

Marko Robić¹, Mira Ristić¹, Stjepko Krehula¹ and Svetozar Musić^{1,2}

1 - Division of Materials Chemistry, Ruđer Bošković Institute, P.O. Box 180, HR-10002 Zagreb, Croatia

2 - Croatian Academy of Sciences and Arts, Zrinski square 11, 10000 Zagreb, Croatia

Marko.Robic@irb.hr

Introduction

Hematite (α -Fe₂O₃) is the oldest known Fe oxide mineral. Because of its stability, it is commonly found in nature. Hematite can be obtained in a variety of ways. In nature, hematite can be formed by atmospheric weathering of iron ores [1]. On the other hand, the simplest method of preparing hematite in the laboratory is by calcination of oxyhydroxides (such as goethite and akaganeite). Hematite can also be prepared hydrothermally by forced hydrolysis of Fe(III) salts (chloride, nitrate, sulphate, etc.). In this research, hematite is produced by calcination of composite fibres (consisting of organic and inorganic components) obtained by electrospinning method. Electrospinning is a well-known, low-cost method that uses high voltage to produce fibres from various materials such as glasses, polymers, ceramics, etc. The fibres produced by electrospinning can be very thin, resulting in a material with a high specific surface area [2].

It is known that the properties of hematite can be varied in many ways, for example, by changing the particle size and morphology (rods, platelets, cubes). The properties of hematite are also influenced by different dopants. In this study, the influence of Er³⁺ on the Fe oxide phase obtained after calcination is investigated. ErFeO₃ (orthoferrite) and Er₃Fe₅O₁₂ (garnet) were also prepared by electrospinning method. In order to gain a better insight into the properties of the fabricated fibrous ceramics, various characterization methods were applied. These include ⁵⁷Fe Mössbauer spectroscopy, X-ray powder diffraction (XRPD) and electron microscopy (FE SEM).

Experimental

Cation salts: Fe(NO₃)₃ · 9H₂O
Er(NO₃)₃ · 5H₂O
Solvent: ethanol and water
pH adjustment: glacial acetic acid
Polymer: PVP (1 300 000 M)

Electrospinning solution (I)

The solutions of the cation salts were added to the acidified viscous PVP solution; stirred for 3 hours.

Electrospinning (II)

tip to collector distance: 11 cm
flow rate: 1 mL / h
voltage: 20 kV

Drying (III)

laboratory oven
90-110 °C, 24 h

Calcination (IV)

10 °C / min
600-1100 °C, 1-3h

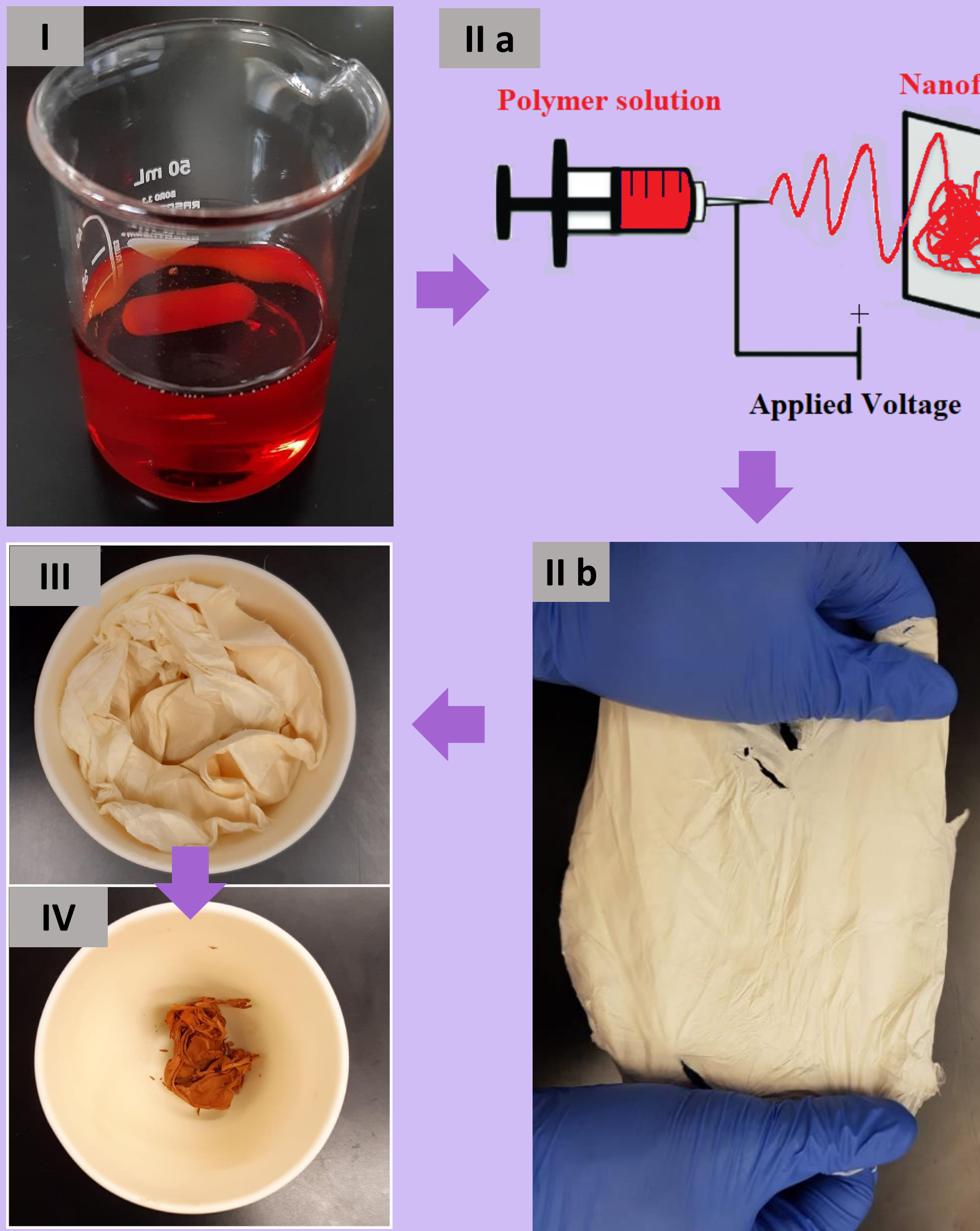


Fig. 1. Electrospinning procedure
I - electrospinning solution (example: Er0)
II a - electrospinning (apparatus)
II b - electrospun (composite) fibre mat (Er5)
III - dried fibres (Er5) in Al₂O₃ crucible before calcination
IV - sample Er5 (after calcination)

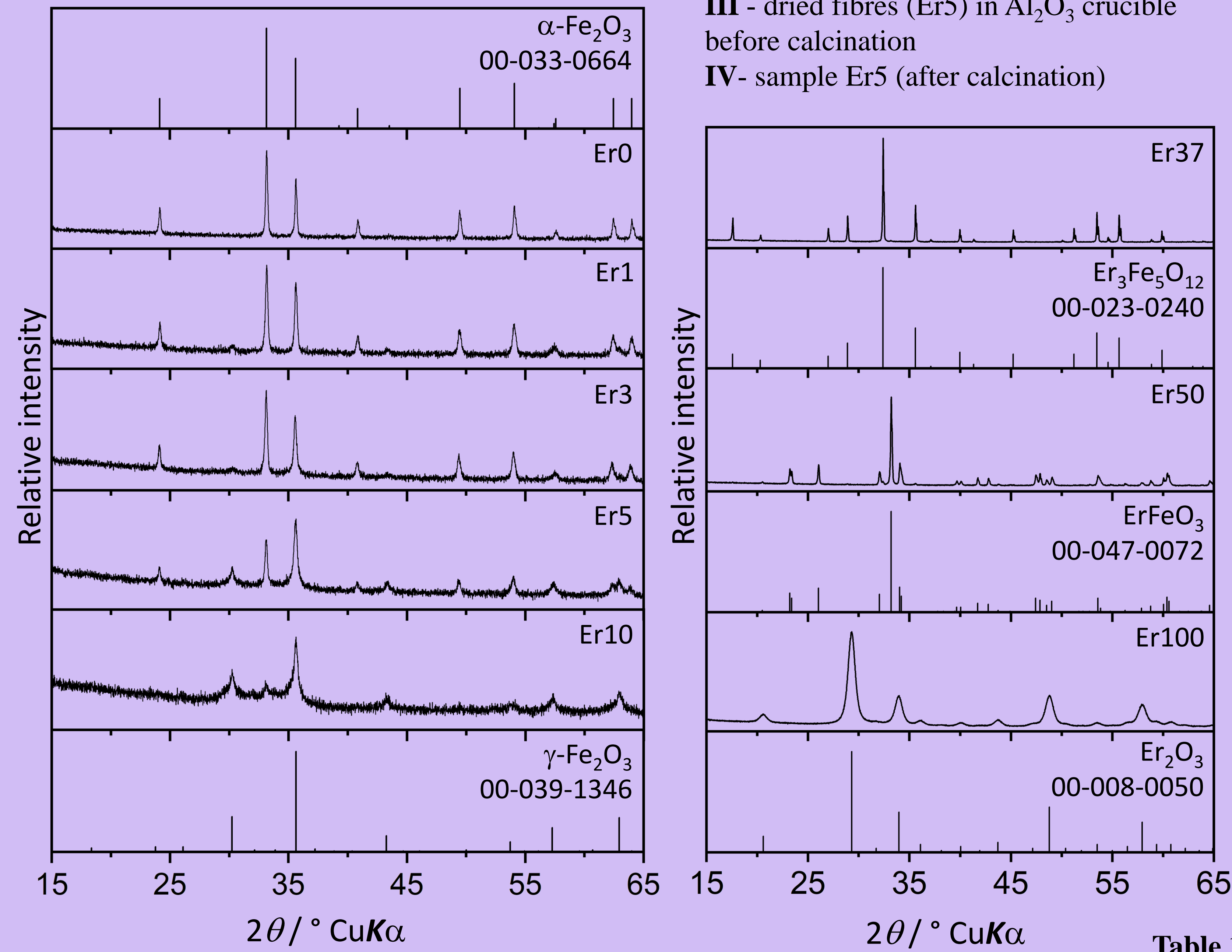


Fig. 2. XRPD patterns of prepared samples.

Conclusions

- Electrospinning has proved to be a very practical method for the preparation of various ceramics. It is possible to synthesize various oxides and their mixtures (α -Fe₂O₃, γ -Fe₂O₃, ErFeO₃, Er₃Fe₅O₁₂, Er₂O₃) by simply varying the ratio of Fe³⁺ and Er³⁺ cations in the initial viscous PVP solution.
- With increasing amount of Er³⁺ in the electrospinning solution, the content of γ -Fe₂O₃ phase increased. A decrease in crystallinity is observed with increasing amount of erbium.
- FE SEM analysis showed that the morphology of the electrospun nanofibres was preserved after calcination of samples Er0, Er1, Er3, Er5, Er10 and Er100, while the morphology was partially preserved for samples Er37 (Er₃Fe₅O₁₂) and Er50 (ErFeO₃).

References

- [1] R. M. Cornell, U. Schwertmann, The Iron Oxides: Structure, Properties, Reactions and Uses, Second ed., Wiley-VCH GmbH & Co KgaA, Weinheim, 2003.
- [2] S. Ramakrishna, K. Fujihara, W. E. Teo, T. C. Lim, Z. Ma: An introduction to electrospinning and nanofibers, World Scientific Publishing Co., Pte. Ltd., Singapore, 2005.

Acknowledgement

This work is financially supported by Croatian Science Foundation (HRZZ), project number IP-2016-06-8254.



Results

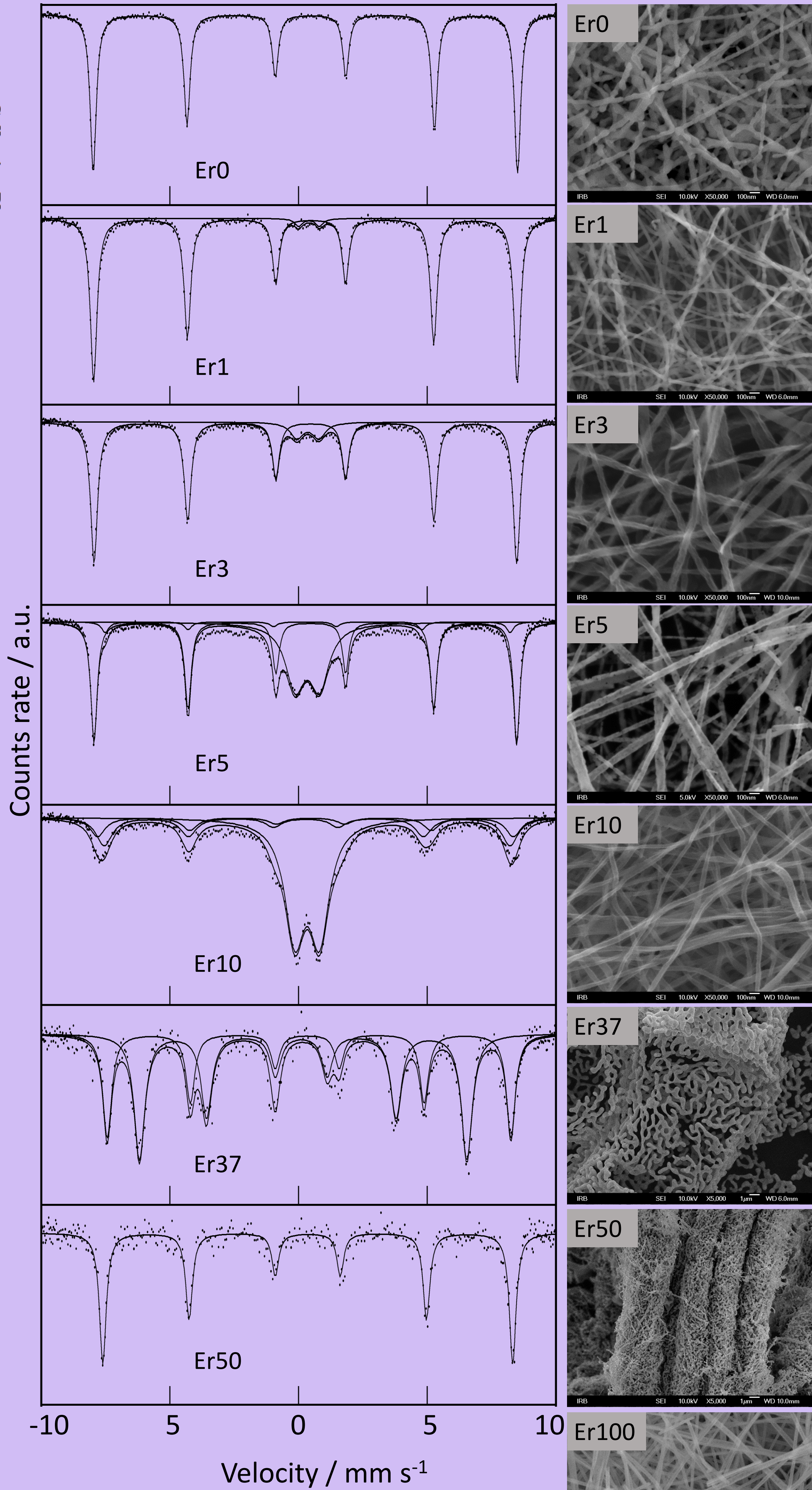


Fig. 3. ⁵⁷Fe Mössbauer spectra of iron-containing electrospun fibres obtained after calcination, recorded at 295 K.

Fig. 4. FE SEM images of the calcined electrospun fibres.

Table 1. ⁵⁷Fe Mössbauer parameters recorded at 295 K.

Sample	Line	δ / mm s ⁻¹	Δ or E_q / mm s ⁻¹	B_{hf} / T	Γ / mm s ⁻¹	Area / %
Er0	<i>M</i>	0.37	-0.21	51.3	0.29	100.0
Er1	<i>M</i>	0.36	-0.19	51.2	0.31	97.7
	<i>Q</i>	0.40	-0.81	-	0.34	2.3
Er3	<i>M</i>	0.37	-0.21	51.1	0.33	91.1
	<i>Q</i>	0.36	0.86	-	0.60 (f)	8.9
Er5	<i>M</i> ₁	0.37	-0.21	51.1	0.30	55.4
	<i>M</i> ₂	0.30 (f)	0.10	48.9	0.32	5.3
	<i>Q</i>	0.34	0.94	-	0.90 (f)	39.3
Er10	<i>M</i> ₁	0.36	-0.20 (f)	50.3	0.69 (f)	15.3
	<i>M</i> ₂	0.31	0.05	49.0	0.74	24.1
	<i>Q</i>	0.33	-0.96	-	0.93	60.6
Er37	<i>M</i> ₁	0.14	0.07	39.5	0.50	59.7
	<i>M</i> ₂	0.37	0.07	48.8	0.41	40.3
Er50	<i>M</i>	0.36	0.00	49.5	0.32	100.0

Key: δ =isomeric shift relative to α -Fe at 295 K, B_{hf} = hyperfine magnetic field, Δ or E_q =quadrupole splitting, Γ =linewidth, *M*=sextet, *Q*=quadrupole doublet, f=parameter is fixed during fitting

Errors: δ and E_q or Δ = \pm 0.01 mm s⁻¹, B_{hf} = \pm 0.2 T