Mössbauer study of iron perovskites of Er, Sm and Nd.

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Abstract. In solid state chemistry the perovskite structure is very important due to their interesting technological properties between this as ceramic pigments. In this work we present the synthesis of ErFeO₃, SmFeO₃ and NdFeO₃. Its characterization by X-ray diffraction, SEM, energy dispersive X-ray analysis and Mössbauer spectroscopy was performed. Energy dispersive X-ray analysis on the compounds was also conducted to confirm the assumptions made from X-ray diffraction results as well as Mössbauer spectroscopy showing the iron as Fe (III).

1. Introduction
A number of LnFeO₃ perovskites have been reported in 1960 years in relation to their magnetic properties and Mössbauer studies and were obtained by the ceramic method from the oxides Ln₂O₃ and Fe₂O₃ and heated to 1380-1420°C for 16h in air [1-4]. In the last years are reported as chemical sensors, in particular SmFeO₃ [5], and the development of ceramic pigments as LaFeO₃ and HoFeO₃ because have high temperature stability and colorimetric properties in the reddish range color. [9]

In this work the ferrites of Erbium, Samarium and Neodymium were synthesized by precursor method from 800°C to 1300°C with the idea of using them as ceramic pigments. These perovskites present reddish colors and great stability and resistance under high temperature and corrosive atmosphere during firing. Their perovskite structures were established by powder X-ray diffraction, their morphology and size particles were determined by SEM, their elemental analysis by EDX and the iron oxidation state by Mössbauer spectroscopy.

2. Experimental
The LnFeO₃ (Ln = Er, Sm, Nd) were synthesized using Ln (NO₃)₃·H₂On. They were heated to dryness in a stove at 110°C; once dry they were weighed and dissolved in deionized water and gauged to 100ml. Aliquots of each were taken and the stoichiometric amounts of FeCl₃·6H₂O were added in a 1:1 ratio each of them. These samples were put in a platinum crucible and heated to complete dryness in an electric plate. The dry samples were calcined in an electric furnace at 800°C, 1000°C and finally at 1300°C for 12 hours, every time with intermittent grinding in an agate mortar in each of the thermal process.

The X-ray diffraction patterns of these samples were taken with a Siemens D5000 diffractometer using Cu, Ka radiation (λ = 1.5406Å) and a Ni filter in a 5-85° 20 range. Details of the microstructure and morphology were done by a (SEM) scanning electron microscope JEOL model JSM- 5900LV. Energy dispersive X-ray analysis (EDX) shows the microanalysis of the elements in the samples. Mössbauer
spectra were obtained at 77 K using a constant acceleration Austin Scientific Associates S-600 spectrometer and a 370 MBq (10 mCi) $^{57}$Co/Rh source, calibration was carried out using a natural iron foil and the spectra were fitted by using the NORMOS program [8].

3. Results and Discussion

The examination of the X-ray diffractogram of SmFeO$_3$ (see figure 1) is representative of the perovskite structure of these phases: ErFeO$_3$, NdFeO$_3$ with traces of lanthanide oxides. These compounds are isomorphous, their structure is similar and the space group is $Pbnm$ which is a distorted perovskite in where each iron remains essentially octahedral; however the axes of four octahedral sites, equivalent at four iron ions, are in different directions. [1]

![Figure 1. X-ray diffractogram of SmFeO$_3$.](image1)

![Figure 2. Microphotograph of SmFeO$_3$.](image2)

Figure 2 shows a representative SEM micrograph. All have the same morphology and similar particle sizes in the range of 1-2 μm.

Figure 3 shows a typical energy dispersive X-ray spectrum of the erbium compound to confirm the assumptions made from the X-ray diffraction powder results.

The Mössbauer results of Fe$^{57}$ in LnFeO$_3$ (Ln = Sm, Er and Nd) at 77 K, have a characteristic sextet pattern for the three compounds, meaning that all the iron atoms are in equivalent sites, in agreement with the crystallographic structure of these compounds. Figure 4 shows the spectrum for SmFeO$_3$.

![Figure 3. X-ray energy dispersive analysis.](image3)

![Figure 4. Mössbauer spectroscopy of SmFeO$_3$.](image4)
A comprehensive study of the magnetic properties of orthoferrites by M. Eibschütz [3] shows among other things that the internal magnetic field at the iron nucleus does not result only from the iron ion, but it is also influenced by the environment, this effect can be seen in the values given for the magnetic field and the values for the isomeric shift are very close for the three compounds and they are in agreement with the values expected for a 3d⁵ configuration of the Fe⁺³ ion (see table 1).

The quadrupole splitting is proportional to the electric field at the site of the Fe⁵⁷ nucleus and reflects the crystalline structure; bellow the Néel temperature, which is our case (77 K), the quadrupole interaction, is a small perturbation on the magnetic nuclear field and the values for QS are given.

4. Conclusions

The ferrites of erbium, samarium and neodymium were synthesized by precursor method to 1300°C, different to the ceramic method realized to 1420°C, may be was necessary to rise the temperature because the X-ray diffractograms show traces of lanthanide oxides. Nevertheless, these perovskites of Er, Nd and Sm present reddish dark colors increasing the darkness respectively. The micrographics of these pigments show fine particle size and present thermal stability and resistance at high temperature. These qualities give good possibilities of using as ceramic pigments.

Table 1. Mössbauer parameters of the iron perovskites

| Sample    | IS (mm/s) | QS (mm/s) | H/eff (T) | Oxidation state |
|-----------|-----------|-----------|-----------|----------------|
| SmFeO₃    | 0.430±.02 | 0.034±.01 | 55.6      | Fe⁺³           |
| ErFeO₃    | 0.392±.02 | 0.011±.01 | 53.5      | Fe⁺³           |
| NdFeO₃    | 0.422±.02 | 0.101±.01 | 54.4      | Fe⁺³           |

5. References

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