Rietveld structure refinement to optimize the correlation between cations disordering and magnetic features of $CoFe_2O_4$ nanoparticles

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Supplementary material: More details about Rietveld structure refinement, model accuracy, and effectiveness of studied responses

S.1. XRD patterns and corresponding Rietveld structure refinements

In this part, the XRD patterns and corresponding Rietveld structure refinement details of analyzed samples with different parameters of synthesis process are presented. In this work, Rietveld refinement was done using Reflex program on the raw data of X-ray diffraction patterns based on the copper source with wavelength of λ_1=1.540562 and λ_2=1.54439 angstrom in the 2-theta range between 20 and 80 degrees, while the values of I2/I1 and polarization equal to 0.50. In addition, the single monochromator with dhkl and angle values equal to 1.000 angstrom and 50.379129 degree, respectively. The refinement was carried out based on Rietveld type and fine convergence quality. After pattern processing, the refinement was done based on Pseudo-Voigt and Thompson-Cox-Hasting functions for peaks profile and Bragg-Brentano function for line shift and zero point shift corrections. The standard pattern as

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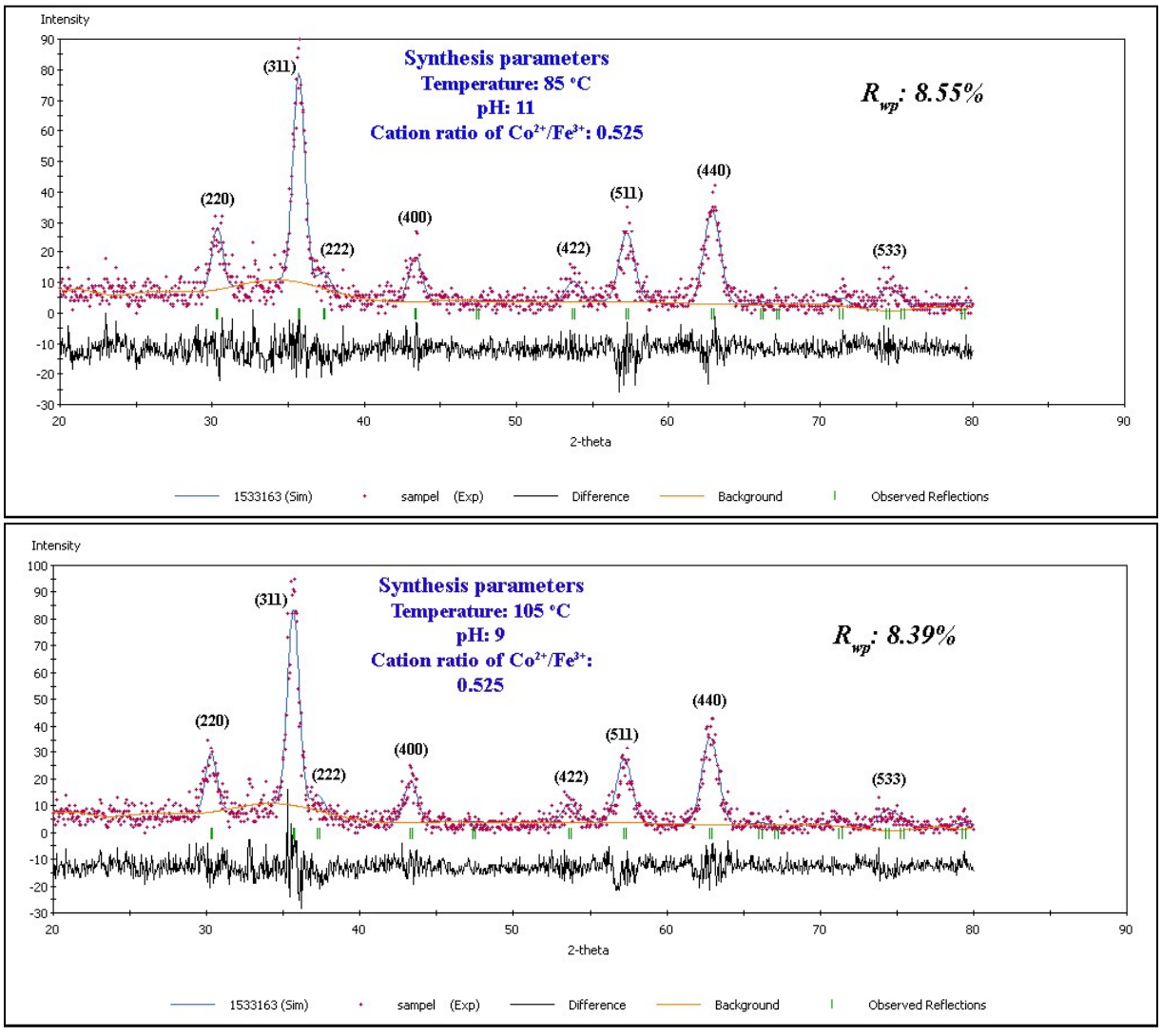
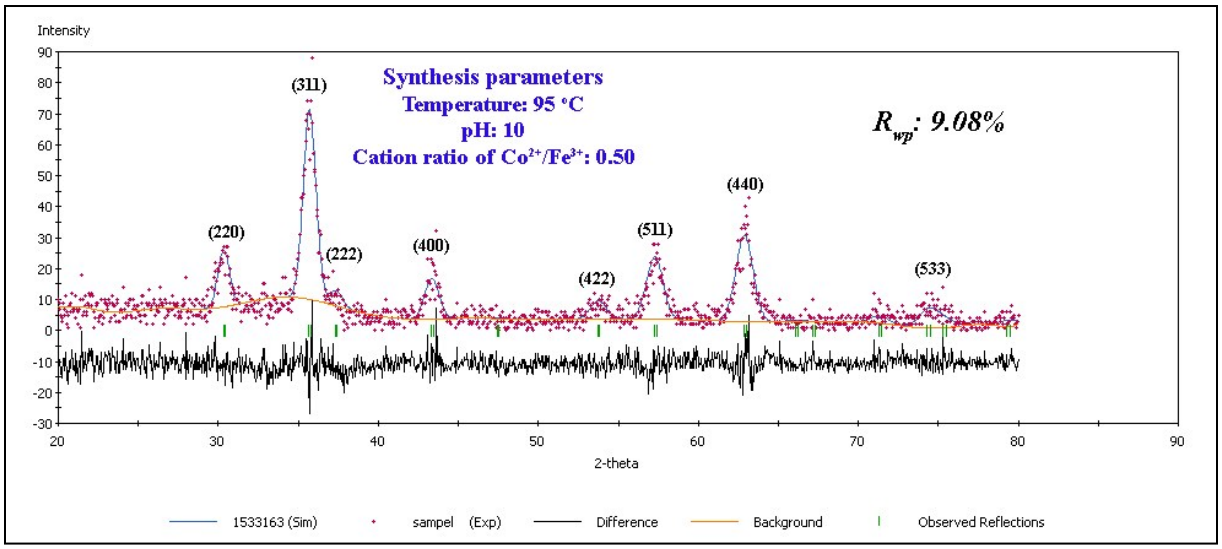
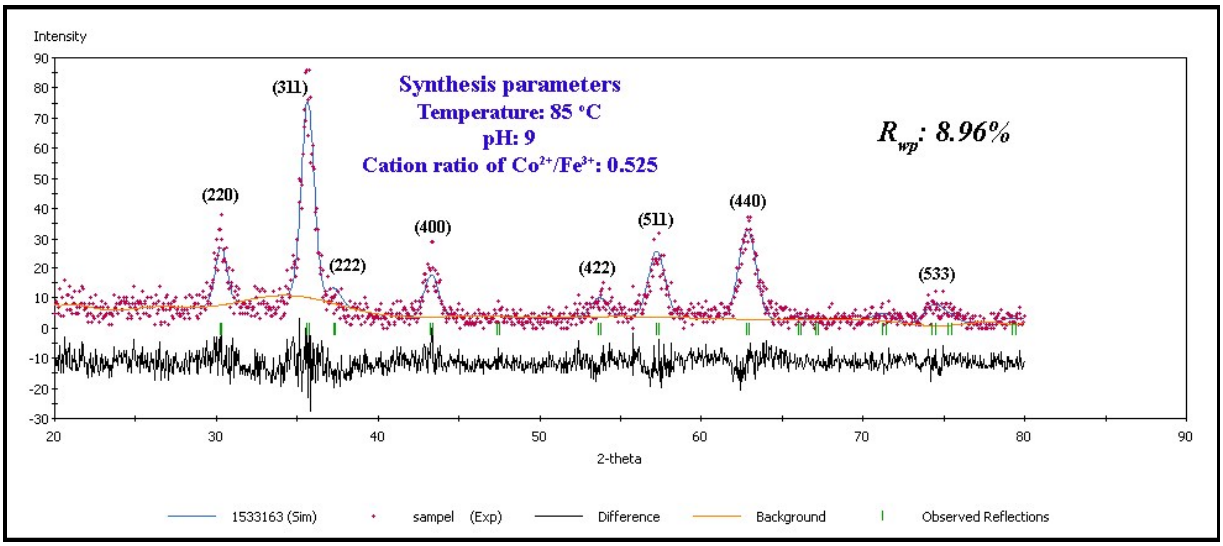
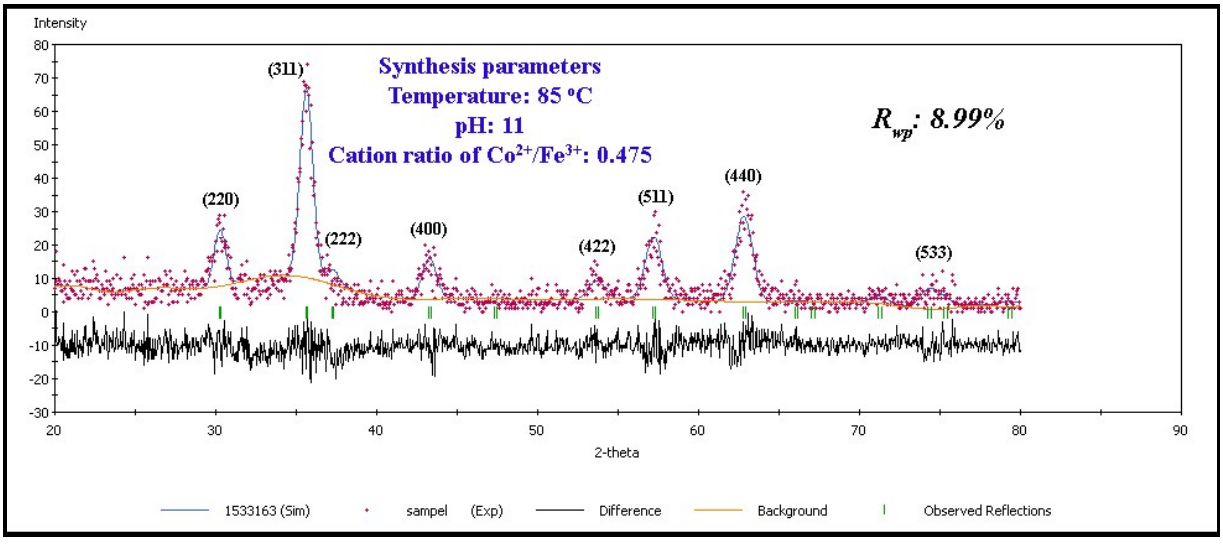
a “CIF” file with number of 1533163 was used as a reference. In addition, the crystallinity degree of samples was determined by using phase analyses approach with comparing of samples patterns with standard background. These processes were done for all designed samples with different parameters of synthesis process such as reaction temperature, pH value of reaction medium, and initial cation ratio of Co^{2+}/Fe^{3+}. The XRD patterns and corresponding Rietveld structure refinement details of some typical samples with different parameters of synthesis process are presented in following. In all of these patterns, the contribution of different parts is clearly determined. Moreover, the values of R_{wp} factor are lower than 10% which confirm the suitable peaks fitting and appropriate refinement.




Intensity
Synthesis parameters
Temperature: 95 °C
pH: 10
Cation ratio of Co2+/Fe3+: 0.50
Rwp: 9.08%
(220)
(311)
(222)
(400)
(422)
(511)
(440)
(533)
2-theta
1533163 (Sim)
sampel (Exp)
Difference
Background
Observed Reflections


Intensity
Synthesis parameters
Temperature: 85 °C
pH: 9
Cation ratio of Co2+/Fe3+: 0.525
Rwp: 8.96%
(220)
(311)
(222)
(400)
(422)
(511)
(440)
(533)
2-theta
1533163 (Sim)
sampel (Exp)
Difference
Background
Observed Reflections


Intensity
Synthesis parameters
Temperature: 85 °C
pH: 11
Cation ratio of Co2+/Fe3+: 0.475
Rwp: 8.99%
(220)
(311)
(222)
(400)
(422)
(511)
(440)
(533)
2-theta
1533163 (Sim)
sampel (Exp)
Difference
Background
Observed Reflections

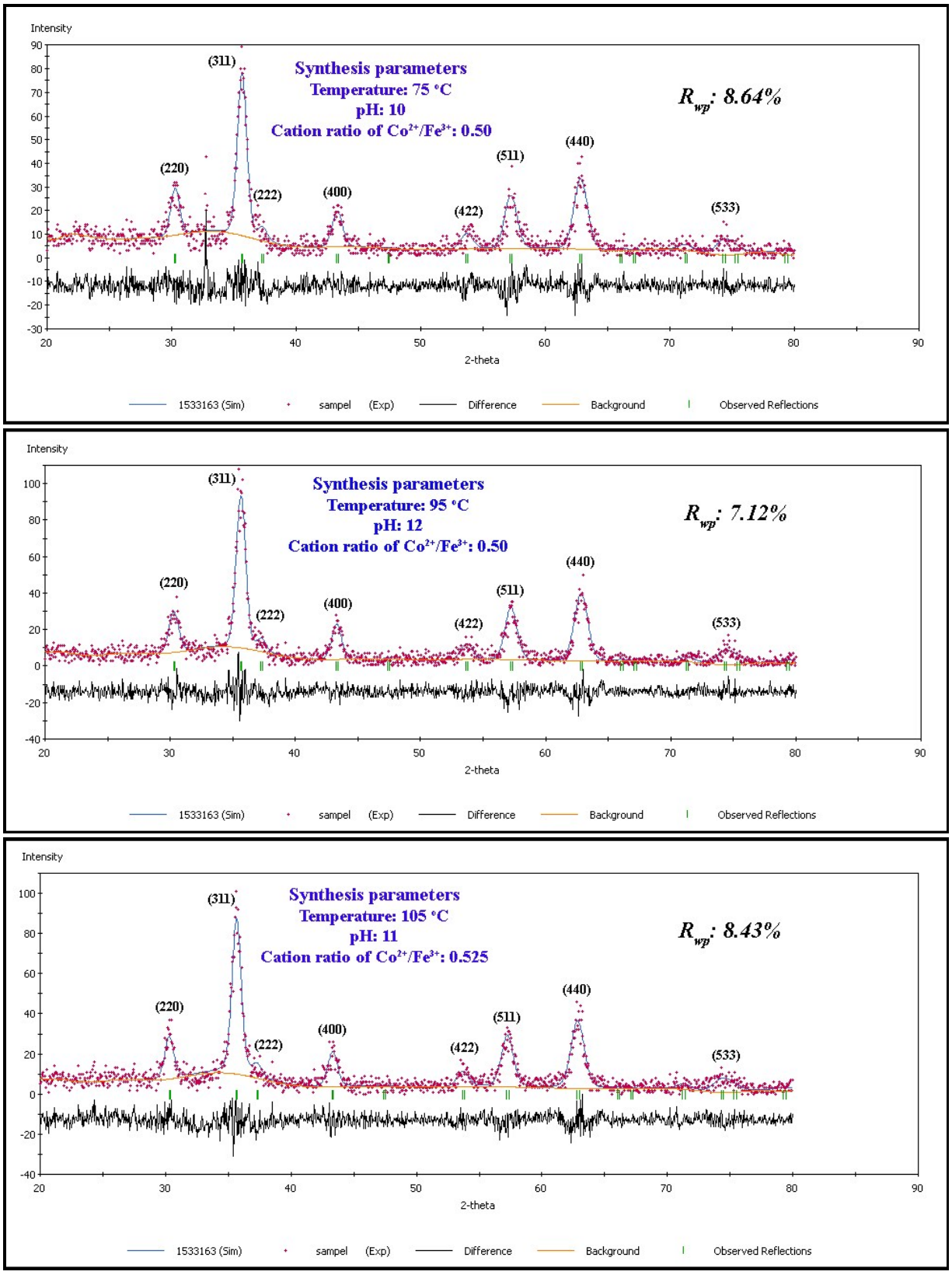


Fig. S1. The XRD patterns and corresponding Rietveld structure refinement details of some typical samples with different parameters of synthesis process fitting by Reflex program (CIF#1533163). The values of R_{wp} factor and synthesis parameters of each sample are presented above of each pattern.

S.2. R-squared diagrams of defined responses

In this part, in order to investigate the accuracy and reliability of suggested models for three defined responses include crystallite size, crystallinity degree, and amount of saturation magnetization ($M_{0.85T}$) as a function of some critical parameters of synthesis method such as reaction temperature, initial pH amount, and initial cation ratio of Co^{2+}/Fe^{3+}, the graphs of relationship between predicted values of each response by suggested model and actual values of these responses can be very useful, while these graphs present the graphically views of R-squared (R^2) amounts. The R^2 graphs for three mentioned responses have been presented in figures S2 (a, b, and c). Based on these graphs, it can be seen the considerable matching between predicted and actual data that confirms the appropriate quality of suggested models [1-3].

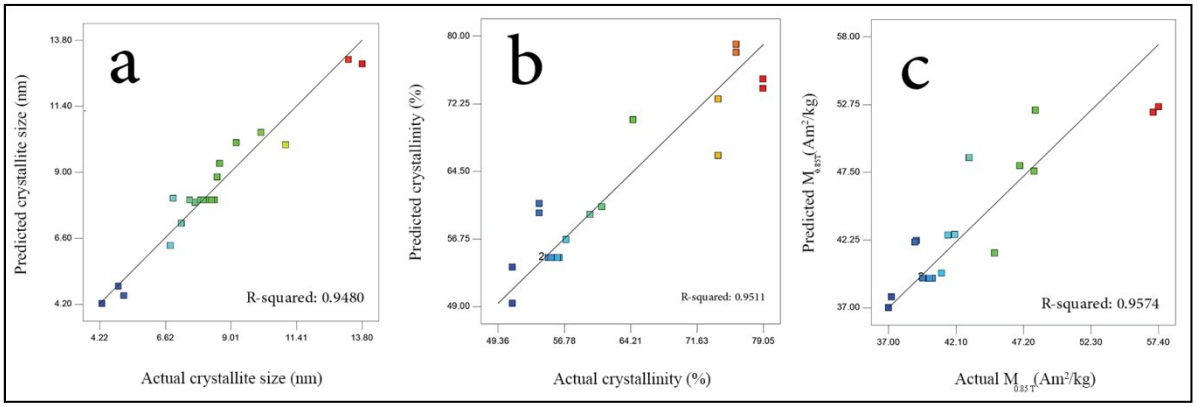


Fig. S2. The R^2 graphs for three mentioned responses. (a) Crystallite size, (b) Crystallinity degree, (c) amount of saturation magnetization ($M_{0.85T}$).

S.3. Model accuracy and factors effectiveness of structural cation distribution

In this part, in order to more accurate study of effectiveness of different term-factors on the response of cation distribution factors (X_B-X_A) in the tetrahedral and octahedral spatial sites in inverse-spinel structure of $CoFe_2O_4$ nanoparticles, the Pareto diagram of effectiveness is showed in figure S3. Accordingly, it is clear that the most influential factor on the structural cation distribution is the initial cation ratio of Co^{2+}/Fe^{3+}, while the reaction temperature and

pH amount have low effects on this response. In addition, among interaction term-factors, the term-factors of temperature interaction with pH amount and initial cation ratio (X_1X_2 and X_1X_3 terms, respectively) illustrate highest effects on cation distribution factors (X_B-X_A). Furthermore, to evaluate the prediction quality of suggested model for this response, it can be presented the R-squared diagram in figure S4. Based on this figure, the matching between predicted and actual values is very considerable [28, 29, 38].

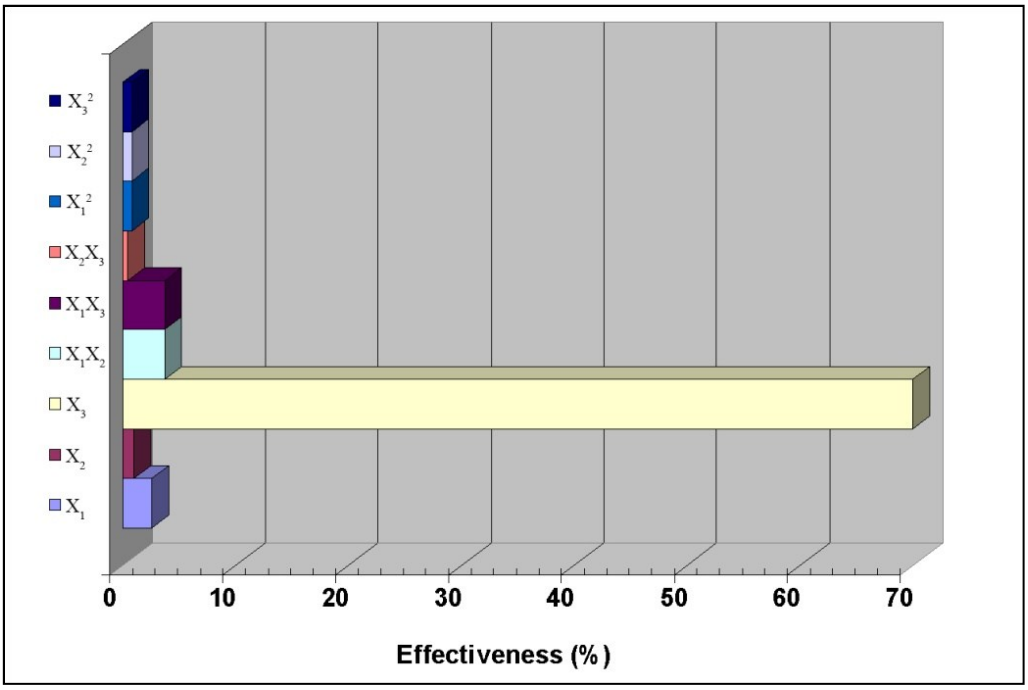


Fig. S3. The Pareto diagram of effectiveness of different term-factors on the response of cation distribution factors (X_B-X_A).

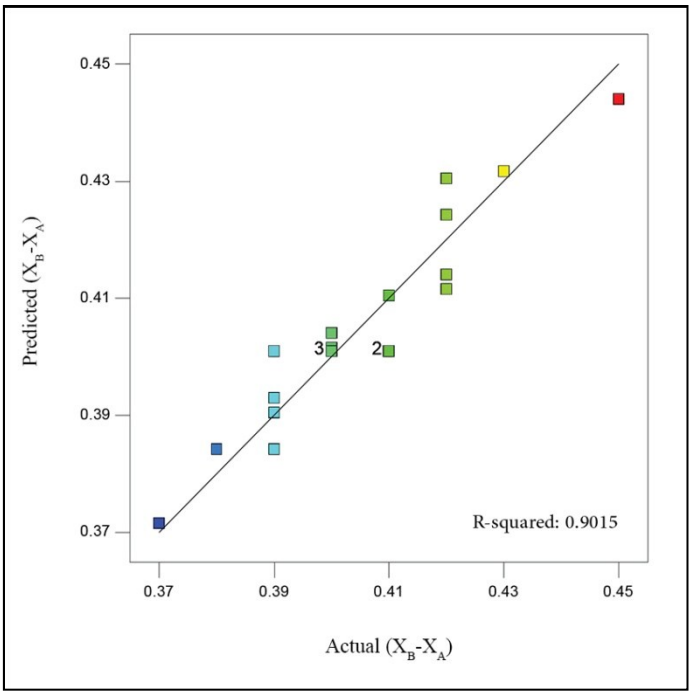


Fig. S4. The R^2 graphs for the response of cation distribution factors (X_B-X_A).

S.4. Correlation model between structural cation distribution and magnetic features

In this research, the response surface methodology (RSM) approach was utilized to study of correlation between structural cation distribution and magnetic features, while the prediction model for saturation magnetization amount ($M_{0.85T}$) is suggested as a function of some essential factors such as crystallite size, crystallinity degree, and cation distribution factors (X_B-X_A). Thus, to evaluate the reliability of this model, the R^2 diagram can be utilized which is presented in figure S5. Based on this diagram, the matching of predicted and actual values is acceptable while the amount of R^2 is located in acceptable level [1-3].

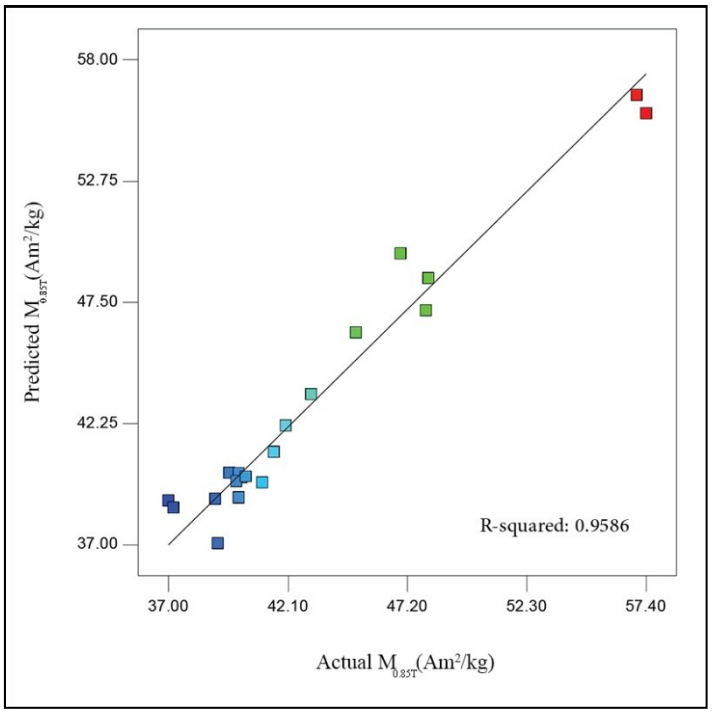


Fig. S5. The R^2 graphs for the response of saturation magnetization amount ($M_{0.85T}$).