\text{Yb}_3\text{Fe}_5\text{O}_{12}$ ,  $\text{Ho}_3\text{Fe}_5\text{O}_{12}$  or  $\text{Tb}_3\text{Fe}_5\text{O}_{12}$ ) are rather scarce and focus only on their magnetic properties [6-8].

To extend the use of iron garnets in photonic applications, they can be further doped by an activating luminescent ion. Doping with erbium is suitable for use in the third telecommunication window because of its photoluminescence at around 1530 nm. When the photoluminescence of Er-doped  $\text{Y}_3\text{Fe}_5\text{O}_{12}$  and  $\text{Bi}_3\text{Fe}_5\text{O}_{12}$  thin films was investigated [2], the  $\text{Er}^{3+}$  emission bands at 540 and 980 nm disappeared while the bands in the range 1530–1560 nm remained intensive. This was due to both strong absorption in the broad charge transfer band at lower wavelengths and the sensitizing effect between the  $^4\text{T}_{1g}$  energy level of  $\text{Fe}^{3+}$  and the  $^4\text{I}_{11/2}$  energy level of  $\text{Er}^{3+}$ . Co-doping with ytterbium can



further enhance the absorption cross-section of  $\text{Er}^{3+}$  ions. The energy transfer from the ytterbium  ${}^2\text{F}_{7/2}$  energy level to the erbium  ${}^4\text{I}_{11/2}$  energy level is well known [9] and was also tested in ytterbium aluminium garnets in which ytterbium was both a co-dopant and a constituent part of the matrix [10, 11].

In terms of magnetic properties, exchange interactions were described for undoped  $\text{Yb}_3\text{Fe}_5\text{O}_{12}$  (YbIG) [12-14] and their influence on the splitting of  $\text{Yb}^{3+}$  energy levels in YbIG was reported [8, 15]. For the  $\text{Yb}_2\text{O}_3$ – $\text{FeO}$ – $\text{Fe}_2\text{O}_3$  system [16, 17], phase equilibria were described and four stable ternary phases identified:  $\text{YbFeO}_3$ ,  $\text{YbFe}_2\text{O}_4$ ,  $\text{Yb}_3\text{Fe}_5\text{O}_{12}$  and  $\text{Yb}_2\text{Fe}_3\text{O}_7$ .

However, to our best knowledge, no paper has yet been published about the optical and magnetic properties of Er-doped ytterbium iron or ytterbium iron-aluminium garnets. Here, we present series of Er-doped ytterbium aluminium-iron garnets. The effect on properties is studied across the complete concentration range of Al-Fe substitution in bulk samples with a fixed erbium content:  $\text{Yb}_{2.94}\text{Er}_{0.06}(\text{Al}, \text{Fe})_5\text{O}_{12}$ . To ensure the homogeneous distribution of dopants, the samples were prepared using a sol-gel method based on Pechini polyesterification. The samples were compared by measuring the  $\text{Er}^{3+}$  photoluminescence properties and evaluating their magnetic characteristics.

## 2. Experimental

### *Preparation of samples*

A set of bulk samples of a general stoichiometry  $\text{Yb}_{2.94}\text{Er}_{0.06}\text{Fe}_{5-x}\text{Al}_x\text{O}_{12}$  ( $x = 0, 1, 2, 3, 4, 5$ ) was produced from precursors prepared by a sol-gel process. These samples have a constant content of erbium dopant and differ in the ratio of iron and aluminium atoms; they are labelled according to this ratio (e.g.  $\text{Yb}_{2.94}\text{Er}_{0.06}\text{Fe}_4\text{Al}_1\text{O}_{12}$  is F4A1, etc.)

The method chosen for the precursors' preparation was based on the Pechini patent. As a source of cations,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  (p.a., Honeywell),  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (p.a., Sigma-Aldrich),  $\text{Yb}(\text{CH}_3\text{COO})_3 \cdot x\text{H}_2\text{O}$  (99.9%, Strem Chemicals) and  $\text{Er}(\text{CH}_3\text{COO})_3 \cdot x\text{H}_2\text{O}$  (99.9%, Strem Chemicals) were used. Citric acid (p.a., Lach-Ner) and ethylene glycol (p.a., Penta) were used for the polyesterification reaction. The chlorides were dissolved in water to a concentration of approx. 10 g of Al per L and 15 g of iron per L; the actual concentration was measured by means of gravimetry. The acetates were dehydrated by heating at 200 °C for 12 hours prior their use.

First, citric acid was dissolved in the aqueous solution of  $\text{Al}^{3+}$ . The aqueous solution of  $\text{Fe}^{3+}$  was then added, followed by solid dehydrated acetates of ytterbium and erbium. After all solid was completely dissolved, ethylene glycol was added and the mixture was magnetically stirred for 30 minutes. Water was evaporated at 85 °C and then the temperature of the mixture was elevated to 130 °C to start a polyesterification process. Amorphous gel was then dried for 2 hours at 240 °C and decomposed at 600 °C (2 hours) and 900 °C (1.5 hours). The precursor was pressed into pellets and sintered at 1250 °C in oxygen atmosphere for 144 hours (the effect of annealing atmosphere was also studied as will be discussed in the Results section).

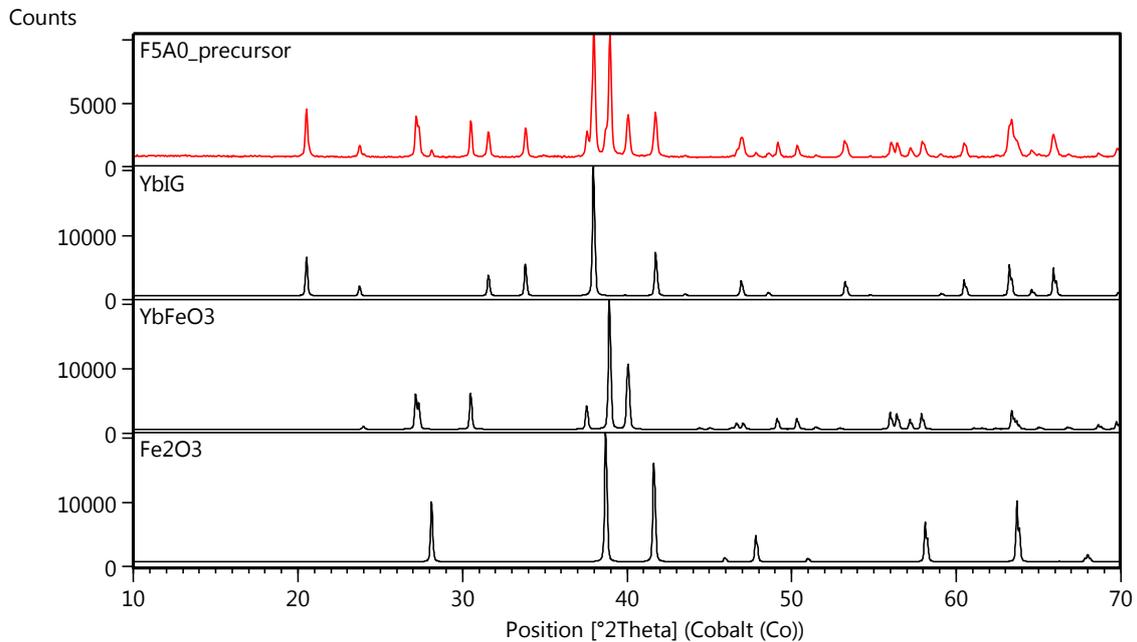
### *Characterization*

The phase composition of the prepared films was determined by XRD analysis. Data were collected at room temperature with Bruker-AXS D2 Phaser powder diffractometer with parafocusing Bragg–Brentano geometry using  $\text{CoK}_\alpha$  radiation in a range of 10–100°  $2\theta$  with a step size of 0.02°. The phase analysis was performed in the HighScore Plus program using the PDF-4 database.

For the photoluminescence (PL) measurement, the excitation radiation of a wavelength of 980 nm emitted by a semiconductor laser POL 4300 was used and the light was processed by a double grated SLD-1 monochromator. Luminescence was detected by a Ge detector J16-2TE (Teledyne Judson Technologies). The spectra were measured in a wavelength region of 1450–1650 nm that corresponds to the  $\text{Er}^{3+}$  transitions from the manifold  ${}^4\text{I}_{13/2}$ . All measurements were carried out at room temperature. For evaluation, all luminescence spectra were transposed to the base level and normalized to a standard sample (an  $\text{Er}^{3+}/\text{Yb}^{3+}:\text{LiNbO}_3$  single crystal used as a reference).

### 3. Results

After the decomposition of precursor powder and prior to annealing, an XRD analysis of precursor phase composition was performed; the results for the sample F5A0 ( $(\text{Yb,Er})_3\text{Fe}_5\text{O}_{12}$ ) are shown in figure 1.

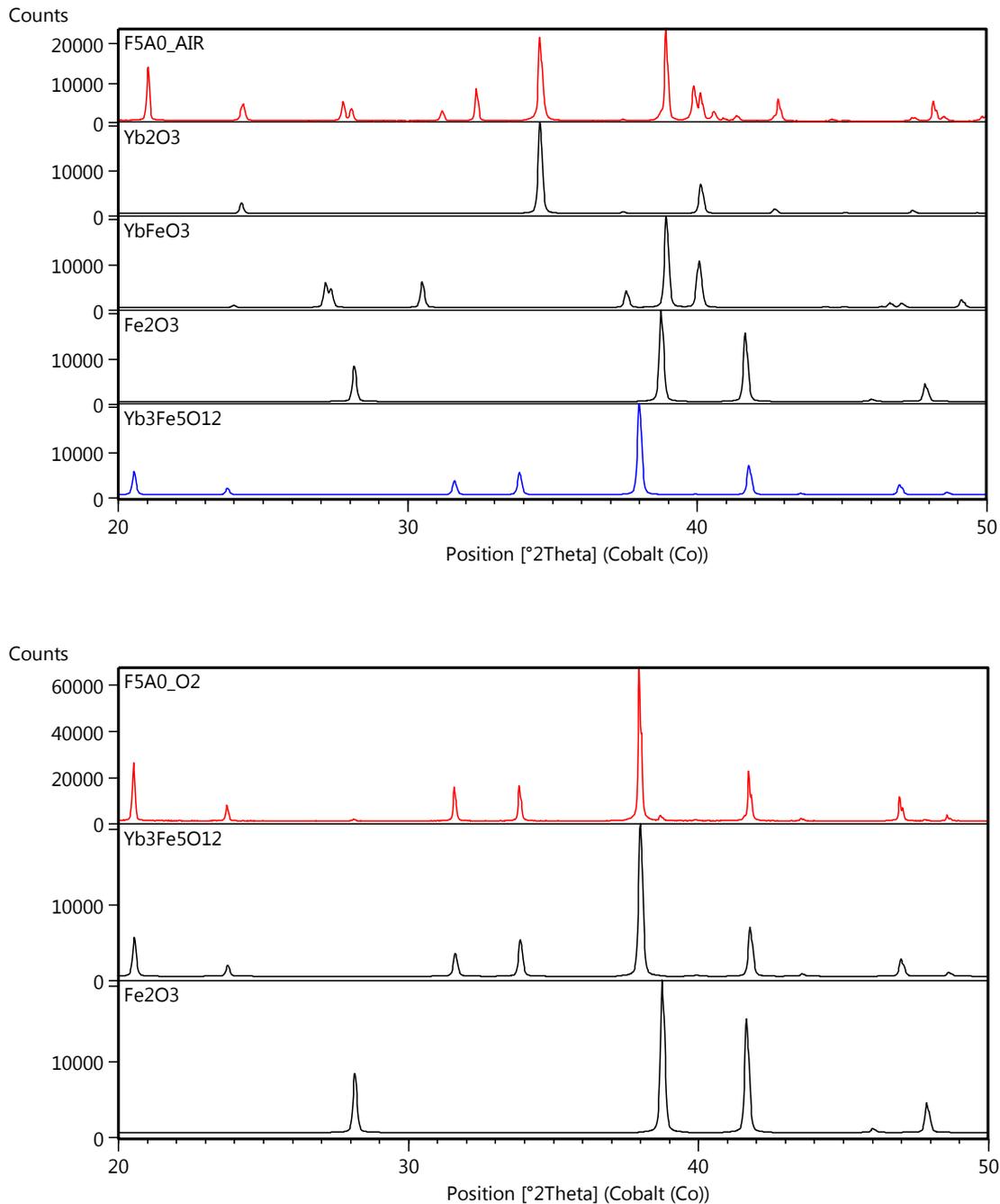


**Figure 1.** XRD patterns of the precursor powder (F5A0) and reference patterns of the identified phases ( $\text{Yb}_3\text{Fe}_5\text{O}_{12}$ ,  $\text{YbFeO}_3$  and  $\text{Fe}_2\text{O}_3$ ).

As can be seen, the precursor contained the desired garnet phase, together with ytterbium-iron perovskite (YbIP) and iron oxide (hematite) already after the gel was decomposed. Here, the advantage of producing highly reactive particles via sol-gel methods is apparent – garnet is formed after 1.5 hours at as low a temperature as 900 °C, while it would need to be annealed for much longer time and at a temperature almost twice as high if solid state reaction was used.

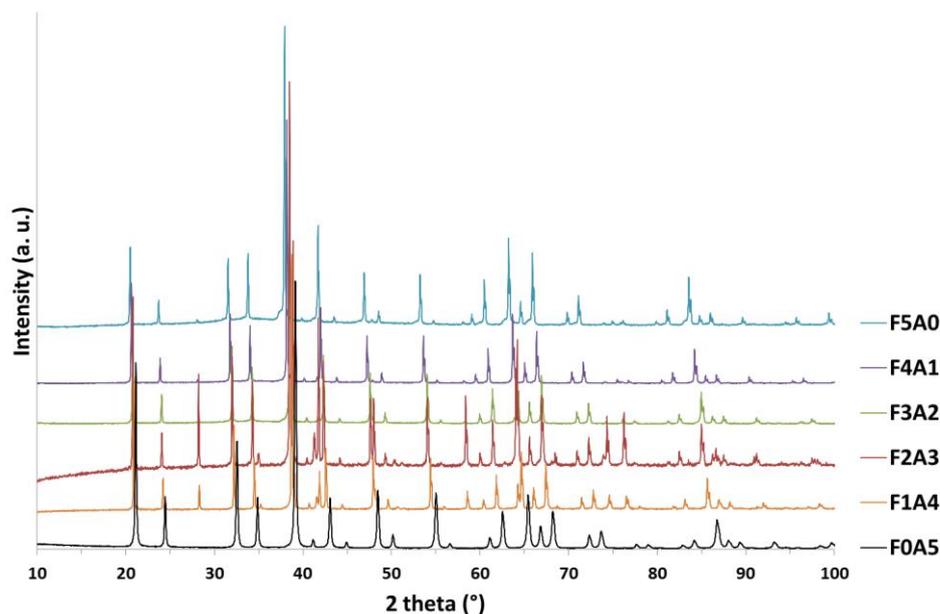
The effect of the annealing atmosphere on the phase composition of final samples was studied as well. The precursor F5A0 was pressed into pellets that were then annealed in air at 1300 °C for 3 days or in oxygen flow at 1200 °C for 4 days. The phase composition of the prepared samples was determined with XRD analysis again (a section of 20–50° of 2theta is shown in figure 2).

Even though the precursor powder contained the YbIG garnet phase, after it was annealed in air, most of it decomposes to YbIP perovskite,  $\text{Yb}_2\text{O}_3$  and iron oxides ( $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  – pattern not included in figure 2). This effect corresponds to the fact that  $\text{Fe}_2\text{O}_3$  tends to decompose at high temperature with a simultaneous reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  [18]. In oxygen flow, on the other hand, almost single phase YbIG was obtained with a small fraction of  $\text{Fe}_2\text{O}_3$  impurity. In order to maintain iron cations in their higher oxidation state, an increased partial pressure of oxygen is necessary. This is why oxygen atmosphere was introduced when the whole series was annealed.



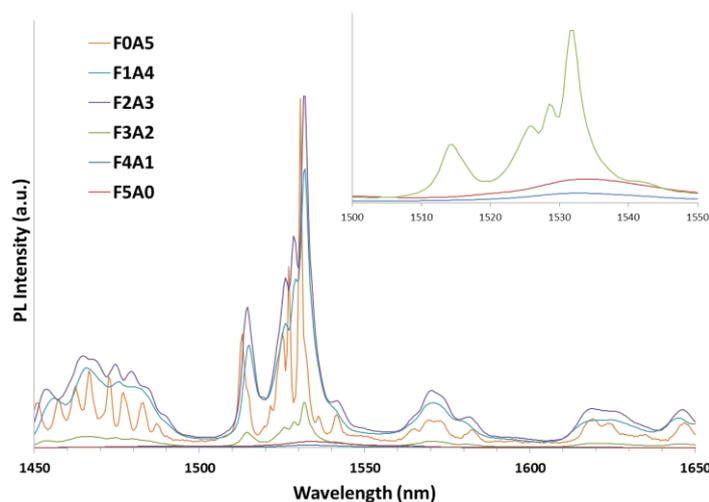
**Figure 2.** XRD patterns of the sample F5A0 annealed in air (left) or oxygen (right).

Figure 3 shows XRD patterns of all prepared samples. Since  $\text{Fe}^{3+}$  cation is slightly larger than  $\text{Al}^{3+}$ , with the increasing content of iron cations the lattice cell parameter increases as well and garnet structure reflections shift towards smaller  $2\theta$  value. All samples contained a small fraction of  $\text{Fe}_2\text{O}_3$  impurity that, based on the Rietveld refinement and subsequent phase analysis, was determined to be around 7.5%. In the Yb/Y-Fe-Al-O system, there are probably competitive processes – garnet vs perovskite thermodynamic stability, the decreasing stability of  $\text{Fe}^{\text{III}}$  with temperature etc. – causing difficulties in the pure-phase YbIG preparation. Nevertheless, for the evaluation of  $\text{Er}^{3+}$  luminescence properties in the  $\text{Yb}_3(\text{Fe,Al})_5\text{O}_{12}$  matrix, the presence of  $\text{Fe}_2\text{O}_3$  phase does not play any role.



**Figure 3.** XRD patterns of all prepared samples

The room temperature emission of erbium cation ( ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$  energy transfer) was measured in a range of 1450–1650 nm; the results of this photoluminescence measurement are shown in figure 4. The sample FOA5, that contains no iron, shows discretely resolved fine splitting that corresponds to the transitions from the  ${}^4I_{13/2}$  manifold and demonstrates homogeneous distribution of doped  $\text{Er}^{3+}$  cations in the garnet matrix and their regular crystal vicinity. When iron is introduced into the garnet matrix, this fine splitting disappears, but, up to 40 % doping of Fe, the PL intensity is comparable with the sample without any iron introduced. The luminescence intensity decreases until it is almost completely lost in samples with the highest content of iron, as shown in the inset of figure 4. The decrease (or disappearance in the case of the highest Fe doping) is probably caused by an energy transfer between  $\text{Fe}^{3+}$  and  $\text{Er}^{3+}$  energy levels that suppresses the radiative transition of erbium ions.



**Figure 4.** Photoluminescence of the samples (samples with weaker emission (F3A2–F5A0) shown in the inset)

#### 4. Conclusion

Bulk samples of a general stoichiometry  $\text{Yb}_{2.94}\text{Er}_{0.06}\text{Fe}_{5-x}\text{Al}_x\text{O}_{12}$  ( $x = 0-5$ ) were prepared via Pechini-based polyesterification. The oxygen atmosphere was used to stabilize the higher oxidation state of Fe and to prevent the decomposition of the garnet phase during annealing. Prepared samples were almost single phase garnets with a small fraction of  $\text{Fe}_2\text{O}_3$  impurity. Erbium luminescence was studied in the ytterbium garnet matrix. With the increasing content of iron, the intensity of emission is comparable with an un-doped sample up to 40 % iron content and then it decreases down to the full loss of erbium  $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$  energy radiative transition (in the case of 80 and 100 % iron doping).

#### Acknowledgment

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