

Structural and magnetic properties of Copper substituted Bismuth ferrite nanoparticles

G. Pushpalatha¹, T.Ravindra Reddy², K. Suresh Babu^{1,3*}, S. Lakshmi Reddy⁴

¹Department of Chemistry, BEST Innovation University, Gownaripalli, Gorantla, Andhra Pradesh 515231, India. ²Department of Physics, Annamacharya Institute of Technology and Sciences, Kadapa, India. ³Department of Chemistry, Marri Laxman Reddy Institute of Technology and Management, Hyderabad, India. ⁴Department of Physics, SVD College, Cuddapah 516003, India.

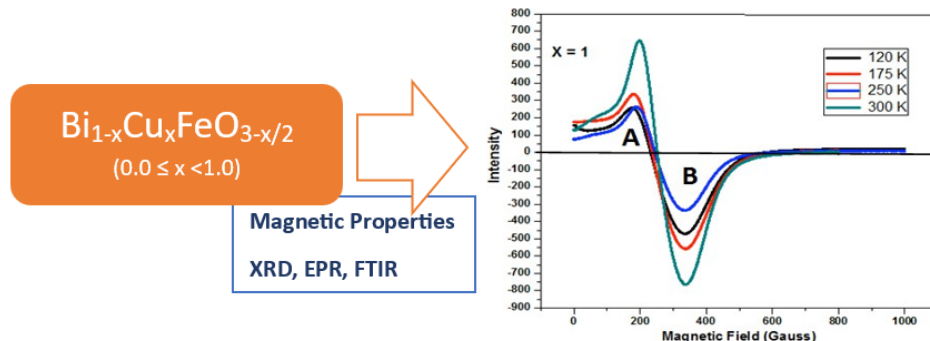
Submitted on: 21-Jan-2025, Accepted and Published on: 04-Apr-2025

Article

ABSTRACT The influence of Cu²⁺ substitution on magnetic properties of nano particles of ferrite of basic composition Bi_{1-x}Cu_xFeO_{3-x/2} (0.0 ≤ x < 1.0) synthesized by solid-state reaction method have been analyzed in this report. X-ray diffraction (XRD), Electron paramagnetic resonance (EPR) spectroscopy and Fourier transformation infrared (FTIR) spectroscopy techniques were used to

investigate the structural and magnetic properties of the synthesized nanoparticles. XRD results confirm that all the samples are in single-phase with rhombic structure. The unit cell parameters "a" and "c" are calculated and found that these change with variation of composition. The average crystallite size of the synthesized nanoparticles is obtained through Scherrer formula and is found to be 54 nm and it decreases with increase in the concentration of doping. EPR spectrum exhibits only one broad resonance with g about 2.56 suggesting the presence of oxygen vacancy and Fe³⁺ in rhombic structure. EPR results indicate that the compound is in single phase only. The g value calculated for Fe(III) for all the samples is almost the same and is about 2.56. EPR results further confirming that metal ion is placed in rhombic crystal structure. It is found that the magnetic phase transition for pure BFO is due to spin-reorientation. Temperature dependence EPR signals like resonance field, g-factor, line-width, intensity, and asymmetric parameter are doping dependent. Temperature dependence magnetic measurements are strongly support the EPR results and indicate that there are two magnetic phases at low temperature and after 250 K only paramagnetic behaviour is present in the compound. FTIR spectrum indicates the presence of M-O bands along with OH vibrations.

Keywords: Copper doped bismuth ferrite, XRD, EPR, IR, Magnetic properties, Metal oxide nanoparticles.



INTRODUCTION

The ideal perovskite structure is cubic with composition ABO₃. The B ions are surrounded by regular octahedral oxygens which share corners to form a three dimensional frame work. The A ions occupy larger holes between the octahedra and each is surrounded by twelve oxygens. The A ions are considerably substituted by rare earths, alkalis, Ca, Nb, Ta for Ti. Generally, perovskites and related compounds exhibit multiferroic, photo catalytic, and magnetic properties. For specific new applications, we require a material with definite chemical composition,

homogeneity, particle size and shape. When bismuth and iron are doped in perovskite, its structure and the properties change. These properties of the compound may be useful in the manufacture of thin film capacitors, nonvolatile memories, nonlinear optics and photo electrochemical cells [1-5].

Bismuth ferrite (BFO) has stability in a narrow temperature range. Even today it is challenging issue to synthesize single-phase bismuth ferrite. However, using rapid liquid phase sintering technique Wang *et al* [6-7] prepared pure phase bismuth ferrite. In the present study bismuth ferrite nano compound has been synthesized by substitution of different cation or combination of cations under varying conditions. In this study, we focus synthesis of copper doped bismuth nano ferrite. Its structural and other properties are studied by using XRD, EPR and IR spectra. XRD analysis is used to confirm the phase of the compound and EPR is used to know the magnetic properties and FTIR is employed to confirm the bond formation of the nano compound. Mostly studied single phase AB₂O₃ type perovskite

*Corresponding Author: Dr. K. Suresh Babu, Professor, Dept of Chemistry, MLRIT, Hyderabad, India. E-mail: sureshbabumlritm@gmail.com



DOI:10.62110/sciencein.mns.2025.v12.1183
URN:NBN:sciencein.mns.2025.v12.1183
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multi ferro icsare BiFeO₃. It possesses rhombohedral distorted perovskite structure, which can also be known by hexagonal lattice constants 'a' and 'c'.

Material and Methods

All of the reagents were of analytical grade (AR) and used without further purification.

The powdered samples of the mixed bismuth ferrites Bi_{1-x}Cu_xFeO_{3-x/2} with variable composition (x = 0 to 1.00 in steps of 0.25) are synthesized by using solid-state reaction method.

Characterization

Phase structure analysis and microstructure of the nanosized Bi_{1-x}Cu_xFeO_{3-x/2} (x = 0 to 1.00 in steps of 0.25) ferrite powders are determined by means of Philips X-ray diffractometer operated in reflection geometry at 30mA, 40kV with Cu-K α ($\lambda=1.54060$ Å) (XRD pattern). EPR spectra of the samples (x= 0.0, 0.50 and 1.00) are also recorded from 150 K to 300K on Carl JES X3 series ESR spectrometer operating at X band frequency ($\nu=9.195$ GHz) having a 100 KHz field modulation to obtain first derivative EPR spectrum. DPPH with a g value of 2.0036 is used for g factor calculations. For all the samples IR spectra are recorded in the range 400 to 4000cm⁻¹ at room temperature (RT) on Bruker instrument. Magnetic properties of the nano compound are measured using vibration sample magnetometer (VSM).

RESULTS AND DISCUSSION

XRD analysis

Figure 1 shows the recorded X-ray diffraction pattern of all the Cu doped nano BFO samples at room temperature (RT). All the diffraction peaks are sharper and have high intensity within 2 θ range of 20 $^{\circ}$ to 60 $^{\circ}$ while some small minor peaks are also found beyond 60 $^{\circ}$.

DopingwithCu²⁺ on the A site of BFO reduces the number of Bi³⁺ ions which will in turn reduce the collective number of stereo-chemically active 6s² lone pairs. Simultaneously charge balance occurs through the creation of oxygen vacancies. This affects the degree of the FeO₆ octahedra and thus also the multiferroic properties of BFO. Due to this, rhombohedral phase structure occurs. [8]. It indicates crystallites with proper orientation developed for the nano-composite. The phase obtained from XRD indicates the presence of perovskite bismuth ferrite with file no: JCPDS File No 86-1518. Angle 2 θ of highest intensity (100%) is found to be 31.79 (x=0.0, 0.25 and 0.50) and 35.56 (x=0.75 and 1.00) [9-10]. The X ray diffraction patterns of copper doped BFO show that all the species have similar diffraction patterns which indicates that all have distorted perovskite crystal structures. The values of the crystal lattice constants "a" and "c" for all the samples determined from X ray data which are in the range 5.23 to 3.85 [5.23, 5.14, 5.21, 4.00 and 3.85](Å) and c = 13. 35 (Å). Generally rhombohedral peak splitting XRD of BFO appears at 31.79 $^{\circ}$ and 32.10 $^{\circ}$ and gradually decreases when divalent ions are doped into it. In the present study similar splitting is noticed. This suggest that the compound possess rhombohedral structure. This is in consistence with the work of other researchers [11,12]. It further supports that our compound is in single phase. In XRD of copper doped BFO pattern majority of peaks disappear and remaining are shifted

towards higher angle side. It is assumed that Bi³⁺ is replaced by ions of Cu²⁺ ions. This suggests that copper replaces bismuth place in the ferrite system by creating oxygen vacancies. The lattice constant 'a' is found to decreasing with increase of Cu concentration. Shift of reflections towards higher angle and no splitting of peaks with the increasing Cu concentration show that Cu atoms have incorporated into the tetrahedral 'A' site of ferrite structure.

The lattice constant "a" decreases for the ferrites with x = 0.00 to x = 1.00, suggesting that bismuth is reducing in the ferrite and is replaced by Cu without disturbing the lattice symmetry. The decrease in lattice constants and unit cell volume is expected due to the stoichiometric replacement of Bi³⁺ with a smaller ionic radii substituent of Cu²⁺. A comparison of lattice parameters themselves reveals a single- phase compound is formed. The effect of copper doping is further reflected in the EPR spectra shown in Figure2. It is clear that increase of 'x' gives rise to broad and less intense IR bands associated with the normal modes in pure BFO while there is no appearance of extra bands in the doped samples. Thus, it appears that doping with Cu²⁺ in BFO affects the perovskite related phonon modes which are associated with a tilting of the FeO₆ a octahedral, the motion of oxygen atoms associated with the Bi site and the off-centering of the Fe from its special crystallographic position [12]. This suggests that the samples synthesized are in single phase.

The average particle size of the compound is evaluated from the line broadening of the peaks using Debye-Scherrer equation.

$$D_{(hkl)} = \frac{0.89\lambda}{\beta_{\frac{1}{2}} \cos \theta}$$

Here D is the particle size of the crystal, λ is the wavelength of incident X ray, θ is the corresponding Bragg angle, $\beta_{\frac{1}{2}}$ is the full width at the half maximum height (FWHM) of the peak.

The evaluated D values are in the range 54 to 30 nm (54, 40, 38, 33, and 30nm). It is noticed that the average particle size goes on decreasing as the doping concentration increases. The maximum size obtained is about 54 nm only.

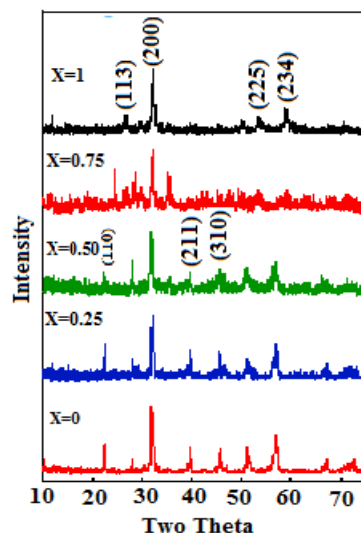


Figure 1. XRD pattern of Bi_{1-x}Cu_xFeO_{3-x/2}

EPR spectral analysis

EPR measurements are useful for obtaining information related to the location of the transitional metal ion impurities within the lattice of the nano BFO compound. The EPR spectrum of $\text{Bi}_{1-x}\text{Cu}_x\text{FeO}_{3-x/2}$ ($x = 0.00, 0.50$ and 1.00) in the temperature range 120K to 300K is shown in Figure 2 is characteristic of Fe(III). The spectrum at all temperatures reveals only one resonance line. From the position of the peak in the EPR spectrum, the calculated spectroscopic splitting factor 'g' values along with other parameters are given in Table 1.

Most of the researchers felt that Fe(III) is placed in rhombic symmetry in the crystal field. For the rhombic symmetry spin-orbit coupling constant, λ , is calculated with the following relation [13].

$$H_R(\text{mT}) = \frac{21419.49}{g\lambda(\text{cm})} = \frac{0.07144775}{g} \nu(\text{MHz})$$

λ obtained for each g tensor is 32.60. For axial symmetry, λ is zero. If rhombic character in the crystal field is increased, it results in the increase of λ up to a maximum of 1/3 [15]. In the present case, the observed value of λ is 1/3 (32.60). Thus, the EPR results indicate that the pure and Cu doped BFO is in perfect rhombic structure. These results agree with the XRD.

The observed resonance in the EPR spectrum shown in Figure 2 is temperature dependent. Variation of magnetic structure with temperature is studied using the resonance shift (H_c), the g-factor, the peak-to-peak width (ΔH_{pp}), the integrated intensity (I_{EPR}), and the asymmetry parameter.

Temperature dependence of the g-factor of the EPR spectra is plotted in Figure 3. It is noticed from the Figure 3 that when the compound contains Bi, g values decrease when temperature is increased. This may be due to gradual build-up of the orbital ordering at low temperature [16]. This in turn causes the change in spin-orbit coupling as well as the crystal-field parameters. A sharp decrease in g value is noticed at 180, 200 and 260 K. This may be due to the exchange of Bi(III) and Fe(III) ions in the ideal perovskite structure contributing to multiferroic properties [17]. These ion displacements will break the centrosymmetry of BFO and induce a spin-reorientation in the 180 K, 200 K and 260 K.

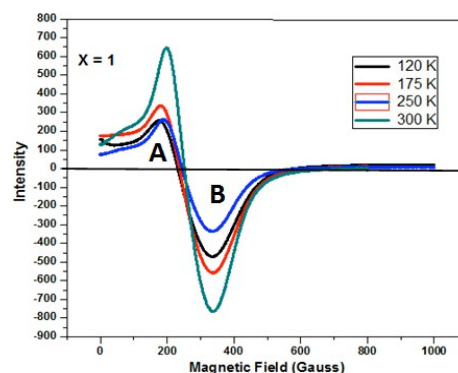
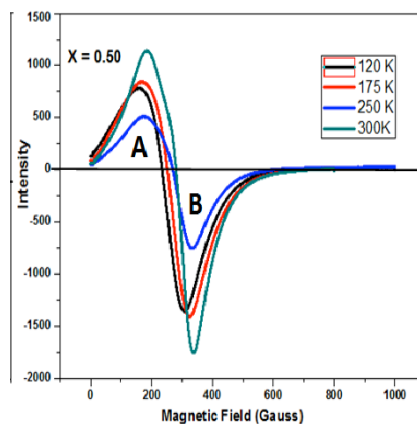
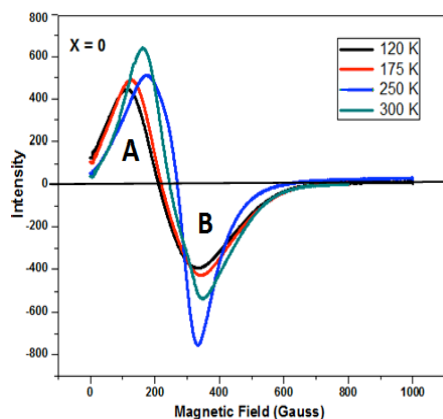


Figure 2 EPR spectrum of $\text{Bi}_{1-x}\text{Cu}_x\text{FeO}_{3-x/2}$

Temperature versus EPR intensity (I_{EPR}) graph is shown in Figure 3. Generally, EPR intensity is proportional to the dc susceptibility (χ) of the spins. The EPR intensity for the concentrations $x=0$ and $x=0.50$ is linear and parallel to temperature axis up to 180K and increases with increase of temperature for $x=0.00$ and decreases for $x=0.50$ concentration. This may be due to magnetic fluctuations occurring at 180 K and 260 K, it may slow down the spin reorientation transition [18]. The temperature dependence of the peak-to-peak line width ΔH is shown in Figure 3. The line width decreases with increasing temperature, which is found to be common in antiferromagnetic materials [19-20]. The observed narrowing of the EPR peaks with the increase in temperature in the present case can be attributed to an exchange interaction between unlike spins. The temperature dependence of the asymmetric parameter A/B is also shown in Figure 3. This asymmetric parameter is an indication of the extent of anisotropy in the magnetic structure of the sample [21]. As can be seen in Figure 3, the spin-reorientation behavior occurs at 180 and 260 K. The large value of A/B for BFO indicates a large magneto crystalline anisotropy in the magnetic interactions.

Magnetic measurements

Figure 4 shows temperature (T) dependences of magnetization (M) measured in zero-field-cooled (ZFC) and field-cooled (FC) modes in a field of 1000 Oe. It is seen that at different temperatures and with different compositions, the curves start to differ from each other and the difference grows as temperature is lowered. This implies that below room temperature the behavior of the sample is not purely paramagnetic (PM), i.e. ferromagnetic

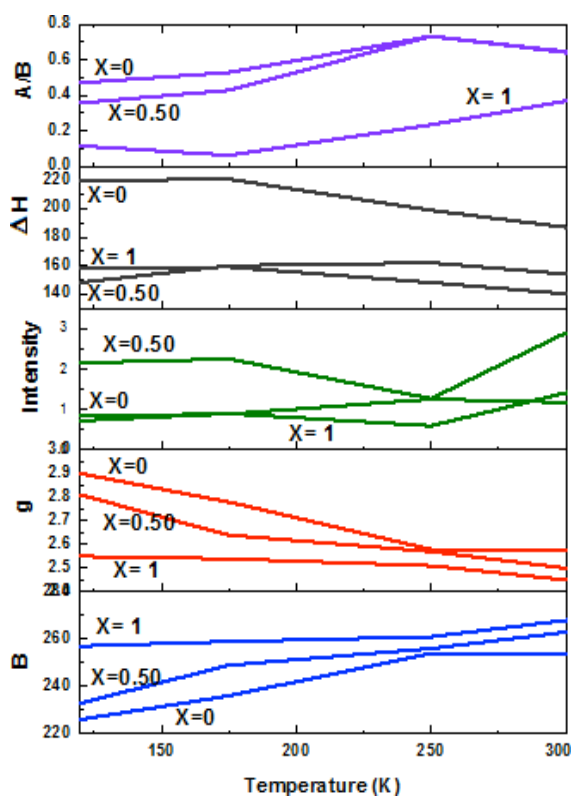


Figure 3. Temperature versus various EPR parameters $H_c, g, I_{EPR}, \Delta H, A/B$.

Table 1. Various EPR parameters for the ferrite $\text{Bi}_{1-x}\text{Cu}_x\text{FeO}_{3-x/2}$

Temperature	Parameter							x
	Field(H) Gauss	g	$\lambda=21419.49/\text{gH}$	Intensity(I)	A/B	ΔH	$\Delta H \text{ XT}$	
120	226	2.90	32.68	0.84	0.470	220	24000	0.00
175	236	2.78	32.64	0.89	0.529	221	38675	
250	254	2.58	32.68	1.25	0.733	199	49750	
300	254	2.58	32.68	1.25	0.647	187	56100	
120	233	2.81	32.73	2.15	0.36	148	17760	0.50
175	248	2.64	32.63	2.25	0.43	160	28000	
250	255	2.57	32.64	1.26	0.73	162	40500	
300	262	2.50	32.63	2.89	0.64	154	46200	
120	257	2.55	32.68	0.72	0.12	158	18960	1.00
175	259	2.54	32.68	0.90	0.06	158	27825	
250	261	2.51	32.68	0.60	0.24	148	37000	
300	268	2.45	32.68	1.40	0.37	140	42000	

(FM) phase starts it is already present near room temperature. This may be at high temperature the spins are in a paramagnetic state. At lower temperature the ordered spin clusters are formed which freeze below temperature into random directions. It is assumed that the freezing temperature corresponds to the maximum of ZFC susceptibility.

In the case of pure bismuth ferrite (BiFeO_3) up to 90 K both paramagnetic and ferromagnetic behavior is present, and then increases of temperature the sample exhibit only paramagnetic behavior. As bismuth content is decreasing or copper doping is

increasing the transition temperature is increasing. When $x=0.25$ the transition temperature is about 120K. But in the case of $x=0.75$ and 0.50 magnetization (M) is almost same and transition temperature (180K) is also identical. This may be due to the exchange of Bi(III) and Fe(III) ions and causes to multi ferroic properties [22,23]. This suggests that the formula of $\text{Bi}_{0.50}\text{Cu}_{0.50}\text{FeO}_3$ holds good.

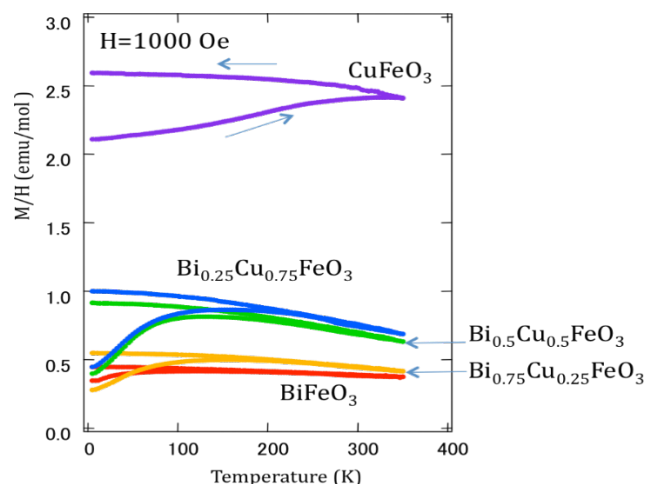


Figure 4. Temperature dependences of ZFC and FC magnetizations measured in field of 1000 Oe.

FTIR analysis

The infrared spectra recorded at RT in the range 400 to 4000cm^{-1} for $\text{Bi}_{1-x}\text{Cu}_x\text{FeO}_{3-x/2}$ with variable composition from $x=0$ to 1.00 in steps of 0.25 are shown in Figure 5. It is seen from the Figure 5 that BFO powders of all composition show almost all the common bands at 3435, 2925, 2848, 1626, 1391, 1023, 814 and 553cm^{-1} .

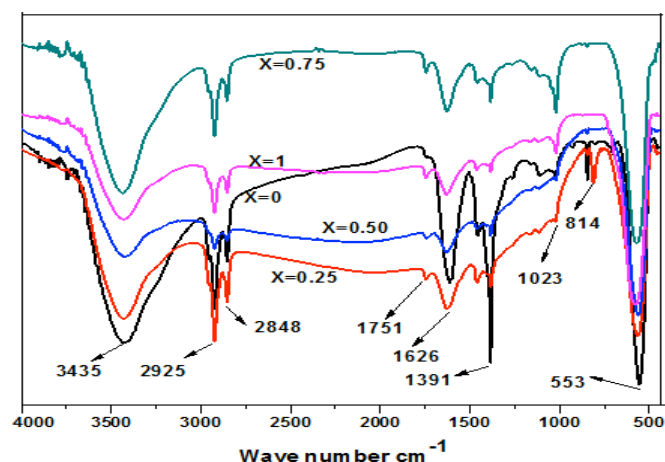


Figure 5. FTIR spectrum of $\text{Bi}_{1-x}\text{Cu}_x\text{FeO}_{3-x/2}$ nanocompound at RT.

Literature survey shows stretching vibration occurs for M-O tetrahedral site in the range of $620\text{--}550\text{cm}^{-1}$. Accordingly, very sharp band with maximum intensity observed at 553cm^{-1} is assigned to M-O-tetrahedral site [24]. The other common bands noticed at 3435, 2925 are ascribed to free or adsorbed water fundamentals of ν_3, ν_2 of OH. The band at 1626cm^{-1} with shoulder

on either side corresponds to bending vibration of H₂O. Very sharp band at 1391 cm⁻¹ is due to the presence of trapped nitrates [25]. Low intensity sharp bands observed at 814 and 2848 cm⁻¹ are assigned to the existence of nitrate ions (NO₃⁻). The other weak band at 1023 cm⁻¹ is first overtone of the fundamental M-O-H bending mode.

CONCLUSION

In conclusion, well dispersed BFO and Cu doped BFO ferrite powders have been synthesized successfully using bismuth nitrate [Bi(NO₃)₃·5H₂O], iron nitrate [Fe(NO₃)₃·9H₂O] and copper nitrate [Cu(NO₃)₂·3H₂O]. Three Cu(II) atoms can replace two atoms of Bi (III). It means that the formula Bi_{1-x}Cu_xFeO_{3-x/2} holds good only for x = 0.50. Structural characterization such as X-ray diffraction studies confirm rhombic phase of the samples. A decrease in the lattice parameters has been observed with increasing Cu doping level. XRD reveals that particle size is about 54nm. EPR studies indicate that the structure is rhombic. Also, these studies suggest that there are two phases at low temperature. Temperature dependence magnetic measurements suggesting that there are two phases at low temperature and at above 250K only paramagnetic is present in the sample. IR studies suggest that the formed powder is nano rhombic ferrite. Further nitrate ions exist in the powder sample as trapped particles. From IR studies, we confirm the ferrite powder contain some water molecules as adsorbed water.

DECLARATION OF INTEREST

The authors declare that they have no conflicts of interest related to this work. No financial support was received for this research. The authors have no competing interests or affiliations that could influence the study.

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