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PERSPECTIVE PEROVSKITES

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Abstract: *Today the term 'perovskite' is used to designate the crystalline structure of a wide variety of ABX_3 ionic compounds. However, historically this name was coined specifically for a mineral, calcium titanate ($CaTiO_3$). The paper describes crystallographic structure of perovskite materials in connection with geometry of dual polyhedra and applications of one class of such materials (metal halides perovskites) for solar energy conversion. History of discovery of mineral perovskite is also discussed.*

Keywords: Dual polyhedra; Perovskite; Solar cells; Crystal Structure; History of Science.

INTRODUCTION

The discovery of the metal halide perovskite (*MHP*) semiconductor as an absorber for photovoltaics (*PV*) (Kojima *et al.*, 2009) and the subsequent meteoritic rise of the efficiency of solar cells based on this type of hybrid organic-inorganic materials are among the most important scientific achievements of recent years. Dominated on the solar electricity market, silicon *PV* almost reached their maximum theoretical efficiency, and it was unclear where to move on further. The development of *MHP PV* has changed the situation, paving the way to attempts to create the so-called dual-junction, or tandem, perovskite/silicon cell consisting of two sub-cells with perovskite on top (closer to the sunlight capturing surface) and with silicon sub-cell on the bottom. What makes this solution so attractive is that adding the cheap *MHP* sub-cell does not increase the cost of the entire tandem all that much, but substantially enhances its efficiency. Today's silicon cells have a record efficiency of ~26%, while the perovskite/silicon tandem devices have already achieved an efficiency of ~30%, thus exceeding a "psychological" barrier of sorts (Green, 2021). The prospects of raising the efficiency of tandem elements to 30-35% is under discussed now. It is for this reason that hundreds if not thousands of laboratories around the world are working on this issue and investing heavily in research and manufacturing industrial prototypes.

This paper describes crystal structure of perovskite materials as well as the background of discovery of mineral perovskite and the life stories of the personalities involved.

DUAL POLYHEDRA AND CRYSTAL STRUCTURE OF PEROVSKITES

Table 1 summarizes some characteristic parameters of Platonic polyhedra. The data can tell a lot about properties of these polyhedra (Katz, 2016). For example, the numbers of faces (F) and vertices (*V*) are interchangeable for cube and octahedron (*6,8*) – (*8,6*), respectively, and for icosahedron and dodecahedron (*20,12*) – (*12,20*), respectively. The same feature holds true for parameters m and n. In this case mathematicians talk about duality of polyhedra. Cube and octahedron are dual to each other; icosahedron is dual to dodecahedron (and vice versa) and tetrahedron is dual to itself. When one forms the dual of a given polyhedron, one creates a new polyhedron in which the faces and vertices of the dual correspond to the vertices and faces of the original polyhedron, respectively. For example, centroids of the faces of the cube define the vertices of the regular octahedron. It happens through the process of polar reciprocation (Coxeter, 1947).

Table 1. Summary of formatting options used in the Styles of this document. Characteristics of Platonic solids.

Polyhedron	Number of edges per each face, *m*	Number of edges that connect in each vertex), *n*	Number of faces, *F*	Number of edges, *E*	Number of vertices, *V*
Tetrahedron	3	3	4	6	4
Cube	4	3	6	12	8
Octahedron	3	4	8	12	6
Icosahedron	3	5	20	30	12
Dodecahedron	5	3	12	30	20

In each pair of dual polyhedra the number of edges is the same, but the number of faces of one is the number of vertices of the other, and vice-versa.

These relationships between the Platonic solids were clearly described by Luca Pacioli in his book "De divina proportione" (Pacioli, 1509) and were known to Kepler, as can be deduced from the following quotation from his book "Mysterium Cosmographicum" (Kepler, 1597): "The octahedron interchanges with the cube, the icosahedron with the dodecahedron, its number of bases and angles. For the cube has six bases and the icosahedron six vertices: the former eight vertices, the latter eight bases. Similarly, the bases of the dodecahedron and the vertices of the icosahedron are twelve in each case: correspondingly the vertices of the former and the bases of the latter are twenty".

An important feature of a pair of dual polyhedra is that both possess the same symmetry properties and have the same number of edges. The dual of an isogonal polyhedron, having equivalent vertices, is one which is isohedral, having equivalent faces. Indeed, this operation permits to inscribe (to circumscribe) polyhedra in their duals. Nature can successfully utilize this property. For example, in 2003 inorganic complexes with the following structure were synthesized: icosahedron with twelve *Ni* atoms in the vertices, Ni_{12}, and one *As* atom in the centre is inscribed in its dual dodecahedron with twenty *As* atoms in vertices, As_{20}. As a result, an ion $[As@Ni_{12}@As_{20}]^{3-}$ is formed. Today an entire class of such complexes, *keplerates*, has been demonstrated.

A brilliant example of dual polyhedral crystallography is a crystalline structure of *MHP*, where $[MX_6]^{4-}$ octahedral anion surrounded by organic cations in cubic or tetrahedral arrangement (Figure 1, left). Here, *A* is an organic or inorganic cation, *M* is a divalent metal cation, and *X* is a halide anion. Their general chemical formula is AMX_3. Methyl ammonium (*MA*) lead halide perovskites ($MAPbX_3$) is the most studied class of such perovskite materials, with the additional advantage of tuning their properties by varying the type of halide ions (I^-, Br^-, Cl^-).

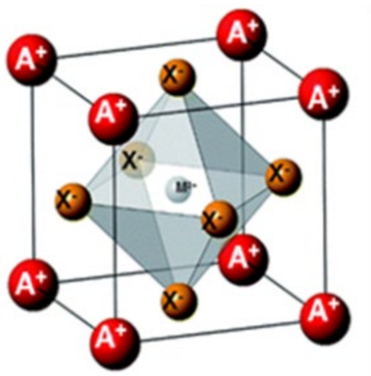

Figure 1 (Left) Unit cell of *MHP* crystal structure. (Right) Sample of mineral perovskite ($CaTiO_3$) from mineralogical collection of the Museum für Naturkunde Berlin. Photos by the author

DISCOVERY OF MINERAL PEROVSKITE

The term "perovskite" was coined for a calcium titanium oxide mineral composed of calcium titanate ($CaTiO_3$). Today this term is used to designate a wide range of ABX_3 compounds with similar type of ionic crystalline structure. The $CaTiO_3$ mineral was discovered in the Ural Mountains of

Russia. The first sample of the mineral was handed over by the founder of Russian Mineralogical Society Alexander Bogdanovich Kemmerer (1789-1858) from Saint Petersburg to Berlin in 1839. Kemmerer gave the sample (shown in Figure 1, right) for further investigation to German mineralogist and crystallographer Gustav Rose (1798-1873) (Figure 2, left) who determined its physical properties and chemical composition. On Kemmerer's suggestion, Rose named the mineral after the Russian politician (Minister of Internal Affairs under Nicholas I of Russia) and mineralogist Count Lev Aleksevich Perovski (1792–1856) (Figure 2, right).

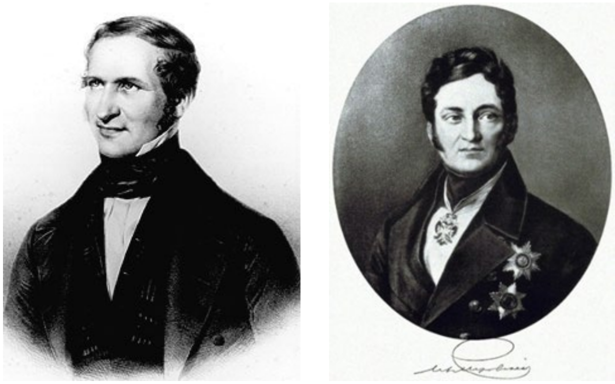

Figure 2 (Left) Gustav Rose. (Right) L*ev* Alekseyev ich Perovski[1].

GUSTAV ROSE

Gustav Rose was born in Berlin on March 18, 1798, in a family that counted at least four generations of distinguished scientists. His grandfather, Valentin Rose the Elder (1736 - 1771), pharmacist and chemist, was the founder of this scientific dynasty. He is known for inventing a low melting temperature alloy composed of bismuth, tin and lead, so-called Rose metal, today widely used as a solder. Since 1761 he owned and managed the apothecary 'At the White Swan' ('Zum Weißen Schwan') which was a real scientific laboratory. In 1771 a young journeyman and Rose's assistant started to work in the pharmacy. It was Martin Heinrich Klaproth (1743 - 1817) who later became the first professor of chemistry at the University of Berlin and discovered such chemical elements as uranium and zirconium. Valentin Rose the Elder died the same year, and Klaproth became the pharmacy manager and took over the care and education of Valentin's two sons. One died while young; the other Valentine Rose the Younger (1762-1807) grew up to become a father of two sons himself: a chemistry professor in University of Berlin Heinrich Rose (1795-1864) and his younger brother Gustav, the main hero of our narrative.

The actual pharmacy "Zum Weißen Schwan" on Spandauer Straße in Berlin has not survived to this day. However, we can precisely identify its location since the pharmacy was situated just opposite to the oldest church in Berlin "Heilige Geist Kirche" ("Holy Ghost Church", built in the 14^{th} century) directly across the Spandauer Straße (Figure 3).

Brought up by Klaprot, Valentin Rose the Younger in 1785 became a provisor in ‘Zum Weißen Schwan’ pharmacy, of which he gained ownership of in 1791. He is credited with the discoveries of a number of important organic compounds and their synthesis.

Figure 3 On the left is Heilig-Geist-Kapelle, now belonging to Humboldt University (the part of Heilige Geist Kirche survived to this day). It faces Spandauer Straße. Rose’s apothecary “Zum Weißen Schwan” was situated across the street at what is now a faceless multi-story building with shops on the ground floor. Photo by the author.

Gustav Rose studied mineralogy at the University of Berlin and later under the great physical chemist Jöns Jakob Berzelius (1779–1848) in Stockholm. For our perovskite discovery narrative, it is important that in 1829 Gustav Rose accompanied the great naturalist Alexander von Humboldt (1769–1859) on his famous scientific expedition to the Ural, Siberia, and the region of the Caspian Sea of Russian Empire. After returning from the trip to Russia, Rose intensively examined the collected minerals and rocks over the period of ten years. 117 different minerals were identified. Some of them (including cancrinite, rhodizite and chevkinite) were described for the first time. Rose summarized the results in the paper (Rose, 1839). There is no doubt that Kämmerer’s visit to Rose in 1839 with a request to explore a new mineral (later to be named perovskite) directly follows the expedition and Rose’s mineralogical activity and intensive contacts in Russia. Therefore, he included the newly identified perovskite in the paper devoted to the description of Ural minerals collected in the expedition (Rose, 1839).

Gustav Rose died on 15th of July 1873 and was buried at St. Marien and St. Nikolai I Cemetery in Berlin. It is probably symbolic that Rose’s tombstone is made of a rose-color marble (Figure 4). Unfortunately, the inscription on his tombstone faded over time and can hardly be read: “In memory of Gustave Rose, Professor of Minerology at University of Berlin, 18 March 1798 – 15 July 1873”. However, his other monument is not in danger of time, and he will never require a restoration. This is the mineral *roselite* ($Ca_2 (Co, Mg) [AsO_4]_2 \cdot H_2O$), named after the mineralogist.

LEV ALEKSEVICH PEROVSKI

Lev Perovski was born on September 9/20, 1792. He was an illegitimate son of the Senator, Trustee of Moscow University, botanist, bibliophile and Freemason Count Alexei Kirillovich Razumovsky and the commoner Maria Mikhailovna Sobolevskaya. Officially Lev and his three brothers and five sisters were considered as adopted children of their own father. Thus, a new noble family appeared, named after the village of Perovo, on the Razumovsky's estate.

Figure 4. Gravestone of Gustav Rose at St. Marien and St. Nikolai I Cemetery, Berlin. Photo by the author.

During the Napoleon invasion of Russia, 1812, Perovski took part in all the major battles of this war. In 1818 he joined the Decembrist Union of Prosperity. However, he did not support the military Decembrist Revolt. After the revolt was suppressed, the new emperor Nicholas I did not punish Perovski for participating in the Union of Prosperity, but on the contrary gave him high government posts: Vice-President of the Appanage Department of the Ministry of the Imperial Court (1829) and Minister of Internal Affairs (1841). He was an extremely energetic person and got a reputation as an active opponent of serfdom. Since 1842, his Ministry became the main headquarter for the preparation of the peasants' liberation. Unfortunately, Nikolai I did not implement these reforms. Serfdom in Russia was abolished only after Perovski's death, by Alexander II in 1861. However, there is no doubt that Lev Perovski was one of those who prepared this most important reform in the history of Russia of the 19th century. The mining industry (including gemstone production) in the Russian Empire belonged to the Appanage Ministry. Perovski contributed much to the development of the mining and lapidary industries as well as mineralogy research in Russia. Being neither a chemist nor a mining engineer, Lev Perovski earned the glory of a zealous collector and a fine connoisseur of minerals. Along with perovskite, his name was directly related to the discovery of two other minerals: phenakite and alexandrite.

AUGUST ALEXANDER KÄMMERER

August Alexander Kämmerer was born in 1789 in the Thuringian town of Artern (then belonging to Saxony). Kämmerer was brought to St. Petersburg by parents at the age of eight. After receiving his initial schooling, he enrolled as a pupil in a private pharmacy. In 1809 he passed the exam for a pharmacist, and already in 1812, he opened his own pharmacy. In 1824, he became the chief-chemist at the laboratory of the Department of Mining and Salt Affairs, and then, in 1826, he headed the newly founded Main Mining Pharmacy. This new position allowed Kämmerer to devote most of his time to his favorite activity - mineralogy. He published many articles and in 1829 Heidelberg University awarded him a PhD degree.

We certainly know from Gustav Rose's publication (Rose 1838) that the new mineral (which eventually came to be known as perovskite) brought to him by Kämmerer in the summer 1839 was found in the South Ural Mountains. From the same source we know that Gustav Rose named the new mineral after Lev Perovski upon Kämmerer's suggestion. What preceded Kämmerer's visit to Berlin? Who found the samples of the new mineral in Russia? From whom did Kämmerer receive these samples? These questions remain open.

IN LIEU OF CONCLUSIONS

In 1845 Alexander von Humboldt wrote: "Every law of nature that reveals itself to the observer suggests a higher law, yet unknown" (von Humboldt, 1848). Without the discovery of the mineral perovskite and the subsequent studies in the 19^{th} century, many of the outstanding achievements of modern science would not have been possible. In 1987, the Nobel Prize in Physics was awarded to Georg Bednorz and Alex Müller for the discovery of High Temperature Superconductivity (*HTSP*) in Perovskite-Type Oxides (Bednorz and K. Müller, 1987) Another Nobel Prize in physics (2007) was awarded for the discovery of Giant Magnetoresistance (*GMR*), an abnormally high change in resistance of a conductor when it is placed in an external magnetic field. This quantum mechanical effect is observed in an alternating sequence of ferromagnetic and non-magnetic conductive nanolayers (Baibich *et al.*, 1988; Binasch *et al.*, 1989). The discovery of the *GMR* effect gave rise to an increased interest in finding related effects in bulk materials. Resistance changes in an applied magnetic field several magnitudes higher than for GMR was observed in certain manganese perovskites (Jonker, 1950; Volger, 1954; Kusters *et al.*, 1989; von Helmolt *et al.*, 1993; Jin, 1994). The observed phenomenon became known as colossal magnetoresistance (CMR). Recent development of efficient MHP-based PV can be considered as the third 'perovskite revolution' of modern time. A Nobel Prize is to be expected.

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[1] Both images are from *Wikipedia*, public domain, as well as the left image in Figure 1.

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Eugene A. Katz is professor at the Ben-Gurion University of the Negev. He received his MSc degree (1982) in Semiconductor Materials Science and Ph. D. (1990) in solid state physics from the National University of Science and Technology "MISIS". His research interests include studies and development of a wide range of materials and devices for solar energy conversion. He has published 141 peer-reviewed papers on these topics as well as popular-scientific book and a number of articles on science history and fullerene-like structures in nanomaterials, living organisms and architecture. Based on the latter activity he has developed and is teaching an interdisciplinary course "Bridges between fine art and natural sciences: cases of fullerenes, polyhedra, symmetry". In 2018 Prof. Katz was awarded the IAAM Medal (by the International Association of Advanced Materials) for the outstanding research in the field of New Energy Materials & Technology.