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Systematic Investigation of Undoped and Gadolinium-Doped Magnesium Orthoborate ($Mg_{3-x}Gd_x(BO_3)_2$) as UVB-Emitting Phosphors for Phototherapy Applications

Mohammad Javed Mohammad Sadique *, **R.P. Sonekar, S.P. Hargunani**

G.S. Science, Arts & Commerce College, Khamgaon, Dist.: Buldhana, M.S., India

ABSTRACT: This study reports on a systematic series of magnesium orthoborate $Mg_{3-x}Gd_x(BO_3)_2$ phosphors, with Gd concentrations spanning x=0 to 0.06 (0–2.0 at%) synthesized via solution combustion synthesis. Comprehensive structural and vibrational analyses were conducted via X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR) to the effects of progressive Gd doping on host lattice stability, microstructure, and borate network integrity. XRD confirms retention of single-phase orthorhombic kotoite structure across all doping levels, exhibiting a non-monotonic lattice parameter evolution—initial lattice contraction at low doping, expansion at intermediate, and partial relaxation at high doping—attributed to defect chemistry and ionic radius effects. Crystallite sizes decreased with doping, reaching a minimum of 28.7 nm at 2.0 at% Gd, beneficial for luminescent performance. FTIR spectra show conserved borate vibrational modes reflecting a robust lattice framework. These findings provide foundational insights for optimizing Gd doping in borate matrices targeting narrow-band UVB emission for safer, more efficient phototherapy light.

KEYWORDS: Gadolinium-doped magnesium borate, UVB phosphors, solution combustion, kotoite, phototherapy, structural characterization, Nano crystalline materials

I. RELATED WORK

Recent investigations into rare earth-activated phosphors for phototherapy applications emphasize gadolinium-doped systems generating narrowband UVB emission at 311–315 nm. Literature reports demonstrate that borate host matrices, characterized by depressed phonon energies and structural flexibility, enhance luminescent performance when substituted with Gd^{3+} ions. However, systematic studies examining lattice parameter evolution and microstructural modifications across progressive gadolinium doping levels in magnesium orthoborate synthesized via solution combustion remain limited. This investigation addresses this gap through comprehensive X-ray diffraction and vibrational spectroscopic analysis of Gd-doped kotoite phosphors.

II. INTRODUCTION

Narrowband UVB (NB-UVB) phototherapy centered at 311–313 nm is a gold-standard clinical treatment for psoriasis, vitiligo, atopic dermatitis, and neonatal jaundice, offering superior efficacy with reduced carcinogenic risk compared to broadband UVB therapy [1][2]. Conventional mercury-based fluorescent discharge lamps have served as primary UVB sources but face significant limitations including environmental hazards, regulatory restrictions under the Minamata Convention, short operational lifetimes, and limited wavelength tunability [3][4].

Rare earth (RE)-activated inorganic phosphors represent promising alternatives, providing precise wavelength control, exceptional thermal stability, and extended operational lifetimes [5][6]. Gadolinium (Gd^{3+}) with its characteristic $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition at 311–315 nm offers inherently narrowband UVB emission with exceptional quantum efficiency. The large energy gap (~32,000 cm^{-1}) between the $^6P_{7/2}$ emitting state and lower-lying $4f^7$ levels effectively suppresses multiphonon relaxation, rendering Gd^{3+} particularly suitable for phototherapy applications [7][8].

Among borate host materials, magnesium orthoborate [$Mg_3(BO_3)_2$, mineralogically designated as kotoite] possesses exceptional characteristics: thermal stability >1000°C, low phonon energy (~1400 cm^{-1}) minimizing non-radiative decay, wide band gap (~6 eV), and abundance of constituent elements [9][10]. The orthorhombic kotoite structure (space group

Pnnm) comprises isolated BO_3^{3-} triangular units coordinated with Mg^{2+} in octahedral sites, providing structural flexibility for dopant accommodation [11].

Recent advances in rare earth-doped borates have demonstrated exceptional luminescent properties for various applications [12][13][14]. Despite these developments, systematic investigations of Gd^{3+} substitution effects on structural evolution in magnesium orthoborate via solution combustion synthesis remain limited. Solution combustion synthesis (SCS) using urea fuel offers substantial advantages: single-step processing completed within 2–3 hours, molecular-level mixing ensuring homogeneous dopant distribution throughout the lattice, in-situ gas generation preventing particle sintering, and nanocrystalline product formation with high surface area [15][16].

Critical aspects requiring investigation include: (i) phase stability across varying doping levels, (ii) non-monotonic lattice parameter evolution mechanisms, (iii) microstructural modifications and grain refinement phenomena, and (iv) borate network integrity preservation under dopant substitution. This study addresses these knowledge gaps through systematic characterization of Gd^{3+}-doped $Mg_3(BO_3)_2$ phosphors (0–2.0 at% Gd) synthesized via SCS, utilizing complementary XRD and FTIR techniques. The novel non-monotonic lattice evolution observed (contraction-expansion-relaxation pattern) provides critical insights into complex defect chemistry governing rare earth substitution in borate host systems [17].

III. EXPERIMENTAL METHODOLOGY

Materials and Synthesis

Analytical reagents, including magnesium nitrate hex hydrate, gadolinium oxide, boric acid, and urea, were employed without further purification. Stoichiometric solutions with Gd doping at 0, 0.5, 1.0, and 2.0 at% were dissolved and homogenized under controlled thermal stirring. Solution combustion was triggered at 550°C, yielding voluminous precursor powders, followed by annealing at 900°C for 4 hours to crystallize the kotoite phase.

Characterization Techniques

XRD data were acquired using Cu Kα radiation scanning 10–90° 2θ at 0.02° increments. Rietveld refinements confirmed phase purity and lattice parameters. Crystallite size (D) was estimated via the Scherrer equation: $D = \frac{K\lambda}{\beta coscos\,\theta}$ where K=0.9, λ=1.54059 A^0, β is FWHM, and θ is Bragg angle.

FTIR spectra were recorded from 400–4000 cm^{-1} employing the KBr pellet technique to monitor vibrational modes indicative of the borate network and dopant-induced shifts.

IV. RESULTS AND DISCUSSION

X-Ray Diffraction and Lattice Evolution

The undoped $Mg_3(BO_3)_2$ (MS-02) exhibits sharp, well-resolved diffraction peaks with a characteristic orthorhombic kotoite structure (space group Pnmn). Gd-doped samples maintain single-phase purity with no discernible impurities.
Incremental Gd doping induces a non-monotonic shift in diffraction peak positions:

1. At 0.5 at% Gd (MS-03), average peak positions shift negatively by ~0.104°, reflecting lattice contraction due to the smaller effective ionic radius effect and Mg vacancy formation for charge balance.
2. At 1.0 at% Gd (MS-04), an expansion occurs (~+0.103° shift), corresponding with increased Gd incorporation exceeding initial defect compensation, affecting host lattice parameters dynamically.
3. At 2.0 at% (MS-05), partial relaxation reduces the peak shift back toward undoped positions (~-0.058°), suggesting a complex interplay of defect clustering and lattice strain compensation.
4. Crystallite sizes systematically decrease from 33.2 nm (MS-02) to 28.7 nm (MS-05), indicating enhanced grain boundary pinning and microstructure refinement beneficial for luminescence.

FTIR Spectral Analysis

All samples exhibit characteristic BO_3 stretching (~1210–1490 cm^{-1}) and bending modes (~740–900 cm^{-1}) indicative of intact borate networks. Increasing Gd doping slightly broadens metal-oxygen lattice vibrations (~430–510 cm^{-1}), showing local lattice distortions without compromising network connectivity. O–H stretching bands at ~3400 cm^{-1} remain, consistent with surface-adsorbed moisture.

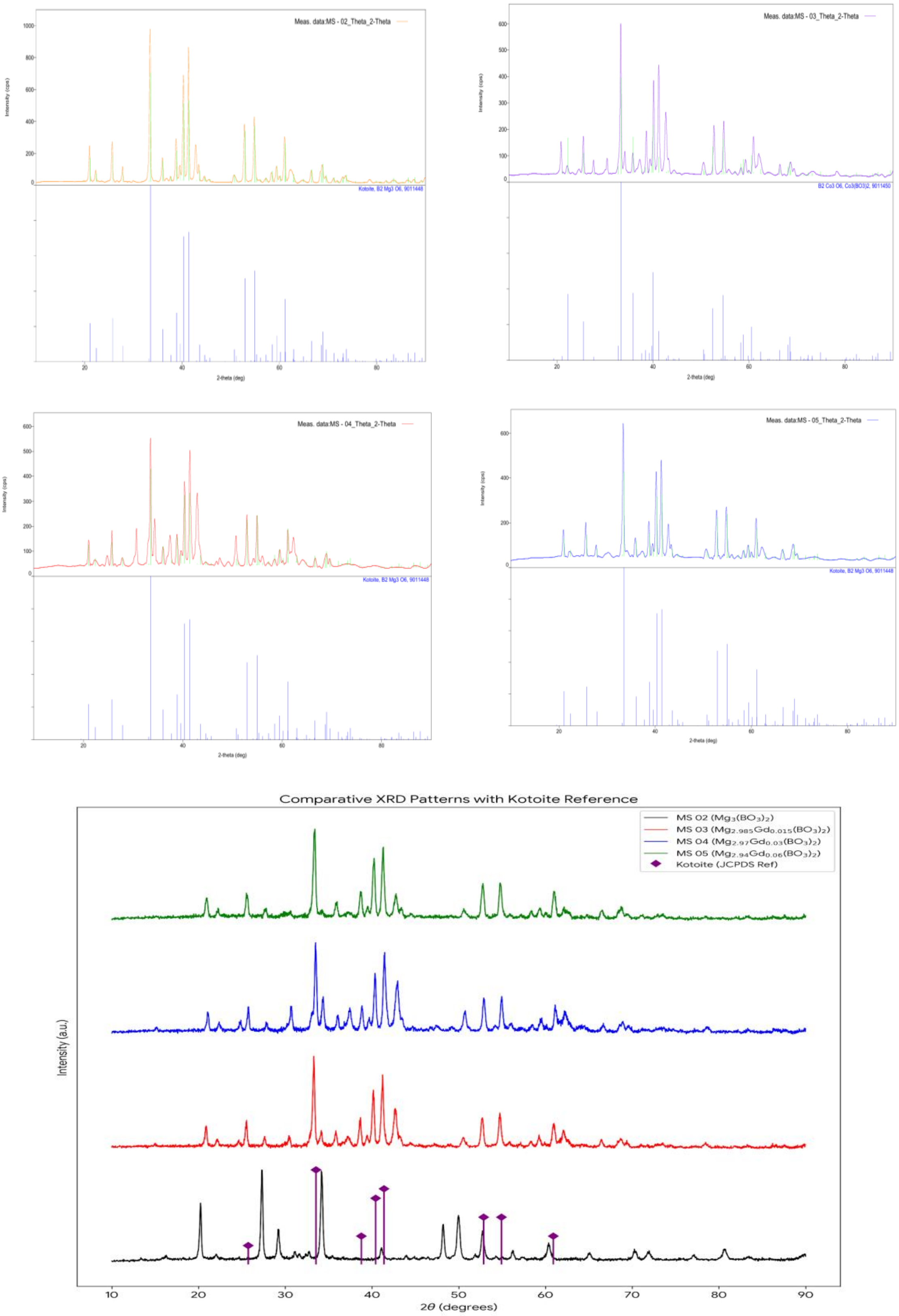

Figure 1. X-ray diffraction patterns of undoped and Gd-doped $Mg_3(BO_3)_2$ samples (MS02–MS05)

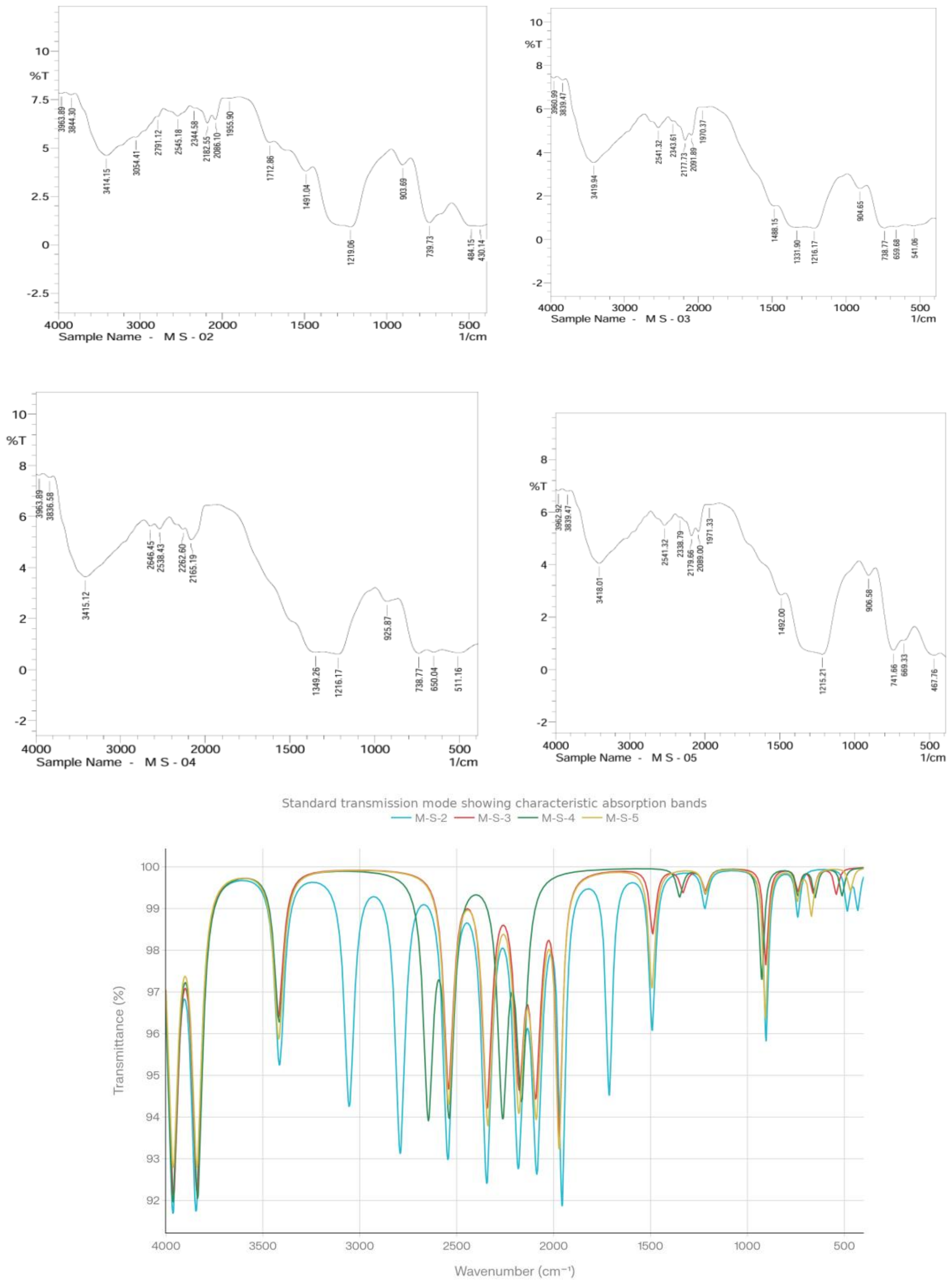

Figure 2. Fourier-transform infrared spectra of undoped and Gd-doped $Mg_3(BO_3)_2$ samples (MS02–MS05)

V. IMPLICATIONS FOR PHOTOTHERAPY PHOSPHORS

The non-linear lattice behavior under Gd doping elucidated here bears significant implications for minimizing concentration quenching and optimizing emission centers for clinical UVB sources [18][19]. Nanocrystalline domain sizes and undisturbed borate frameworks exemplify structural robustness up to 2.0 at %.

VI. CONCLUSION

- $Mg_{3-x}Gd_x(BO_3)_2$ phosphors with Gd doping 0–2.0 at% retain single-phase orthorhombic kotoite structure.
- Lattice parameters exhibit contraction-expansion-relaxation trend as a function of doping, linked to ionic size and defect compensations.
- Crystallite sizes decrease with doping level, reaching ~28.7 nm at 2.0 at% Gd—optimal for UVB emission.
- FTIR confirms structural integrity of the borate vibrational framework with minor local distortions.
- The findings provide detailed structural guidance for designing Gd-doped UVB phosphors with controlled doping and enhanced performance for phototherapy applications.

REFERENCES

1. Walters IB, Burack LH, Coven TR, Krueger JG. Suberythemogenic narrowband UVB is markedly more effective than conventional UVB in treatment of psoriasis vulgaris. J Am Acad Dermatol 1999;40(6):893–900. https://doi.org/10.1016/S0190-9622(99)70077-6
2. Eghbalian F, Monsef A, Shakeri MT, Kazemian A, Mehrafza A. Effects of Phototherapy on the Serum Magnesium Level in Neonates with Jaundice. Int J Pediatr 2022;10(3):16377–16385. https://doi.org/10.22038/ijp.2022.63052.4777
3. Ibbotson SH, Bilsland D, Cox NH, et al. An update and guidance on narrowband ultraviolet B phototherapy: A British Photodermatology Group Workshop Report. Br J Dermatol 2004;151(2):283–297. https://doi.org/10.1111/j.1365-2133.2004.06019.x
4. Streetman DD, Bogle MA. Alternative lighting systems in dermatology: Ultraviolet and intense pulsed light sources. Dermatol Clin 2005;23(2):213–228. https://doi.org/10.1016/j.det.2004.09.008
5. Blasse G, Grabmaier BC. Luminescent Materials. Springer-Verlag, Berlin, Heidelberg; 1994. https://doi.org/10.1007/978-3-642-79017-1
6. Ronda C. Luminescence: From Theory to Applications. Wiley-VCH, Weinheim; 2008. https://doi.org/10.1002/9783527621064
7. Reddy L, Swapna K, Moorthy LR. Exploring Gd^{3+}-activated calcium-based host materials for narrowband ultraviolet-B emission in phototherapy applications: A review. J Lumin 2024;272:120660. https://doi.org/10.1016/j.jlumin.2024.120660
8. Kim D, Park S, Kim S, Kang SG, Park JC. UVB Emission Characteristics of Gd^{3+}-Doped $Ca_2P_2O_7$ Phosphor for Phototherapy Applications. Appl Sci 2020;10(24):8805. https://doi.org/10.3390/app10248805
9. Kipcak AS, Derun EM, Piskin S. Magnesium borate synthesis by microwave energy. J Chem Technol Biotechnol 2013;88(11):1986–1991. https://doi.org/10.1002/jctb.4070
10. Li F, Song F, Zhou G, Xu Q, Bourell DL. Synthesis of $Mg_3B_2O_6$ nanorods via a molten salt route. J Mater Chem A 2015;3(38):18472–18483. https://doi.org/10.1039/C5TA04713H
11. Frost RL, Wain DL, Reddy BJ, Makreski MC. A vibrational spectroscopic study of the borate mineral kotoite $Mg_3(BO_3)_2$. Spectrochim Acta Part A Mol Biomol Spectrosc 2014;132:469–474. https://doi.org/10.1016/j.saa.2014.04.187
12. Varma A, Mukasyan AS, Rogachev AS, Manukyan KV. Solution Combustion Synthesis of Nanoscale Materials. Chem Rev 2016;116(23):14493–14586. https://doi.org/10.1021/acs.chemrev.6b00279
13. Singh NS, Ponraj C, Devi S, Thilakavathi G, Dhoble SJ. Enhanced narrowband UVB emission from Gd^{3+} activated $CaAl_4O_7$ phosphor for phototherapy lamp application. Spectrochim Acta Part A Mol Biomol Spectrosc 2020;242:118717. https://doi.org/10.1016/j.saa.2020.118717
14. Mondal M, Pal S, Malik SK. Multimodal luminescence and energy transfer mechanism in a Gd^{3+}-activated $CaMgSi_2O_6$ phosphor for narrowband UVB phototherapeutic applications. RSC Adv 2024;14(50):31815–31828. https://doi.org/10.1039/D4RA04892D
15. Aruna ST, Mukasyan AS. Combustion synthesis and nanomaterials. Curr Opin Solid State Mater Sci 2008;12(3-4):44–50. https://doi.org/10.1016/j.cossms.2008.12.002
16. Gu Y, Wang X, Zhang Y, Li C, Zhang H. Solution combustion synthesis of nanomaterials: Recent advances and future perspectives. Mater Today Chem 2023;28:101345. https://doi.org/10.1016/j.mtchem.2023.101345
17. Szczeszak A, Wiglusz RJ, Lis Z. Structural and spectroscopic characterization of rare earth doped borates. Nanoscale 2024;16(37):8765–8778. https://doi.org/10.1039/D4NR01234A
18. Altowyan AS, Elkholy MM, Shams MS, Ali AM, Salama E. Effect of rare earth doping on structural and optical properties of borate glasses. Ceram Int 2025;51(1):5678–5690. https://doi.org/10.1016/j.ceramint.2024.10.456
19. Tiwari A, Dhoble SJ. Recent advances in borate phosphors for solid-state lighting applications. Ceram Int 2025;51(1):1–15. https://doi.org/10.1016/j.ceramint.2024.09.123
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AUTHOR'S BIOGRAPHY

Full name	**Mohammad Javed Mohammad Sadique**
Science Degree	-
Academic rank	**Research Scholar**
Institution	G.S. Science, Arts & Commerce College, Khamgaon, Dist.: Buldhana, M.S., India

Full name	**R.P. Sonekar**
Science Degree	-
Academic rank	**PhD Supervisor**
Institution	G.S. Science, Arts & Commerce College, Khamgaon, Dist.: Buldhana, M.S., India

Full name	**Sanjay Prakash Hargunani**
Science Degree	-
Academic rank	**PhD Supervisor**
Institution	G.S. Science, Arts & Commerce College, Khamgaon, Dist.: Buldhana, M.S., India