Rare-Earth Perovskites in the Quantum Age: Bridging Materials Science and Technologies

R Djoumessi Fobasso[1], **B. Sondezi** [1]

[1]Rare Earth-Based oxides and Nano Group, Department of Physics, University of Johannesburg, Auckland Park 2006, South Africa

E-mail: redrissed@uj.ac.za

Abstract. Perovskite materials are known to have unique optoelectronic and quantum properties. These make them good candidates for the next generation of quantum technologies. This article reviews the properties of perovskites that make them good candidates for bridging materials science with cutting-edge quantum applications. These applications include but are not limited to quantum computing, quantum dots, spin qubits, communication, superconducting systems, and sensing. The first part focuses on the structural properties of perovskites and the second part focuses on fundamental properties such as quantum spin liquid and photoluminescence that make them ideal candidates for quantum-enabled devices. Next, the review highlights the challenges and future prospects for the development of perovskite materials from a quantum perspective. Finally, a preliminary investigation of the new perovskite $YbInO_3$ is made based on Monte-carlo simulation method.

1 Introduction

Getting affordable and clean energy is the 7^{th} UN Sustainable Development Goal. One way of achieving this goal is to ensure that renewable energy sources like solar, wind, and thermal energy are accessible at reasonable prices to everyone. Solar energy is recognized as an effective way to deal with environmental pollution and global warming and, most importantly, make electricity accessible to everyone. Most of the photovoltaic cells were silicium based. Discovered in the 1830's, the existence of perovskites revolutionized the world of science 180 years later. Indeed, it was only in 2010 that Tsutomu Miyasaka highlighted its potential in the photovoltaic industry. They serve as a good example for bridging quantum technologies and materials science. Due to their characteristics, perovskite materials have significant technical significance across various real-world applications such as solar cells with their exceptional optoelectronic properties, photocatalysts, light-emitting devices, energy conversion and storage, sprintronic devices, gas sensing, etc... [1, 2, 3, 4]. This article aims to illuminate the path toward perovskite-driven quantum technologies, which are potentially important materials for technological applications, especially in solar cells, offering insights for researchers across materials science, physics, and engineering. Specifically, we will explore how perovskites materials serve as a bridge in material science and subdomains such as quantum light sources, spin-based quantum technologies.

2 Crystal structure and phase formation

The perovskites of interest here are materials with general chemical formula ABO_3 where A is a rare-earth, B is a transition metal, and form within the Pm-3m space group (n^o. 221). In this group, the A cation is assigned the coordinates (0, 0, 0), the B cation is positioned at (1/2, 1/2, 1/2), and the O anions are situated at (1/2, 1/2, 0), (1/2, 0, 1/2), and (0, 1/2, 1/2) locations. Figure 1 gives a schematic representation of the perovskite crystal structure. The rare-earth atoms occupy the center of the cube. The B atoms occupy the corners of the cube and

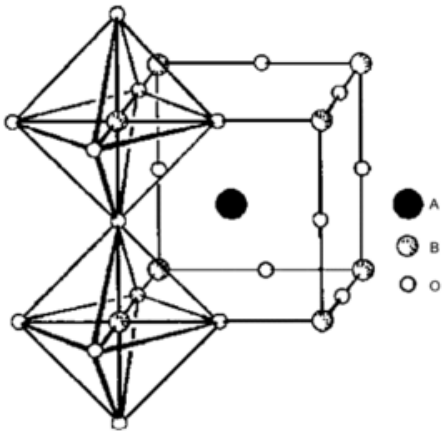

Figure 1: General crystal structure representation of perovskites with general chemical formula ABO_3.

the O atoms occupy the faces of the cube. The corner-sharing BX_6 octahedra form a 3D network as seen on the picture. It is possible to customize the properties of perovskites by substituting atoms in different sites (A, B, and O). For instance, substituting Pb^{2+} ions with Sn^{2+} on the B site in halide perovskites [5] reduces the toxicity of the material while affecting the band structure.

One of the earliest report on the series is in 1950's with the crystal structure study of $GdFeO_3$ by Geller [6] and its magnetic property studies by Gilleo [7]. The first and most comprehensive study on the series ABO_3 was conducted by V. M. Goldschmidt and his colleagues, who synthesized a substantial quantity of ABO_3 compounds and then identified their overall structural characteristics [8]. Among others, Goldschmidt examined the components that determine the kind of structure and provided clear evidence of the significant effect of ionic radius and ionic polarizability as variables. He derived the so-called "tolerance factor t" given by equation (1), which determine the type of structure expected depending on the ionic radii.

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)}, \tag{1}$$

where R_A and R_B are the ionic radius of the A and B cations respectively, R_O is the ionic radius of oxygen. For $t = [0.77 - 1.00]$, a perovskite structure is obtained. Specifically, a cubic perovskite structure is obtained for $t = [0.8 - 1.0]$. It also indicates whether ferroelectricity is present in a material or not. In 2014, S. C. TIDROW [9] developed a new model based on some physical constraints and compared it with the Goldschmidt formalism. First, he found that for low-symmetry crystals, there is a structural volume instability which is consistent with the Goldschmidt's tolerance in the interval $0.77 < T < 1.00$. Second, he found that, that structural instability increases in the region close to the upper limit of the Goldschmidt tolerance interval t = 1.00. Third, he found that the cubic phase can form in perovskite even for tolerance factor value far from 1.00 and outside the tolerance factor range $0.77 < T < 1.05$.

3 Quantum Phenomena in Perovskites and Applications in Quantum Technologies

There are several quantum phenomena that are likely to arise in perovkistes due to several factors such as electron structure and correlations, spin-orbit entanglement, lattice dynamics, and spin-orbit coupling (SOC). The latter leads to several quantum mechanical phenomena which plays a key role in condensed matter physics by influencing the electronic, magnetic and optical properties of materials. For instance, quantum spin liquids can arise in rare-earth perovskites because of the SOC which hybridize the spin and orbital degrees of freedom and sometimes prevent a magnetic order to happen at even lower temperatures. That is the case in $YbAlO_3$ which is a quasi-1D quantum magnet [10] exhibiting a quantum spin liquid state due to the SOC splitting the Yb^{3+} Kramers doublet, leading to fractionalized spinon excitations. This material has potential in quantum information science, optoelectronics and spintronics [11, 12]. A disorder-induced spin liquid state has also been found in $TbInO_3$ [13, 14].

Topological quantum states were also found to occur in rare-earth perovskites due to SOC. That is the case of $NdNiO_3$, a perovskite quantum material which under strain shows SOC-induced Dirac crossings in its electronic structure [15]. This is an example of SOC-Driven Band Inversions. SOC introduces the Dzyaloshinskii-

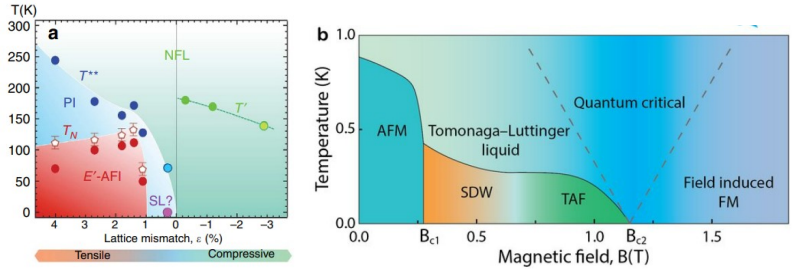

Figure 2: Left panel:Change in the transition temperature and possible quantum spin liquid state in $NdNiO_3$. Right panel: Phase diagram of $YbAlO_3$ highlighting the crossovers between Luttinger liquid and quantum critical (QCP).

Moriya Interaction (DMI), stabilizing quantum skyrmions as it is the case in $GdFeO_3$ which hosts nanometer-scale skyrmions under magnetic fields [16]. In the field of quantum coherence and qubits, long coherence quantum bits can be formed from the SOC-split energy levels of rare-earth ions such as Er^{3+} and Nd^{3+}. In the presence of quantum fluctuations, long-range ordering can be suppressed in rare-earth perovskites, giving rise to paraelectricity. It's the case of $SrTiO_3$ which is a non-rare earth material quantum paraelectric and is often doped with rare-earth element such as La. Furthermore, features such as zero dielectric loss confirm the quantum paraelectric state at low temperatures in $EuTiO_3$ [17]. In materials such as $YAlO_3$, the single-photon emission for quantum communication is enabled when doped with rare-earth ions such as Eu^{3+} and Yb^{3+} [18]. These rare-earth perovskites demonstrate how quantum effects can be used to create quantum networks and non-volatile memory, among other next generation technologies.
The unique mix of spin, optical, and electrical features of rare earth perovskites has made them a viable platform for quantum technologies. Long coherence periods and strong SOC are made possible by these materials' use of rare earth ion shielded 4f electrons, which is an essential combination for quantum applications. A number of material systems have demonstrated exceptional potential. $CsPbBr_3$ is an all-inorganic halide perovskite material. With its orthorhombic perovskite structure, it is proned to photoluminescence quantum yields, long carrier diffusion lengths, and narrow emission bandwidths. These properties open the door to several applications in optoelectronics, photovoltaics, photodetectors and quantum technologies. It was demonstrated that doping $CsPbBr_3$ with rare-earth elements greatly enhance his properties. For instance, Eu^{3+} with its hyperfine structure permits microwave control for quantum information storage [19]. When used as a dopant in $CsPbBr_3$, the obtained material has great potential to be used as quantum memory with optically addressable 4f-4f transitions exhibiting millisecond-scale coherence times at cryogenic temperatures. When doped with Nd^{3+} or Yb^{3+}, the quantum coherence and near-infrared emission in $CsPbBr_3$ is enhanced [20]. These properties make it a good candidate for spintronic devices and quantum light sources.

4 Challenges and Limitations

Perovskite materials confront numerous obstacles that prevent their widespread use, despite their exceptional optoelectronic qualities and potential for quantum technology. Performance gradually deteriorates due to stability problems in the presence of external elements like oxygen, heat, and moisture. For instance, when doped with rare-earth such as Yb^{3+} and Er^{3+}, halide perovskites such as $CsPbCl_3$ can degrade quickly due to moisture and thermal stress encountered due to lattice distortions or when the ion migrates within the structure [21]. Perovskites such as $LaCoO_3$ and $NdAlO_3$ can segregate under prolonged excitation. This can reduce their photoluminescence properties [22].

Inconsistencies in defect densities and film homogeneity further complicate the scalability of high-quality perovskite synthesis for industrial applications. Lead-based perovskites' toxicity creates health and environmental issues, necessitating the development of safer substitutes without sacrificing performance. Deeper theoretical and experimental understanding is also needed because the basic knowledge of charge-carrier dynamics and quantum behaviour in perovskites is still developing. To completely close the gap between perovskite invention and useful quantum technologies, these issues must be resolved.

5 Case study: Monte Carlo simulation of the new material $YbInO_3$

The preliminary investigation of the new perovskite material $YbInO_3$ was carried out. The Goldschmidt parameter introduced earlier was calculated to determine the crystal structure of the compound. A tolerance factor of 0.8 suggests an orthorhombic structure, according to B. Philipp et al. [25]. The database of quantum materials (OQMD) [26], which is a database of DFT-calculated thermodynamic and structural properties of materials,

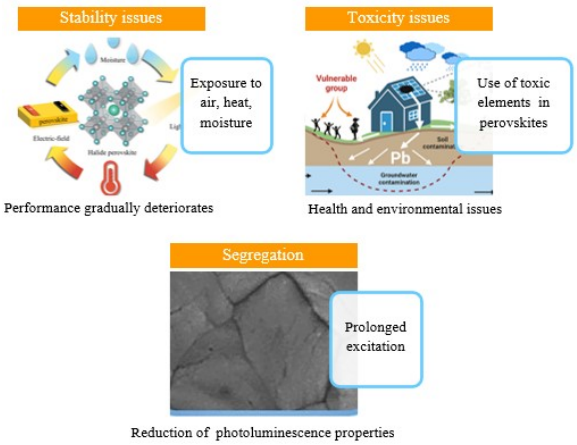

Figure 3: Perovskite materials confront numerous obstacles that prevent their widespread use, despite their exceptional optoelectronic qualities and potential for quantum technology [23, 24].

was used to estimate the lattice constants in the absence of experimental data in the $YbInO_3$ system. These are a = 5.973 Å, b = 7.488 Å, and c = 5.696 Å. The starting point for our analysis is the hamiltonian H where only the first nearest neighbor was considered:

$$H = -\sum_{\langle ij \rangle} J_{ij} S_i S_j \tag{2}$$

where J_{ij} is the exchange coupling parameter; $\langle ij \rangle$ denotes the first nearest neighbors; and S_i and S_j are spins at site i and j, respectively. The energy of the system E = -5.74 eV used was obtained from the OQMD. Monte Carlo simulation combined with Metropolis algorithm has been performed in the frame of Ising model ti simulate the energy of the system; magnetization; magnetic susceptibility (χ); and specific heat (C_v) using the following formula:

$$E = \frac{< H >}{N}, \tag{3}$$

$$M = \frac{|\sum_{\mathrm{i}}^{\mathrm{Yb}} - \sum_{\mathrm{i}}^{\mathrm{In}}|}{N}, \tag{4}$$

$$\chi = \frac{(\langle M^2 \rangle - \langle M \rangle^2)}{k_{\mathrm{B}} T}, \tag{5}$$

$$C = \frac{(\langle E^2 \rangle - \langle E \rangle^2)}{k_{\mathrm{B}} T^2}, \tag{6}$$

where k_{B} is the Boltzmann constant, T the temperature, and N the number of spins in the system. The physical quantities were simulated as function of the lattice size ranging from L = 8 to L = 24. The transition temperature T_{C} has been found by this simulation around 65 K for small lattice sizes. The sharp drop in the energy curve at 65 K is a sign of a magnetic phase transition in the material. This phase transition is consistent with the peak observed in the magnetic susceptibility and specific heat curve. The gradual increase in the energy curve is a sign of thermal population of excited states. This increase is followed by a plateau which is a sign of energy saturation. The sample therefore enters a paramagnetic state. The increase in lattice size stabilizes the ordered phase as observed in all four graphs.

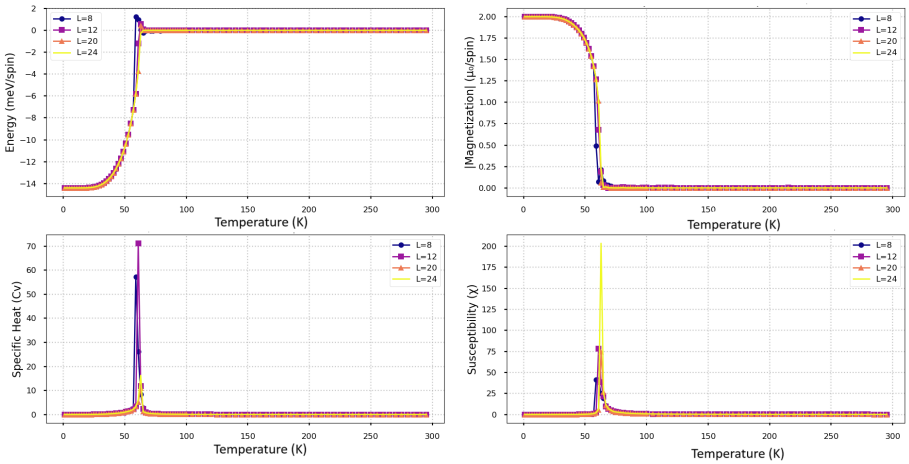

Figure 4: (a): Internal energy as a function of temperature for different lattice sizes. (b): Total magnetization as a function of temperature for different lattice sizes. (c): Specific heat as a function of temperature for different lattice sizes. (d): Magnetic susceptibility as a function of temperature for different lattice sizes.

6 Conclusion

Rare-earth perovskites offer a unique interplay of electron correlations, strong spin-orbit coupling, and structural versatility. These make them stand at the forefront of the quantum materials revolution. They offer a platform to discover and study materials such as quantum spin liquids and qubit hosts. By combining theory, computational and experimental work, rare-earth perovskites will open up new possibilities in fields such as spintronics and quantum computing. Preliminary structural and DFT results of $YbInO_3$ suggest a magnetic ordering in the material. Knowing that this material is prone to frustration due to the geometry of the lattice, it is worth investigating the experimental physical properties to get an insight into the features of the material.

References

[1] L. Zhu, R. Ran, M. Tade, W. Wang, and Z. Shao, "Perovskite materials in energy storage and conversion," *Asia-Pacific Journal of Chemical Engineering*, vol. 11, no. 3, pp. 338–369, 2016.

[2] H. Khan, S. E. Lofland, J. Ahmed, K. V. Ramanujachary, and T. Ahmad, "Emerging rare earth perovskite nanostructures for efficient electrochemical energy conversion and storage," *International Journal of Hydrogen Energy*, vol. 58, pp. 954–963, 2024.

[3] L. Zhang, L. Mei, K. Wang, Y. Lv, S. Zhang, Y. Lian, X. Liu, Z. Ma, G. Xiao, Q. Liu *et al.*, "Advances in the application of perovskite materials," *Nano-Micro Letters*, vol. 15, no. 1, p. 177, 2023.

[4] H. Yamamoto, S. Okamoto, and H. Kobayashi, "Luminescence of rare-earth ions in perovskite-type oxides: from basic research to applications," *Journal of Luminescence*, vol. 100, no. 1-4, pp. 325–332, 2002.

[5] G. Volonakis, M. R. Filip, A. A. Haghighirad, N. Sakai, B. Wenger, H. J. Snaith, and F. Giustino, "Lead-free halide double perovskites via heterovalent substitution of noble metals," *The Journal of Physical Chemistry Letters*, vol. 7, no. 7, pp. 1254–1259, 2016.

[6] S. Geller, "Crystal structure of gadolinium orthoferrite, $GdFeO_3$," *The Journal of Chemical Physics*, vol. 24, no. 6, pp. 1236–1239, 1956.

[7] M. Gilleo, "Magnetic properties of a gadolinium orthoferrite, $GdFeO_3$, crystal," *The Journal of Chemical Physics*, vol. 24, no. 6, pp. 1239–1243, 1956.

[8] V. M. Goldschmidt and D. Holmsen, *Geochemische Verteilungsgesetze Der Elemente*. In Kommission bei J. Dybwad, 1927, no. 1.

[9] S. C. Tidrow, "Mapping comparison of goldschmidt's tolerance factor with perovskite structural conditions," *Ferroelectrics*, vol. 470, no. 1, pp. 13–27, 2014.

[10] L. Wu, S. Nikitin, Z. Wang, W. Zhu, C. D. Batista, A. Tsvelik, A. M. Samarakoon, D. A. Tennant, M. Brando, L. Vasylechko *et al.*, "Tomonaga–luttinger liquid behavior and spinon confinement in $\mathrm{YbAlO_3}$," *Nature communications*, vol. 10, no. 1, p. 698, 2019.

[11] S. Nikitin, T. Xie, A. Podlesnyak, and I. A. Zaliznyak, "Experimental observation of magnetic dimers in diluted Yb: $\mathrm{YbAlO_3}$," *Physical Review B*, vol. 101, no. 24, p. 245150, 2020.

[12] L. Wu, S. E. Nikitin, M. Brando, L. Vasylechko, G. Ehlers, M. Frontzek, A. T. Savici, G. Sala, A. D. Christianson, M. D. Lumsden *et al.*, "Antiferromagnetic ordering and dipolar interactions of $\mathrm{YbAlO_3}$," *Physical Review B*, vol. 99, no. 19, p. 195117, 2019.

[13] L. Clark, G. Sala, D. D. Maharaj, M. B. Stone, K. S. Knight, M. T. Telling, X. Wang, X. Xu, J. Kim, Y. Li *et al.*, "Two-dimensional spin liquid behaviour in the triangular-honeycomb antiferromagnet $\mathrm{TbInO_3}$," *Nature Physics*, vol. 15, no. 3, pp. 262–268, 2019.

[14] J. Kim, X. Wang, F.-T. Huang, Y. Wang, X. Fang, X. Luo, Y. Li, M. Wu, S. Mori, D. Kwok *et al.*, "Spin liquid state and topological structural defects in hexagonal $\mathrm{TbInO_3}$," *Physical Review X*, vol. 9, no. 3, p. 031005, 2019.

[15] A. Arab, X. Liu, O. Köksal, W. Yang, R. U. Chandrasena, S. Middey, M. Kareev, S. Kumar, M.-A. Husanu, Z. Yang *et al.*, "Electronic structure of a graphene-like artificial crystal of $\mathrm{NdNiO_3}$," *Nano letters*, vol. 19, no. 11, pp. 8311–8317, 2019.

[16] A. Moskvin, "Dzyaloshinskii interaction and exchange-relativistic effects in orthoferrites," *Journal of Experimental and Theoretical Physics*, vol. 132, pp. 517–547, 2021.

[17] T. Katsufuji and H. Takagi, "Coupling between magnetism and dielectric properties in quantum paraelectric $\mathrm{EuTiO_3}$," *Physical Review B*, vol. 64, no. 5, p. 054415, 2001.

[18] M. Persson, "Stark shifts and ion-ion interaction in europium doped $\mathrm{YAlO_3}$-on the road to quantum computing," *Lund Reports in Atomic Physics*, 2002.

[19] W. Zheng, P. Huang, Z. Gong, D. Tu, J. Xu, Q. Zou, R. Li, W. You, J.-C. G. Bünzli, and X. Chen, "Near-infrared-triggered photon upconversion tuning in all-inorganic cesium lead halide perovskite quantum dots," *Nature Communications*, vol. 9, no. 1, p. 3462, 2018.

[20] H. Huang, R. Li, S. Jin, Z. Li, P. Huang, J. Hong, S. Du, W. Zheng, X. Chen, and D. Chen, "Ytterbium-doped $\mathrm{CsPbCl_3}$ quantum cutters for near-infrared light-emitting diodes," *ACS Applied Materials & Interfaces*, vol. 13, no. 29, pp. 34 561–34 571, 2021.

[21] N. Fiuza-Maneiro, J. Ye, S. K. Sharma, S. Chakraborty, S. Gómez-Graña, R. L. Hoye, and L. Polavarapu, "Unlocking brightness in $\mathrm{CsPbCl_3}$ perovskite nanocrystals: Screening ligands and metal halides for effective deep trap passivation," *ACS Energy Letters*, vol. 10, no. 4, pp. 1623–1632, 2025.

[22] T. Long, D. Song, Y. Zhou, X. Yu, X. Wang, C. Li, H. Chen, G. Li, and F. He, "Modulating activity of lattice oxygen of $\mathrm{ABO_3}$ perovskite oxides in redox reactions: A review," *ACS Applied Materials & Interfaces*, vol. 17, no. 14, pp. 20 590–20 612, 2025.

[23] J.-P. Correa-Baena, M. Saliba, T. Buonassisi, M. Grätzel, A. Abate, W. Tress, and A. Hagfeldt, "Promises and challenges of perovskite solar cells," *Science*, vol. 358, no. 6364, pp. 739–744, 2017.

[24] D. Liu, X. Liang, X. Yin, Y. Yang, G. Wang, M. Wang, and W. Que, "Modulation of photoinduced phase segregation and stress-driven nanoscale cracking in hybrid halide perovskite solar cells," *ACS Applied Materials & Interfaces*, vol. 16, no. 18, pp. 23 109–23 121, 2024.

[25] J. Philipp, P. Majewski, L. Alff, A. Erb, R. Gross, T. Graf, M. Brandt, J. Simon, T. Walther, W. Mader *et al.*, "Structural and doping effects in the half-metallic double perovskite $\mathrm{A_2CrWO_6}$ (A= Sr, Ba, and Ca)," *Physical Review B*, vol. 68, no. 14, p. 144431, 2003.

[26] J. E. Saal, S. Kirklin, M. Aykol, B. Meredig, and C. Wolverton, "Materials design and discovery with high-throughput density functional theory: the open quantum materials database (oqmd)," *Jom*, vol. 65, no. 11, pp. 1501–1509, 2013.