ISSN 1330-3651 (Print), ISSN 1848-6339 (Online)
https://doi.org/10.17559/TV-20210716122507
Subject Review

Perovskite Oxides for Energy Applications

Andreja ŽUŽIĆ*, Veljko FILIPAN, Igor SUTLOVIĆ, Jelena MACAN

Abstract: Industrial and population growth is constantly increasing energy consumption. Since 81.3% of consumed energy is produced from fossil fuels, the high pollution and emission rates are leading to climate changes resulting in extreme weather conditions. The development of new materials and technology is necessary to achieve sustainable societal growth and development. In the field of new materials, perovskites are the main subject of much scientific research conducted in the last decade. Perovskites are usually divided into two groups: halides and oxides. The application of perovskite halides in photovoltaic and solar cells is already well-known and investigated. On the other hand, perovskite oxides do not possess optical and light-absorption properties comparable to perovskite halides, but they have promising electrical and magnetic properties and high reducibility rates. This review is dedicated to the perovskite oxides, preparation methods of this material and their application for energy transformation and storage applications. The perovskite oxides have high potential as working materials in solid oxide fuel cells (SOFC), Ca batteries, thermochemical energy storages (TCES) and ambient temperature magnetic refrigerators (MR).

Keywords: batteries; energy storage; magnetic refrigerators; perovskite oxides; solid oxide fuel cells

1 INTRODUCTION

Industrial development and population growth are constantly increasing the energy demand. According to the statistical data [1], the biggest individual driver of primary energy growth was China followed by India and Indonesia as the next largest contributors. 81.3% of consumed energy comes from fossil fuels (oil, gas, coal) which leads to the increase of greenhouse gases emissions causing climate changes. Therefore, it is very important to develop new technologies and materials for efficient energy conversion and storage. In the development of new materials, materials engineering has the main role. During the last decade, a group of ceramic called perovskites was the subject of scientific research due to the promising electrical, magnetic, photovoltaic and redox properties with possible energy applications [2]. Perovskites can be divided into two groups: perovskite halides and perovskite oxides. The light absorption properties of perovskite halides as well as their application in photovoltaic and solar cells are already well-known and investigated [3]. However, perovskite oxides are less investigated although they also possess promising energy application properties as reported by Goodenough [4] in 1955. This review gives an overview of the perovskite oxides structure, synthesis methods and potential applications for energy purposes (SOFCs, batteries, solar energy storages and magnetic refrigerators).

1.1 Perovskite Structure

The mineral form of calcium titanate ($CaTiO_3$) was discovered in the Ural mountains by German scientist Gustav Rose in 1839 and named 'perovskite' in honour of Count Lev Alekseyevich von Perovski, a Russian statesman and mineralogist [5]. Nowadays, perovskites are a broad group of materials described with the general formula ABX_3. In this formula A represents an alkaline earth metal ion (Ca, Sr, Ba) or a rare-earth metal (La, Nd, etc.) ion. The B-site is occupied by a transition metal (Mn, Fe, Cr, Ti, Pb) ion which is octahedrally coordinated by halogen (Cl, Br, I, F) or oxygen ions, generally marked with X. The ideal perovskite structure is cubic with the space group $Pm3m$ shown in Fig. 1.

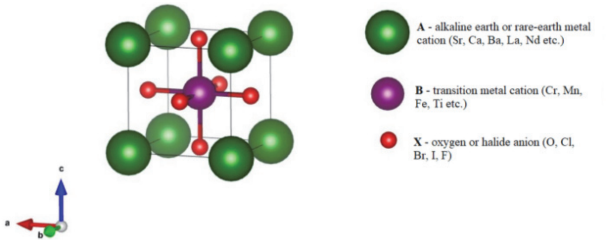

Figure 1 The ideal cubic perovskite structure [6]

Due to the chemical flexibility of perovskites and the possibility to substitute A and B-site metal ions, cell distortion can occur. The distortion leads to the structural stabilization and is described using the Goldschmidt tolerance factor t defined as follows [7]:

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

where R_A, R_B and R_X represent the ionic radius of A-site cation, B-site cation and X-site anion. The perovskites with $1.00 < t < 1.13$ will exhibit hexagonal symmetry (Fig. 2a), while compositions with $t < 1.00$ are associated with cubic (Fig. 1) and orthorhombic (Fig. 2b) symmetry. According to the research conducted by Hines et al. [8], the perovskite structure will be cubic for $0.90 < t < 1.00$, and orthorhombic for $0.75 < t < 0.90$. For $t < 0.75$, the hexagonal ilmenite structure characteristic for $FeTiO_3$ will be obtained [8].

The structure distortion and defects of perovskite oxides play the main role in their transport properties required for energy applications. Oxygen ion transport in perovskite oxides is mediated via a vacancy mechanism. If trivalent A-site ion is substituted with divalent ion, the oxygen vacancies will form to preserve the electroneutrality and enhance oxygen ionic conductivity [9]. Furthermore, the oxygen nonstoichiometry leads to the mixed-valence state of B-site ions [10]. The presence of multiple valences enables Zerner double exchange mechanism [11] described as follows:

$$\begin{aligned} &B^{n+} - O^{2-} - B^{(n+1)+} \rightarrow B^{(n+1)+} - O^{-} - B^{(n+1)+} \rightarrow \\ &\rightarrow B^{(n+1)+} - O^{2-} - B^{n+} \end{aligned} \tag{2}$$

The Zerner double exchange mechanism is a type of magnetic exchange that occurs between ions in different oxidation states spanned by oxygen anion. When O gives up its spin-up electron to $B^{(n+1)+}$, its vacant orbital can be filled by an electron from B^{n+}. In one double exchange process, an electron moves between neighbouring cations retaining its spin [10, 11].

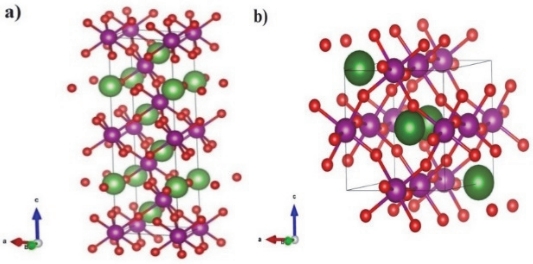

Figure 2 The hexagonal (a) and orthorhombic (b) distortion of perovskite structure [6]

1.2 Properties of Perovskite Oxides

Perovskite materials exhibit many interesting properties (Tab. 1) due to their tendency to oxygen nonstoichiometry and cell distortion. In this review, the focus will be on ferroelectric, magnetic and redox properties important for energy applications.

Table 1 Some properties of perovskite materials [10]

Properties	Example of material
Electrical conductivity	$SrFeO_3$, $LaCoO_3$, $LaNiO_3$, $LaCrO_3$
Superconductivity	$La_{0.9}Sr_{0.1}CuO_3$
Ionic conductivity	$CaTiO_3$, $BaZrO_3$, $SrZrO_3$, $BaCeO_3$
Piezoelectricity	$PbZrO_3$, $PbTiO_3$, $BiTiO_3$, $NaTiO_3$
Magnetic properties	$LaMnO_3$, $LaFeO_3$
Catalytic properties	$LaCoO_3$, $LaMnO_3$, $BaCuO_3$
Redox properties	$CaMnO_3$, $LaMnO_3$

1.2.1 Ferroelectric Properties

Ferroelectricity is the phenomenon of spontaneous electric polarization of the material when an external electric field is applied. The ferroelectric materials possess a dielectric constant which is two magnitudes larger compared to those in an ordinary dielectric. Materials with ferroelectric properties can be applied in infrared cameras, vibration sensors, memory devices and capacitors [12].

1.2.2 Magnetic Properties

Magnetic properties are the main characteristic of the rare-earth manganites described with the general formula $Re_{1-x}A_xMnO_3$ in which Re represents a trivalent rare-earth metal ion (La, Nd, Pr, etc.) and A is a divalent alkaline earth metal ion (most often Sr). These materials possess the property of colossal magnetoresistance (CMR) which allows them to change their electric resistance in the presence of a magnetic field [13]. When a material possesses both electric and magnetic properties it is called multiferroic material. Those kinds of materials are highly applicable in spintronics, a new technology for data storage. Such devices utilise the spin degree of freedom of electrons and/or holes and the interaction with their orbital moments to store two times more data on the device of the same dimensions [14]. Furthermore, perovskite oxides with magnetic properties are nowadays investigated as working materials in magnetic refrigeration systems [12].

1.2.3 Redox Properties

The oxygen nonstoichiometric perovskite oxides containing multiple valence ions are highly valuable for applications as redox materials. The thermochemical cycle is a combination of a high-temperature step, at which the oxide is partially reduced under the release of oxygen, and a low-temperature oxidation step. These thermochemical cycles can be applied for combustion of organic fuels, H_2O or CO_2 splitting as well as in solar energy storage [15].

2 PREPARATION OF PEROVSKITE OXIDES

2.1 Solid-State Reactions

In solid-state reactions, perovskites are synthesized by mixing oxides or carbonates of the A and B-site metal ions. The mixing can be conducted in agate mortar with a pestle or in a planetary ball mill. The disadvantages of the solid-state reactions are inhomogeneity of the reaction mixture, incorporation of different impurities during repeated grinding and heating process and big particle size unsuitable for coatings. Neagu et al. [16] have reported that by administering the composition and nonstoichiometry, the growing nanoparticles from perovskite oxides can be accomplished through solid-state synthesis. To further improve synthesis procedures, methods from the solution were developed [14].

2.2 Synthesis Procedures from the Solution

2.2.1 Sol-Gel Process

The sol-gel alkoxide route is the very common synthesis procedure in the field of ceramics. It can be described as the formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid. In this process, several stages are identified and the first one is the formation of sol from the precursors' solution via the condensation process. The advancing condensation process leads to gel formation followed by drying and calcination to obtain ceramics [12, 17].

This process is broadly applied to aluminate and titanate and generally nanosized particles preparation. The use of the sol-gel process is limited due to the stability of the precursor and it is not suitable for the preparation of manganites, which are the most important magnetic perovskites [13]. Furthermore, the control of the air humidity, concentration and pH value of the solution is necessary for synthesis optimization.

2.2.2 Pechini Method

The Pechini method is a variation of the typical sol-gel procedure which compensates previously stated disadvantages. This method is also called the polymeric precursor or mixed liquids method. The principle of this method is the formation of a chelate between A and B-site cations and carboxylic acid. The most often used carboxylic acid is citric acid. After the homogenous solution of metal-citrate chelates is obtained, the ethylene glycol is added to achieve the formation of a covalent network with uniformly distributed metal cations and the resulting solution is heated (150 - 250 °C) leading to the condensation between COOH and OH groups. The process is finished when the resin mass is formed. The last step is calcination in order to achieve phase transformation of the resin precursor into a perovskite [12, 17].

2.2.3 Citrate-Nitrate Autocombustion (CNA) Method

The CNA method is analogous to the Pechini method with the exception that no ethylene-glycol is added. In this method, citric acid has two roles; the first as a chelating agent of cations and the second as the fuel in the combustion process. The formation of a gel is achieved by heating citrate-nitrate chelates solution at temperatures above 300 °C. Further gel heating leads to gel drying and its combustion into a precursor powder which is then calcined to obtain ceramics [17].

2.2.4 Coprecipitation Method

The coprecipitation method is the least explored method for the perovskite oxides preparation. The principle of the method is the dissolution of A and B-side metal cation sources in a convenient solvent (e.g. aqueous nitric acid). The simultaneous precipitation (coprecipitation) of different cations in the solution occurs after the addition of a chemical reagent that decreases the solubility of the present compounds. To achieve coprecipitation of all cations in the solution and to obtain homogeneous products, the control of the temperature, concentration, pH value and homogeneity of the solution is essential. The ammonium carbonate is the most popular precipitation agent since the carbonates degrade during the calcination process and leave the system in the form of CO_2. The pH value of the solution is most often controlled by the addition of liquid ammonia or urea and the homogeneity of the solution is achieved by stirring [12].

2.2.5 Hydrothermal Synthesis

The main principle of hydrothermal synthesis is the conduction of the reaction in the aqueous solution or suspension of the precursor at high temperature and pressure. The difference of this method compared to the previously listed methods is that crystalline powders can be obtained without the calcination step. Furthermore, the advantage of this method is the possibility to change particle size and shape by controlling reaction temperature, pH, time and concentration of the reactants [12, 18].

2.3 Synthesis of Nanostructured Perovskite Oxides

Although the nanostructured perovskite oxides can be synthesised by previously mentioned sol-geland hydrothermal methods [17, 18], they are often prepared by the molten salt method [19]. In this method, sources of metal ions (oxides) are mixed with salt (NaCl and KCl) and then sintered at a temperature above the melting point (950 °C) of the salt. At this temperature, the oxides particles rearrange and then diffuse rapidly in a liquid state of the salt. With further sintering, particles of the perovskite phase are formed through the nucleation and growth processes. In the field of nanostructured perovskite oxides, barium ($BaTiO_3$) and lead ($PbTiO_3$) titanates are the most investigated for their application in capacitors, sensors and acoustic transducers [19].

3 APPLICATIONS OF PEROVSKITE OXIDES

3.1 Perovskites in Solid Oxide Fuel Cell (SOFC)

SOFCs are nowadays introduced as an efficient and environmentally friendly source of electric power. They operate at high temperatures (about 1000 °C) and allow the transport of oxygen ions through the ceramic components of the cell. To lower the working temperature to the intermediate temperature range (650 - 850 °C), ceramics with higher electronic and ionic conductivity are necessary and perovskite oxides are ideal candidates for that purpose. Further requirements for perovskite oxides application in SOFCs are their chemical stability, porosity, oxygen deficiency and low cost [20]. The schematic of SOFC is shown in Fig. 3. The fuel (steam-reformed natural gas) enters the cell at the anode side, while air enters the fuel cell at the cathode side. Oxygen from the air combines with free electrons to form oxide ions at the cathode and these oxides travel from the cathode to the anode through the solid electrolyte. At the anode, oxide ions react with hydrogen to form water steam and with CO to form CO_2, releasing free electrons. These free electrons travel to the cathode through the external circuit, producing electricity [10].

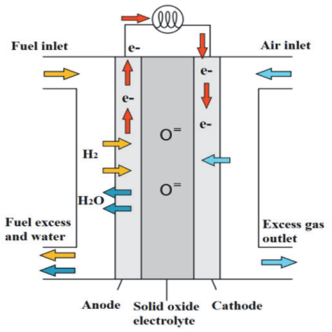

Figure 3 Schematic of SOFC [10]

3.1.1 Perovskites as Cathodes

Perovskite oxides possess electric conductivity due to the Zerner double exchange mechanism. The electric conductivity increases with temperature until the value when the material starts to melt or degrade (above 1300 °C). To start the electrochemical reaction, oxygen molecules absorbed on the cathode need to be transformed into the oxygen anions which then diffuse through the cathode and electrolyte [20]. Taking that into account, the structure of the perovskite cathode needs to be porous. Moreover, the electric conductivity of perovskites depends on symmetry. The research has shown that the cubic perovskites have the highest conductivity which decreases with the increase of the crystal structure distortion. On the other hand, ionic conductivity can be improved by the A-site cation substitution which causes the formation of oxygen vacancies to neutralize the charge of the system. To sum up, the convenient cathode material needs to have ionic conductivity 10^{-3} - 10^{-5} S/cm, and electronic conductivity higher than 100 S/cm [10, 20]. In the first high-temperature SOFCs, strontium doped lanthanum manganites ($La_{1-x}Sr_xMnO_3$, LSMO) were investigated as cathode materials due to their compatibility with yttria-stabilized zirconia (YSZ) electrolyte. Unfortunately, the disadvantage was material poisoning caused by Cr from the Cr_2O_3 interconnectors. Furthermore, lanthanum cobaltite ($LaCoO_3$) was investigated as a potential cathode material. Since it degrades in a chemical reaction with YSZ, it is convenient in SOFCs with doped cerium oxides as electrolytes. Strontium doped $LaCoO_3$ with chemical formula $La_{1-x}Sr_xCoO_3$ (LSCO) possess ionic conductivity and significantly higher electric conductivity of 1000 S/cm. The main disadvantage of LSCO is low stability. To increase stability, a part of Co is substituted with Fe resulting in a stable perovskite phase with a chemical formula $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$ (LSCFO). Even though this substitution decreases electric conductivity, for $x = 0.4$ and $y = 0.2$, its value of 300 S/cm is enough for the SOFCs application [10, 21].

3.1.2 Perovskites as Anodes

The most often used anodes in fuel cells are Ni cermets, composite materials prepared from ceramics and metal. These materials have excellent performance when pure H_2 is used as fuel. When fuel contains impurities as S, H_2S or CO, the corrosion and degradation of Ni electrodes will occur. Perovskites are a good alternative due to their high ionic and electronic conductivity, stability in reducing atmospheres and possibility to change chemical composition via substitution. As anodes, titanates and chromites are widely investigated, especially $SrTiO_3$ and yttria doped $SrTiO_3$. Despite that, the main challenge is to develop perovskite oxide with a catalytic activity comparable to Ni [10, 22].

3.1.3 Perovskites as Electrolytes and Interconnectors

Ionic conductivity is the main requirement for the application of perovskite oxide as an electrolyte in SOFCs. Furthermore, chemical compatibility with electrode materials and stability for different oxygen partial pressures are very important. Moreover, mechanical stability is an important criterion for the SOFCs geometry. Strontium doped lanthanum gallates ($La_{1-x}Sr_xGaO_3$, LSGO) possess good ionic and electronic conductivity that could be additionally increased by partial substitution of Ga with Mg ($La_{1-x}Sr_xGa_{1-y}Mg_yO_3$, LSGMO). Although the decrease in electrolyte thickness contributes to the resistance decrease, the electrolyte should not be too thin in order to maintain the cell potential. In the case of the LSGMO electrolyte, the optimal electrolyte thickness is 100 µm [23]. As interconnectors in SOFCs, $LaCrO_3$ compounds are used. Their role is to separate the fuel and gaseous oxidant. Besides that, interconnectors need to possess high electric conductivity at temperatures about 1000 °C. Furthermore, the good interconnector material needs to be impermeable for gases, chemically stable for fuel and oxidant and thermochemically compatible with other cell components. To satisfy listed requirements, La and Cr in $LaCrO_3$ are often substituted with Ca^{2+}, Mg^{2+} and Sr^{2+} [23].

3.2 Perovskite as Cathodes in Batteries

The widely used lithium-ion batteries (LIB) enabled the development of portable electronic devices and they are nowadays present in every mobile phone. However, these batteries have reached their maximum in the aspect of energy density, i.e. the amount of energy that can be stored in a given mass of a substance or system. The promising alternatives are calcium-based batteries, which can provide 2 electrons per atom, achieving double energy density compared to lithium. With a mass ratio of 3.56%, Ca is the fifth most abundant element in the Earth's crust, it is nontoxic and its standard reduction potential is –2.87 V. Moreover, the theoretical energy density of Ca batteries is 2.06 Ah/cm^3, which is twice as much as LIB [24]. Ca battery cells are analogous with LIBs on the cathode side. During the battery discharge, the carrier ion (Ca^{2+}) migrates from the anode to the cathode through the electrolyte and electrons are flowing through an external circuit (Fig. 4). During the battery charging, these processes are reversed [24]. Although the research of Ca batteries started in 1935, the main problem was to find materials suitable for reversible intercalation of Ca^{2+} ions, as well as an electrolyte that enables battery charging at room temperatures. Due to that, the development of Ca batteries was stopped and it resumed in the last decades due to the development of new materials-perovskites [24].

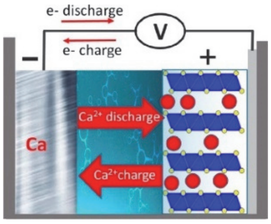

Figure 4 Schematic of a Ca battery using a Ca metal anode and an intercalation perovskite cathode [24]

For the research of suitable cathode materials, the density-functional theory (DFT) is widely used. DFT is based on the computational quantum mechanical modelling method to investigate the electronic structure of particular atoms, molecules and condensed phases. According to the DFT, the most suitable cathode materials for Ca batteries are perovskite oxides with a general formula $CaMO_3$ (M = Mo, Cr, Mn, Fe, Co, Ni) [24-27].

Arroyo et al. [26] have investigated the application of $CaMoO_3$ as cathode material in Ca batteries with 0.4 M $Ca(BF_4)_2$ in propylene and ethylene carbonate as electrolytes. The DFT study marked $CaMoO_3$ as potential cathode material due to its high electric conductivity, no crystal defects and activity in the voltage range 2 - 3 V. Despite this, deintercalation of Ca^{2+} ions was not achieved since the diffusion of Ca^{2+} inside the perovskite structure was too low. Pathreeker et al. [27] have prepared $CaMnO_3$ as cathode material, while 0.5 M $Ca(BF_4)_2$ in acetonitrile was used as electrolyte. In this case, the reversible intercalation and deintercalation of Ca was achieved, which was confirmed by X-ray diffractometry (XRD) showing the formation of new phases-cation deficient $Ca_{1-x}MnO_3$ and MnO_2. The disadvantage is that phase transformation occurred after only one working cycle which could be a significant problem for multi-cycling investigations. Even though the perovskite structure is stable, transitional metals show a tendency to crystallize forming a related spinel structure. DFT studies have shown that $CaCo_2O_4$ is a promising cathode material in Ca batteries due to the high specific capacity and rate of ionic diffusion. This was investigated by Cabello et al. [28] who have prepared $CaCo_2O_4$ based cathodes and observed reversible capacity of 30 - 100 mAh/g^1 after 30 cycles.

3.3 Perovskites in Solar Energy Storage

The concentrating solar power (CSP) technology is a promising concept for the energy supply and sustainable development. The thermal energy storage (TES) combined with CSP plants offers the opportunity to balance the supply and energy demand by reducing undesirable impacts of the intermittent availability of solar energy. The concept of the TES system relies on two-tank, molten-salt storage that enables the supply of solar energy during the off-sun hours. These two-tank molten-nitrate salt systems have a temperature limit of around 560 °C and a low specific storage capacity of < 450 kJ/kg. The system performance can be improved by increasing operating temperature above 600 °C or by the increase of the molten-salt quantities [29]. Due to the listed system limitations, the current researches are directed to the reducible perovskite oxides for thermochemical energy storage (TCES) applications. The concept of the TCES system is given in Fig. 5.

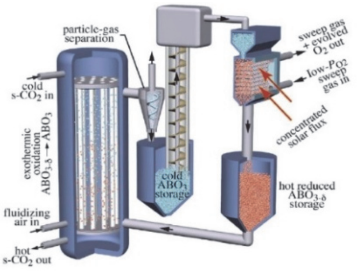

Figure 5 Schematic of a concentrating solar power plant receiver with perovskite oxide thermochemical energy storage and fluidized bed re-oxidation and heat transfer [29]

Particles in cold storage are lifted to the top of the concentrated solar radiation receiver where they are irradiated as they travel down. The receiver is operated under the vacuum or with a sweep of gas to provide low oxygen partial pressure necessary for particle reduction and heating necessary for energy storage. Afterwards, the hot reducing particles from the receiver are stored in a hot storage tank and are discharged into a bubbling fluidized bed reactor. This reactor is supplied with air to fluidize and exothermically oxidize the particles. The resulting heat is transferred to the power cycle working fluid in order to produce electrical energy. The O_2 necessary for the process can be supplied from the air, which simplifies the storage plant construction and reduces the cost. This concept allows energy storage and release over a broad temperature range [30].

Studies of TCES redox cycles of simple multivalent cation oxides such as Co_3O_4/CoO, Fe_3O_4/FeO and Mn_3O_4/Mn_2O_3 found that the main disadvantages were low applicability for large-scale systems due to the high cost and slow re-oxidation kinetics. La-rich perovskites were identified as the most suitable material from the reversibility aspect, but their high cost is motivating the new researchers to look for low-cost perovskite materials. Oxygen deficient $CaMnO_{3-\delta}$ is that kind of material and has shown redox stability up to 1250 °C. Furthermore, the A and B-site doped $CaMnO_{3-\delta}$, such as $Ca_{1-x}Sr_xMnO_{3-\delta}$ and $CaMn_{1-y}Cr_yO_{3-\delta}$ are identified as promising TCES materials. The research conducted by Imponenti et al. [30] has shown that $Ca_{1-x}Sr_xMnO_{3-\delta}$ ($x \leq 0.1$) compositions possess the highest specific energy storage with a thermodynamic limit of about 700 kJ/kg at 900 °C and partial oxygen pressure of 10^{-4} bar. Moreover, > 50% of energy storage was attributed to chemical energy storage due to the reduction process. Babiniec et al. [31] have studied Al and Ti-doped $CaMnO_{3-\delta}$ which were showing lower specific energy capacity of 390 kJ/kg at temperatures above 1000 °C. The newest research conducted by Jin et al. [32] investigated the application of $CaCo_{0.05}Mn_{0.95}O_{3-\delta}$ in the TCES systems. The results have shown an energy capacity of about 424 kJ/kg without losing reversibility. Even the low Co doping ($x = 0.05$) can weaken the metal-oxygen bonds and facilitate the lattice oxygen diffusion to the surface-active oxygen sites. Although the listed materials have great potential for TCES applications, future research needs to be focused on the preparation of low molecular weight materials with a high oxygen deficiency ($\delta \geq 0.25$) to achieve high reduction enthalpy and redox capacity.

3.4 Perovskites in Magnetic Refrigerators

Ambient temperature magnetic refrigeration (MR) technology has the potential to replace classical gas compression technology. The main advantages are low power consumption, non-toxicity and eco-compatibility of working media. The MR technology is based on a magnetocaloric effect (MCE), which is defined as a tendency of certain materials to heat up when placed in a magnetic field and to cool down when the magnetic field is removed [33].

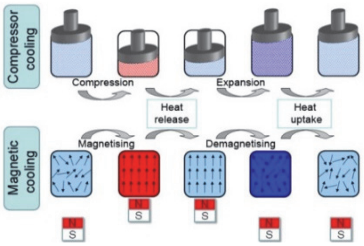

Figure 6 Schematic comparison of a classic compressor and innovative magnetic cooling process [33]

The material suitable for MR needs to possess large magnetic entropy change (ΔS_M), large adiabatic temperature change and high relative cooling power. Gadolinium (Gd) is considered as the most active material (ΔS_M = 3.25 J/kgK in a magnetic field of 1 T) for application as working media in ambient temperature MR. The main disadvantage of the Gd application is its high price, so it is necessary to investigate other lower-cost materials. Lanthanum manganites ($LaMnO_3$) and related doped compounds of a general formula $La_{1-x}A_xMn_{1-y}M_yO_3$ have been studied since the 1950s due to their astonishing magnetic properties originated from the superexchange mechanism. The superexchange mechanism is also called Kramers-Anderson superexchange and is described as strong antiferromagnetic coupling between two nearest neighbour cations through non-magnetic anion [33].

It is well known that the effect of mixed valence and spin states is significant for the magnetic properties of the material [4]. In pure $LaMnO_3$, Mn is present in a +3 oxidation state. Since $LaMnO_3$ is stable in air in an oxygen-excess form, the mixed +3/+4 Mn valence will occur. The convenient way to achieve Mn mixed-valence is to substitute a part of La with an alkaline earth metal cation, usually Sr or Ba. Rostamnejadi et al. [34] have researched on the magnetic properties of $La_{0.67}Sr_{0.33}MnO_3$ comparing it to the other magnetic materials. The material has shown paramagnetic to ferromagnetic transition at about 100 °C making it suitable for the ambient temperature MR. Furthermore, the measured ΔS_M was 5.15 J/kgK which was even higher than for Gd. Phan et al. [35] have investigated magnetic properties of a $LaMnO_3$ doped with Ca and Ba. The obtained results for $La_{0.7}Ca_{0.18}Ba_{0.12}MnO_3$ and $La_{0.7}Ca_{0.06}Ba_{0.24}MnO_3$ materials have shown significantly lower ΔS_M of around 1.70 J/kgK in comparison to the pure Gd. The same research group has prepared Ca and Pb doped $LaMnO_3$ materials and the largest ΔS_M was measured for $La_{0.7}Ca_{0.1}Pb_{0.2}MnO_3$ (3.72 J/kgK). $La_{0.6}Ca_{0.2}Pb_{0.1}MnO_3$ had a lower ΔS_M of about 2.50 J/kgK. Moreover, it was observed that the large magnetic entropy change of the prepared materials occurred around 25 °C, allowing the water to be used as a heat transfer fluid. According to the investigations, rare-earth manganites have the potential to replace Gd and to become promising working materials for magnetic refrigeration in household air conditioning systems and refrigerators.

4 CONCLUSIONS AND FUTURE REMARKS

The perovskite oxides (ABO_3) are the subject of much scientific research due to their promising electric, magnetic and redox properties necessary for energy applications. These materials can be prepared using solid-state reactions or procedures from the solution or melt. By synthesis parameters optimization, it is possible to prepare nanosized materials with controlled oxygen nonstoichiometry required for the transport properties.

Most publications in the field of perovskite oxides are dedicated to the group of rare-earth manganites, especially $LaMnO_3$, which possess astonishing electric and magnetic properties due to the uncoupled electron in the 5d orbital of La. These properties can be easily improved by the partial substitution of La^{3+} with an alkaline earth metal ion, most often Sr^{2+}. Furthermore, the potential development of Ca batteries has brought $CaMnO_3$ materials into the spotlight. Additionally, it was observed that $CaMnO_3$ has promising properties for thermochemical energy storage application due to its high reducibility and redox stability at temperatures above 1000 °C.

To sum up, perovskite oxides are promising new materials in the development of new technologies necessary for sustainable social development. They are a low-cost alternative to noble-based materials with high functionality and stability. The main disadvantage of perovskite oxides is harsh preparation conditions requiring high temperatures (> 1000 °C). Furthermore, the large-scale preparation of perovskite oxides is a great challenge, as most of the published work is limited to a laboratory scale. Therefore, for broad perovskite oxides application, it will be necessary to develop new low-cost and mild-temperature preparation procedures. However, the high number of publications in this field promises the future development of proposed perovskite oxides applications.

Acknowledgements

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. This work has been supported in part by Croatian Science Foundation under the project IP-2018-01-5246.

5 REFERENCES

[1] See https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/statistical-review/bp-stats-review-2020-full-report.pdf

[2] Zhang, W., Eperon, G. E., & Snaith, H. J. (2016). Metal halide perovskites for energy applications. *Nature Energy*, *1*, 16048 (1-8.). https://doi.org/10.1038/nenergy.2016.48

[3] Kim, J. Y., Lee, J. W., Jung, H. S., Shin, H., & Park, N. G. (2020). High-efficiency perovskite solar cells. *Chemical Reviews*, *120*(15), 7867-7918. https://doi.org/10.1021/acs.chemrev.0c00107

[4] Goodenough, J. B. (1955). Theory of the role of covalence in the perovskite-type manganites [La,M(II)]MnO_3. *Physical Review*, *100*(2), 564-573. https://doi.org/10.1103/PhysRev.100.564

[5] Attfield, J. P., Lightfoot, P., & Morris, R. E. (2015). Perovskites. *Dalton Transactions*, *44*, 10541-10542. https://doi.org/10.1039/c5dt90083b

[6] Momma, K. & Izumi, F. (2011). VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography*, *44*, 1272-1276. https://doi.org/10.1107/S0021889811038970

[7] Bartel, C. J., Sutton, C., Goldamith, B. R., Ouyang, R., Musgrave, C. B., Ghiringhelli, L. M., & Scheffler, M. (2019). New tolerance factor to predict the stability of perovskite oxides and halides. *Science Advances*, *5*(2). https://doi.org/10.1126/sciadv.aav0693

[8] Hines, R. I. (1997). *Atomistic simulation and ab-initio studies of polar solids*, Doctoral dissertation, Bristol University.

[9] Song, J., Zhu, S., Ning, D., & Bouwmeester, H. J. M. (2021). Defect chemistry and transport properties ofperovskite-type oxides $La_{1-x}Ca_xFeO_{3-\delta}$. *Journal of Materials Chemistry A*, *9*, 974-989. https://doi.org/10.1039/D0TA07508F

[10] Sunarso, J., Hashim, S. S., Zhu, N., & Zhou, W. (2017). Perovskite oxides applications in high temperature oxygen separation, solid oxide fuel cell and membrane reactor: A review. *Progress in Energy and Combustion Science*, *61*, 57-77. https://doi.org/10.1016/j.pecs.2017.03.003

[11] Orgiani, P., Galdi, A., Aruta, C., Cataudella, V. De Filippis, G., Perroni, C. A., Marigliano Ramaglia, V., Ciancio, R., Brookes, N. B., Moretti Sala, M., Ghiringhelli, G., & Mariato, L. (2010). Multiple double-exchange mechanism by Mn^{2+}-doping in manganite compounds. *Physical Review B*, *82*(20), 205122 (1-4). https://doi.org/10.1103/PhysRevB.82.205122

[12] Assirey, E. A. R. (2019). Perovskite synthesis, properties and their related biochemical and industrial application. *Saudi Pharmaceutical Journal*, *27*(6), 817-829. https://doi.org/10.1016/j.jsps.2019.05.003

[13] Baldini, M., Muramatsu, T., Sherafati, M., Mao, H. K., Malavasi, L., Postorino, P., Satpathy, D., & Struzhkin, V. V. (2015). Origin of colossal magnetoresistance in $LaMnO_3$ manganite. *Proceedings of the National Academy of Sciences of the United States of America*, *112*(35), 10869-10872. https://doi.org/10.1073/pnas.1424866112

[14] Yakout, S. M. (2020). Spintronics: Future technology for new data storage and communication devices. *Journal of superconductivity and novel magnetism*, *33*, 2557-2580. https://doi.org/10.1007/s10948-020-05545-8

[15] Bulfin, B., Vieten, J., Starr, D. E., Azarpira, A., Zachäus, C., Hävecker, M., Skorupska, M., Schmücker, M., Roeb, M., & Sattler, C (2017). Redox chemistry of $CaMnO_3$ and $Ca_{0.8}Sr_{0.2}MnO_3$ oxygen storage perovskites. *Journal of Materials Chemistry A*, *5*, 7912-7919. https://doi.org/10.1039/C7TA00822H

[16] Neagu, D., Tsekouras, G., Miller, D. N., Ménard, H., & Irvine, J. T. S. (2013). In situ growth of nanoparticles through control of non-stoichiometry. *Nature Chemistry*, *5*(11), 916-923. https://doi.org/10.1038/nchem.1773

[17] Danks, A. E., Hall, S. R., & Schnepp, Z. (2016). The evolution of 'sol-gel' chemistry as a technique for materials synthesis. *Materials Horizons*, *3*, 91-112. https://doi.org/10.1039/C5MH00260E

[18] Ban, T., Kaiden, T., & Ohya, Y. (2019). Hydrothermal synthesis of layered perovskite-structured metal oxides and cesium tungstate nanosheets. *Crystal Growth and Design*, *19*, 6903-6910. https://doi.org/10.1021/acs.cgd.9b00515

[19] Ahda, S., Misfadhila, S., Parikin, P., & Putra, T. Y. S. P. (2017). Molten salt synthesis and structural characterization of$BaTiO_3$nanocrystal ceramics. *Materials Science and Engineering*, *176*, 012048 (1-6). https://doi.org/10.1088/1757-899X/176/1/012048

[20] Cascos, V., Troncoso, L., Larralde, A. L., Fernandez-Diaz, M. T., & Alonso, J. A. (2020). Performance of $SrCo_{1-x}Ir_xO_{3-\delta}$ ($x = 0.10$ and 0.15) perovskites as potential cathode materials for intermediate-temperature solid oxide fuel cells (IT-SOFC). *ACS Applied Energy Materials*, *3*, 6709-6716. https://doi.org/10.1021/acsaem.0c00848

[21] Kaur, P. & Singh, K. (2020). Review of perovskite-structure related cathode materials for solid oxide fuel cells. *Ceramics International*, *46*(5), 5521-5535. https://doi.org/10.1016/j.ceramint.2019.11.066

[22] Wang, W., Qu, J., Julião, P. S. B, & Shao, Z. (2017). Recent advances in the development of anode materials for solid oxide fuel cells utilizing liquid oxygenated hydrocarbon fuels: A mini review. *Energy Technology*, *7*, 33-44. https://doi.org/10.1002/ente.201700738

[23] Ishihara, T. (2009). *Perovskite oxide for solid oxide fuel cells, Fuel cells and hydrogen energy*, Springer. https://doi.org/10.1007/978-0-387-77708-5

[24] Arroyo-de Dompablo, M. E., Ponrouch, A., Johansson, P., & Palacín, M. R. (2020). Achievements, Challenges, and prospects of calcium batteries. *Chemical Reviews*, *120*, 6331-6357. https://doi.org/10.1021/acs.chemrev.9b00339

[25] Torres, A., Bardé, F., & Arroyo-de Dompablo, M. E. (2019). Evaluation of cobalt oxides for calcium battery chatode applications. *Solid State Ionics*, *340*, 115004 (1-8). https://doi.org/10.1016/j.ssi.2019.115004

[26] Arroyo-de Dompablo, M. E., Krich, C., Nava-Avendãno, J., Palacín, M. R., & Bardé, F. (2016). In quest of cathode materials for Ca ion batteries: the $CaMO_3$ perovskites (M = Mo, Cr, Mn, Fe, Co, Ni). *Physical Chemistry Chemical Physics*, *18*, 19966-19972. https://doi.org/10.1039/C6CP03381D

[27] Pathreeker, S., Reed, S., Chano, P., & Hosein, I. D. (2020). A study of calcium ion intercalation in perovskite calcium manganese oxide. *Journal of Electroanalytical Chemistry*, *874*, 114453 (1-6). https://doi.org/10.1016/j.jelechem.2020.114453

[28] Cabello, M., Nacimiento, F., Gonzáles, J. R., Ortiz, G., Alcántara, R., Lavela, P., Pérez-Vicente, C., & Tirado, J. L. (2016). Advancing towards a veritable calcium-ion battery: $CaCo_2O_4$ positive electrode material. *Electrochemistry Communications*, *67*, 59-64. https://doi.org/10.1016/j.elecom.2016.03.016

[29] Albrecht, K. J., Jackson, G. S., & Braun, R. J. (2018). Evaluating thermodynamic performance limits of thermochemical energy storage subsystems using reactive perovskite oxide particles for concentrating solar power. *Solar Energy*, *167*, 179-193. https://doi.org/10.1016/j.solener.2018.03.078

[30] Imponenti, L., Albrecht, K. J., Kharait, R., Sanders, M. D., & Jackson, G. S. (2018). Redox cycles with doped calcium manganites for thermochemical energy storage to 1000 °C. *Applied Energy*, *230*, 1-18. https://doi.org/10.1016/j.apenergy.2018.08.044

[31] Babiniec, S. M., Coker, E. N., Miller, J. E., & Ambrosini, A. (2015). Doped calcium manganites for advanced high-temperature thermochemical energy storage. *International Journal of Energy Research*, *40*, 280-284. https://doi.org/10.1002/er.3467

[32] Jin, F., Xu, C., Yu, H., Xia, X., Ye, F., Li, X., Du, X., & Yang, Y. (2021). $CaCo_{0.05}Mn_{0.95}O_{3-\delta}$: A promising perovskite solid solution for solar thermochemical energy storage. *ACS Applied Materials & Interfaces*, *13*, 3856-3866. https://doi.org/10.1021/acsami.0c18207

[33] Hussain, I., Anwar, M. S., Khan, S. N., Lee, C. G., & Koo, B. H. (2018). Magnetic properties and magnetocaloric effect in ordered double perovskites $Sr_{1.8}Pr_{0.2}FeMo_{1-x}W_xO_6$. *Korean Journal of Materials Research*, *28*(8), 445-451. https://doi.org/10.3740/MRSK.2018.28.8.445

[34] Rostamnejadi, A., Salamati, H., & Kameli, P. (2012). Magnetic properties of interacting $La_{0.67}Sr_{0.33}MnO_3$ nanoparticles. *Journal of Superconductivity and Novel Magnetism*, *25*, 1123-1132. https://doi.org/10.1007/s10948-011-1378-z

[35] Phan, M. H., Peng, H. X., Yu, S. C., Tho, N. D., Nhat, H. N., & Chau, N. (2007). Manganese perovskites for room temperature magnetic refrigeration applications. *Journal of Magnetism and Magnetic Materials*, *316*(2), 562-565. https://doi.org/10.1016/j.jmmm.2007.03.021

Contact information:

Andreja ŽUŽIĆ, MSc cheming. and PhD student
(Corresponding author)
University of Zagreb, Faculty of Chemical Engineering and Technology,
Marulićev trg 19, 10 000 Zagreb, Croatia
E-mail: azuzic@fkit.hr

Veljko FILIPAN, Full professor
University of Zagreb, Faculty of Chemical Engineering and Technology,
Marulićev trg 19, 10 000 Zagreb, Croatia
E-mail: vfilipan@fkit.hr

Igor SUTLOVIĆ, Full professor
University of Zagreb, Faculty of Chemical Engineering and Technology,
Marulićev trg 19, 10 000 Zagreb, Croatia
E-mail: isutlo@fkit.hr

Jelena MACAN, Full professor
University of Zagreb, Faculty of Chemical Engineering and Technology,
Marulićev trg 19, 10 000 Zagreb, Croatia
E-mail: jmacan@fkit.hr