



Comparative Structural, Vibrational, and Optical Properties of Ba(Ni_{0.5}M_{0.5})O₃ (M = Cu, Co, Cr) Perovskites: A Study Using XRD, FTIR, and UV-Vis Spectroscopy

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Abstract:

This study presents the synthesis and comparative analysis of Ba(Ni_{0.5}Co_{0.5})O₃, Ba(Ni_{0.5}Cu_{0.5})O₃, and Ba(Ni_{0.5}Cr_{0.5})O₃ perovskite compounds, focusing on their structural, vibrational, and optical properties. The sol-gel method was employed to synthesize the materials, and X-ray diffraction (XRD) confirmed the formation of a cubic perovskite structure in all three compounds with high crystallinity. The calculated crystallite sizes were found to be in the nanometer range (24.77–29.53 nm), with slight lattice expansion observed for Cu and Cr substitutions. Fourier-transform infrared (FTIR) spectroscopy confirmed the presence of metal-oxygen bonds, characteristic of the perovskite structure, and indicated successful phase formation without impurities. UV-Vis spectroscopy revealed band gap energies of 2.68 eV for Ba(Ni_{0.5}Co_{0.5})O₃, 2.92 eV for Ba(Ni_{0.5}Cu_{0.5})O₃, and 3.18 eV for Ba(Ni_{0.5}Cr_{0.5})O₃, suggesting their potential for optoelectronic and photocatalytic applications. These results demonstrate the efficacy of the sol-gel synthesis method in producing high-purity perovskite materials with desirable structural, vibrational, and optical properties, making them suitable for advanced technological applications such as photocatalysis, solar cells, and other optoelectronic devices.

Introduction:

Perovskite materials, particularly those with the general formula ABO₃, have garnered considerable attention due to their versatile structural and functional properties, making them valuable for a wide range of applications such as catalysis, solid oxide fuel cells, and electronic devices. These materials exhibit a unique cubic structure that allows for various elemental substitutions at both the A and B sites, providing a platform for fine-tuning their properties for specific uses (Sebastian, 2008). Recent studies have explored the effect of elemental doping on the performance of perovskites in catalytic applications. Zhang, Wang, and Chen (2021) investigated the role of elemental doping in ABO₃ perovskites during low-pressure gas nitriding, demonstrating that doping can significantly enhance catalytic activity by altering the surface properties and redox behavior of the material. Similarly, the catalytic oxidation properties of ABO₃-type perovskites were studied by Poplawski et al. (2000), further highlighting the importance of the B-site elements in determining the material's reactivity and stability.

The synthesis and development of perovskites for applications such as solid oxide fuel cells (SOFCs) also remain an active area of research. Domínguez-Crespo et al. (2024)

synthesized ABO₃ perovskites using the Pechini method and analyzed their structural and electrical properties, confirming that elemental substitutions at the B-site can enhance conductivity and stability, making them promising cathode materials in SOFCs. The Pechini method, known for producing high-purity perovskites, is particularly advantageous for fabricating materials with controlled microstructures (Domínguez-Crespo et al., 2024).

Furthermore, advanced oxidation processes (AOPs) have been a major focus in the environmental application of perovskites. Mamba, Mafa, and Rtimi (2022) reviewed heterogeneous AOPs over ABO₃ perovskites and concluded that structural modifications due to doping can enhance the photocatalytic efficiency, making these materials highly effective in pollutant degradation. This reinforces the importance of tailoring perovskite structures for environmental applications.

The study of structural, electronic, and optical properties of perovskites has also been advanced through computational methods. Parvaiz, Khalil, and Tahir (2024) conducted density functional theory (DFT) investigations on inorganic perovskites, revealing that substitutions at the B-site lead to significant changes in electronic and optical properties, which are critical for applications in photosensitive devices.

Given the broad scope of perovskite research, this paper aims to conduct a comparative analysis of $\text{Ba}(\text{Ni}_{0.5}\text{Cu}_{0.5})\text{O}_3$, $\text{Ba}(\text{Ni}_{0.5}\text{Co}_{0.5})\text{O}_3$, and $\text{Ba}(\text{Ni}_{0.5}\text{Cr}_{0.5})\text{O}_3$ perovskites. The study will focus on the structural, vibrational, and optical properties of these materials using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and UV-Vis spectroscopy. By comparing the effects of different B-site substitutions (Cu, Co, Cr), this research seeks to provide insights into how these substitutions influence the material's properties and potential applications.

Experimental

The $\text{Ba}(\text{Ni}_{0.5}\text{Co}_{0.5})\text{O}_3$, $\text{Ba}(\text{Ni}_{0.5}\text{Cu}_{0.5})\text{O}_3$, and $\text{Ba}(\text{Ni}_{0.5}\text{Cr}_{0.5})\text{O}_3$ perovskites were synthesized using the sol-gel method, a versatile technique that provides excellent control over the composition and homogeneity of the final product. Barium nitrate [$\text{Ba}(\text{NO}_3)_2$], nickel nitrate [$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], cobalt nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], copper nitrate [$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$], and chromium nitrate [$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] were used as precursors in the respective stoichiometric ratios (1 mol Ba, 0.5 mol Ni, and 0.5 mol of Co, Cu, or Cr). Each nitrate was dissolved in distilled water, and the solutions were mixed under constant stirring to ensure homogeneity. Citric acid (1:1 molar ratio with the total metal ions) and ethylene glycol were added to chelate the metal ions and promote gelation. The mixture was heated at 80°C with continuous stirring until a viscous gel formed, which was then dried at 120°C for 12 hours to remove any residual water and solvents. The dried gel was ground into fine powder and calcined in a muffle furnace. For $\text{Ba}(\text{Ni}_{0.5}\text{Co}_{0.5})\text{O}_3$, the powder was calcined at 900°C for 4 hours, while for $\text{Ba}(\text{Ni}_{0.5}\text{Cu}_{0.5})\text{O}_3$ and $\text{Ba}(\text{Ni}_{0.5}\text{Cr}_{0.5})\text{O}_3$, calcination was performed at 850°C for 5 hours and 950°C for 6 hours, respectively. The heating rate was controlled, with a soak period at the final temperature to ensure complete phase formation. Finally, the powders were cooled naturally inside the furnace to prevent thermal shock and ensure stable crystalline structures. This process ensured high-purity perovskite materials, ready for further characterization.

Results and Discussion

Structural Analysis (XRD)

X-ray diffraction (XRD) analysis was conducted to determine the crystalline structure and phase purity of the synthesized $\text{Ba}(\text{Ni}_{0.5}\text{Co}_{0.5})\text{O}_3$, $\text{Ba}(\text{Ni}_{0.5}\text{Cu}_{0.5})\text{O}_3$, and $\text{Ba}(\text{Ni}_{0.5}\text{Cr}_{0.5})\text{O}_3$ perovskites. The XRD patterns of all three compounds were compared with the standard Joint Committee on Powder Diffraction Standards (JCPDS) data, confirming the successful formation of cubic perovskite structures. The diffraction peaks in all cases showed sharp intensity, indicating high crystallinity and well-ordered structures. The peak

positions and lattice parameters varied slightly due to the substitution of different B-site cations (Co, Cu, and Cr).

For $\text{Ba}(\text{Ni}_{0.5}\text{Co}_{0.5})\text{O}_3$, the average crystallite size was calculated to be 29.53 nm using the Debye-Scherrer equation. The $\text{Ba}(\text{Ni}_{0.5}\text{Cu}_{0.5})\text{O}_3$ and $\text{Ba}(\text{Ni}_{0.5}\text{Cr}_{0.5})\text{O}_3$ compounds showed slightly smaller crystallite sizes of 26.86 nm and 24.77 nm, respectively, suggesting that the substitution of Cu and Cr results in finer particle sizes. These small crystallite sizes are beneficial for applications where higher surface area and reactivity are essential, such as in catalysis or electronic devices. The lattice constants also varied, with Cu and Cr ions causing slight expansion of the lattice due to their larger ionic radii compared to Co, consistent with the observed diffraction data. Overall, the XRD results confirmed that all three perovskites were successfully synthesized with high phase purity and nanocrystalline structures.

Vibrational Analysis (FTIR)

Fourier-transform infrared (FTIR) spectroscopy was performed to confirm the presence of key functional groups and the metal-oxygen bonding characteristic of perovskite structures in $\text{Ba}(\text{Ni}_{0.5}\text{Co}_{0.5})\text{O}_3$, $\text{Ba}(\text{Ni}_{0.5}\text{Cu}_{0.5})\text{O}_3$, and $\text{Ba}(\text{Ni}_{0.5}\text{Cr}_{0.5})\text{O}_3$. The FTIR spectra for all samples exhibited strong absorption bands in the range of $600\text{--}400\text{ cm}^{-1}$, which are attributed to the stretching vibrations of Ni-O, Co-O, Cu-O, and Cr-O bonds within the perovskite lattice. These metal-oxygen stretching bands are crucial for verifying the successful incorporation of the B-site metal ions into the perovskite framework. In the case of $\text{Ba}(\text{Ni}_{0.5}\text{Co}_{0.5})\text{O}_3$, the Ni-O and Co-O stretching bands were observed at around 550 cm^{-1} and 490 cm^{-1} , respectively. For $\text{Ba}(\text{Ni}_{0.5}\text{Cu}_{0.5})\text{O}_3$, the Cu-O bond vibrations appeared at slightly higher wavenumbers, around 600 cm^{-1} , reflecting the differences in bond strength and mass between the metal cations. $\text{Ba}(\text{Ni}_{0.5}\text{Cr}_{0.5})\text{O}_3$ showed Cr-O stretching bands in the range of 580 cm^{-1} to 460 cm^{-1} . The absence of broad peaks around 3600 cm^{-1} , which would indicate the presence of surface-adsorbed water or hydroxyl groups, suggested effective drying of all samples. Additionally, no significant peaks corresponding to organic residues or unreacted precursors were observed, confirming the successful formation of the perovskite phase without contamination. The FTIR results provide further evidence of the high chemical purity and structural integrity of the synthesized perovskites.

Optical Properties (UV-Vis Spectroscopy)

The optical properties of the $\text{Ba}(\text{Ni}_{0.5}\text{Co}_{0.5})\text{O}_3$, $\text{Ba}(\text{Ni}_{0.5}\text{Cu}_{0.5})\text{O}_3$, and $\text{Ba}(\text{Ni}_{0.5}\text{Cr}_{0.5})\text{O}_3$ compounds were studied using UV-Vis spectroscopy to evaluate their potential for optoelectronic and photocatalytic applications. The UV-Vis absorption spectra for all three samples

showed distinct absorption edges, which correspond to electronic transitions from the valence band to the conduction band. These absorption edges were analyzed using the Tauc plot method to estimate the optical band gap (Eg) of each compound.

Ba(Ni_{0.5}Co_{0.5})O₃ exhibited an absorption edge at around 460 nm, corresponding to a direct band gap energy of 2.68 eV. This value indicates that the material is a wide-band-gap semiconductor, suitable for applications such as photocatalysts and solar cells. Ba(Ni_{0.5}Cu_{0.5})O₃, with a slightly higher absorption edge at around 425 nm, was found to have a band gap of 2.92 eV. This higher band gap suggests improved thermal and chemical stability, making it a promising candidate for applications in harsh environments. Ba(Ni_{0.5}Cr_{0.5})O₃ showed the highest band gap energy of 3.18 eV, with an absorption edge around 390 nm. This wide band gap indicates strong potential for use in ultraviolet light absorption and high-energy optoelectronic devices. The differences in band gap energies among the three perovskite compounds can be attributed to the electronic configuration and bonding environment of the B-site cations. The higher band gaps of Ba(Ni_{0.5}Cu_{0.5})O₃ and Ba(Ni_{0.5}Cr_{0.5})O₃ suggest that these materials have higher potential for applications that require stability and efficiency under UV and visible light. Overall, the UV-Vis spectroscopy results demonstrate the excellent optical properties of these perovskite compounds and their suitability for advanced technological applications.

Conclusion:

In this study, Ba(Ni_{0.5}Co_{0.5})O₃, Ba(Ni_{0.5}Cu_{0.5})O₃, and Ba(Ni_{0.5}Cr_{0.5})O₃ perovskite compounds were successfully synthesized using the sol-gel method, demonstrating the versatility and effectiveness of this technique in producing high-quality nanocrystalline materials. X-ray diffraction (XRD) confirmed the formation of a cubic perovskite structure with high phase purity and crystallinity for all samples. The slight variations in lattice parameters and crystallite sizes due to different B-site substitutions were consistent with expectations, highlighting the influence of cation size on the structural properties of perovskites. Fourier-transform infrared (FTIR) spectroscopy further validated the formation of the metal-oxygen bonds, confirming the successful incorporation of Co, Cu, and Cr into the perovskite structure. The absence of impurities and residual precursors in the FTIR spectra supported the high chemical purity of the synthesized compounds. UV-Vis spectroscopy revealed distinct optical band gaps for each compound, with values of 2.68 eV, 2.92 eV, and 3.18 eV for Ba(Ni_{0.5}Co_{0.5})O₃, Ba(Ni_{0.5}Cu_{0.5})O₃, and Ba(Ni_{0.5}Cr_{0.5})O₃, respectively. These band gaps suggest that the materials are suitable for applications in optoelectronics, photocatalysis, and

other technologies requiring precise band gap control. Overall, this study highlights the potential of these perovskite materials for advanced technological applications and underscores the effectiveness of the sol-gel method in synthesizing high-purity perovskite compounds.

References:

1. Chengsong Zhang, Yun Wang, Yunxia Chen. (2021). Effect of elemental doping on the catalytic activity of ABO₃ perovskite oxides during low-pressure gas nitriding. *Applied Surface Science*, 548, 149276. <https://doi.org/10.1016/j.apsusc.2021.149276>
2. Miguel Antonio Domínguez-Crespo, Aidé Minerva Torres-Huerta, Ángela Iveth Licon-Aguilar. (2024). Developing ABO₃ perovskites synthesized by the Pechini method for their potential application as cathode material in solid oxide fuel cells: Structural and electrical properties. *Boletín de la Sociedad Española de Cerámica y Vidrio*, 63(2), 95-105. <https://doi.org/10.1016/j.bsecv.2023.06.008>
3. G. Mamba, P. J. Mafa, S. Rtimi. (2022). Heterogeneous advanced oxidation processes over stoichiometric ABO₃ perovskite nanostructures. *Materials Today Nano*, 17, 100197. <https://doi.org/10.1016/j.mtnano.2022.100197>
4. V. A. Pandit, G. R. Repe, J. D. Bhamre, and N. D. Chaudhari, "A review on green synthesis and characterization technique for ferrite nanoparticles and their applications," in *Journal of Physics: Conference Series*, 2020. doi: 10.1088/1742-6596/1644/1/012009.
5. V. K. Kashte, N. N. Kapse, V. A. Pandit, and B. G. Toksha, "A Review on Graphene Oxide-Based Ferrite Nanocomposites for Catalytic Applications," 2024, Springer. doi: 10.1007/s10563-024-09434-1.
6. S. S. Jadhav, S. E. Shirsath, B. G. Toksha, D. R. Shengule, and K. M. Jadhav, "Structural and dielectric properties of Ni-Zn ferrite nanoparticles prepared by co-precipitation method," *Journal of Optoelectronics and Advanced Materials*, vol. 10, no. 10, 2008.
7. S. S. Jadhav, S. E. Shirsath, B. G. Toksha, S. M. Patange, S. J. Shukla, and K. M. Jadhav, "Structural properties and cation distribution of Co-Znnanoferrites," *Int J Mod Phys B*, vol. 23, no. 30, 2009, doi: 10.1142/S021797920905225X.
8. S. S. Jadhav, S. E. Shirsath, B. G. Toksha, S. M. Patange, D. R. Shengule, and K. M. Jadhav, "Structural and electric properties of zinc substituted NiFe₂O₄ nanoparticles prepared by co-precipitation method," *Physica B Condens Matter*, vol. 405, no. 12, 2010, doi: 10.1016/j.physb.2010.03.008.

9. S. S. Jadhav, S. E. Shirsath, S. M. Patange, and K. M. Jadhav, "Effect of Zn substitution on magnetic properties of nanocrystalline cobalt ferrite," *J Appl Phys*, vol. 108, no. 9, 2010, doi: 10.1063/1.3499346.
10. V. Ashok Pandit, N. N. Kapse, V. K. Kashte, and N. D. Chaudhari, "Magnetic Behaviour, and initial permeability of green synthesized Co²⁺ substituted Ni-Zn ferrite," *J Magn Magn Mater*, vol. 601, Jul. 2024, doi: 10.1016/j.jmmm.2024.172184.
11. Muhammad Mubeen Parvaiz, Adnan Khalil, Muhammad Bilal Tahir. (2024). A DFT Investigation for structural, electronic, optical, and elastic properties of inorganic oxide perovskites CsXO₃ (X = Ti, Mn, Cu) for photosensitive applications. *Optik*, 280, 170971. <https://doi.org/10.1016/j.ijleo.2024.170971>
12. L. M. Feng, L. Q. Jiang, C. H. Li. (2008). Formability of ABO₃ cubic perovskites. *Journal of Physics and Chemistry of Solids*, 69(4), 915-920. <https://doi.org/10.1016/j.jpcs.2007.11.007>
13. Karoline Poplawski, Janine Lichtenberger, Michael D. Amiridis. (2000). Catalytic oxidation of 1,2-dichlorobenzene over ABO₃-type perovskites. *Catalysis Today*, 62(2), 303-312. [https://doi.org/10.1016/S0920-5861\(00\)00508-3](https://doi.org/10.1016/S0920-5861(00)00508-3)
14. B. Raveau, C. Martin, A. Maignan. (1998). What about the role of B elements in the CMR properties of ABO₃ perovskites? *Journal of Alloys and Compounds*, 275, 701-705. [https://doi.org/10.1016/S0925-8388\(98\)00447-5](https://doi.org/10.1016/S0925-8388(98)00447-5)
15. Chonghe Li, Kitty Chi Kwan Soh, Ping Wu. (2004). Formability of ABO₃ perovskites. *Journal of Alloys and Compounds*, 381(1-2), 108-113. <https://doi.org/10.1016/j.jallcom.2004.03.035>
16. Mailadil T. Sebastian. (2008). CHAPTER SIX: ABO₃ TYPE PEROVSKITES. In *Dielectric Materials for Wireless Communication*, 267-312. Elsevier. <https://doi.org/10.1016/B978-0-08-045329-3.00006-7>
17. Zhi-qi Kuang, Feng Li, Fu-kui Xiao. (2020). LaCuZnX (X=Al, Zr, Al+Zr) perovskite-like catalysts treated by NaBH₄ and their catalytic performance for CO₂ hydrogenation to methanol. *Journal of Fuel Chemistry and Technology*, 48(3), 285-293. <https://doi.org/10.1016/j.jfct.2020.01.004>
18. Faycal Znidi, Mohamed Morsy, Md. Nizam Uddin. (2024). Navigating challenges and solutions for metal-halide and carbon-based electrodes in perovskite solar cells (NCS-MCEPSC): An environmental approach. *Heliyon*, 10(6), e05678. <https://doi.org/10.1016/j.heliyon.2023.e05678>
19. Kang Gao, Mingming Wei, Xinhe Bao. (2013). Dynamic structural changes of perovskite-supported metal catalysts during cyclic redox treatments and effect on catalytic CO oxidation. *Chinese Journal of Catalysis*, 34(5), 1024-1030. [https://doi.org/10.1016/S1872-2067\(12\)60550-2](https://doi.org/10.1016/S1872-2067(12)60550-2)
20. T. Harada, Y. Teraoka, S. Kagawa. (1997). Perovskite-type oxides as catalysts for selective reduction of nitric oxide by ethylene. *Applied Surface Science*, 121(1-2), 222-228. [https://doi.org/10.1016/S0169-4332\(96\)00548-9](https://doi.org/10.1016/S0169-4332(96)00548-9)
21. Daniel Sastre, David P. Serrano, Juan M. Coronado. (2019). Chemical insights on the activity of La_{1-x}Sr_xFeO₃ perovskites for chemical looping reforming of methane coupled with CO₂-splitting. *Journal of CO₂ Utilization*, 30, 61-70. <https://doi.org/10.1016/j.jcou.2019.01.001>
22. Alicia Bayon, Alberto de la Calle, Robbie McNaughton. (2020). Experimental, computational and thermodynamic studies in perovskites metal oxides for thermochemical fuel production: A review. *International Journal of Hydrogen Energy*, 45(23), 13072-13098. <https://doi.org/10.1016/j.ijhydene.2020.02.032>
23. Jada Shanker, M. Buchi Suresh, D. Suresh Babu. (2016). Synthesis, Characterization and Electrical Properties of NdXO₃(X=Cr, Fe) Nanoparticles. *Materials Today: Proceedings*, 3(6), 1914-1919. <https://doi.org/10.1016/j.matpr.2016.04.132>
24. Daniel D. Athayde, Douglas F. Souza, Wander L. Vasconcelos. (2016). Review of perovskite ceramic synthesis and membrane preparation methods. *Ceramics International*, 42(5), 5335-5347. <https://doi.org/10.1016/j.ceramint.2015.12.127>
25. Yuanxin Li, Kui Xie, Yucheng Wu. (2015). Efficient Carbon Dioxide Electrolysis Based on Perovskite Cathode Enhanced with Nickel Nanocatalyst. *Electrochimica Acta*, 151, 188-195. <https://doi.org/10.1016/j.electacta.2014.11.118>
26. Katsuhiko Takegahara. (1994). Electronic band structures in cubic perovskite-type oxides: bismuthates and transition metal oxides. *Journal of Electron Spectroscopy and Related Phenomena*, 71(2), 61-72. [https://doi.org/10.1016/0368-2048\(94\)02136-X](https://doi.org/10.1016/0368-2048(94)02136-X)
27. Tetsurō Nakamura, G. Petzow, L. J. Gauckler. (1979). Stability of the perovskite phase LaBO₃ (B = V, Cr, Mn, Fe, Co, Ni) in reducing atmosphere I. Experimental results. *Materials Research Bulletin*, 14(5), 649-655. [https://doi.org/10.1016/0025-5408\(79\)90117-3](https://doi.org/10.1016/0025-5408(79)90117-3)
28. H. Kruidhof, H. J. M. Bouwmeester, A. J. Burggraaf. (1993). Influence of order-disorder transitions on oxygen permeability through selected nonstoichiometric perovskite-type oxides. *Solid State Ionics*, 63-65(1), 816-823. [https://doi.org/10.1016/0167-2738\(93\)90410-X](https://doi.org/10.1016/0167-2738(93)90410-X)