



X-Ray Diffraction Investigation of Transition Metal Doped $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ High Temperature Superconductors

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Abstract

X-ray diffraction (XRD) technique was employed to investigate the structural properties of undoped and transition metal doped $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ high temperature superconductors. In the present work, a series of transition metal ions Chromium (Cr), Manganese (Mn), Iron (Fe), Cobalt (Co), and Nickel (Ni) were substituted at the Cu site with the objective of studying their influence on the crystal structure of the $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ system. Samples were synthesised using the conventional solid-state reaction method. Analysis of the XRD pattern of the undoped sample confirms the formation of the orthorhombic Er 123 superconducting phase. The doped samples exhibit slight variations in peak positions, intensities, and broadening compared with the undoped sample. These variations indicate the successful incorporation of dopant ions into the crystal lattice of the samples. Comparative analysis of the diffraction patterns reveals that although transition-metal substitution introduces lattice distortions, the fundamental orthorhombic structure of the $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ high temperature superconductors remains preserved.

Keywords: $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ high temperature superconductors; Doping; Lattice distortion; Lattice parameters; Orthorhombicity; X-ray diffraction.

1. Introduction

Superconductivity, first discovered in 1911 by H. K. Onnes, has advanced from mercury's vanishing resistance at cryogenic temperatures to complex high-temperature superconductors capable of operating well above liquid nitrogen levels [1]. The advent of cuprates such as $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) and subsequent families including Bi, Tl, and Hg based oxides revolutionised the field [2–41]. Despite these advances, the mechanisms underlying high- T_c superconductivity remain unresolved, with theories ranging from spin fluctuations to electron-phonon coupling [42–65]. Structural factors, particularly oxygen ordering and lattice arrangements, have proven critical in determining superconducting behaviour, making rare earth barium copper oxides ($\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$) a focal point of research. Within this family, $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Er123) has attracted attention for its structural stability and favourable superconducting characteristics. The Cu–O planes and oxygen ordering in the lattice play a decisive role in its electrical transport properties, while doping at the Cu site with transition metal ions offers a pathway to probe structural modifications and their impact on superconductivity [2–65]. Such doping not only provides insights into pairing mechanisms but also help refine material performance for technological applications. Building on this, X-ray diffraction studies have consistently confirmed that the orthorhombic structure is essential for superconductivity in $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (RE123) systems. While earlier investigations examined undoped and Cr doped Er123 samples, establishing the presence of the orthorhombic

superconducting phase, systematic comparative studies across multiple dopants remain limited. Transition metals such as Mn, Fe, Co, and Ni, with their distinct ionic radii and electronic configurations, are expected to influence the $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ lattice differently. The present work therefore aims to conduct a comparative structural analysis of $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ doped with Cr, Mn, Fe, Co, and Ni using X-ray diffraction technique, thereby advancing understanding of how targeted substitutions shape the superconducting phase.

2. Experimental Method

2.1 Synthesis of Samples

Polycrystalline samples of undoped and transition-metal-doped $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ were synthesised using the conventional solid-state reaction method [63-66]. High-purity precursor powders of Er_2O_3 , BaCO_3 , and CuO (99.99%) were used as starting materials. For the undoped $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ sample (total batch mass of 5.0 g), the precursor masses were calculated stoichiometrically as follows:

- Er_2O_3 : 1.285 g
- BaCO_3 : 2.651 g
- CuO : 1.603 g

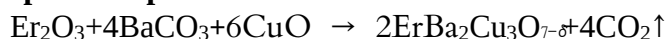
For the doped compositions, transition-metal ions were substituted at the Cu site according to the general formula: $\text{ErBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-\delta}$ $x=0.2$. Where $\text{M}=\text{Cr, Mn, Fe, Co, or Ni}$. Doping was restricted exclusively to the copper site, while erbium and barium concentrations were kept unchanged. All doped compositions were prepared for a fixed total batch mass of 5.0 g. The CuO content was reduced according to the substitution level ($x=0.2$), and a corresponding stoichiometric quantity of dopant oxide was introduced.

The calculated precursor masses for each doped composition were:

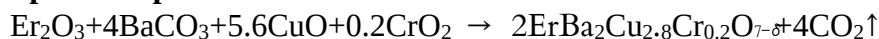
- Cr-doped ($\text{ErBa}_2\text{Cu}_{2.8}\text{Cr}_{0.2}\text{O}_{7-\delta}$): $\text{Er}_2\text{O}_3 = 1.296$ g, $\text{BaCO}_3 = 2.676$ g, $\text{CuO} = 1.294$ g, $\text{Cr}_2\text{O}_3 = 0.309$ g
- Mn-doped ($\text{ErBa}_2\text{Cu}_{2.8}\text{Mn}_{0.2}\text{O}_{7-\delta}$): $\text{Er}_2\text{O}_3 = 1.294$ g, $\text{BaCO}_3 = 2.669$ g, $\text{CuO} = 1.291$ g, $\text{MnO}_2 = 0.353$ g
- Fe-doped ($\text{ErBa}_2\text{Cu}_{2.8}\text{Fe}_{0.2}\text{O}_{7-\delta}$): $\text{Er}_2\text{O}_3 = 1.293$ g, $\text{BaCO}_3 = 2.666$ g, $\text{CuO} = 1.289$ g, $\text{Fe}_2\text{O}_3 = 0.316$ g
- Co-doped ($\text{ErBa}_2\text{Cu}_{2.8}\text{Co}_{0.2}\text{O}_{7-\delta}$): $\text{Er}_2\text{O}_3 = 1.293$ g, $\text{BaCO}_3 = 2.668$ g, $\text{CuO} = 1.287$ g, $\text{CoO} = 0.297$ g
- Ni-doped ($\text{ErBa}_2\text{Cu}_{2.8}\text{Ni}_{0.2}\text{O}_{7-\delta}$): $\text{Er}_2\text{O}_3 = 1.294$ g, $\text{BaCO}_3 = 2.668$ g, $\text{CuO} = 1.287$ g, $\text{NiO} = 0.296$ g

The precursor powders were weighed according to the required stoichiometric ratios and thoroughly mixed using an agate mortar and pestle to obtain a homogeneous mixture. Except for the variation in precursor stoichiometry due to Cu-site substitution, all undoped and doped samples were synthesised under identical experimental conditions. The homogeneous prepared powder mixtures were transferred carefully into acetone-cleaned alumina/silica crucibles. The crucibles were placed at the central zone of a horizontal tube furnace. The furnace temperature was increased gradually from ambient temperature ($\sim 30^\circ\text{C}$) to 900°C , which was reached in approximately 3 hours. The temperature was maintained at 900°C for 24 hours to promote solid state reactions and initial phase formation. The reactions occurring during the initial calcination stage can be represented by the following stoichiometric equations:

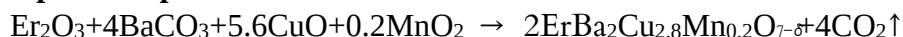
a) Undoped Composition



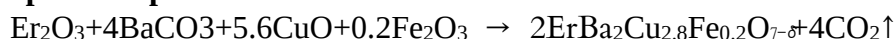
b) Cr doped Composition



c) Mn doped Composition



d) Fe doped Composition



e) Co doped Composition



f) Ni doped Composition



The calcined mass was carefully crushed and reground for 40 to 45 minutes to additionally maintain the homogeneity. The reground powder of compositions was then placed in a silica boat crucible and subjected to a second heat treatment (sintering). The temperature was raised from ambient temperature to 970°C , followed

by natural cooling to ambient temperature. This sintering step enhanced grain growth, densification, and crystalline order. Minor cracking observed after sintering was attributed to thermal stresses developed during heating and cooling. The sintered material was again lightly ground for 30-40 minutes. The fine powder was pelletized using a hardened steel die of 10 mm diameter under a uniaxial hydraulic pressure of approximately 1000-1200 psi. The pellets were placed carefully in silica consist boat crucibles as well as subjected to a final heat-treatment cycle to enhance mechanical stability and microstructural uniformity, making them appropriate for further characterization.

2.2 Characterization of Samples

The structural characteristics of the prepared samples were analysed using X-ray diffraction. This investigation represents a fundamental, non destructive testing technique used for material characterization. The diffraction patterns were recorded over a suitable 2θ range using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). The obtained XRD patterns were analysed to identify crystal symmetry, phase formation, peak positions, and structural changes resulting from dopant substitution. In X-ray diffraction (XRD), Bragg's condition ($n\lambda = 2d \sin\theta$) plays a crucial role in determining the diffraction pattern and interplanar spacing of crystalline high temperature superconductors. The XRD diffraction patterns were recorded over a 2θ range of 20° – 80° with a step size of 0.02° . The obtained diffraction peaks were compared with standard reference literatures and previous studies to identify the phases as well as were indexed as per as the characteristic planes of the $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ structure. The lattice parameters a , b , and c and unit cell volume (V) were calculated from the indexed peak positions using least-square refinement. Structural variations caused by dopant substitution were analysed through changes in lattice parameters, orthorhombicity ($\delta = (b-a)/(b+a)$), and shifts in diffraction peak positions. The crystallite size was estimated from the full width at half maximum (FWHM) of the peaks using the Scherrer equation, which provides information about microstructural characteristics influencing the superconducting properties.

3. Results and Discussion

The structural characteristics of the synthesized prepared samples were examined by X-ray diffraction (XRD), and the diffraction patterns were analysed to determine phase purity and structural changes due to doping. The X-ray diffraction (XRD) patterns of the undoped and transition metal doped $\text{ErBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-\delta}$ ($M = \text{Cr, Mn, Fe, Co and Ni}$; $x = 0.2$) samples clearly confirm the formation of the characteristic $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (RE 123) orthorhombic phase. The diffraction graph patterns indicate well-defined peaks with respect to the characteristic reflections of the Er 123 ceramic structure, peak values such as (013)/(103), (014)/(104), (006), (020), and (213), showing good crystallinity of the synthesised samples. No evident impurity peaks are observed, which was suggesting that the high temperature superconducting samples are principally single phase and that the transition-metal substitution does not significantly disturb the basic crystal structure of the material. The XRD patterns of the undoped and transition-metal-doped samples are shown in Figures 1-6.

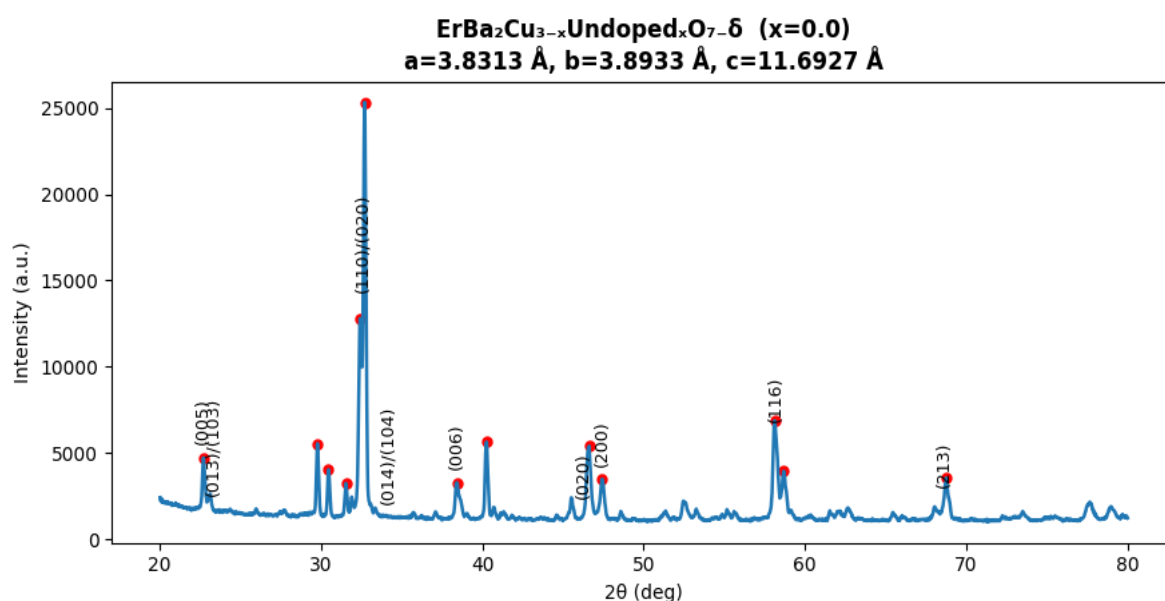


Figure 1: XRD Pattern of Pure $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$

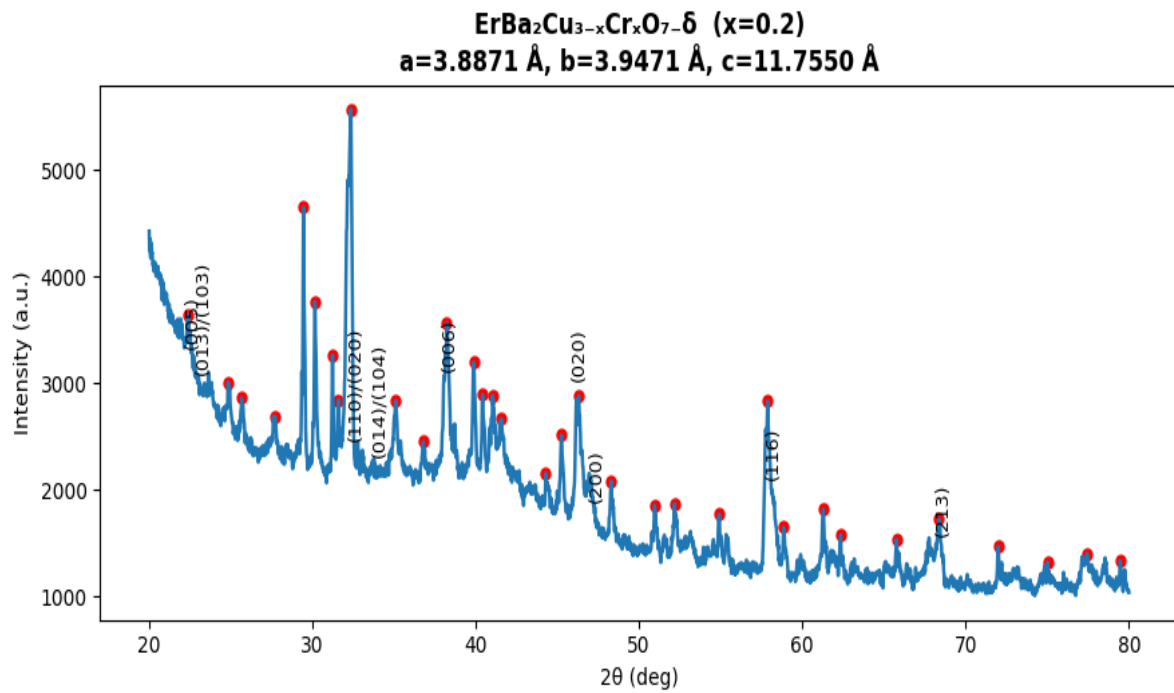


Figure2: XRD pattern of pure $\text{ErBa}_2\text{Cu}_{3-x}\text{O}_{7-\delta}$

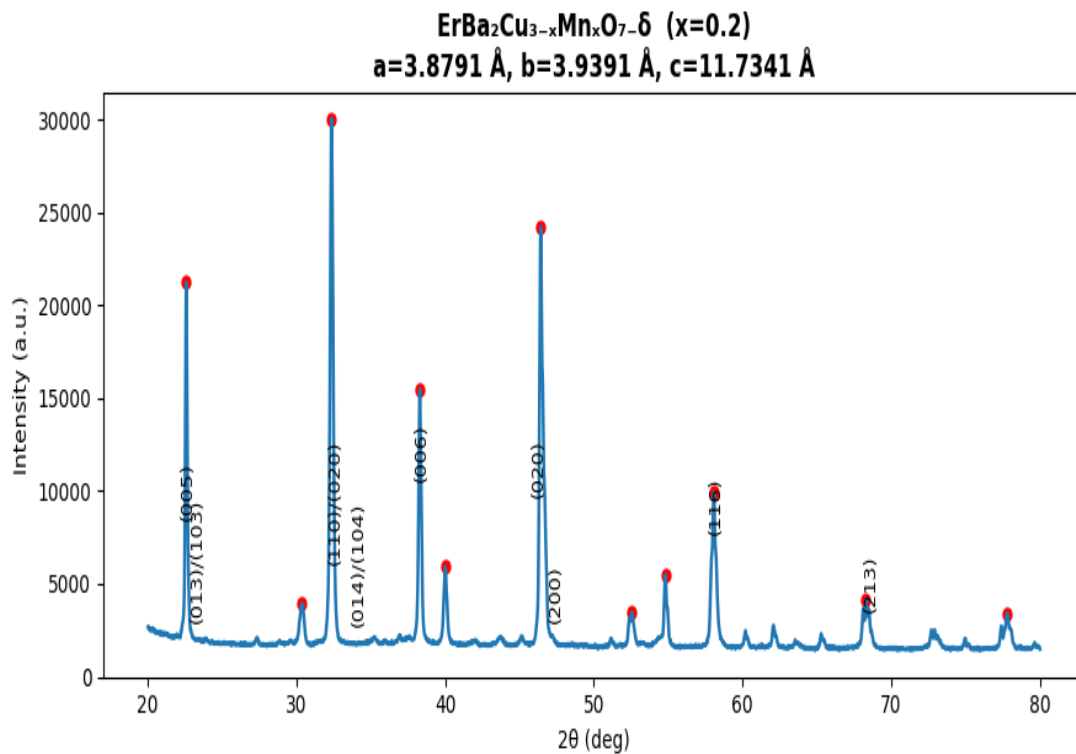


Figure3: XRD pattern of Mn-doped $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

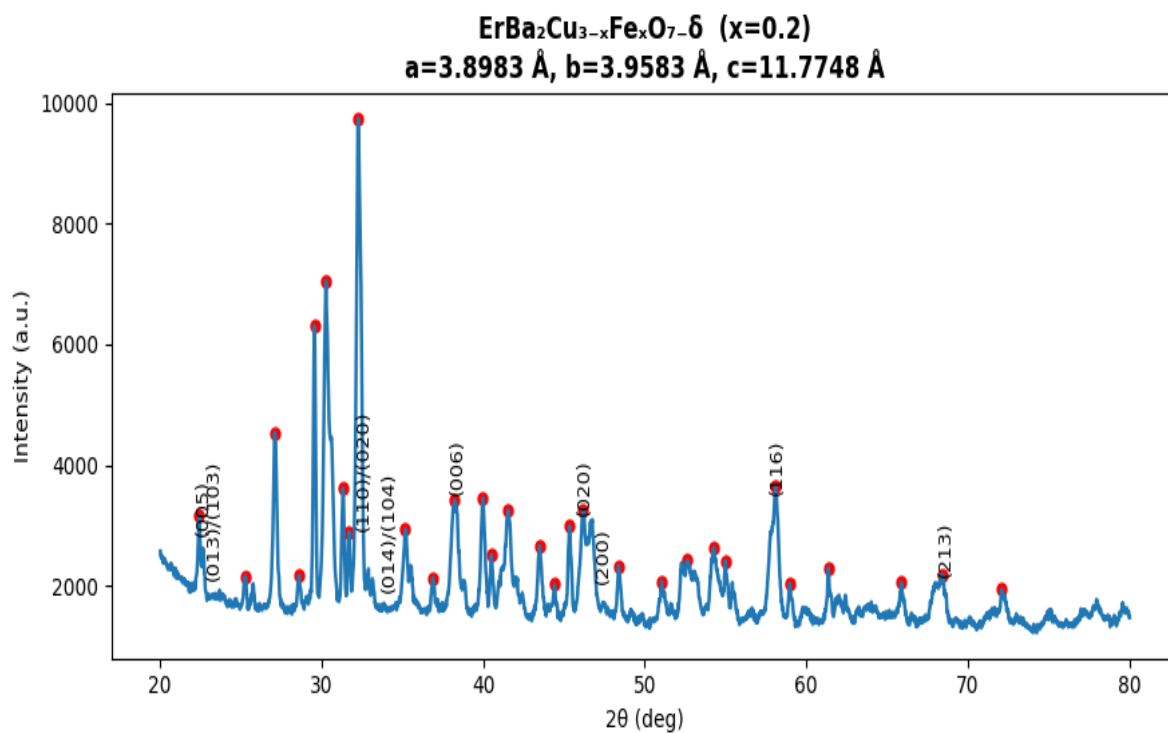


Figure 4: XRD pattern of Fe-doped ErBa₂Cu₃O_{7-δ}.

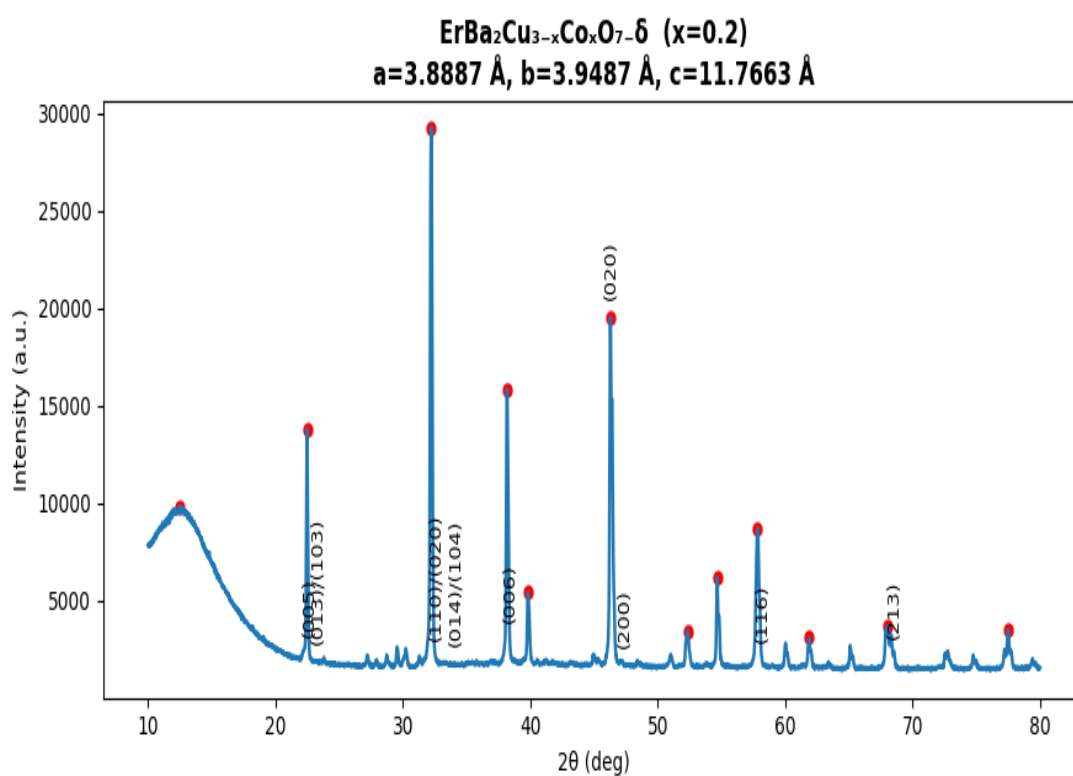


Figure 5: XRD pattern of Co-doped ErBa₂Cu₃O_{7-δ}.

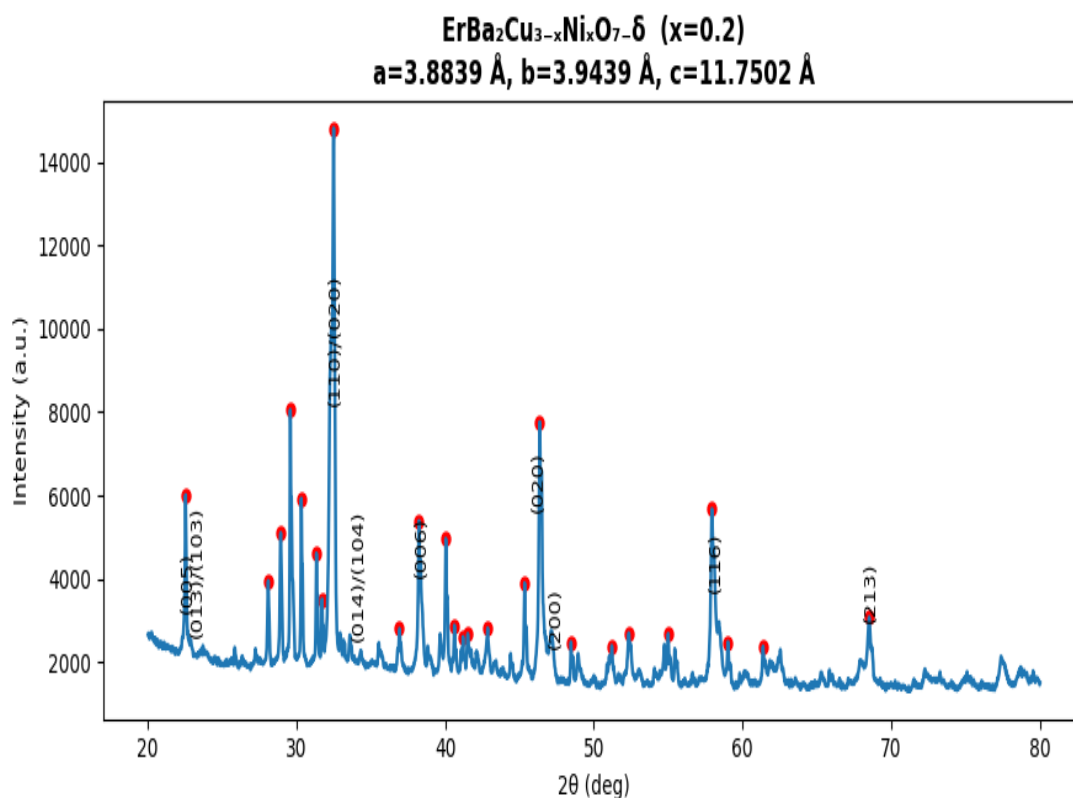


Figure 6: XRD pattern of Ni-doped ErBa₂Cu₃O_{7-δ}.

For the undoped ErBa₂Cu₃O_{7-δ} sample, the calculated lattice parameters are $a = 3.8313$ Å, $b = 3.8933$ Å, and $c = 11.6927$ Å, which are consistent with the described orthorhombic structure of the ErBa₂Cu₃O_{7-δ} high temperature superconducting system. Afterward partial substitution of Cu with transition-metal ions, slight variations in peak positions as well as intensities are observed. These changes arise due to the difference observed in ionic radii between the dopant ions a Cu²⁺, which introduces small lattice distortions. Lattice parameters calculated for undoped and doped samples of Er 123 high temperature superconductors are mentioned in Table 1. The variations in these parameters confirms that the dopants have been incorporated at copper site of the ErBa₂Cu₃O_{7-δ} lattice without significantly affecting the fundamental crystal framework of ErBa₂Cu₃O_{7-δ} high temperature superconductors.

Table 1: Lattice parameters of the samples.

Sample	a (Å)	b (Å)	c (Å)	Orthorhombicity
Undoped Er 123	3.8313	3.8933	11.6927	0.008030
Cr doped Er 123	3.8871	3.9471	11.7550	0.007658
Mn doped Er 123	3.8791	3.9391	11.7341	0.007637
Fe doped Er 123	3.8983	3.9583	11.7748	0.007674
Co doped Er 123	3.8887	3.9487	11.7663	0.007656
Ni doped Er 123	3.8839	3.9439	11.7502	0.007665

Overall, the XRD results reveal that the doping of transition-metal ions at the Cu site leads to minor changes in lattice parameters and small peak shifts in the diffraction patterns due to lattice strain. However, the fundamental orthorhombic crystal framework of ErBa₂Cu₃O_{7-δ} remains intact for all doped samples. This indicates that the transition metal doping modifies the lattice slightly without destroying the structural stability of the Er123 superconducting phase, which may influence the physical and superconducting properties of the material.

4. Conclusion

In this study, undoped and transition-metal-doped $\text{ErBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-\delta}$ ($\text{M} = \text{Cr, Mn, Fe, Co, and Ni}$) samples were successfully synthesised and their structural properties were investigated using X-ray diffraction (XRD) technique. The analysis of diffraction patterns confirm the formation of the characteristic orthorhombic $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Er 123) phase for all samples. The absence of significant impurity peaks indicates that the synthesised samples are predominantly single phase. Slight variations in lattice parameters and small shifts in diffraction peaks were observed after the doping of transition metal ions at the Cu site, indicating the successful incorporation of dopant ions into the crystal lattice. The calculated orthorhombicity values remain non zero for all doped samples, confirming that the orthorhombic structure is preserved despite the introduction of transition metal ions. These results suggest that the transition metal substitution causes only minor lattice distortions without significantly affecting the fundamental crystal framework of $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ high temperature superconductor. Therefore, the structural stability of the Er 123 superconducting phase is maintained, although slight modifications in the lattice may influence the physical and superconducting properties of the material.

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