Comprehensive study of structural, physical, and spectroscopic properties of Co-Ni substituted BaMg$_2$Fe$_{16}$O$_{27}$ W-type hexaferrites

Wasim Tahir$^{a}$, Muhammad Azhar Khan$^{a, b}$, Shagufta Gulbadan$^a$, Abdul Majeed$^{a, b}$ and Khalid Mahmood$^c$

$^a$Institute of Physics, The Islamia University of Bahawalpur, Bahawalpur, Pakistan; $^b$Department of Physics, Bahawalnagar Campus, The Islamia University of Bahawalpur, Bahawalnagar, Pakistan; $^c$Department of Physics, Government College University, Faisalabad, Pakistan

**ABSTRACT**

Cobalt and nickel substituted BaMg$_2$Fe$_{16}$O$_{27}$ W-type hexaferrite nanoparticles were synthesized via citric acid-assisted sol–gel auto-combustion technique. XRD results revealed the single-phase W-type hexagonal structure of these nanomaterials. The decrease in lattice parameters and unit cell volume is accredited to smaller ionic radii of substituted ions as compared to that of host ions. The variations in Raman spectra as a function of substitution content (x, y) are ascribed to the induction of strain in the unit cell. The PL spectra of synthesized samples revealed all emissions invisible (red) regions with PL intensity near 661 nm. Furthermore, the semiconducting nature of synthesized materials has been assessed based on bandgap energy $E_g = 1.875$ eV. FTIR investigations endorsed the successful settlement of substituents at tetrahedral and octahedral sites. SEM images exhibit non-homogenous hexagonal platelet-shaped particles. The research outcomes suggest the promising applications of synthesized compounds with suitable cationic substitution for microwave devices.

1. Introduction

Owing to ferrites unique structural and magnetic characteristics, these are immensely used in numerous applications of technological importance [1,2] such as permanent magnets, magnetism based recording media, electronic appliances, communication gadgets, RAMs, stealth combat aircraft, and high frequency (HF) applications [3]. Hexagonal ferrites have been attracted huge attention due to their high resistivity, high magnetic moment of ferrites are significant beneficial. Environmental safety and chemical resistance are additional undeniable advantages of these substances. Ferrites in nanoform have better qualities than their micro-sized counterparts and are significantly more promising [5,6]. Barium-based hexaferrite has been designated as the most efficient magnetic compound with outstanding structural and magnetic properties [7–9]. Due to dissimilar crystal structures, these ferrites have been categorized into seven classes namely: M-, W-, R-, X-, U-, Y-, and Z-type. The magnetic characteristics of hexagonal ferrites are owing to the super exchange interaction, and they are all ferrimagnetic in nature. W-type hexaferrite has the general formula: $A$Me$_2$Fe$_{16}$O$_{27}$, where $A = $ (Sr, Ba), and Me represent divalent cation (e.g. Co$^{2+}$, Ni$^{2+}$, Mg$^{2+}$, Mn$^{2+}$, Zn$^{2+}$, Cu$^{2+}$ or any other suitable divalent cation), the combination of suitable cations can also be used [10].

The crystal structure of W-type hexagonal ferrites comprises of alternate stacking of S (Fe$_6$O$_8$) and R (BaFe$_8$O$_{11}$) blocks along the c-axis in the sequence RSSR$S^*$S$^*$, where the asterisk (*) symbol designates 180° rotation of the respective block. Here, S stands for spinel block that comprises two oxygen layers and R designates rhombohedral block containing three oxygen layers [11]. Seven different sub-lattices are located in these blocks and are denoted by 12k, 4f$_{IV}$, 6g, 4f, 4f$_{V}$, and 2d. Of these seven sub-lattices, the first four (12k, 4f$_{IV}$, 6g, 4f) own octahedral site, sub-lattice 2d has special bipyramidal site, and the remaining two (4e, 4f$_{V}$) possess tetrahedral site [12].

The simultaneous existence and distribution of trivalent as well as divalent cations amid seven lattice sites fascinate the researchers to investigate W-type hexaferrite for various scientific applications [13] because...
their properties can be tuned by appropriate divalent and trivalent cationic substitution. Various factors like preparation technique, type of substitution, substitution content, and sintering temperature greatly affect the structural, electrical, and magnetic characteristics of W hexaferrites [14]. EM materials, a combination of magnetic filler and polymer, can decline electromagnetic interference (EMI) effectively, and W hexaferrite can be utilized as high-frequency magnetic fillers because of their substantial magnetic loss at FMR point [15,16].

Because, un-substituted ferrites do not have the characteristics needed for a specific application, the replacement of divalent or trivalent metal ions in hexaferrites has a lot of promise. Such replacements assist a lot with resistivity, permittivity, permeability, and magnetic properties including saturation magnetization ($M_s$) and magnetic coercivity ($H_c$), which are important for high-frequency applications. The magnetic, electrical, and dielectric characteristics of microwave absorbers may be affected by the chemical composition and crystal structure of ferrites. W-type hexaferrites are prospective microwave absorbent materials due to their soft magnetic character. Many individuals have examined W-type hexagonal ferrites because they have good magnetic and electromagnetic characteristics [17,18].

Raman spectroscopy is a non-destructive characterization tool that has been used by many researchers for vibrational analysis of various spinel ferrites as well as M-type hexaferrite with powdered, pellet, or film-shaped samples [19–23]. However, to the best of our knowledge, not any noteworthy Raman spectroscopic work has been reported for W-type hexaferrite except R. Sagayaraj et al. [24].

In BaMg$_2$Fe$_{16}$O$_{27}$, the divalent magnesium ions are positioned at tetrahedral and octahedral sites of spinel block, while barium ions are located in R-block [25]. The effect of Ni substitution on magnetic and dielectric properties of BaCo$_2$ W-type hexaferrite has been investigated by A. M. Abo El Ata et al. [26]. With Ni substitution, the optimized X-band microwave characteristics of ZnFe$_2$O$_4$ have been reported [27]. Recently, antibacterial activity of Zn substituted BaCu$_2$ W-type hexaferrite nanoparticles has been reported and published [24].

M. H. Won and C. S. Kim mentioned the fabrication of material through the replacement of Co by Ni in Ba$_2$Co$_2$ Y-type hexaferrite, that can be used in antenna applications (GHz range) [28]. Imran Khan et al., probed the Nd-Ni substitution effect in SrCo$_2$W hexaferrite showing the potential of their fabricated materials for high-density recording media [29]. Majid Niaz Akhter et al. found the enhancement in saturation magnetization, remanence, and coercivity with the increment in Ce$^{3+}$ substitution level in Ce-substituted Cu nanoferrite materials. Additionally, the maximum value of saturation was measured using law of approach (LOA). They looked at several features of Ce-substituted Cu nanosized ferrites having different characteristics as potential material for core, security, sensing, switching, multilayer chip induc- tor, microwave absorption and biomedical applications [30]. Majid Niaz Akhter and M. Azhar Khan [31] prepared Ce substituted Ni-Zn spinel ferrites. According to them, the reduction in saturation magnetization, remanence, initial permeability, and Bohr magneton was observed whereas the enhancement in coercivity with Ce$^{3+}$ substitution. The increment in Yafet and Kittel (Y-K) angles were found with Ce substituted NiZn nanoferrites from $x = 0$ to $x = 0.04$ correspondingly. The evaluation regarding switching field distribution (SFD) for Ce substituted NiZn nanoferrites was calculated by taking first derivative of the demagnetization data accordingly. M. N. Akhter et al. [32] proposed synthesis of spinel ferrites with Pr substitution, and observed decrement in magnetic saturation, coercivity, remanence as well as anisotropy constant with Pr concentration in Cu spinel ferrite. However, Y–K angles were enhanced with Pr substitution level in Cu spinel nanoferrites. The evaluation of microwave frequency response was done that established the application of these Pr substituted Cu spinel nanoferrites in the range of 5.2–9.5 GHz correspondingly. These Pr doped Cu spinel nanoferrites’ characteristics suggested that they may be employed in microwave devices, memory devices, and recording media. M. N. Akhter et al. [33] prepared Co-Ce based spinel ferrites with Cu-substitution. They found reduction in the magnetic parameters including saturation magnetization, remanence, coercivity, Bohr magnetic moment and anisotropy constant of the Cu doped Co–Ce nanoferrites were decreased. However, Yafet-Kittel (Y-K) angles were found to be enhanced with Cu doped Co–Ce nanoferrites. The saturation data of the samples was also used to examine the high frequency response of the Cu substituted spinel nanoferrites in the microwave region. All the Cu doped Co–Ce nanoferrites samples were suggested to be used in microwave for X-band regime. M. N. Akhter et al. [34] proposed the preparation of Rare earths (Res) substituted Mn spinel nanoferrites having chemical composition Mn${_2}$Co$_{16-x}$Fe$_{x}$O$_{4}$ (Res = Tb, Pr, Ce, Y and Gd) using sol gel method. They found the enhancement in saturation magnetization from 1.332 to 38.097 emu/g whereas increment in remanence was observed from 1.096 to 25.379 emu/g correspondingly. Other magnetic characteristics including initial permeability, magnetic anisotropy, and magnetic moments were also improved. Furthermore, with Res doping in Mn ferrites, Y–K angles exhibited a substantial reaction.

In this research article, by keeping iron content constant, we have substituted Mg$^{2+}$ ions with Ni$^{2+}$ ions, and replaced Ba$^{2+}$ ions by Co$^{2+}$ ions. It was also established that the addition of Co$^{2+}$ and Ni$^{3+}$ cations enhanced and changed the structural, spectroscopic, electric, and magnetic characterizations. Different methods have been utilized for the preparation of ferrites, such as micro-emulsion, aerosol pyrolysis, rotary
evaporation, sol–gel auto-combustion, and co-precipitation [35]. The sol–gel auto-combustion method is applied for the synthesis of W-type hexaferrite with the composition \( \text{Ba}_1-x\text{Co}_x\text{Mg}_2-y\text{Ni}_y\text{Fe}_{16}\text{O}_{27} \) because of its various advantages including excellent chemical homogeneity, low synthesis temperature, energy efficiency, atomic level precursors’ mixing, low cost, facile operation, narrow-size distribution, short reaction time, and extraordinary purity of samples as well as the simplicity of method, highest crystallinity, and high surface area of particles [17,36–38]. The key motivation of the present study is to synthesize W-type hexaferrite nanoparticles substituted by Co-Ni that were not reported earlier with best of our knowledge.

A comprehensive structural study was carried out using the XRD technique. Moreover, the substitution effect of (Co, Ni) ions on spectroscopic and optical properties of \( \text{BaMg}_2\text{W} \)-hexaferrite have been investigated by FTIR, Raman, and PL spectroscopy.

2. Experimental details

\( \text{Ba}_1-x\text{Co}_x\text{Mg}_2-y\text{Ni}_y\text{Fe}_{16}\text{O}_{27} \) nanoparticles with substitution contents \( x = 0.0, 0.1, 0.2, 0.3, 0.4 \) and \( y = 0.0, 0.2, 0.4, 0.6, 0.8 \) were synthesized via sol–gel process owing to extraordinary chemical homogeneity attained by this procedure. For the present compositions, technical grade raw materials; \( \text{Ba(NO}_3\text{)}_2 \) (Merck; 99%), \( \text{Fe(NO}_3\text{)}_3\cdot9\text{H}_2\text{O} \) (Merck; 99%), \( \text{Mg(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} \) (UNI-CHEM; 99%), \( \text{Ni(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} \) (UNI-CHEM; 99%), \( \text{Ni(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} \) (PRS Panreac; 98%) were used. The aqueous solutions using stoichiometric molar amounts of these metallic and nonmetallic nitrates, and citric acid (Chem Lab; 99.5%), were prepared separately with the help of deionized water. From these prepared solutions, stoichiometric volumes were taken and five mixtures were prepared as per samples’ compositions. The presence of citric acid in the ratio 1:1 with metal ions supports the binding of metal ions, lowers the reaction temperature as well as acts as fuel for self-burning of the material. Each resultant solution was stirred and heated to 40 °C to accomplish the chelation process of metallic ions that results in their segregation as well as unvaried distribution. Ammonia liquor is added dropwise to increase solution pH to 7. After neutralization of the solution, each solution is heated to 80 °C along with continuous stirring. After continuous heating plus stirring for 2.5 h, each solution is converted into a viscous gel that undergoes auto-combustion to yield fine powders as the final product. The samples were placed in the laboratory microwave oven at 200 °C for two hours to eradicate any moisture. The powdered samples were grinded in an agate mortar and pestle, and then annealed in a muffle furnace at 1250 °C for 6 h. These powders were then cooled to ambient temperature. Each sintered powder was again grinded for further characterization. Crystallographic probing of samples was done by XRD apparatus (Bruker D8) equipped with CuKα source emitting monochromatic radiations of 0.154 nm wavelength. Optical characterizations were accomplished by employing a Raman spectrometer (MN STEX-PR1100), and a PL spectrometer (MN STEX-PR1100 Daangwoon optron). FTIR analysis of prepared materials was done by FTIR (Bruker Tensor27) spectrometer at room temperature in order to probe the stretched atomic vibrations, and structure as well. To investigate the morphology, shape, and grain size of unsubstituted and substituted \( \text{BaMg}_2\text{WHF}_5 \), scanning electron microscopy (SEM) (Emcrrafts; cube 1100; SK) was employed.

3. Results and discussion

3.1. X-ray Diffraction (XRD) analysis

To investigate the structural characteristics of prepared W-type hexaferrite samples having chemical composition \( \text{Ba}_1-x\text{Co}_x\text{Mg}_2-y\text{Ni}_y\text{Fe}_{16}\text{O}_{27} \) \( x = 0.0, 0.1, 0.2, 0.3, 0.4; y = 0.0, 0.2, 0.4, 0.6, 0.8 \), X-ray diffraction technique was employed. The plot of X-ray Diffraction (XRD) patterns is displayed in Figure 1. The diffraction patterns confirmed the occurrence of the W-type hexagonal phase (ICDD # 01-078-0134) in all fabricated samples exhibiting the fine atomic level blending of entire integrant elements via the sol–gel technique. The highest intensity peak for the samples \( x = 0.0, y = 0.0 \) and \( x = 0.1, y = 0.2 \) was found ~ [116]. However, for the samples \( x = 0.2, y = 0.4 \), \( x = 0.3, y = 0.6 \), \( x = 0.4, y = 0.8 \) the maximum intensity peak shifted to [011], [110] and [201], respectively. Thus, at a higher substitution level, the switching of maximum intensity peak to different angles as well as the appearance of new peaks confirmed the required Co-Ni substituting effect in the structure of these materials. Moreover, the variations in peak intensities for synthesized samples can be attributed to substitutions Co-Ni cations [39]. The effective use of X-ray Diffraction (XRD) data yielded various important crystallographic details of powdered hexaferrite samples such as lattice constants \( a, c \), cell volume \( V \), the crystallite size \( D \), X-ray density \( d_4 \), bulk density \( d_b \), porosity \( \%P \), dislocation density \( \delta \) and lattice strain \( \epsilon \) that are represented in tabular form in Table 1.

Lattice parameters \( a, c \) were calculated with the help of cell software (version 5.0, Copyright (C) 1986 by K. Dwight) using \( h k l \). The measured lattice parameters are displayed in Table 1, and their values are closely related to those reported in the previous literature. The values of lattice parameter “a” decreased with enhancement in substitution contents \( x, y \) as shown in Figure 2. This variation can be attributed to the comparatively smaller ionic radius of \( \text{Co}^{2+} (0.74 \text{Å}) \) [40] as compared to \( \text{Ba}^{2+} (1.35 \text{Å}) \) [41] ions, and the slightly smaller ionic radius of \( \text{Ni}^{2+} (0.69 \text{Å}) \) [42] replacing \( \text{Mg}^{2+} (0.72 \text{Å}) \) ions [43,44]. The greater variations in lattice parameters “c”
than "a" can be justified based on the fact that in W-type hexaferrite, the c-axis; being perpendicular to the basal plane bears the easy axis character causing an easy orientation of spin directions in its direction. Because of the varying ionic radii of the substituents, the crystal structure usually undergoes a distortion (shrinking or stretching) after the cation replacement. For all samples, the calculated crystallographic axis ratio c/a is presented in Table 1. As per Verstegen & Stevels, the assessment of structure type may be carried out by calculation of the c/a ratio. If this ratio is less than 5.585 then the structure can be of W-type, and the c/a ratio of the currently synthesized materials is less than 5.585 [3,45].

The inter-planar spacing \( d_{hkl} \) and cell volume \( V_{cell} \) of each sample were measured by using relations (1) and (2), respectively. The variation in cell volume is attributed to the variation in lattice parameters \( a \) and \( c \) as displayed in Table 1. With the increase in substitution level \( (x, y) \), a decreasing trend in cell volume (Figure 3) was observed that might be due to the above-mentioned decreasing behaviour of lattice parameters. The reduction in cell volume might be due to the compression of unit cell. Moreover, the tabulated values of \( d_{hkl} \) \( (\AA) \) and \( V_{cell} \) \( (\AA^3) \) are in good agreement with earlier reported literature for W-type hexaferrite.

\[
\begin{align*}
  d_{hkl} & = \frac{1}{\sqrt{\frac{1.33(h^2+k^2+l^2)}{a^2} + \frac{2}{c^2}}} \\
  V_{cell} & = a^2c\sin120^\circ = (0.866)a^2c
\end{align*}
\]

Here, \( h, k, \) and \( l \) are the miller indices of the most intensive peak of each material, while "a" and "c" represent the lattice parameters.

For each synthesized sample, the crystallite size \( (D) \) was determined by applying Gaussian fit to the highest intensity peak and resultant D values are obtained from Scherrer's relation (3); which was found to be in the range of 14–22 nanometres. When the crystallite size is

**Figure 1.** XRD patterns of \( \text{Ba}_{1-x}\text{Co}_x\text{Mg}_{2-y}\text{Ni}_y\text{Fe}_{16}\text{O}_{27} \) W-type hexaferrites \((x = 0.0, 0.1, 0.2, 0.3, 0.4 \text{ and } y = 0.0, 0.2, 0.4, 0.6, 0.8)\).

**Table 1.** Structural parameters of \( \text{Ba}_{1-x}\text{Co}_x\text{Mg}_{2-y}\text{Ni}_y\text{Fe}_{16}\text{O}_{27} \) W-type hexaferrite powders from XRD analysis.

| Parameters | \( x = 0.0 \) | \( x = 0.1 \) | \( x = 0.2 \) | \( x = 0.3 \) | \( x = 0.4 \) |
|-----------|---------------|---------------|---------------|---------------|---------------|
| \( a(\AA) \) | 5.9101        | 5.9064        | 5.9018        | 5.8806        | 5.9016        |
| \( c(\AA) \) | 32.934        | 32.901        | 32.766        | 32.897        | 32.8967       |
| \( d_{hkl}(\AA) \) | 2.6020        | 2.6001        | 2.5478        | 2.9403        | 2.5477        |
| \( V_{cell}(\AA^3) \) | 3 996.21      | 993.97        | 988.35        | 985.18        | 992.22        |
| \( \text{Molecular weight}(\text{amu}) \) | 1511.45       | 1510.49       | 1509.53       | 1508.57       | 1507.61       |
| \( \text{Crystallite size}(\text{nm}) \) | 22             | 13             | 15             | 16             | 16             |
| \( \text{X-ray density}(g/cm}^3 \) | 5.04           | 5.05           | 5.07           | 5.08           | 5.04           |
| \( \text{Bulk density}(g/cm}^3 \) | 2.58           | 2.27           | 2.95           | 3.00           | 3.00           |
| \( \%\text{porosity} \) | 68             | 49             | 55             | 42             | 40             |
| \( \text{Specific surface area}(10^7\text{cm}^2\text{g}^{-1}) \) | 54.11          | 84.87          | 78.90          | 73.82          | 74.40          |
| \( \text{Dislocation density}(10^{-3}\text{nm}^{-2}) \) | 2.149          | 5.463          | 4.233          | 3.853          | 4.041          |
| \( \text{Microstrain}(10^{-3}) \) | 5.397          | 8.584          | 7.311          | 8.208          | 7.119          |
| \( \text{Stacking fault coefficient}(\alpha) \) | 0.00413        | 0.00307        | 0.01364        | 0.07400        | 0.01507        |
tiny, the surface area is bigger, indicating that the number of atoms at the surface is greater, i.e. the covered surface by atoms at the material’s surface is more relevant when the crystallite size is small. The ferrimagnetic materials with $D < 50$ nm can be potentially employed for the reduction of signal-to-noise ratio in numerous high density recording, and microwave applications [3,46–48]. So, we can made conclusion that the prepared samples are potential candidate for microwave applications. The deviation of d-spacing and crystallite size with substituted contents are shown in Figure 4.

The microstrain was calculated utilizing equation (4), and its increasing behaviour might be due to the difference in ionic radii of substituent ions versus host ions causing strain in the crystal structure. Moreover, an increase in dislocation density ($\delta$) and stacking fault coefficient ($\kappa$) is because of the decrement in crystallite size caused by the difference of ionic radii regarding the host and substituted ions. Physically, dislocation density describes the linear defects in the crystal lattice, while the stacking fault coefficient designates the planar defects. Stacking faults are common

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**Figure 2.** Variation of lattice parameters (a & c) as a function of substituted contents ($x = \text{Co}$ and $y = \text{Ni}$) for $\text{Ba}_{1-x}\text{Co}_x\text{Mg}_{2-y}\text{Ni}_y\text{Fe}_{16}\text{O}_{27}$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$ and $y = 0.0, 0.2, 0.4, 0.6, 0.8$) W-type hexaferrites.

**Figure 3.** Variation of unit cell volume and c/a ratio versus substituted contents ($x = \text{Co}$ and $y = \text{Ni}$) content ($x, y$) for $\text{Ba}_{1-x}\text{Co}_x\text{Mg}_{2-y}\text{Ni}_y\text{Fe}_{16}\text{O}_{27}$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$ and $y = 0.0, 0.2, 0.4, 0.6, 0.8$) W-type hexaferrites.
Figure 4. Variation of d-spacing and crystallite size with substituted contents \((x = \text{Co} \quad \text{and} \quad y = \text{Ni})\) for \(\text{Ba}_1-x\text{Co}_x\text{Mg}_{2-y}\text{Ni}_y\text{Fe}_{16}\text{O}_{27}\) \((x = 0.0, 0.1, 0.2, 0.3, 0.4 \quad \text{and} \quad y = 0.0, 0.2, 0.4, 0.6, 0.8)\) W-type hexaferrites.

in closely packed structures like WHFs, and mainly arise during crystal growth. The variations in strain \((\epsilon)\), dislocation density \((\delta)\), and stacking fault probability \((\alpha)\) as a function of substituted contents \((x, y)\) are depicted in Figure 5.

\[
D = \frac{K\lambda}{\beta \cos \theta} \quad (3)
\]

\[
\beta \cos \theta = \frac{K\lambda}{D} + 4\epsilon \sin \theta \quad (4)
\]

In the above relations, the parameter "K" called shape factor; accounts for the difference in \(h\kappa l\) values and crystallite shapes. For W-type hexagonal ferrite, its value is fixed and is equal to 0.89. While, \(\lambda\), \(\beta\) (rad), and \(\theta\) (rad) denotes the wavelength of used X-rays \((= 1.5406 \text{ Å})\), full width at half maximum, and Bragg’s angle, respectively.

With the help of X-ray Diffraction (XRD) data, the physical properties like X-ray density \((\rho_X; \text{Equation (5)})\), bulk density \((\rho_B; \text{Equation (6)})\), and porosity \((\% P; \text{Equation (7)})\) were also measured by the following relations, and are given in Table 1.

\[
\rho_X = \frac{ZM}{N_A V_{\text{cell}}} \quad (5)
\]

\[
\rho_B = \frac{m}{\pi r^2 h} \quad (6)
\]

Here \(Z\) denotes the effective number of molecules in a unit cell, and in the present case, its value is 2. \(M\) represents the molecular weight; \(N_A \left(6.023 \times 10^{23} \text{ per mole}\right)\) stands for Avogadro’s number and \(V_{\text{cell}}\) denotes the cell volume. The obvious increasing behaviour of X-ray density can be linked with a decrease in cell volume; as X-ray density varies inversely with cell volume.

The bulk density was found to be increase from 1.61 to 3.00 g cm\(^{-3}\) with the enhancement of substituted contents \((x, y)\). This variation can be justified, because the density of substituent elements Co (8.9 g/cc) and Ni (8.9 g/cc) is fairly higher than those of host elements Ba (3.59 g/cc) and Mg (1.738 g/cc).

Figure 5. Variation of strain \((\epsilon)\), dislocation density \((\delta)\), and stacking fault coefficient \((\alpha)\) as a function of substituted contents \((x = \text{Co} \quad \text{and} \quad y = \text{Ni})\) for \(\text{Ba}_1-x\text{Co}_x\text{Mg}_{2-y}\text{Ni}_y\text{Fe}_{16}\text{O}_{27}\) \((x = 0.0, 0.1, 0.2, 0.3, 0.4 \quad \text{and} \quad y = 0.0, 0.2, 0.4, 0.6, 0.8)\) W-type hexaferrites.
attributed to the formation of grains of smaller size with composition. The greater value of X-ray density as compared to that of bulk-density is because of the tiny pores formation during the synthesis of materials as well as during sintering process [49]. A decrease in porosity (68–40%), measured by Equation (7), was also observed for studied materials, and can be linked with the increase of apparent density with increment in substitution level ($x, y$).

$$\% P = \left(1 - \frac{\rho_{app}}{\rho_{X}}\right) \times 100$$ (7)

The porosity decreased as a result of the substituted ions, demonstrating that the replacement of Co-Ni improved the densification process [49].

The specific surface area ($S$) of crystallites calculated by employing Equation (8), indicates an increasing trend with ($x, y$). The increase in $S$ may be due to the reduction in crystallite size. The smaller the crystallite size, the greater will be the number of surface atoms, and the larger will be the surface area.

$$S = \frac{6000}{(\rho_{X} \times D)}$$ (8)

### 3.2. Raman spectroscopic analysis

Raman spectroscopy is an attractive technique that is employed for spectroscopic probing of substituted hexaferrite materials [50,51]. It yields information about vibrational as well as rotational energy states provided that the effective derivative of polarizability ($\partial \alpha / \partial Q$) should be non-zero. In hexaferrite, the use of $D_{6h}$ symmetry-based group theory suggests the presence of 42 active Raman modes (i.e. $14E_{1g} + 11A_{1g} + 17E_{2g}$), where the letters A and E represent one and two-dimensional motions correspondingly [51]. The existence of all mentioned Raman modes is accredited to the activity of metal–oxygen ions or only O$^{-2}$ ions [52–54].

Many researchers have probed the phonon modes of barium hexaferrites (BHFs) in thin-film or pellet shapes. However, the detailed investigation of barium hexaferrites in powder form via the Raman spectroscopic method has not been extensively reported in the literature survey [55]. Moreover, to the best of our knowledge, not any noteworthy Raman work has been carried out for W-type hexaferrites. Therefore, in this article Raman spectroscopy of our synthesized W-type nanoferrite powders ($\text{Ba}_{1-x}\text{Co}_{x}\text{Mg}_{2-y}\text{Ni}_{y}\text{Fe}_{16}\text{O}_{27}$) has been carried out for a better understanding of structural variations of substituted metal cations. Raman spectroscopy not only provides information about crystal structure but also stipulates impurity concentration as well as crystal deformations [56–59].

It is quite clear from Figure 6 that the Raman spectra for substituted samples are different from that of the un-substituted one, and this difference is highest for the sample with the highest degree of substitution (i.e. $x = 0.4, y = 0.8$), thus revealing the requisite substitution effect. The peaks present in Raman spectra arise mostly because of vibrations of atomic bonds, and are thus capable of identifying even with a small amount of impurity [51,60]. The changes in Raman peak broadness happen due to variations of substitution concentration in chemical composition, cell dimension, bond extent, atomic radii, and magnetic structure [61]. The analysis of Raman spectra reveals the presence of 10 active Raman modes at $\nu_1 = (85–87)\text{ cm}^{-1}$, $\nu_2 = (178–181)\text{ cm}^{-1}$, $\nu_3 = (208–211)\text{ cm}^{-1}$, $\nu_4 = (282–290)\text{ cm}^{-1}$, $\nu_5 = (328–332)\text{ cm}^{-1}$, $\nu_6 = (407–412)\text{ cm}^{-1}$, $\nu_7 = (462–466)\text{ cm}^{-1}$, $\nu_8 = (521–524)\text{ cm}^{-1}$, $\nu_9 = (608–613)\text{ cm}^{-1}$, $\nu_{10} = (677–681)\text{ cm}^{-1}$. All these modes along with their respective symmetry and assigned polyhedra are listed in Table 2. The variations in the position of vibrational modes can be ascribed to the placement of substituent ions amid different available interstitial lattice sites present in the crystal structure. The band 178–181 cm$^{-1}$ belongs to the vibrations of the entire spinel block. The Raman bands 208–211 cm$^{-1}$ and 282–290 cm$^{-1}$ arise because of metal–oxygen vibrations at octahedral (2a) sites. The occurrence of the vibrational band at $\nu_1 = 328–332\text{ cm}^{-1}$, $\nu_2 = 407–412\text{ cm}^{-1}$, $\nu_4 = 521–524\text{ cm}^{-1}$ may be because of metal–oxygen vibrations at octahedral (12k) sites. The vibrations corresponding to octahedral (12k, 2a) lattice sites are responsible for the $\nu_3 = 462–466\text{ cm}^{-1}$ band. The metal–oxygen vibrations at 4f$_2$ (4f$_{VI}$) octahedral sites caused by the emergence of Raman band at $\nu_5 = 608–613\text{ cm}^{-1}$. The presence of a band at $\nu_6 = 677–681\text{ cm}^{-1}$ can be due to atomic vibrations at the bi-pyramidal 2b site [50–52,60,61]. The variations in the broadness and intensity of peaks are obvious from the graph that can be justified on the basis of local strain induced inside the
Table 2. Raman spectral bands in Ba$_{1-x}$Co$_x$Mg$_{2-y}$Ni$_y$Fe$_{16}$O$_{27}$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$ and $y = 0.0, 0.2, 0.4, 0.6, 0.8$) W-type hexaferrites.

| $x = 0.0, y = 0.0$ | $x = 0.1, y = 0.2$ | $x = 0.2, y = 0.4$ | $x = 0.3, y = 0.6$ | $x = 0.4, y = 0.8$ | Symmetry | Assigned Polyhedra |
|-------------------|-------------------|-------------------|-------------------|-------------------|----------|-------------------|
| 87                | 86                | 86                | 85                | 86                | E1g      | Whole S-block     |
| 181               | 180               | 180               | 178               | 180               | E1g      | Octahedral (12k)  |
| 211               | 208               | 208               | 208               | 208               | E1g      | Octahedral (2a)   |
| 282               | 282               | 287               | 290               | 287               | A1g      | Octahedral (12k)  |
| 332               | 330               | 330               | 328               | 329               | E1g      | Octahedral (12k)  |
| 412               | 409               | 409               | 407               | 407               | E1g      | Octahedral (12k)  |
| 466               | 464               | 466               | 462               | 462               | A1g      | Octahedral (12k)  |
| 524               | 521               | 521               | 524               | 521               | A1g      | Octahedral (12k)  |
| 613               | 612               | 608               | 612               | 610               | A1g      | Octahedral (4f)   |
| 679               | 677               | 678               | 681               | 681               | A1g      | Bipyramidal (2b)  |

Table 3. The intensity of highest peak in PL spectra of each powder sample regarding Ba$_{1-x}$Co$_x$Mg$_{2-y}$Ni$_y$Fe$_{16}$O$_{27}$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$ and $y = 0.0, 0.2, 0.4, 0.6, 0.8$) W-type hexaferrites.

| Composition | PL intensity (a.u.) |
|-------------|---------------------|
| Ba$_{0.9}$Co$_{0.1}$Mg$_{1.8}$Ni$_{0.2}$Fe$_{16}$O$_{27}$ | 673.5 |
| Ba$_{0.8}$Co$_{0.2}$Mg$_{1.6}$Ni$_{0.4}$Fe$_{16}$O$_{27}$ | 803.11 |
| Ba$_{0.7}$Co$_{0.3}$Mg$_{1.4}$Ni$_{0.6}$Fe$_{16}$O$_{27}$ | 550.31 |
| Ba$_{0.6}$Co$_{0.4}$Mg$_{1.2}$Ni$_{0.8}$Fe$_{16}$O$_{27}$ | 695.86 |
| Ba$_{0.5}$Co$_{0.4}$Mg$_{1.8}$Ni$_{0.2}$Fe$_{16}$O$_{27}$ | 220.84 |

unit cell (also observed in XRD analysis) due to smaller ionic radii of Co$^{2+}$ and Ni$^{2+}$ ions as compared to host Ba$^{2+}$ and Mg$^{2+}$ ions. This observation is clear-cut evidence of the incorporation of Co$^{2+}$ and Ni$^{2+}$ ions in the Ba-W sub-lattices that in turn caused local strain inside the crystal structure [22].

3.3. Photoluminescence (PL) spectroscopic analysis

Owing to its contactless and non-destructive character, photoluminescence (PL) spectroscopy can be considered as the workhorse among various optical probing tools. This technique produces information regarding intrinsic and extrinsic transitions as well as imperfections and impurities [62,63]. The principle of PL (photoluminescence) spectroscopy is “photoluminescence” that corresponds to light emission of specific wavelengths from a material through optical excitation. If material is exposed to light of appropriate energy (wavelength), the electronic excitations took place within the material by the absorption of photons’ energy. The relaxation (radiative) of these electronic excitations to the ground state leads to the emission of photons of a specific wavelength that are characteristics of the material. This phenomenon, photoluminescence, is highly dependent on the energy of exciting light that ultimately govern the number of excited electrons as well as holes [64].

In this work, PL (photoluminescence) spectroscopy is carried out under an excitation wavelength of 536 nm. The measurement of Photoluminescence spectra for all synthesized W-type hexaferrite samples was carried out at ambient temperature to probe their optical behaviour. The resultant intensity (a. u.) versus wavelength (nm) graphs for different substitution contents of Co-Ni (i.e. 0.0/0.0, 0.1/0.2, 0.2/0.4, 0.3/0.6, 0.4/0.8) are presented in Figure 7 revealing the existence of emission peaks in the range 620–700 nm. Eight clear peaks in the visible (red) region corresponding to wavelengths 633, 639, 646, 650, 652, 655, 658, and 661 nm were observed in all samples. Very small shifting of peaks towards shorter wavelength was detected that can be linked with the decrease in crystallite size as revealed from XRD (X-ray Diffraction) data. The most intense peak of spectra was observed around 661 nm in all samples. The occurrence of these peaks can be ascribed to free electronic excitation transitions starting from localized energy state located below conduction band, and ending at valence band [65]. A non-linear variation in PL intensity with substitution of Co and Ni in the samples (Ba$_{1-x}$Co$_x$Mg$_{2-y}$Ni$_y$Fe$_{16}$O$_{27}$) was observed, and the highest Photoluminescence (PL) intensity was found for the sample with composition Ba$_{0.9}$Co$_{0.1}$Mg$_{1.8}$Ni$_{0.2}$Fe$_{16}$O$_{27}$. The intensity of the highest peak in PL (photoluminescence) spectra of each powder sample of Ba$_{1-x}$Co$_x$Mg$_{2-y}$Ni$_y$Fe$_{16}$O$_{27}$ is listed in Table 3. The calculated energy bandgap values for all samples are nearly equal to 1.875 eV, and thus revealing the semiconducting nature of synthesized materials [66].

3.4. Fourier Transform Infrared (FTIR) spectroscopic analysis

Infrared spectroscopic studies enable to probe the structural and chemical changes as well as the development of the required phase in the synthesized materials. The Fourier Transform Infrared (FTIR) spectra of prepared W-type hexaferrite nanoparticles having composition Ba$_{1-x}$Co$_x$Mg$_{2-y}$Ni$_y$Fe$_{16}$O$_{27}$ were measured in the wavenumber range of 600–4000 cm$^{-1}$, and are depicted in Figure 8. The occurrence of more than five peaks in all spectra exhibits the complex nature of the investigated materials [67]. The IR absorption band marked at 1622 cm$^{-1}$ occurred due to the absorption of CO$_2$ present in the environment by the highly porous nature of materials [68]. The broad absorption band at 3124–3554 cm$^{-1}$ is because of O-H stretching vibrations of water due to the presence of moisture in
Figure 7. Photoluminescence spectra of $\text{Ba}_{1-x}\text{Co}_x\text{Mg}_{2-y}\text{Ni}_y\text{Fe}_{16}\text{O}_{27}$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$ and $y = 0.0, 0.2, 0.4, 0.6, 0.8$) W-type hexaferrites.

Figure 8. FTIR spectra for $\text{Ba}_{1-x}\text{Co}_x\text{Mg}_{2-y}\text{Ni}_y\text{Fe}_{16}\text{O}_{27}$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$ and $y = 0.0, 0.2, 0.4, 0.6, 0.8$) W-type hexaferrites.

The broadness of the 3124–3554 cm$^{-1}$ peak is associated with hydrogen-bonded chains. The vibrations of inorganic metallic ions located in the crystal lattice are responsible for IR bands in the range 600–1000 cm$^{-1}$ [70,71]. The emergence of 1125 and 1398 cm$^{-1}$ vibrational bands in the FTIR spectrum corresponds to the bridging connection of metal–oxygen ions like $\text{Ba-O-Ba}$, $\text{Ba-O-Co}$, $\text{Fe-O-Fe}$, and $\text{Mg-O-Ni}$ [72,73]. The existence of a 2358 cm$^{-1}$ peak can be attributed to N-H stretching vibrations corresponding...
Figure 9. SEM images of all the five synthesized samples of WTHs.
to ammonia traces; that was used during the synthesis process for pH maintenance [73,74]. The variations in the FTIR (Fourier transform infrared) spectrum confirm the successful substitution of Co$^{2+}$ and Ni$^{2+}$ in the lattice, and these variations can also be due to the change in lattice parameters extracted from X-ray Diffraction (XRD) data. So, the above Fourier Transform Infrared (FTIR) results are completely in agreement with our X-ray Diffraction (XRD) findings, and thus justify the synthesis of nano-ferrites with a W-type hexagonal structure.

3.5. Scanning Electron Microscopic (SEM) analysis

Microstructural analysis has vital importance in determining the desired characteristics of synthesized W-type hexaferrites in the field of microwave absorption [75]. Figure 9(a–e) represents the Scanning Electron Microscope (SEM) images of (Co, Ni)-substituted BaMg$_2$W-hexaferrites. Micrographs clearly indicate that co-substitution of Co and Ni in the hexagonal lattice has modified the grain morphology. The presence of pores in all images indicates the synthesis of highly porous materials. Figure 9(a) belongs to an un-substituted compound, and shows the growth of condensed grains with sharp edges about mixed morphology like hexagonal, rectangular, and triangular shapes. For substituted compound (Figure 9(b)), the particles with hexagonal shape are dominant, and are stacked irregularly. Figure 9(c) shows that the particles are aggregated possessing intra-granular pores. Figure 9(d,e) representing samples with maximum substitution level contain hexagonal platelet-like grains but their orientation is random. The presence of hexagonal morphology of grains in SEM micrographs satisfied our X-ray Diffraction (XRD) predicted results, and hence signifies the importance of the sol–gel self-combustion route for synthesizing pure hexaferrites. The assessed values of average grain size by ImageJ software were found to be in the range of 1.6–3.2 micron and are depicted in Figure 10. The development of these quite large grains confirms the polycrystalline nature of investigated compounds, and is because of higher sintering temperature and duration [68]. Also, larger grains can lead to greater absorption of microwaves [76]. Moreover, the synthesized materials contain hexagonal-shaped platelet-like grains and thus can be efficiently used in microwave absorbing coatings [77,78].

4. Conclusion

W-type barium hexaferrite Ba$_{1-x}$Co$_x$Mg$_{2-y}$Ni$_y$Fe$_{16}$O$_{27}$; $x = 0.0, 0.1, 0.2, 0.3, 0.4$ and $y = 0.0, 0.2, 0.4, 0.6, 0.8$ were prepared using sol–gel auto-combustion technique, which is cost-effective, bottom-up, wet chemical method vigorously employed by researchers for the synthesis of very fine ferrite powders at nanosize. A decrement in (a) and (c) lattice parameters, and hence in unit cell volume (V) is also observed owing to local strain instigated by the shorter ionic radii of Ni$^{2+}$ (0.69 Å) and Co$^{2+}$ (0.96 Å) replacing respective host ions Mg$^{2+}$ (0.72 Å) and Ba$^{2+}$ (1.35 Å). The enhancement in X-ray density may be due to reducing trend of cell volume. Maximum values of dislocation density and lattice strain are observed for the sample with $x = 0.1, y = 0.2$. The crystallite size is found in the range of 13–22 nm. Raman spectra indicate the existence of ten active vibrational modes. Moreover, the differences in intensity and wideness of peaks were attributed to the substitution-induced local strain inside the unit cell. Eight emission peaks in the visible region are obvious from PL spectra in all materials. Very small shifting of PL peaks towards shorter wavelength because of a decrement in crystallite size is observed. The calculated energy bandgap of 1.875 eV from all samples signifies that the synthesized materials exhibit semiconducting behaviour. The presence of large grains of average size 1.6–3.2 μm suggested their usage in the manufacturing of microwave absorbing materials (MAMs).

Disclosure statement

No potential conflict of interest was reported by the author(s).

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ORCID

Muhammad Azhar Khan http://orcid.org/0000-0002-1463-3031
References

[1] El Ata AA, Ahmed M. Dielectric and AC conductivity for BaCo2–xCuxFe16O27 ferrites. J Magn Magn Mater. 2000;208(1–2):27–36. doi:10.1016/S0304-8853(99)00547-8

[2] Hessien MM, Rayan DA, Mahmoud MHM, et al. Controlling the structural, microstructure and magnetic properties of barium W-type hexaferrite elaborated using tartaric acid precursor strategy. J Mater Sci: Mater Electron. 2018;29(12):9771–9779. doi:10.1007/s10854-018-9016-1

[3] Akhtar MN, Javed S, Ahmad MR, et al. Sol gel derived MnTi doped Co2 W-type hexagonal ferrites: structural, physical, spectral and magnetic evaluations. Ceram Int. 2020;46(6):7842–7849. doi:10.1016/j.ceramint.2019.12.003

[4] Ahmad M, Grössinger R, Kriegisch M, et al. Magnetic and microwave attenuation behavior of Al-substituted Co2W hexaferrites synthesized by sol-gel auto-combustion process. Curr Appl Phys. 2012;12(6):1413–1420. doi:10.1016/j.cap.2012.02.038

[5] Darwish MA, Abosheisha HF, Morchenko AT, et al. Impact of the Zr-substitution on phase composition, hexaferrite. J Alloys Compd. 2009;470(1–2):332–335.

[6] Hessien MM, Rayan DA, Mahmoud MHH, et al. Control-structure, magnetic, and microwave properties of the BaM hexaferrite. Ceram Int. 2021;47(12):16752–16761. doi:10.1016/j.ceramint.2021.03.041

[7] Dimri MC, Kashyap SC, Dube DC. Electrical and magnetic properties of barium hexaferrite nanoparticles prepared by citrate precursor method. Ceram Int. 2004;30(7):1623–1626. doi:10.1016/j.ceramint.2003.12.173

[8] Ahmed M, Okasha N, Oaf M, et al. The role of Mg substitution on the microstructure and magnetic properties of BaM hexagonal ferrite. Ceram Int. 2021;47(12):16752–16761. doi:10.1016/j.ceramint.2021.02.247

[9] Akhtar MN, Javed S, Ahmad MR, et al. Systematic study of Mn substituted Sr-hexaferrites by self-propagation high-temperature synthesis. J Rare Earths. 2008;26(1):81–84. doi:10.1016/S1002-0721(08)60042-3

[10] Rehman AU, Shaukat SF, Haidyrah AS, et al. Synthesis and investigations of structural, magnetic and dielectric properties of Cr-substituted W-type hexaferrites for high frequency applications. J Electroceram. 2021;46(3):93–106. doi:10.1007/s10832-021-00246-7

[11] You L, Qiao L, Zheng J, et al. Magnetic properties of La-Zn substituted Sr-hexaferrites by self-propagation high-temperature synthesis. J Rare Earths. 2008;26(1):81–84. doi:10.1016/S1002-0721(08)60042-3

[12] Rehman AU, Shaukat SF, Haidyrah AS, et al. Synthesis and investigations of structural, magnetic and dielectric properties of Cr-substituted W-type hexaferrites for high frequency applications. J Electroceram. 2021;46(3):93–106. doi:10.1007/s10832-021-00246-7

[13] Rehman AU, Shaukat SF, Haidyrah AS, et al. Synthesis and investigations of structural, magnetic and dielectric properties of Cr-substituted W-type hexaferrites for high frequency applications. J Electroceram. 2021;46(3):93–106. doi:10.1007/s10832-021-00246-7

[14] Pullar RC. Hexagonal ferrites: A review of the synthesis, properties and applications of hexaferrite ceramics. Prog Mater Sci. 2012;57(7):1191–1334. doi:10.1016/j.pmatsci.2012.04.001

[15] Liu Q, Wu C, Wang Y, et al. Microstructure and electromagnetic properties of oriented strontium W-type hexaferrite with rare-earth Gd3+ substitution. Ceram Int. 2019;45(9):12205–12210. doi:10.1016/j.ceramint.2019.03.126
[31] Akhtar MN, Khan MA. Effect of rare earth doping on the structural and magnetic features of nanocrystalline spinel ferrites prepared via sol gel route. J Magn Magn Mater. 2018;460:268–277. doi:10.1016/j.jmmm.2018.03.069

[32] Akhtar MN, Babar M, Qamar S, et al. Structural rietveld refinement and magnetic features of prosademiun (Pr) doped Cu nanocrystalline spinel ferrites. Ceram Int. 2019;45(8):10187–10195. doi:10.1016/j.ceramint.2019.02.069

[33] Akhtar MN, Khan AA, Akhtar MN, et al. Structural rietveld refinement, morphological and magnetic features of Cu doped CoCe nanocrystalline ferrites for high frequency applications. Phys B. 2019;561:121–131. doi:10.1016/j.physb.2019.02.055

[34] Akhtar MN, et al. Preparations and tailoring of structural, magnetic properties of rare earths (REs) doped nanoferrites for microwave high frequency applications. Ceram Int. 2020;46(17):26521–26529. doi:10.1016/j.ceramint.2020.07.118

[35] Shouhstry Veisi SS, Yousefi M, Amini MM, et al. Magnetic and microwave absorption properties of Cu/Zr doped M-type Ba/Sr hexaferrites prepared via sol-gel auto combustion method. J Alloys Compd. 2019;773:1187–1194. doi:10.1016/j.jallcom.2018.09.189

[36] Almessiere MA, Slimani Y, Gungunes H, et al. Investigation of the effects of Tm3+ on the structural, microstructural, optical, and magnetic properties of Sr hexaferrites. Results Phys. 2019;13:102166. doi:10.1016/j.rinp.2019.10.016

[37] Mackenzi JD. Applications of the sol-gel process. J Non-Cryst Solids. 1988;100(1–3):162–168. doi:10.1016/0022-3093(88)90013-0

[38] Almessiere MA, Slimani Y, Gungunes H, et al. AC susceptibility and hyperfine interactions of vanadium substituted barium nanoferrites. Ceram Int. 2018;44(15):17749–17758. doi:10.1016/j.ceramint.2018.06.242

[39] Akhtar MN, et al. Sol gel derived MnTi doped CoZ ferrite-based hexagonal ferrites: structural, physical, spectral and magnetic evaluations. Ceram Int. 2020;46(6):7842–7849.

[40] Yang Y, Liu X, Jin D, et al. Structural and magnetic properties of La–Co substituted Sr–Ca hexaferrites synthesized by the solid state reaction method. Mater Res Bull. 2014;59:37–41. doi:10.1016/j.materresbull.2014.06.003

[41] Liu J, Wang Lng, Yin Xiaohui, et al. Effect of ionic radius on colossal permittivity properties of (A, Ta) co-doped TiO2 (A = alkaline-earth ions) ceramics. Ceram Int. 2020;46(8):12059–12066. doi:10.1016/j.ceramint.2020.01.247

[42] Almessiere MA, Slimani Y, Korkmaz AD, et al. Comparative study of sonochemically synthesized Co-Zr and Ni-Zr substituted Sr-hexaferrites: magnetic and structural investigations. J Magn Magn Mater. 2020;497:165996. doi:10.1016/j.jmmm.2019.165996

[43] Huang K, Yu J, Zhang L, et al. Synthesis and characterization of magnesium and titanium doped M-type barium calcium hexaferrites by a solid state reaction method. J Alloys Compd. 2020;825:154072. doi:10.1016/j.jallcom.2020.154072

[44] Akhtar MN, Khan MA. Structural, physical and magnetic evaluations of Ce-Zn substituted SrCo2 W-type hexaferrites prepared via sol gel auto combustion route. Ceram Int. 2018;44(11):12921–12928. doi:10.1016/j.ceramint.2018.04.104

[45] Tang J, Liu X, Mehmood Ur Rehman K, et al. Microstructure and characterization of W-type hexaferrite Ba1−xLaхFe2xFe63+αOy prepared by solid state method. J Magn Magn Mater. 2019;452:354–359. doi:10.1016/j.jmmm.2017.12.105

[46] Carol T, TT, Mohammed J, Batoo KM, et al. Crystal-structure analysis, Raman spectroscopy, dielectric measurements, magnetic and optical properties of Cr3+–Ni2+–substituted Co2Y-type barium hexaferrites. Mater Res Bull. 2022;145:111564. doi:10.1016/j.materresbull.2021.111564

[47] Ahmad I, Shah SM, Zafar MN, et al. Synthesis, characterization and charge transport properties of Pr–Ni Co-doped SrFe2O4 spinel for high frequency devices applications. Ceram Int. 2021;47(3):3760–3771. doi:10.1016/j.ceramint.2020.09.233

[48] Hambali S, Doyan A. Synthesis and characterization barium M-hexaferrites (BaFe12−2xCoMnxNixO19) as a microwave absorbent material. Solid State Phenom. 2021;317:46–52. doi:10.4028/www.scientific.net/SSP.317.46

[49] Abdeen AM, Hemedah OM, Assem EE, et al. Structural, electrical and transport phenomena of Co ferrite substituted by Cd. J Magn Magn Mater. 2002;238(1):75–83. doi:10.1016/S0304-8853(01)00465-6

[50] Kreisel J, Lucazeau G, Vincent H. Raman study of substituted barium ferrite single crystals, BaFe12−2xMe xCoO19 (Me = Ir, Ti). J Raman Spectros. 1999;30(2):115–120. doi:10.1002/(SICI)1097-4555(199902)30:2<115::AID-JRS353>3.0.CO;2-D

[51] Kreisel J, Lucazeau G, Vincent H. Raman spectra and vibrational analysis of BaFe12019hexagonal ferrite. J Solid State Chem. 1998;137(1):127–137. doi:10.1006/jssc.1997.7737

[52] Jasrotia R, Singh VP, Kumar R, et al. Raman spectra of sol-gel auto-combustion synthesized Mg2Ag-Mn and Ba-Nd-Cd-In ferrite based nanomaterials. Ceram Int. 2020;46(1):618–621. doi:10.1016/j.ceramint.2019.09.012

[53] John N, George S. Raman spectroscopy. In: Spectroscopic methods for nanomaterials characterization Vol. Vol. 2: Elsevier; 2017. p. 95–127.

[54] Wolveinor DS. Characterization of Semiconductor heterostructures and nanostructures: Chapter 17. In: Raman spectroscopy. Elsevier Inc.; 2008. p. 249–288.

[55] Kumar S, Laha R, Kar M. Raman characterization of polycrystalline barium hexaferrite nanoparticles: SERS of nanoparticles in powder form. Phys B. 2020;579:411833. doi:10.1016/j.physb.2019.411833

[56] Yang XX, Zhou ZF, Wang Y, et al. Raman spectroscopy determination of the debye temperature and atomic cohesive energy of CdS, CdSe, Bi2Se3, and Sb2Te3 nanocrystals. J Appl Phys. 2012;112(8):083508. doi:10.1063/1.4759207

[57] Zhang X, Qiao X-F, Shi W, et al. Phonon and Raman scattering of two-dimensional transition metal dichalcogenides from monolayer, multilayer to bulk material. Chem Soc Rev. 2015;44(9):2757–2785. doi:10.1039/C4CS00282B

[58] Davydov SY. On estimating the G-peak shift in graphene Raman spectra. Phys Solid State. 2017;59(3):629–632. doi:10.1134/S1068745617030088

[59] Hu L-W, Liu X, Le G-M, et al. Morphology evolution and SERS activity of the nanoporous Au prepared by dealloying sputtered Au-Ag film. Phys B. 2019;558:49–53. doi:10.1016/j.physb.2019.01.019

[60] Kumar S, Kumar Manglam M, Supriya S, et al. Lattice strain mediated dielectric and magnetic properties in La doped barium hexaferrite. J Magn Magn Mater. 2019;473:312–319. doi:10.1016/j.jmmm.2018.10.085
[61] Velhal N, Kulkarni G, Mahadik D, et al. Effect of Ba+ 2 ion on structural, magnetic and microwave properties of screen printed BaSr1-XFe12O19 thick films. J Alloys Compd. 2016;682:730–737. doi:10.1016/j.jallcom.2016.04.310

[62] Torvik JT. Chapter 2 – dopants in GaN. In: Manasreh O, editor. III-Nitride semiconductors: electrical, structural and defects properties. Amsterdam: Elsevier; 2000. p. 17–49.

[63] Chapter 3 – The Current situation in ultra-precision technology – silicon single crystals as an example. In: Doi T, Marinescu ID, Kurokawa S, editors. Advances in CMP polishing technologies. Oxford: William Andrew Publishing; 2012. p. 15–111.

[64] Singh RK, Narayan A, Prasad K, et al. Thermal, structural, magnetic and photoluminescence studies on cobalt ferrite nanoparticles obtained by citrate precursor method. J Therm Anal Calorim. 2012;110(2):573–580. doi:10.1007/s10973-012-2728-1

[65] Pubby K, Babu KV, Narang SB. Magnetic, elastic, dielectric, microwave absorption and optical characterization of cobalt substituted nickel spinel ferrites. Mater Sci Eng B.. 2020;255:14513. doi:10.1016/j.mseb.2020.114513

[66] Costa JCS, Taveira RJS, Lima CFRAC, et al. Optical band gaps of organic semiconductor materials. Opt Mater. 2016;58:51–60. doi:10.1016/j.optmat.2016.03.041

[67] Nandiyanto ABD, Oktiani R, Ragadhita R. How to read and interpret FTIR spectroscopy of organic material. Indones J Sci Technol. 2019;4(1):97–118. doi:10.17509/jiost.v4i1.15806

[68] Ahmad M, Grössinger R, Kriegisch M, et al. Characterization of Sr-substituted W-type hexagonal ferrites synthesized by sol–gel auto combustion method. J Magn Magn Mater. 2013;332:137–145. doi:10.1016/j.jmmm.2012.12.039

[69] Ghasemi A, Gordani GR, Ghaseemi E. Co2W hexaferrite nanoparticles-carbon nanotube microwave absorbing nanocomposite. J Magn Magn Mater. 2019;469:391–397. doi:10.1016/j.jmmm.2018.09.010

[70] Priyadharsini P, Pradeep A, Rao PS, et al. Structural, spectroscopic and magnetic study of nanocrystalline Ni–Zn ferrites. Mater Chem Phys. 2009;116(1):207–213. doi:10.1016/j.matchemphys.2009.03.011

[71] Gulbadan S, Ejaz SR, Nizamani AH, et al. Structural elucidation and dielectric behavior evaluation of sol-gel synthesized Co–Al co-substituted M-type hexaferrite materials. Ceram Int. 2020;46(4):4914–4923. doi:10.1016/j.ceramint.2019.10.228

[72] Ashraf GA, Zhang L, Abbas W, et al. Synthesis and characterization of Al-Sm substituted Ba-Sr M-type hexagonal ferrite nanoparticles via sol-gel route. Ceram Int. 2018;44(15):18678–18685. doi:10.1016/j.ceramint.2018.07.096

[73] Bibi F, et al. Evaluation of structural, dielectric, magnetic and photocatalytic properties of Nd and Cu co-doped barium hexaferrite. Ceram Int. 2021;47(21):30911–30921.

[74] Ali I, Islam MU, Awan MS, et al. Structural, electrical, and microstructure properties of nanostructured calcium doped Ba-hexaferrites synthesized by sol-gel method. J Supercond Novel Magn. 2013;26(11):3277–3286. doi:10.1007/s10948-013-2167-7

[75] Gordani GR, Mohsenedi M, Ghaseemi A, et al. Microstructure, magnetic and microwave absorptive behavior of doped W-type hexaferrite nanoparticles prepared by co-precipitation method. Mater Res Bull. 2016;76:187–194. doi:10.1016/j.materresbull.2015.12.021

[76] Goldman A. Modern ferrite technology. 2ndSpringer; 2006.

[77] Huang K, Liu X, Feng S, et al. Structural and magnetic properties of Ca-substituted barium W-type hexagonal hexaferrites. J Magn Magn Mater. 2015;379:16–21. doi:10.1016/j.jmmm.2014.11.018

[78] Xu J, Zou Haifeng, Li Hongying, et al. Influence of Nd3+ substitution on the microstructure and electromagnetic properties of barium W-type hexaferrite. J Alloys Compd. 2010;490(1–2):552–556. doi:10.1016/j.jallcom.2009.10.079