Ruddlesden–Popper phase $A_2B_04$ oxides: Recent studies on structure, electrical, dielectric, and optical properties

Gurudeo NIRALA, Dharmendra YADAV, Shail UPADHYAY*

Department of Physics, Indian Institute of Technology (BHU), Varanasi-221005, India

Received: October 1, 2019; Revised: January 29, 2020; Accepted: February 4, 2020

© The Author(s) 2020.

Abstract: In the last two decades, structure and properties of Ruddlesden–Popper phase (RP) $A_2B_04$ oxides with $K_2NiF_4$ structure, have been widely investigated. But to the best of our knowledge, no review article is available in the literature on recent studies on these oxides. Therefore, in this article, recent studies on structure, electrical, dielectric, and optical properties of these oxides have been reviewed. Special attention is put on to highlight the effect of doping and oxygen stoichiometry on the structure and properties of these oxides. Further, important applications of these oxides have also been mentioned in this article.

Keywords: Ruddlesden–Popper (RP) phase; $A_2B_04$ oxides; electrical conductivity; dielectric

1 Introduction

Ruddlesden–Popper (RP) phases are described with the general formula of $A_{n+1}B_nO_{3n+1}$. This formula can also be written as $AO(ABO_3)_n$, where $n$ perovskite layers are stacked between $AO$ rock-salt layers along the crystallographically $c$-axis [1]. The first member of the series, $A_2B_04$ ($n = 1$), adopts the $K_2NiF_4$ structure. Figure 1 represents the ideal tetragonal unit-cell of a RP-phase $A_2B_04$ oxide, which corresponds to the stoichiometric compound crystallized in $I4/mmm$ space group. This is also a two-dimensional (2D) layered perovskite structure. Commonly, $A_2B_04$ oxides consist of rare or alkaline earth element as $A$-site cations with transition or post-transition metals on the $B$-site, forming an extensive series of compositions. The $A$-site cations have a coordination number of “9”, locating at the boundary between the two types of layers, while the $B$-site cations are positioned at the center of an octahedron formed by six oxygen anions. RP oxides have shown very attractive and versatile physical properties such as superconductivity [2–6], magnetoresistance [7–11], mixed ionic and electronic conductivity [12–15], giant and colossal dielectric [16–19], low loss microwave dielectric [20–24], photoluminescence [25–29], catalytic activity [30–32], thermoelectric [33–35], etc., which are useful for many energy and electronic devices. The $A_2B_04$ layered perovskites have recently attracted attention owing to their great environmental stability and versatile applications. The alkaline earth element (AE) doped and undoped $RE_2MO_4$ layered perovskites (where $RE$ is rare earth element and $M$ is transition metal) have been considered as alternatives for cathode application in Solid Oxide Fell Cells (SOFC)/Solid Oxide Electrolysis Cells (SOEC), due to their superior mixed ionic and electronic conductivities in comparison to traditionally used perovskite oxides [36–39]. $Sr_2CeO_4, AE_2SnO_4$ ($AE = Ca, Sr, Ba$) are found to be suitable host for photoluminescence applications
Fig. 1 Ideal tetragonal unit cell of stoichiometric \( A_2BO_4 \) layered perovskite crystalized in \( I4/mmm \) space group.

[40–42]. Doped and undoped lanthanide nickelates show giant/colossal dielectric properties [43–45].

In the last several years, rapid growth in solar cells and optoelectronic devices based on 3D organic–inorganic halide-based perovskites is observed. But their inherent instabilities over moisture, light, and heat strongly hindered this growth. Recently 2D organic–inorganic based layered perovskites received increasing attention owing to their superior ambient stability. These 2D perovskites have demonstrated to exhibit abundant and tunable optoelectronic properties, high quantum efficiency, and large specific surface area, which hold a good prospect for a range of electronic and optical applications [46,47].

During 1980–1990, Rao and his group [48,49] carried extensive research work on structure and magnetic properties of \( A_2BO_4 \) oxides. Magnetic properties of these oxides were investigated more extensively than transport properties. They published a few review articles and chapters in the book on these oxides [50].

After observation of superconductivity up to 35 K in the Ba-doped \( La_2CuO_4 \) ternary compound by George Bednorz and Alex Müller of IBM Zurich Laboratory in 1986 [51], research works on \( A_2BO_4 \) oxides further intensified. However, in the last two decades, these oxides have attracted attention because of their applications based on their electrical, optical, and dielectric properties. Recently two review articles have been published in the literature on diffusion/transport of oxide ion [52,53]. To the best of our knowledge, no recent review articles on the overall development of structure, properties, and applications of \( A_2BO_4 \) layered perovskites are available in the literature.

Fig. 2 (a) Half unit cell of \( T \)-type \( La_2NiO_4 \) layered perovskite. (b) Unit cell of \( T' \)-type \( Pr_2CuO_4 \) ternary oxide.

Therefore, in this article structure, electrical, dielectric, and optical properties of \( A_2BO_4 \) along with various applications have been reviewed. In addition, various strategies for enhancing their properties using suitable doping at \( A \)- as well as \( B \)-sites are discussed. We expect that this article will intensify research on \( A_2BO_4 \) layered perovskites and finally commercialization of devices based on these oxides.

2 Structure and oxygen stoichiometry

The \( A_2BO_4 \) compounds crystallize in two major structural forms: \( T \)-type and \( T' \)-type [54]. The schematic structure of \( T \)-type \( La_2NiO_4 \) ternary oxide is shown in Fig. 2(a). For clarity, only half cell \( (a/2 \times b/2 \times c) \) is shown. The \( Ni \) cations are located at the center of apically elongated octahedra, also known as \( NiO_6 \) octahedra; the six \( Ni-O \) distances are: \( Ni-O_{b1}(O(1)) \times 4 = 1.947 \) Å and \( Ni-O_{ap}(O(2)) \times 2 = 2.267 \) Å; two long distant atoms are along the \( c \)-axis. The \( La \) cation is surrounded by nine oxygen atoms, four \( O_{ap} \) atoms (in the same level of \( La \) atom), four \( O_{bs} \) atoms (in \( Ni \) level, above (below)), and one \( O_{ap} \) atom (head-below (head-above) from \( La \) atom). These nine \( O \) atoms make a \( LaO_9 \) polyhedra. The \( La \) atom is not located at the center of this polyhedra, but it is little shifted towards the capping \( O_{ap} \). The \( NiO_6 \) octahedra and \( LaO_9 \) polyhedra share faces with each other and each \( NiO_6 \) octahedra is connected with four nearest neighboring \( NiO_6 \) octahedra in \( ab \)-plane by common shared \( O_{bs} \) atoms. Each \( NiO_6 \) octahedra with eight \( La \) atoms of \( O_{ap} \) level makes a \( LaNiO_3 \) perovskite unit. Between two perovskite units, there is a \( LaO \) rocksalt layer in \( ab \)-plane. Therefore, the
La₂NiO₄ structure can be described as an intergrowth of an alternative layer of LaNiO₃ perovskite and LaO rocksalt along the c-axis. Thus T'-type A₂BO₄ ternary oxides are known as A₂BO₄ layered perovskite or RP-phase layered perovskite. K₂NiF₄ has a similar structure. Hence, this structure is also commonly referred as K₂NiF₄ structure.

In contrast to T-type structure in T'-type structure, the cationic arrangement is the same, but the anionic arrangement is different [55]. Basal oxygens, O₉₅, do not change its position but apical oxygens, O₉₆, are shifted to the face of the unit cell, between the levels of cation A, designated as O₇. The schematic structure of T'-type Pr₂CuO₄ ternary oxide is shown in Fig. 2(b). The Cu cation is surrounded by four O₉₅ atoms and their interionic distances are 1.98 Å. The Pr cations are surrounded by eight O atoms: four O₉₅ atoms are in the Cu level and four O₉₇ are between the level of Pr atoms, making a PrO₈ cube.

The A₂BO₄ compounds can also be visualized as alternative stacking of BO₂ and A₂O₂ bilayers along c-axis [56]. In La₂NiO₄, four halves shared (between unit cells) O₉₅ atoms and one Ni atom makes NiO₂ layer, similarly two O₉₆ and two La atoms make La₂O₂ bilayer, as shown in Fig. 2(a), so the structure of La₂NiO₄ compromises the following sequences of layers.

\[(\text{NiO}_9)_0(\text{LaO}_9)_c(\text{LaO}_9)_o(\text{NiO}_9)_c(\text{LaO}_9)_o \ldots\]

The subscript o and c indicate whether the cation is at the origin or center of the mesh, respectively. Similar stacking of BO₂ and A₂O₂ bilayers in T'-type structured Pr₂CuO₄ is also schematically shown in Fig. 2(b). The A₂BO₄ compounds also crystallize in T'-type structure, which is a hybrid of T- and T'-type structure [54]. Recently several research groups have investigated the T- and T'-type structures using well known Goldschmidt tolerance factor t as a criterion. The tolerance factor is based on the analysis of perovskite supercells (also known as perovskite tolerance factor) and given as follows [57]:

\[ t = \frac{r_{A} + r_{O}}{\sqrt{2(r_{B} + r_{O})}} \]  

where, \( r_{A} \), \( r_{B} \), and \( r_{O} \) are ionic radii of cation A, cation B, and oxygen, respectively. The tolerance factor "t" for T-type structure is found in the range of 0.99 ≥ t ≥ 0.87 while for T'-type structure the tolerance factor lies in the range of 0.86 > t ≥ 0.83. Under high pressure, the lower limit of t for T'-type structure extends up to 0.81. The T'-type structure exists for a narrow range of tolerance factors, lies in between the t of T- and T'-type structure [54].

Most of the A₂BO₄ layered perovskites crystallize either in orthorhombic structure or in tetragonal structure. The tolerance factor t for tetragonal and orthorhombic structure lies in the range of 0.99 ≥ t ≥ 0.88 and 0.88 ≥ t ≥ 0.865, respectively [56]. The A₂BO₄ layered perovskites can be further subdivided in two groups, one of which consists rare earth element (RE = La, Nd, Pr, etc.) as cation “A” and the other of which consists alkali earth element (AE = Ca, Sr, Ba) as cation “A”. The layered perovskites consisting RE as cation “A”, consists transition metal(s) (M = Ni, Cu, Co, etc.) in divalent state as cation “B” and the other group which consists AE as cation “A”, consists of transition element(s) or post-transition element(s) (M = Mn, Sn, Ti, etc.) in the tetravalent state, as cation “B”. These two groups of layered perovskites are named as RE₂MO₄ and AE₂M’O₄ in this article, respectively. In recent years another group of A₂BO₄ layered perovskites or doped A₂BO₄ layered perovskites are also studied, which consist of both rare earth and alkaline earth elements in the form of cation “A” and cation “A” in equal or unequal stoichiometries. The general structural formula for this group of compounds is sometimes written as “AₓA’₂-xBO₄”. Majority of RE₂M₀₄, crystallize in orthorhombic structure with space group Bmab, P4₁/nmc, Pccn, etc. while AE₂M’O₄ crystallize in tetragonal structure with space group I4/mmm, P4₁/mmm, etc. There are also some exceptions as well, marked as “±” in Table 1, which do not follow this general categorization.

In orthorhombic RE₂M₀₄, tensile stress in the RE₂O₂ layer and compressive stress in the MO₂ layer are present. In La₂NiO₄, the basal Ni – O₉₅ interatomic distances (1.94 Å) are shorter than the sum of the ionic radii (2.09 Å, using \( r_{\text{Ni}^{2+}} = 0.73 \) Å and \( r_{O^{2-}} = 1.40 \) Å) and three out of four basal Li – O₉₆ interatomic distances (2.797 Å and 3.15 Å ) are longer than the sum of the ionic radii (2.62 Å, using \( r_{\text{La}^{3+}} = 1.216 \) Å) [58,59]. This mismatch of interionic distances and the sum of ionic radii produces stress between interlayers. These interlayer stresses are partially relieved by the systematic canting of NiO₆ octahedra about a fixed rotation axis, which is parallel to the basal plane, i.e., the NiO₂ and La₂O₂ layers are partially buckled to relieve the compressive and
Table 1 Structure, highest experimentally measured electrical conductivity, and activation energy of recently studied ceramics

| Ceramic | Structure         | Total electrical conductivity, $\sigma$ (S·cm$^{-1}$) at temperature (°C) | Activation energy, $E_a$ (eV) | Reference |
|---------|-------------------|--------------------------------------------------------------------------|-------------------------------|-----------|
| Nd$_2$NiO$_{1.2}$ | Orthorhombic | 99 at 900 | 0.081 | [12] |
| Nd$_{1.7}$Ca$_{0.3}$NiO$_{4.11}$ | Tetragonal | 153 at 900 | 0.085 | [12] |
| (Nd$_0.9$La$_{0.1}$)$_2$Ni$_{0.75}$Cu$_{0.25}$O$_4$ | Tetragonal | 114.36 at 500 | 0.083 | [96] |
| Nd$_2$Ni$_0.6$Co$_0.4$O$_4$ | Orthorhombic | 48 at 400 | 0.145 | [97] |
| Nd$_2$Ni$_0.6$Cu$_0.4$O$_4$ | Orthorhombic | 42 at 400 | 0.111 | [97] |
| Nd$_{1.8}$Sr$_{0.2}$Ni$_0.8$Cu$_0.4$O$_{4.01}$ | Tetragonal | 42.7 at 640 | 0.07 | [76] |
| Nd$_2$Ni$_{0.6}$Fe$_{0.4}$O$_4$ | Orthorhombic | 38 at 400 | 0.109 | [97] |
| Nd$_{1.8}$Ce$_{0.2}$Cu$_{0.8}$Ni$_0.2$O$_{4.6}$ | Tetragonal | 0.619 at 700 | 0.11 | [75] |
| Nd$_2$Ni$_0.6$Mn$_0.4$O$_4$ | Orthorhombic | 38 at 400 | 0.119 | [97] |
| La$_2$NiO$_4$ | Orthorhombic | 96 at 800 | 0.07 | [98] |
| La$_2$Ni$_0.8$Cu$_0.2$O$_4$ | Orthorhombic | 57 at 800 | 0.08 | [98] |
| La$_2$Ni$_0.8$Cu$_0.2$O$_4$ | Orthorhombic | 55 at 400 | 0.09 | [99] |
| La$_{1.7}$Sr$_{0.3}$NiO$_4$ | Tetragonal | 180 at 800 | 0.073 | [100] |
| La$_2$Ni$_{0.8}$Mg$_0.2$O$_4$ | Tetragonal | 88.2 at 400 | 0.061 | [101] |
| Pr$_{1.8}$Sr$_{0.2}$NiO$_4$ | Tetragonal | 0.25 at 900 | 0.065 | [102] |
| Pr$_{1.8}$Ni$_0.8$Cu$_{0.2}$O$_4$ | Tetragonal | 100 at 500 | 0.64 | [15] |
| Pr$_{1.8}$Ni$_{0.75}$Cu$_{0.25}$O$_4$ | Tetragonal | 40 at 500 | 0.57 | [15] |
| Pr$_{2.2}$Ni$_{0.8}$Cu$_{0.4}$O$_4$ | Orthorhombic | 130 at 450 | 0.08 | [99] |
| Sm$_{1.8}$La$_{0.2}$Ni$_{0.8}$O$_4$ | Tetragonal | 260 at 700 | 0.06 | [103] |
| Sm$_{1.8}$La$_{0.2}$Ni$_{0.8}$O$_4$ | Orthorhombic | 0.361 at 640 | 0.26 | [104] |
| La$_{1.8}$Sr$_{0.2}$CoO$_4$ | Tetragonal | 0.03 at 400 | 0.451 | [17] |
| Nd$_{2.8}$Sr$_{0.2}$CoO$_{4.6}$ | Tetragonal | 212 at 800 | 0.51 | [105] |
| PrSr$_{0.8}$Mn$_{0.2}$O$_{4.83}$ | Tetragonal | 7 at 900 | 0.42 | [106] |
| Pr$_{1.8}$Sr$_{0.2}$Co$_{0.8}$O$_{4.83}$ | Tetragonal | 23 at 900 | 0.34 | [106] |
| La$_2$CuO$_4$ | Orthorhombic | 10 at 900 | 0.07 | [107] |
| La$_{1.8}$Pr$_{0.2}$Cu$_{0.4}$Sr$_{0.2}$CuO$_{4.04}$ | Tetragonal | 1.8 at 900 | 0.20 | [108] |
| Pr$_{2.2}$Sr$_{0.2}$CuO$_{4}$($x = 0.5, 0.75$) | Tetragonal | 25 at 900 | 0.44 | [108] |
| Pr$_{2.2}$CuO$_{4.05}$ | Tetragonal* | 200 at 1000 | 0.34 | [107] |
| Nd$_{2}$CuO$_{4.04}$ | Tetragonal* | 100 at 1000 | 0.60 | [107] |
| Sm$_{1.8}$Sr$_{0.2}$CuO$_4$ | Tetragonal | 6.8 at 640 | 0.40 | [13] |
| Sm$_{1.8}$Sr$_{0.2}$CuO$_4$ | Tetragonal | 96 at 950 | 0.32 | [109] |
| La$_{0.8}$Sr$_{1.2}$MnO$_4$ | Tetragonal | 5 at 1100 | 0.11 | [110] |
| Nd$_{2}$Sr$_{1.5}$MnO$_{4}$ | Tetragonal | 33.4 at 800 | 0.20 | [111] |
| Nd$_{2}$BaInO$_{3.95}$ | Monoclinic | 3.6 $\times$ 10$^{-5}$ at 858 | 0.91 | [112] |
| Nd$_{0.9}$Ca$_{0.1}$BaInO$_{3.95}$ | Monoclinic | 4.9 $\times$ 10$^{-4}$ at 500 | 0.77 | [113] |
| Nd$_{0.9}$Ba$_{0.1}$InO$_{3.95}$ | Monoclinic | 1.3 $\times$ 10$^{-4}$ at 500 | 0.92 | [113] |
| Nd$_{0.9}$Sr$_{1.2}$BaInO$_{3.95}$ | Monoclinic | 3.0 $\times$ 10$^{-4}$ at 500 | 0.73 | [113] |

Tensile stresses, respectively, as shown in Fig. 3 [60,61].

The other RE$_2$MO$_4$, with similar interlayer stresses as in La$_2$NiO$_4$, the systematic canting of MO$_6$ octahedra are also there, to relieve interlayer stresses in their structure [56]. These distortions in the structure produced by the systematic canting of MO$_6$ octahedra lead to the change in Bmab, P4$_2$/nmc, Pccn, and Fmmm symmetries of the orthorhombic structure. The two nearest neighbor corner shared MO$_6$ octahedra generally cant symmetrically in opposite directions.

www.springer.com/journal/40145
about the fixed rotation axis, as shown in Fig. 3. The azimuthal orientation of rotation axes for neighboring planes of MO₆ octahedra differ by ⁰ in Bmab, 90° in P ⁴/ ²/nm, and between ⁰ and 90° in Pccn. These octahedra canting symmetries are also characterized by long-range ordering. When either distortion is present or correlation length of canting is short, then the structure is best described by the Fmmmm symmetry. The Fmmmm symmetry is also used in assigning an average structure of the material, with uncharacterized incommensurate structure or presence of weak supercell having a dimension larger than \( \sqrt{2a} \times \sqrt{2b} \times c \) [61].

Majority of A₂BO₄ layered perovskites which crystallize in orthorhombic structure transform into the less ordered orthorhombic structure of Fmmmm space group above the room temperature and into a tetragonal structure at moderately high temperature. These structural transformations are referred by abbreviated name as LTO (Low-Temperature Orthorhombic), LTLO (Low-Temperature Less Orthorhombic), and HTT (High-Temperature Tetragonal) for general nomenclature [61]. At high temperature (above room temperature) above-mentioned stresses between the interlayers relaxed due to the thermal expansion of the unit cell and the MO₆ octahedra aligned in tetragonal symmetry groups (14/mmm or P4/mmm). The alignment of MO₆ octahedra disturb the periodic symmetry and produces structural transformations, initially in LTLO above the room temperature and finally in HTT at high moderately temperature. Stoichiometry of oxygen in the structure is also responsible for the structural transformation. But temperature-dependent structural transitions mentioned above are independent of oxygen stoichiometry due to the thermal expansion of unit cell [58,60–63].

The A₂BO₄ layered perovskites are generally synthesized via solid-state reaction method. During high-temperature synthesis processes (> 1000 °C), excess oxygens may accommodate in the structure at the interstitial sites and/or oxygen vacancies are created in the structure. These excess oxygens in the structure are accommodated in the form of doubly ionized oxide ions, O²⁺. In this article, Kröger–Vink notation has been followed to represent charge species and defects. In Kröger–Vink notation, the positively charged species are marked as “•” in superscript. Similarly, the negatively charged species are marked as “’” in superscript. When an oxide ion, O²⁻ accommodates the interstitial sites, two excess holes, h⁺ are created in the structure. Similarly, when an oxygen vacancy, Vₒ⁰⁻ is created two excess electrons, e’ are created in the structure. Generation of these defects are represented by Eqs. (2) and (3) [64].

\[
\frac{1}{2} O₂(g) = O²⁻ + 2h⁺ \tag{2}
\]

\[
O⁰⁻ = Vₒ⁰⁻ + \frac{1}{2} O₂(g) + 2e' \tag{3}
\]

These excess holes may recombine with electrons or with divalent transition metal ions according to Eqs. (4) and (5), respectively;

\[
h⁺ + e' = 0 \tag{4}
\]

\[
M^{2+} + h⁺ = M^{3+} \tag{5}
\]

In RE₂MO₄, RE₂O₂ bilayer is electropositive and MO₂ layer is electronegative. Excess oxide ions mostly accommodate in the RE₂O₂ bilayer interstitials and holes generally go in the MO₂ layer due to their electropositive and electronegative nature, respectively. By this mechanism, excess oxide ions in the structure facilitate in neutralizing the electronic polarity of layers. It is also reported that in RE₂MO₄ oxides, excess oxide ions at interstitial sites minimize the electronic polarity between the RE₂O₂ and MO₂ intergrown layers [65,66]. There are also reports on RE₂MO₄, in which the creation of oxygen vacancies at basal oxygen sites, i.e., in MO₂ layers is discussed [67]. The electronic polarity of intergrown RE₂O₂ and MO₂ layers, inhibits the creation of oxygen vacancy in RE₂O₂ bilayer [66]. Location of oxygen vacancy and interstitial oxygen is schematically shown in Fig. 4 [66]. The oxygen stoichiometry of RE₂MO₄ depends on the number of excess oxide ions at interstitial sites and number of oxygen vacancies in the structure. The interstitial oxide ions O²⁻, in RE₂O₂ bilayers play crucial role in reducing the stresses produced by the above-mentioned mismatch.
of interionic distances of RE−O_{ap} and M−O_{bs} [66]. On the accommodation of oxygen at interstitial sites, the electrostatic repulsion between O'' and neighboring apical oxygen O_{ap} of RE_{2}O_{2} bilayer increases the lattice parameters “a” and “c” which facilitates to release of compressive and tensile stresses present in MO_{2} layer and RE_{2}O_{2} bilayer, respectively. It is also known that ionic radii of transition metal ions in lower oxidation state are smaller than their higher oxidation state. Hence, oxidation of transition metal ions reduces the effective interionic distances of M−O_{bs}. Due to these two processes taking place simultaneously majority of RE_{2}MO_{4} oxides exhibit a structural transformation with increasing concentration of interstitial oxide ions [60,68,69]. For example, the hyper-stoichiometric (oxygen excess) La_{2}NiO_{4+δ} (0.10 < δ < 0.15) transforms from orthorhombic to tetragonal phase [70]. The A_{2}BO_{4} layered perovskites also exhibit a structural transformation on becoming hypo-stoichiometric (oxygen deficient). For example, when Sr_{2}MnO_{4} becomes hypo-stoichiometric, i.e., Sr_{2}MnO_{3.5}, transforms from tetragonal to monoclinic phase [71,72].

The oxygen stoichiometry in structure can also be tailored by substitutions at A and B sites. There are three kinds of substitutions (isovalent, donor, and acceptor) having been done in A_{2}BO_{4} layered perovskites. Further, in the case of isovalent substitution, substituted ion may have smaller or larger ionic radius than the host ion. Isovalent substitution of smaller ionic radii helps in increasing the void space of interstitial sites, thus, supporting accommodation of higher concentration of excess oxygen in the structure. The substitution of larger ionic radii has vice versa effect. The isovalent substitution also helps in increasing or reducing the above-mentioned stresses of intergrown layers, due to increment or decrement in interionic distances, respectively. For example, on substitution of Ni in La_{2−x}Cu_{1−x}Ni_{x}O_{4+δ} oxygen content increases with the increasing content of Ni. The size of octahedra with Ni gets reduced due to the smaller ionic radius of Ni (r_{Ni^{2+}} = 0.69 Å) as compared to Cu (r_{Cu^{2+}} = 0.73 Å). Thus, void space in La_{2}O_{2} bilayer is increased and facilitates easier accommodation of O'' [68].

The donor substitutions are generally done in A{\textsubscript{E}E}_{2}M^{4+}O_{4} by substituting RE ions at the AE site. The RE substitution creates excess electrons in the structure according to Eq. (6). These excess electrons may reduce M^{4+} cation to M^{3+}, according to Eq. (7). On account of this, the RE_{x}A{\textsubscript{E}}_{2−x}O_{2} rocksalt bilayer becomes electropositive and M^{3+}M_{1−y}O_{2} becomes electronegative, which helps in accommodating more O'' in RE_{x}A{\textsubscript{E}}_{2−x}O_{2} rocksalt bilayers. For example, La_{2−x}Sr_{x}MnO_{4+δ}, (0.25 ≤ x ≤ 0.6) consist of excess oxygen in the structure as compared to Sr_{2}MnO_{4} [39]. Excess electrons created due to RE substitution do not only reduces M' cations, but also some of them may recombine with excess holes (according to Eq. (4)) created by interstitial oxide ions (according to Eq. (2)). If these two processes of reduction of M' cation and recombination of electron and hole occurring simultaneously (may make x ≠ y), the concentration of reduced M' ion can be different from twice of concentration of RE substituent.

\[ RE_{2}O_{3} = 2(RE^{3+}_{AE}) + 20^{0} + \frac{1}{2}O_{2}(g) + 2e' \]  \hspace{1cm} (6)

\[ (M^{4+})^{x} + e' = (M^{3+})^{y} \]  \hspace{1cm} (7)

The acceptor substitutions in RE_{2}MO_{4} have been made by replacing RE ions with AE ions. Acceptor dopants normally create excess holes in the structure according to Eq. (8). These excess holes recombine with neutral oxygen vacancies and help them stabilizing as V_{0}^{*}, according to Eq. (9). Another possibility is that these excess holes recombine with divalent (M^{2+}) ions to form trivalent ions (M^{3+}) as given by Eq. (10). The study of Nd_{2−x}Sr_{x}NiO_{4−δ} ceramics confirms this hypothesis. This solid solution is an oxygen-deficient material and the content of oxygen decreases with increasing Sr content [73]. La_{2−x}Sr_{x}CuO_{4−δ} was studied by Kanai et al. [74] as a function of Sr content, oxygen partial pressure, and temperature. This study shows that it is an oxygen deficient material for
\[ x > 0.5 \text{ in } -6 < \log(P(O_2)/\text{atm}) < 0 \] partial pressure range at 900 °C. The variation of oxygen content with oxygen partial pressure is shown in Fig. 5. Similar to Nd\(_{2-x}\)Sr\(_x\)NiO\(_{4-\delta}\), La\(_{2-x}\)Sr\(_x\)CuO\(_{4-\delta}\) also becomes more oxygen deficient with increasing Sr content.

\[
\begin{align*}
\text{AE}^0 &= (\text{AE}^0_{\text{RE}^3+})^\dagger + \frac{1}{2} \text{O}_2(g) + h^* \\
V_0^\dagger + 2h^* &= V_0^{\star\star} \\
(M_{M^2+}^{2+})^X + h^* &= (M_{M^2+}^{3+})^* 
\end{align*}
\]

3 Electrical properties

In the beginning of twenty-first century A\(_2\)BO\(_{4+\delta}\) layered perovskites renewed their interest after the investigation of oxygen transport properties of La\(_2\)NiO\(_{4+\delta}\) at high temperature [75–77]. Electrical properties of A\(_2\)BO\(_{4+\delta}\) layered perovskites at low temperature were extensively studied after the discovery of superconductivity in La\(_2\)CuO\(_{4+\delta}\). But in recent years, more attention has been focused on the study of high-temperature electronic and oxide ion transport properties of A\(_2\)BO\(_{4+\delta}\) layered perovskites. In this context, La\(_2\)NiO\(_{4+\delta}\) is widely studied for their phase stability, oxygen stoichiometry and high-temperature transport properties, and a comparative study with La\(_2\)CuO\(_{4+\delta}\) is established. La\(_2\)NiO\(_{4+\delta}\) shows a semiconductor to metal-like transition at 350 °C and have electrical conductivity 100 \(\Omega^{-1}\) cm\(^{-1}\) at transition temperature which is lower than electrical conductivity of mixed electronic-ionic conducting perovskite oxides [78]. However, oxide ion conductivity of La\(_2\)NiO\(_{4+\delta}\) in the intermediate temperature range is higher than that of mixed electronic–ionic conducting perovskite oxides. Skinner and Kilner [79] have shown that oxide ion conductivity is higher in La\(_2\)NiO\(_{4+\delta}\) than conductivity of La\(_{0.6}\)Sr\(_{0.4}\)Co\(_{0.1}\)Fe\(_{0.8}\)O\(_3\) (LSCF), but, one order lower than the best perovskite oxide ion conductor La\(_{0.3}\)Sr\(_{0.7}\)CoO\(_3\) (LSC) perovskite. Most of the undoped A\(_2\)BO\(_4\) layered perovskites are poor oxide ion conductor due to less oxygen vacancies and interstitial oxide ions [80]. As discussed in Section 2, on partial substitution the oxygen stoichiometry tunes, i.e., material either becomes hypo-stoichiometric or hyper-stoichiometric [39,81]. Oxygen vacancies in the structure provide necessary pathways for oxide ion migration via hopping through the vacant sites [82]. Generally, on acceptor substitution A\(_2\)BO\(_4\) layered perovskites becomes hypo-stoichiometric. But, sometimes even after substituting acceptor ions structure is hyper-stoichiometric. This is because of excess number of interstitial oxide ions than the oxygen vacancies in structure. The interstitial oxide ions also migrate in the structure and contribute to the oxide ion conductivity. Some of acceptor substituted hyper-stoichiometric structures show high mixed ionic and electronic conductivity [79]. The substitution of acceptor cations at A-site also promotes the oxidation of B-cation, according to Eq. (10). Partial oxidation of B-cation enhances the electrical conductivity. Electron bounded with unoxidized B-cation hops to neighboring oxidized B-cation. During this hopping process, the unoxidized B-cation oxidizes and oxidized B-cation reduces and becomes unoxidized. Similarly, hole bounded with oxidized B-cation hops to neighboring unoxidized B-cation, and during this hopping process, the oxidized B-cation reduces and oxidized B-cation oxidizes. Sometimes these hopping processes, also produce a lattice distortion on local level at reducing and oxidizing B-cation sites, due to Jahn–Teller (JT) effect [39,83,84]. Thus, the hopping of electron/hole between the reduced and unreduced B-cation is different from the conduction of electron in metals and conduction of electron/hole in semiconductors. In some materials, local lattice distortion and electron/hole make a bound pair with each other (known as polaron), and conduction of these bound pair is known as polaronic conduction [19,85,86]. Further, when two polarons get closer and

---

Fig. 5 Oxygen content in La\(_{2-x}\)Sr\(_x\)CuO\(_{4-\delta}\) as a function of oxygen partial pressure at 900 °C. Oxygen deficiency is increasing with increasing Sr content. Reproduced with permission from Ref. [74], © Academic Press 1997.
bound with each other to minimize their energy by sharing distortion with each other is known as bound bipolaron. Strongly bounded bipolarons are small in size and have integer spin, and thus, have bosonic properties. Formation of bipolarons without sharing distortion with each other is possible by Bose–Einstein condensation mechanism. This might be a possible mechanism for high-temperature superconductivity. The theme of this article makes this discussion out of the scope of this article.

There are various factors on which oxide ion conductivity in these oxides depends. Some of them are oxygen stoichiometry, temperature, oxygen partial pressure, mobility, etc. The dependence of oxide ion conductivity (σ) on temperature is represented by the Arrhenius relationship, given as follows [87]:

\[ \sigma T = A \exp \left( - \frac{E_a}{kT} \right) \]  
(11)

where \( A \) and \( E_a \) is a pre-exponential factor and activation energy of oxide ion migration, respectively. In Table 1, the values of activation energy and highest value of electrical conductivity (measured experimentally) along with their references are listed. In these studies migration of oxide ions have been emphasized. For example, in La\(_2-x\)Sr\(_x\)CuO\(_4\) the activation energy of oxygen diffusion decreases with increasing concentration of Sr upto \( x \leq 0.7 \), and after that increases for \( 0.7 < x \leq 2.0 \). The increase in the value of activation energy is explained in terms of immobilization of oxygen vacancy due to cluster formation of defects with Cu or ordering of oxygen sublattices [88].

Bochkov et al. [89] studied on La\(_2\)Co\(_2\)Cu\(_{1-x}\)O\(_4\) solid solution and suggested that increasing Co at Cu increases the oxygen content and decreases the electronic conductivity. Oxygen permeation flux also increases with increasing Co concentration for \( 0.02 \leq x \leq 10 \), and after that decreases with further increase in Co concentration, indicates the participation of interstitial oxide ions in oxide ion conduction. The dependence of oxide ion conduction on membrane thickness emphasized the role of surface exchange rates. Oxygen ion diffusion is expected to occur via the interstitial oxygen migration mechanism. But, the oxygen permeability studies in La\(_2\)Ni\(_{0.99}\)Fe\(_{0.02}\)O\(_{4+δ}\) and La\(_2\)Ni\(_{0.88}\)Fe\(_{0.02}\)Cu\(_{0.10}\)O\(_{4+δ}\) by Kharton et al. [90] demonstrated that both interstitial migration and vacancy diffusion mechanisms are contributing in total ionic conductivity.

It is noted that both oxygen hyper-stoichiometric (A\(_2\)BO\(_{4+δ}\)) and hypo-stoichiometric (A\(_2\)BO\(_{4-δ}\)) oxides consist oxygen vacancies, \( V_o^* \) and oxide ions, \( O_i^\prime \) as defects. Consequently, in these materials oxide ion conductivity is mediated by both oxygen vacancies and interstitial oxide ions. Therefore, the diffusion coefficient of oxygen is given as [91]:

\[ D_o = D_V[V_o^*] + D_i[O_i^\prime] \]  
(12)

where \( D_V \) and \( D_i \) are diffusion coefficient of oxygen vacancy and interstitial oxide ion, respectively. Whereas, \( [V_o^*] \) and \( [O_i^\prime] \) represent concentration of oxygen vacancy and interstitial oxide ion, respectively. The oxygen diffusion in these materials is anisotropic in nature. Molecular dynamics (MD) studies of oxide ion conduction in La\(_{1.65}\)Sr\(_{0.3}\)CuO\(_{3.81}\) and La\(_{x}\)Sr\(_{1-x}\)O\(_{3.5}\) showed that the mobility of oxygen species in La\(_{0.5}\)Sr\(_2\)O\(_2\) bilayers and CuO\(_2\) is significantly different and later being more favored for oxide ion conduction [92,93]. Opila et al. [88] have reported the anisotropic nature of oxygen diffusion in \( ab \)-plane (basal plane) and along c-axis in La\(_{2-x}\)Sr\(_x\)CuO\(_4\). Atomic computer simulation of oxide ion conduction mechanisms in tetragonal La\(_2\)NiO\(_4\) was done by Cleave et al. This study, a number of vacancy pathways within the \( ab \)-plane and along the c-axis were considered. Interstitial migration of oxide ion according to interstitial migration mechanism was also considered. This study showed that the activation energy for oxide ion migration via vacancies is lower than the activation energy for migration of oxide ions via interstitial sites. In vacancy mechanism the activation energy for oxide ion migration within the \( ab \)-plane among equatorial sites is 0.55 eV and via apical sites is only 0.35 eV. And, if an oxide ion moves from equatorial site to a vacant site at apical site it has to overcome an energy barrier of 0.77 eV. Whereas, in interstitial migration mechanism oxide ion has to overcome an energy barrier of 0.86 eV for their migration in \( ab \)-plane [82]. Chroneos et al. [94] investigated the conduction pathways of interstitial oxide ions and vacancies in stoichiometric tetragonal La\(_2\)NiO\(_4\) by MD simulation method. This study also shows that the vacancy migration mechanism in \( ab \)-plane is a most favorable mechanism of the oxide ion conduction with the migration activation energy of 0.51 eV in a temperature range of 500 – 800°C. Oxygen stoichiometry does not affect activation energy very significantly. Experimental studies on polycrystalline La\(_2\)NiO\(_4\) by Sayers et al. [95] predicted that the activation energy for oxygen migration is 0.54 eV. This is consistent with the most recent MD studies by Chroneos et al. [94].
4 Dielectric properties

4.1 Giant (colossal) dielectric materials

The discovery of very high dielectric constant ($\varepsilon_r \approx 10^4$ at 300 K) first in CaCu$_3$Ti$_4$O$_{12}$ (CCTO) and later in compounds such as AFe$_{0.5}$Ba$_{0.5}$O$_3$ (A = Ba, Sr, Ca; B = Nb, Ta, Sb), Gd$_{0.6}$Y$_{0.4}$BaCo$_2$O$_{5.5}$, La$_{0.5}$Sr$_{0.5}$Ga$_{0.6-}\text{Ti}_{0.4}$O$_{3-\delta}$ increased the interest of researchers towards investigation of dielectric properties of RP phase oxides including A$_2$BO$_4$ oxides [114–117]. Although, in recent years La$_2$NiO$_4$ has been widely investigated for its mixed ionic and electronic conducting (MIECs) properties useful for SOFCs. But dielectric properties of doped and undoped La$_2$NiO$_4$ oxides have also been investigated due to their very large (giant/colossal) value of the dielectric constant in the wide range of temperature and frequency. Due to high value of dielectric constant these oxides have immense potential for their applications in modern microelectronics and for the development of capacitor-based energy storage devices [118].

Till date the origin of colossal dielectric constant (CDC) is highly debated. Many authors, as Lunkenheimer et al., Sinclair et al., and Cohen et al. assigned the origin of CDC to extrinsic effects, i.e., to Maxwell–Wagner (MW) interfacial polarization at sample–electrode/grain–grain boundary interfaces [114,119–121]. Interfacial polarization or space charge polarization occurs when conducting charge carriers traveling within the grains get pile up at grain–grain boundary interfaces due to insulating nature of grain boundaries. However, some authors claim that intrinsic effect, i.e., small polaronic hopping and hence charge ordering is responsible for the colossal dielectric constant (CDC) [122–124]. There is also another group of authors, who believe that both intrinsic as well as extrinsic effects are responsible for CDC in different range of temperature and frequencies [17,124–126]. Dielectric properties of La$_2$NiO$_4$ oxide have been further modified by substituting different alkaline earth metals (Ca, Sr, and Ba) at La site. Chouket et al. [124] studied LaSrNiO$_4$, and reported dielectric relaxation phenomenon. They attributed dielectric relaxation phenomenon to small polaronic hopping process due to closeness of activation energies of relaxation time and bulk electrical conduction. However, a large difference in activation energies of bulk and grain boundaries electrical conduction confirmed the existence of the MW effect in the ceramic. In another studies on Mn-substituted LaSrNi$_{1-x}$Mn$_x$O$_4$ nickelates, they have reported two dielectric relaxation processes in different temperature ranges [125]. The relaxation process occurring between 200 and 300 K was attributed to MW polarization due to conducting (grain) and insulating (grain boundary) regions. A weaker relaxation process below 150 K was ascribed to charge ordering. Equivalence in activation energies of low temperature and high frequency dielectric relaxation time and bulk electrical conductivity calculated according to small polaronic model confirms the role of adiabatic small polaronic hopping process in dielectric relaxation. Song et al. have studied dielectric properties of La$_{1.75}$Ba$_{0.25}$NiO$_4$ ceramics prepared by spark plasma sintering (SPS) process. In this oxide also two dielectric relaxation processes were observed. The lower temperature relaxation process was credited to the charge ordering and high temperature one to the Maxwell–Wagner polarization. Although the dielectric loss of La$_{1.75}$Ba$_{0.25}$NiO$_4$ is lower than that of some Sr substituted nickelate ceramics, but still it is not suitable for the practical applications due to high dielectric loss [127]. Shi et al. [128] have reported colossal dielectric properties in La$_{2-x}$Ca$_x$NiO$_{4+\delta}$. Among all the samples, at 1 MHz La$_{1.8}$Ca$_{0.2}$NiO$_{4+\delta}$ has the highest value of dielectric constant ($\varepsilon_r = 5103$) whereas La$_{1.7}$Ca$_{0.3}$NiO$_{4+\delta}$ has the lowest loss. Doping of Ca effectively increases the $\varepsilon_r$ and reduces the dielectric loss. Fan et al. [21] tried to explain the dielectric loss from the relationship of two polar-phonon modes and structure. According to their theory, dielectric loss is influenced by (La, Ca)–O(1), (La, Ca)–O(2a), and (La, Ca)–O(2b) bonds and if the normalized values of any cation–oxygen bond approach 1, the dielectric loss attains its minimum value. From La$_3$NiO$_{4+\delta}$ to La$_{2.7}$Ca$_{0.3}$NiO$_{4+\delta}$, normalized bond valences of Ca–O(1), Ca–O(2a), and La–O(2a) approach 1, reducing the dielectric loss greatly. In Ca doped La$_{2.3}$NiO$_4$ La–O(2b) and Ca–O(2b) bonds are heavily compressed; this may be the reason for high dielectric loss. Among all prepared compositions, the minimum elongation of Ca–O(1), Ca–O(2a), and La–O(2a) bonds was observed in La$_{1.7}$Ca$_{0.3}$NiO$_{4+\delta}$ causing lowest dielectric loss for this particular composition. A detailed dielectric investigation on charge ordered La$_{1.75}$Sr$_{0.25}$NiO$_4$ upto 1 GHz frequency have been carried by Krohns et al. [129]. They reported that this sample retains its colossal dielectric constant well into the technically required gigahertz frequency range. The
dielectric properties of $La_{1.5}Sr_{1/6}NiO_4$ are superior to other colossal dielectric materials, including most investigated $GaCu_3Ti_4O_{12}$ (CCTO). Wang et al. [126] studied dielectric properties of the $A_{0.5}Sr_{1/2}Ni_{1-x}AlO_4$ ($A = La, Nd; \ x = 0.2, 0.3$) solid solution. They ascribed giant dielectric response of composition with $x = 0.3$ to the adiabatic small polaronic hopping process, because the value of activation energy of dielectric relaxation and bulk electrical conduction is very close. However, in the composition with $x = 0.2$, both dielectric relaxations were observed, attributed to adiabatic small polaronic hopping process and MW effect. In all the above-mentioned studies on dielectric properties of undoped, doped, and co-doped $La_2NiO_4$ oxides, low temperature ($< 150 \text{ K}$) dielectric relaxation process is attributed to small polaronic hopping mechanism based on the closeness of activation energy values of bulk conductivity and dielectric relaxation. Similarly, high temperature ($> 150 \text{ K}$) dielectric relaxation process is ascribed to Maxwell–Wagner polarization based on the closeness of activation energy values of grain boundaries conduction and high-temperature dielectric relaxation.

The contribution of oxygen vacancy in the giant dielectric constant of $Sm_{1.5}Sr_{0.5}NiO_{4-\delta}$ has been studied by Liu et al. [130]. The giant dielectric response in as-sintered $Sm_{1.5}Sr_{0.5}NiO_{4-\delta}$ ceramic is directly linked to the small polaronic hopping process, while in the annealed sample it is linked to oxygen vacancy concentrations. Annealing in a nitrogen gas atmosphere increases the oxygen vacancies in $Sm_{1.5}Sr_{0.5}NiO_{4-\delta}$, and consequently, the dielectric constant at low temperature is decreased and increased at high temperature. However, the dielectric loss is increased in the overall temperature range. Dielectric studies in oxygen hyper-stoichiometric $Nd_3NiO_{4+\delta}$ ceramic by Liu et al. [19] confirmed the similar mechanism of dielectric relaxation. In hyper-stoichiometric ceramics, excess holes are generated in the structure according to Eq. (2), as mentioned in Section 2. As the content of excess oxygen decreases the concentration of excess holes also decreases and hence the activation energy of dielectric relaxation at low temperature increases. These studies reveal that the dielectric properties of $A_2BO_4$ strongly depends on oxygen stoichiometry.

Jia et al. [16] studied the effect of polaronic concentration on dielectric properties of $Mn$-substituted $Sm_{1.5}Sr_{0.5}NiO_4$ ceramics. They have reported that the dielectric loss decreases with increasing content of $Mn$ ions at Ni sites. At low temperature, on increasing content of $Mn$ ions at Ni sites polaron concentration decreases and its size increases leading to increase in the value of dielectric constant and decrease in the dielectric loss. The change in the microstructure of $La_{1.5}Sr_{0.5}Ni_{1-x}Ga_xO_4$ ceramic as a function of concentration of $Ga^{3+}$ has been carried out. The substitution of $Ga^{3+}$ in $La_{1.5}Sr_{0.5}Ni_{1-x}Ga_xO_4$($x = 0, 0.1, 0.3$) has remarkably influenced the microstructure and increased the value of total resistance [131]. Due to increase in the value of resistance of $La_{1.5}Sr_{0.5}Ni_{1-x}Ga_xO_4$, its dielectric constant has increased and loss has decreased significantly.

The studies of $La_{1.5}Sr_{0.5}Ni_{1-x}Ga_xO_4$ also highlighted the effect of sample electrode interface polarization on the dielectric properties. The effect of DC bias on non-ohmic sample–electrode contact and grain boundary responses were studied in $Mg$ substituted $La_{1.5}Sr_{0.5}Ni_{1-x}Mg_xO_4$ ceramics by Meeporn et al. [43]. For undoped $La_{1.7}Sr_{0.3}NiO_4$, capacitance “C” decreases with increasing DC bias voltage and follows the Mott–Schottky law which confirmed the effect of sample electrode interface on the dielectric properties. However, for $Mg$ substituted $La_{1.7}Sr_{0.3}Ni_{1-x}Mg_xO_4$ the decrease in “C” values with increasing DC bias voltage does not follow the Mott–Schottky law, indicating negligible contribution of sample electrode interface polarization. This decrease in capacitance “C” is attributed to significant increase in the resistance of grain boundaries on $Mg$ substitution.

The dielectric properties of manganese $A_2BO_4$ oxides were also studied. In $Sr_2Mn_{0.5}Ti_{0.5}O_4$ only one high temperature (above $453 \text{ K}$) dielectric relaxation is present, which is attributed to the MW polarization. The low-temperature dielectric relaxation generally originated from adiabatic small polaronic hopping process is absent in $Sr_2Mn_{0.5}Ti_{0.5}O_4$. It was observed that in $Sr_2Mn_{0.5}Ti_{0.5}O_4$ both titanium and manganese ions are in “$4+$” oxidation state that is why the concentration of oxygen vacancies and polarons in the unit cell are almost zero [132]. It is important to notice here that the dielectric constant of $Sr_2Mn_{0.5}Ti_{0.5}O_4$ is not as high as of doped and co-doped $La_2NiO_4$. This is because degree of polyhedral distortions in $Sr_2Mn_{0.5}Ti_{0.5}O_4$ is much less as compared with doped/co-doped $La_2NiO_4$. Further, it is observed that when all the “B” cation are in the same oxidation state, the distortion in the polyhedra is minimum and charge ordering is absent. This results in lowering dielectric
constant values. The effect of charge ordering has been studied in Pr doped Ca$_{2-x}$Pr$_x$MnO$_4$. Undoped Ca$_2$MnO$_4$ does not show charge-order, and the measured intrinsic dielectric constant is only 14. The Pr doping induces charge-order in the system causing noteworthy increase in the value of dielectric constant, $\varepsilon_r$ ($\sim$220) for Ca$_{1.75}$Pr$_{0.25}$MnO$_4$ [133].

4.2 Microwave dielectric materials

There is also another group of A$_2$BO$_4$ layered perovskites, which have been studied for low-loss microwave dielectric applications. The general formula for these ceramics is MLnBO$_4$ (M = Ca, Sr, Ba; Ln = Y, La, Nd, Sm; B = Al, Ga, (M$_{0.5}$Ti$_{0.5}$), (Zn$_{0.5}$Ti$_{0.5}$)) [134]. Among these oxides, CaLaAlO$_4$ and SrYAlO$_4$ are not stable. This is because, for these two oxides the difference between tolerance factor “t” of layered perovskite and its perovskite unit (i.e., LaAlO$_3$ in CaLaAlO$_4$, and YAlO$_3$ in SrYAlO$_4$) is greater than 4.3%. Stability of CaLaAlO$_4$ has been improved by substituting Sr at Ca, in Ca$_{1-x}$Sr$_x$LaAlO$_4$ stability is reported for composition with $x > 0.9$ [135]. In the crystal structure of MLnBO$_4$, large distortion in (M,Ln)O$_9$ polyhedra and BO$_6$ octahedra are observed in the crystal structure. These distortions originate due to a large difference in the ionic radii of M and Ln cations, also leading to an interlayer size mismatch. Between these interlayers static electric polarization may also be present due to “2+” oxidation state of cation M and “3+” oxidation state of cation Ln (discussed in detail in Section 2) [21,134,136,137]. There are several studies in which improvement in $Q \times f$ (where $Q$ = $\frac{\varepsilon_r}{\varepsilon''}$ and $f = \text{frequency}$) has been achieved by reducing interlayer static electric polarization [21,136,138,139]. The solid solution of SrLaAlO$_4$, SrNdAlO$_4$, SrMgAlO$_4$, CaNdAlO$_4$ with Sr$_2$TiO$_4$/Ca$_2$TiO$_4$ (i.e., Sr$_{1+x}$La$_{1-x}$Al$_{1-x}$Ti$_x$O$_4$, Sr$_{1+x}$Nd$_{1-x}$Al$_{1-x}$Ti$_x$O$_4$, Sr$_{1+x}$Sm$_{1-x}$Al$_{1-x}$Ti$_x$O$_4$, Ca$_{1+x}$Nd$_{1-x}$Al$_{1-x}$Ti$_x$O$_4$, respectively) have been extensively studied by several research groups and improvement in $Q \times f$ were reported by co-substitution of Sr(Ca)/Ti cations. Co-substitution reduces the interlayer polarization and results in improving $Q \times f$ value. Co-substitution also decreases the tolerance factor “t” and subsequently interlayer stress increases. Sometimes a new phase MTiO$_3$ also appears. These two effects: decrement in tolerance factor “t” and appearance of the new phase, bring a negative impact on $Q \times f$ improvement [24,136–140]. Although MLnAlO$_4$ ceramics have high $Q \times f$ values (~90000 GHz) and further improvement in $Q \times f$ values is also observed in solid solution with Sr$_2$TiO$_4$/Ca$_2$TiO$_4$. But, relatively low dielectric constant ($\varepsilon_r < 20$) and higher temperature coefficient of the resonant frequency $\tau_f (\sim -30 \text{ ppm/}^\circ\text{C})$ limit their practical applications. The improvement in $\varepsilon_r$ was expected by replacing Al$^{3+}$ with suitable trivalent cation having ionic polarizability higher than 0.78 Å$^3$ of Al$^{3+}$ cation. However, only Ga$^{3+}$ is found to be a suitable cation with ionic polarizability of 1.50 Å$^3$, by considering the stability of A$_2$BO$_4$ layered perovskite structure and electrically insulator (an essential requirement for microwave dielectric ceramics). SrLaGaO$_4$ ceramic has higher dielectric constant ($\varepsilon_r = 20.3$) than SrLaAlO$_4$ ($\varepsilon_r = 17.6$) but lower $Q \times f$ value (16200 GHz) than 95200 GHz of SrLaAlO$_4$. The $\tau_f$ of SrLaGaO$_4$ is -33.5 ppm/$^\circ$C nearly the same as -32 ppm/$^\circ$C of SrLaAlO$_4$. The $Q \times f$ value of single crystal SrLaGaO$_4$ is significantly higher 170000 GHz in comparison to $Q \times f$ value of its ceramic 16200 GHz. It was expected to replace Al$^{3+}$ cation by alogivalent cations such as (M$_{0.5}$Ti$_{0.5}$) or (Zn$_{0.5}$Ti$_{0.5}$)$^{3+}$, which have effectively higher ionic polarizability of 2.135 and 2.515 Å$^3$, respectively. Significant improvement in the dielectric constant was observed in SrLa(Mg$_{0.5}$Ti$_{0.5}$)O$_4$ ($\varepsilon_r = 25.5$) and SrLa(Zn$_{0.5}$Ti$_{0.5}$)O$_4$ ($\varepsilon_r = 29.4$) ceramics compared to the analogs SrLaAlO$_4$ and SrLaGaO$_4$, which is attributed to the increased normalized bond lengths of (Sr/La) – O$_{ap}$ and (Sr/La) – O$_{bs}$ and the higher polarizability of (R$_{0.5}$Ti$_{0.5}$)$^{3+}$ than Al$^{3+}$ and Ga$^{3+}$. In addition, $\tau_f$ also becomes positive (29 ppm/$^\circ$C for SrLa(Mg$_{0.5}$Ti$_{0.5}$)O$_4$ and 38 ppm/$^\circ$C for SrLa(Zn$_{0.5}$Ti$_{0.5}$)O$_4$) with increase in dielectric constant [134]. Although, for these ceramics, the dielectric constant is high but higher $\tau_f$ value limits its practical application in commercial microwave devices, such as dielectric resonators and filters [141].

Recently, Sr$_2$TiO$_4$ and Sr$_2$CeO$_4$ were also studied for low loss microwave dielectric applications by Liu et al. and Dai et al., respectively. The dielectric properties of these two ceramics are $\varepsilon_r = 42$, $Q \times f = 145200 \text{ GHz}$, $\tau_f = 130 \text{ ppm}/^\circ\text{C}$ for Sr$_2$TiO$_4$, and $\varepsilon_r = 14.8$, $Q \times f = 172600 \text{ GHz}$, $\tau_f = -62 \text{ ppm}/^\circ\text{C}$ for Sr$_2$CeO$_4$ [20,142]. High values of $\varepsilon_r$, $Q \times f$, and $\tau_f$ of Sr$_2$TiO$_4$, make it suitable for wireless passive temperature sensors application [141]. Properties
of the solid solution of these two oxides have been also studied by Dai et al. For Sr$_2$Ce$_{0.6}$Ti$_{0.35}$O$_4$ ($\varepsilon_r = 20.7$, $Q \times f = 115550$ GHz ) very small value of $\tau_f (= -1.8$ ppm/°C) was reported [20]. The microwave dielectric properties of some recently studied A$_2$BO$_4$ oxides with respective references are listed in Table 2. A systematic improvement in low-loss microwave dielectric properties is obvious from Table 2. 

Till date, no report is found in the literature on experimental measurements to claim ferroelectric characteristics in A$_2$BO$_4$ layered perovskites. Although theoretical group of researchers have suggested certain compositional and structural modifications to induce highly improper ferroelectricity (HIF) in RP oxides. On the basis of group theory, they have shown that the condensation of two distortion modes; (i) unique symmetric octahedral distortions (Fig. 6) and (ii) a combination of a single octahedral distortion with “compositional” A- or B-cation ordering (Fig. 7), can transform the centrosymmetric structure into a non-centrosymmetric structure (necessary requirement for a crystal to exhibit ferroelectricity) [143, 144]. The general rule that a unique symmetric octahedral distortion for ferroelectric nature, failed to induce HIF in A$_2$BO$_4$ layered perovskite as there are an even number of “A” cations per unit cell. However, symmetrical ordering of “A” cations in (ABO$_3$)A'O layered perovskite can induce ferroelectricity [145]. The relative magnetoelectric properties corresponding to HIF is also explored in ABO$_3$ and A$_3$B$_2$O$_7$. However, till date it is not explored yet in A$_2$BO$_4$ layered perovskites [144].

| Table 2  Dielectric properties of some recently studied ceramics for low-loss microwave applications |
|-----------------------------------------------|
| Ceramic | $\varepsilon_r$ | $Q \times f$ (GHz) | $\tau_f$ (ppm/°C) | Reference |
| CaNdAlO$_4$ | 18.2 | 17980 | -79 | [146] |
| CaSmAlO$_4$ | 18.2 | 51060 | -3 | [146] |
| CaYAlO$_4$ | 18.9 | 39960 | 6 | [146] |
| SrSmAlO$_4$ | 18.3 | 70000 | -1 | [21] |
| SrNdAlO$_4$ | 18.4 | 55300 | -15 | [21] |
| SrLaAlO$_4$ | 17.6 | 65500 | -32 | [21] |
| SrLaGaO$_4$ | 20.3 | 16219 | -33.5 | [147] |
| SrNdGaO$_4$ | 21.4 | 16650 | 7.1 | [147] |
| (Ca$_{0.05}$Sr$_{0.95}$)LaAlO$_4$ | 16.7 | 28171 | -52.4 | [135] |
| SrLa(Mg$_{0.3}$Ti$_{0.7}$)O$_4$ | 25.5 | 72000 | 29 | [134] |
| SrLa(Zn$_{0.5}$Ti$_{0.5}$)O$_4$ | 29.4 | 34000 | 38 | [134] |
| SrLa[Al$_{0.25}$Mg$_{0.75}$]O$_4$ | 22.2 | 89,100 | -0.1 | [23] |
| SrLa[Al$_{0.25}$Zn$_{0.75}$]O$_4$ | 23.5 | 102000 | -3.4 | [22] |
| Ca$_{1.12}$Nd$_{0.88}$Al$_{0.88}$Ti$_{1.12}$O$_4$ | 19.5 | 93400 | -2 | [139] |
| Sr$_{1.8}$Nd$_{0.2}$Al$_{0.8}$Ti$_{1.8}$O$_4$ | 23.6 | 86300 | 10.9 | [138] |
| Sr$_{1.4}$La$_{0.6}$Al$_{0.6}$Ti$_{1.4}$O$_4$ | 18.5 | 95000 | -8.9 | [24] |
| Sr$_2$TiO$_4$ | 42 | 145200 | 130 | [142] |
| Sr$_2$CeO$_4$ | 14.8 | 172600 | -62 | [20] |
| Sr$_2$Ce$_{0.6}$Ti$_{0.35}$O$_4$ | 20.7 | 115550 | -1.8 | [20] |

Fig. 6 (a) The A$_2$am ferroelectric ground state structure of Ca$_3$Ti$_2$O$_7$ and Ca$_3$Mn$_2$O$_7$. Large (blue) spheres correspond to Ca ions. (b) Schematic of the atomic displacements corresponding to the $X_3^0$ rotation mode. The dashed square denotes the unit cell of the $I4/mmm$ reference structure. (c) Schematic of the $X_3^1$ rotation mode. All axes refer to the coordinate system of the $I4/mmm$ reference structure. Reproduced with permission from Ref. [144], © Elsevier Inc. 2012.

Fig. 7 (a) The $n = 2$ Ruddlesden–Popper structure (without octahedral rotations) with a single A-cation. (b) $A/A'$ ordered $n = 2$ phase. (c) $A/A'$ ordered $n = 1$ phase. Reproduced with permission from Ref. [145], © WILEY–VCH Verlag GmbH & Co. KGaA, Weinheim 2013.
5 Optical properties

In recent years commercialization of white light-emitting diodes (WLEDs), flat-panel displays, plasma display panels (PDPs), field emission displays (FEDs), and thin-film electroluminescent devices (TFELs) could be possible due to the development of new phosphor materials with improved optical properties [29,148–150]. For the development of new phosphor materials, the efforts to discover new host materials and high-performance activators are needed [29]. Traditionally sulfide and halide phosphors were extensively studied but in recent years oxide phosphors have received attention of the researchers due to their stability [29,150,151]. Inorthostannates exhibited broad bands just below the fundamental absorption edges, implying that luminescence centers do not consist of the component elements in the host materials. It was suggested that the Ti containing octahedra are possible luminescence centers in these materials, as it was proposed for earlier investigated Ti-doped Mg$_2$SnO$_4$ and Y$_2$Sn$_2$O$_7$ [150,156].

Another phosphor which has drawn wide attention of researchers in recent years for its optical properties is Sr$_2$CeO$_4$, firstly reported by Danielson and his co-workers in 1998 [157]. It is intrinsically luminescent material and has chemically and thermal stability. Sr$_2$CeO$_4$ also possesses some desirable qualities of phosphor materials such as (i) ligands-to-metal charge transfer (CT) transition of Ce$^{4+}$ at ~340 nm, (ii) efficient energy transfer that can occur from the Ce$^{4+}$-O$^{2-}$ CT state to the trivalent rare earth in Sr$_2$CeO$_4$: RE$^{3+}$, (iii) high efficiency for absorbing UV radiation, and (iv) the large band gap [40]. Almost all cerium-based phosphors are known due to their localized Ce$^{3+}$ excited state with luminescence arising from 4f to 5d transitions. However, in Sr$_2$CeO$_4$ the cerium ion is in “4+” oxidation state and the 4f shell is empty, the only possible transition is metal to ligand charge transfer transition originating due to the interaction of central cerium ion with neighboring oxygen ligands in CeO$_6$ octahedra [158]. Figure 8(a) shows the photoluminescence excitation (PLE) spectra of Sr$_2$CeO$_4$ phosphor. The excitation spectra consist of a broad spectrum in UV-region between 200 and 400 nm with a peak at 299 nm and a shoulder at 349 nm. The broadness of the excitation spectrum indicates the possibilities of using Sr$_2$CeO$_4$ phosphor in UV LED chips. Two peaks in the excitation spectra of Sr$_2$CeO$_4$ are associated with two different Ce$^{4+}$–O$^{2-}$ bond-lengths. The excitation from the ground state to the excited states is attributed to the $t_{1g}$–f (terminal) and $t_{1u}$–f (equatorial) charge transfer states of Ce$^{4+}$. The band $t_{1u}$–f is spin forbidden; hence the excitation intensity associated with it is lowered than the band associated with $t_{1g}$–f state [158]. Therefore, the higher energy band (299 nm) originates from charge transfer from apical oxygen, O$_{ap}$ to Ce$^{4+}$ and lower energy band (349 nm) originates from the charge transfer from equatorial oxygen, O$_{eq}$ to Ce$^{4+}$. Figure 8(b) shows photo-luminescence
emission spectra of $\text{Sr}_2\text{CeO}_4$ under the excitation wavelength at 299 nm. The emission spectrum shows board band emission (FWHM $\approx 100$ nm) in blue region with a maximum at 478 nm via radiative transition from the excited charge transfer state to the ground state [158].

The improvement in the emission intensity of $\text{Sr}_2\text{CeO}_4$ has been achieved by increasing sintering temperature as plotted in the inset of Fig. 8(b). It is mentioned that with increasing sintering temperature crystallinity improves, and hence emission intensity increases up to 1100 °C. Above 1100 °C no further improvement in the crystallinity could be achieved due to high agglomeration at a higher temperature, and hence emission intensity starts decreasing. The Commission International De l-Eclairage (CIE) chromaticity coordinates of the $\text{Sr}_2\text{CeO}_4$ phosphors sintering at different temperatures lie in the blue region.

In recent years rare earth (RE$^{3+}$) ions such as Eu$^{3+}$, Ho$^{3+}$, Er$^{3+}$, Tm$^{3+}$, Dy$^{3+}$, Yb$^{3+}$ etc. doped $\text{Sr}_2\text{CeO}_4$ phosphors have attracted lots of attention from the researchers [148]. $\text{Sr}_2\text{CeO}_4$:Eu$^{3+}$ (Dy$^{3+}$, Tm$^{3+}$) phosphors have exhibited strong red (yellow, blue) emission which makes them potential for display applications such as UV-LEDs [159]. Rare earth ions (Ho$^{3+}$, Er$^{3+}$, Tm$^{3+}$, and Yb$^{3+}$) doped $\text{Sr}_2\text{CeO}_4$ phosphors have been studied for their application as lasing materials or spectral conversion materials [159]. Dy$^{3+}$ doped phosphors have shown two intense emission at 484 nm (blue) and 575 nm (yellow) useful for white light emission based optical devices. However, these emission lines (of Dy$^{3+}$) are very sensitive to the chemical environment surrounding the luminophore. The intensity ratios of these two emission bands are host dependent. Therefore, emission of white light can be realized by modulating the intensity of emission, i.e., by compositional modification of the host [40]. In Eu$^{3+}$ and Dy$^{3+}$ co-doped $\text{Sr}_2\text{CeO}_4$, the photoluminescence mechanism of energy transfer between Eu$^{3+}$ and Dy$^{3+}$ for color tunable phosphor applications has been studied by Li et al. [157]. They also studied the energy transfer between Ce$^{4+}$–O$^{2-}$ charge-transfer state (CTS) and Eu$^{3+}$ states by theoretical calculation of the band structure. They found that the efficiency of co-doped phosphors is lowered as compared to single ion doped phosphors due to the reabsorption mechanism between the Eu$^{3+}$ and Dy$^{3+}$ co-dopants. $\text{Sr}_2\text{CeO}_4$:Nd$^{3+}$ nanophosphors exhibit a strong near-infrared (NIR) emission and can be used as high-efficiency laser material based on their peculiar optical properties [157].

Recent research reports have emphasized the role of co-doping of alkali metal ions (Li$^+$, Na$^+$, K$^+$) along with rare-earth ions (RE$^{3+}$) in some of $\text{A}_2\text{BO}_4$ oxides. This approach has been employed in several phosphors, like $\text{CaMO}_4$:Dy$^{3+}$ ($\text{M=WO}_4$, Y$_2\text{Zr}_2\text{O}_7$: Dy$^{3+}$, Y$\text{BO}_3$: Eu$^{3+}$, YPO$_4$: Eu$^{3+}$, etc. [160–163]. The co-doping of monovalent alkali metal ions reduces the charge unbalancing problem originated by doping of trivalent rare-earth ions at divalent alkaline earth metal ions ($\text{Ca}^{2+}$, Sr$^{2+}$, Br$^{2+}$). Co-doping of alkali metal ions (Li$^+$, Na$^+$, K$^+$) along with rare-earth ions (RE$^{3+}$) approach has emerged as an efficient way to enhance the photoluminescence (PL) intensity and emission characteristics of $\text{A}_2\text{BO}_4$ oxides based phosphors [40].
6 Conclusions and perspective

Only those $A_2BO_4$ compounds which crystallize in T-type structure form layered perovskite structure or $K_2NiF_4$ structure. All the investigated $A_2BO_4$ layered perovskites have either orthorhombic or tetragonal crystal structure. At high temperature due to the expansion in the unit cell volume of $RE_2MO_4$ oxides, orthorhombic to tetragonal structural transformation is observed. The structural transformation in these oxides can be induced by varying oxygen stoichiometry and selecting suitable dopants. Both hypo-stoichiometric (less oxygen, $A_2BO_4{-\delta}$) and hyper-stoichiometric (more oxygen, $A_2BO_{4+\delta}$) can be synthesized by changing processing conditions or dopants.

Majority of $A_2BO_4$ oxides are insulator in nature. However, hypo-/hyper-stoichiometric $RE_2MO_4$ and AE doped $RE_2MO_4$ have high value of conductivity due to mixed ionic–electronic conducting properties. Due to a wide range of oxygen stoichiometry and large interstitial space for oxide ion migration, the mixed ion conductivity is higher in $LaNiO_4$ making it useful for cathode in IT-SOFCs. Among all the investigated $RE_2MO_4$, Pr$_{1.3}$Sr$_{0.7}$Ni$_{0.7}$Cu$_{0.3}$O$_4$ shows the highest ($260 \text{ S} \cdot \text{cm}^{-1}$ at 700 °C) mixed ionic–electronic conductivity (MIEC). The stability of $Ln_2NiO_4$ with commonly used electrolytes in SOFCs has been performed but more studies are needed for practical application.

Recently, some of $A_2BO_4$ oxides having giant/colossal dielectric constant were explored. Doped and undoped $LaNiO_4$ have shown very large (“giant”) magnitude of the dielectric constant and thus display immense potential for their applications in modern microelectronics and for the development of capacitor-based energy storage devices. The dielectric properties of $La_{15/8}Sr_{1/8}NiO_4$ are superior to popular high dielectric constant material $CaCu_3Ti_4O_{12}$ (CCTO). Until now no ferroelectric characteristics have been observed experimentally in any $A_2BO_4$ layered perovskites. Theoretical researchers have suggested certain compositional and structural modifications to induce highly improper ferroelectricity (HIF) in RP oxides. But the only compositional ordering of “A” cations found suitable in $(ABO_2)A’O$ layered perovskites.

There is also another group of $A_2BO_4$ layered perovskites which have been studied for low-loss microwave dielectric applications. Very high values of $\varepsilon_r$, $Q \times f$, and $T_f$ of $Sr_2TiO_4$, make it very suitable for wireless passive temperature sensor application.

The $A_2BO_4$ layered perovskites have also been studied for phosphor applications. $M_2SnO_4$ ($M = Ca, Sr, Ba$) and $Sr_2CeO_4$ are extensively studied as a host matrix because of their wide optical band gap ($3–5 \text{ eV}$), stable crystal structure, physical and chemical stability, non-toxicity, and lack of radioactive elements. Among all the investigated $A_2BO_4$ oxides, $Sr_2CeO_4$ has shown self-luminescence in blue region.

In the last two decades researchers have mainly focused attention on $La_2NiO_4$, and studies on the properties of other oxides such as $A_2BO_4$ ($A = Ca, Sr, Ba$ and $B = Sn, Ti, Mn$) are very limited. Dielectric properties of $Sr_2SnO_4$ and $Sr_2MnO_4$ investigated by our research group are promising and need more investigations for further improvement. The understanding about the origin of high dielectric constant in $La_2NiO_4$ is not clear and needs more experimental and theoretical research on this system. Although theoretical researchers have suggested certain compositional and structural modifications to induce HIF in RP oxides, experimentally these modifications are not employed yet.

Acknowledgements

Mr. Gurudeo Nirala and Mr. Dharmendra Yadav are thankful to the Ministry of Human Resource and Development (MHRD), Government of India for the financial support in terms of Senior Research Fellowship (SRF).

References

[1] Ruddlesden SN, Popper P. The compound Sr$_3$Ti$_2$O$_7$ and its structure. Acta Cryst 1958, 11: 54–55.
[2] Hirayama T, Nakagawa M, Sumiyama A, et al. Superconducting properties in $La_xCuO_4$ with excess oxygen. Phys Rev B 1998, 58: 5856–5861.
[3] Tholence JL. Superconductivity of $La_xCuO_4$ and $YBa_2Cu_3O_7$. Phys B+C 1987, 148: 353–356.
[4] Suter A, Logvenov G, Boris AV, et al. Superconductivity drivesagnetism in $\delta$-doped $La_xCuO_4$. Phys Rev B 2018, 97: 134522.
[5] Bates FE, Eldridge JE. Normal modes of tetragonal $La_xNiO_4$ and $La_xCuO_4$ isomorphs of the hight $T_c$ superconductor $La_xSr_xCuO_4$. Solid State Commun 1989, 72: 187–190.
[6] Burns G, Dacol FH, Kliche G, et al. Raman and infrared studies of $Sr_2TiO_4$: A material isomorphic to $(La,Sr)_2CuO_4$ superconductors. Phys Rev B 1988, 37: 3381–3388.
[7] Moritomo Y, Asamitsu A, Kuwahara H, et al. Giant
magnetoresistance of manganese oxides with a layered perovskite structure. *Nature* 1996, **380**: 141–144.

[8] Wang XL, Takayama-Muromachi E, Dou SX, et al. Band structures, magnetic properties, and enhanced magnetoresistance in the high pressure phase of Gd and Y doped two-dimensional perovskite Sr2CoO4 compounds. *Appl Phys Lett* 2007, **91**: 062501.

[9] Gebhardt JR, Roy S, Ali N. Colossal magnetoresistance in Ce doped manganese oxides. *J Appl Phys* 1999, **85**: 5390–5392.

[10] Goodrich R, Hall D, Palm E, et al. Magnetoresistance below 1 K and temperature cycling of ruthenium oxide-bismuth ruthenate cryogenic thermostats. *Cryogenics* 1998, **38**: 221–225.

[11] Zhu M, Peng J, Zou T, et al. Colossal magnetoresistance in a Mott insulator via magnetic field-driven insulator–metal transition. *Phys Rev Lett* 2016, **116**: 216401.

[12] Pikalova E, Sadykov VA, Filonova EA, et al. Structure, oxygen transport properties and electrode performance of Ca-substituted Nd2NiO4. *Solid State Ionics* 2019, **335**: 53–60.

[13] Chaudhari VN, Khandale AP, Bhoga SS. Sr-doped Ca-substituted Nd2NiO4. *Solid State Ionics* 2016, **268**: 140–149.

[14] Kovalevsky AV, Kharton VV, Yaremchenko AA, et al. Stability and oxygen transport properties of Pr2NiO4+δ ceramics. *J Eur Ceram Soc* 2007, **27**: 4269–4272.

[15] Hyodo J, Tominaga K, Ju YW, et al. Electrical conductivity and oxygen diffusivity in Cu- and Ga-doped Pr2NiO4. *Solid State Ionics* 2014, **256**: 5–10.

[16] Jia BW, Liu XQ, Chen XM. Structure, magnetic and dielectric properties in Mn-substituted Sm1.5Sr0.5NiO4 ceramics. *J Appl Phys* 2011, **110**: 064110.

[17] Yang WZ, Song CL, Liu XQ, et al. Dielectric relaxation and polaron hopping in the single-layered perovskite La2−xSrxCuO4 ceramics. *J Mater Sci* 2011, **46**: 6339–6343.

[18] Liu XQ, Jia BW, Yang WZ, et al. Dielectric relaxation and polaronic hopping in Al-substituted Sm1.5Sr0.5NiO4 ceramics. *J Phys D: Appl Phys* 2010, **43**: 495402.

[19] Liu G, Chen TT, Wang J, et al. Effect of excess oxygen on crystal structures and dielectric responses of Nd2NiO4+δ ceramics. *J Alloys Compd* 2013, **579**: 502–506.

[20] Dai QL, Zuo RZ. A novel ultralow-loss Sr2CeO4 microwave ceramic and its property modification. *J Eur Ceram Soc* 2019, **39**: 1132–1136.

[21] Fan XC, Chen XM, Liu XQ. Structural dependence of microwave dielectric properties of SrRAlO4 (R = Sm, Nd, La) ceramics: Crystal structure refinement and infrared reflectivity study. *Chem Mater* 2008, **20**: 4092–4098.

[22] Liu B, Li L, Liu XQ, et al. Structural evolution of SrLaAl1−x(Zn0.5Tb0.5)yO3 ceramics and effects on their microwave dielectric properties. *J Mater Chem C* 2016, **4**: 4684–4691.

[23] Chen GY, Ren GR, Li L, et al. Structure and microwave dielectric properties of SrLa[Al1−x(Mg0.5Ti0.5)x]O3 (x = 0.2–0.8) ceramics. *Ceram Int* 2018, **44**: 1984–1990.

[24] Mao MM, Chen XM, Liu XQ. Structure and microwave dielectric properties of solid solution in SrLaAlO4–Sr2TiO4 system. *J Am Ceram Soc* 2011, **94**: 3948–3952.

[25] Chen YC, Chang YH, Tsai BS. Influence of processing conditions on synthesis and photoluminescence of Eu3+-activated strontium stannate phosphors. *J Alloys Compd* 2005, **398**: 256–260.

[26] Sahu M, Gupta SK, Jain D, et al. Solid state speciation of uranium and its local structure in Sr2CeO4 using photoluminescence spectroscopy. *Spectrochim Acta A Mol Biomol Spectrosc* 2018, **195**: 113–119.

[27] Li J, Li X, Hu SL, et al. Photoluminescence mechanisms of color-tunable Sr2CeO4Eu3+–Dy3+ phosphors based on experimental and first-principles investigation. *Opt Mater* 2013, **35**: 2309–2313.

[28] Gao H, Wang YH. Photoluminescence of Eu3+ activated Ba2SnO4 under ultraviolet–vacuum ultraviolet excitation. *J Mater Res* 2006, **21**: 1857–1861.

[29] Stanulis A, Katelnikovas A, Enseling D, et al. Luminescence properties of Sm3+–doped alkaline earth ortho-stannates. *Opt Mater* 2014, **36**: 1146–1152.

[30] Labbasetwar N, Saravanan G, Kumar Megaranjan S, et al. Perovskite-type catalytic materials for environmental applications. *Sci Technol Adv Mater* 2015, **16**: 036002.

[31] Schön A, Dujardin C, Daquin JP, et al. Enhancing catalytic activity of perovskite-based catalysts in three-way catalysis by surface composition optimisation. *Catal Today* 2015, **258**: 543–548.

[32] Polo-Garzon F, Wu ZL. Acid-base catalysis over perovskites: A review. *J Mater Chem A* 2018, **6**: 2877–2894.

[33] Wu TJ, Gao P. Development of perovskite-type materials for thermoelectric application. *Materials* 2018, **11**: 999.

[34] Lee KH, Kim SW, Ohta H, et al. Thermoelectric properties of layered perovskite-type (Sr1−Ca)x(Ti1−Nb)yO2. *J Appl Phys* 2007, **101**: 083707.

[35] Lee KH, Ohta H, Koumoto K, Thermoelectric properties of layered perovskite-type Nb-doped SrO(SrTiO3)n−1 c2ruddlesden-popper phases, In: Proceedings of the 2006 25th International Conference on Thermoelectrics, 2006: 81–84.

[36] Li Q, Zhao H, Luo LH, et al. Electrode properties of Sr doped La2CuO4 as new cathode material for intermediate-temperature SOFCs. *Electrochem Commun* 2007, **9**: 1508–1512.

[37] Ghorbani-Moghadam T, Kompaa A, Bagheri-Mohagheghi MM, et al. High temperature electrical conductivity and electrochemical investigation of La1−xSr2xCoO4 nanoparticles for IT–SOFC cathode. *Ceram Int* 2018, **44**: 21238–21248.

[38] Garali M, Kahlouqi M, Mohammed B, et al. Synthesis, characterization and electrochemical properties of La2−εEu3+NiO4ε Ruddlesden-Popper-type layered nickelates as cathode materials for SOFC applications. *Int J Hydrogen Energ* 2019, **44**: 11020–11032.

[39] Sandoval MV, Pirovano C, Capoen E, et al. In-depth study of the Ruddlesden–Popper La5Sr3MnO12 family as possible electrode materials for symmetrical SOFC. *Int
J Adv Ceram 2020, 9(2): 129–148

J Hydrogen Energ 2017, 42: 21930–21943.

[40] Monika DL, Nagabhushana H, Krishna RH, et al. Synthesis and photoluminescence properties of a novel Sr2CeO4:Dy3+ phosphor with enhanced brightness by Li+ co-doping. RSC Adv 2014, 4: 38655–38662.

[41] Srinivas M, Appa Rao B, Vithal M, et al. Luminescence properties of Tb3+ doped Sr2SnO3 green phosphor in UV/VUV regions. Luminescence 2013, 28: 597–601.

[42] Xu XH, Wang YH, Gong Y, et al. Effect of oxygen vacancies on the red phosphorescence of Sr2SnO3;Sm3+ phosphor. Opt Express 2010, 18: 16989.

[43] Meeporn K, Chanlek N, Thongpai P. Effects of DC bias on non-ohmic sample-electrode contact and grain boundary responses in giant-permittivity La1.7Sr0.3Ni1-xMg0.5O4 ceramics. RSC Adv 2016, 6: 91377–91385.

[44] Jia BW, Yang WZ, Liu XQ, et al. Giant dielectric response in (Sm1−Nd1)3Sr2NiO4 ceramics: The intrinsic and extrinsic effects. J Appl Phys 2012, 112: 024104.

[45] Liu XQ, Wu YJ, Chen XM, et al. Temperature-stable giant dielectric response in orthorhombic samarium strontium nickelate ceramics. J Appl Phys 2009, 105: 054104.

[46] Chen YN, Sun Y, Peng JJ, et al. 2D Ruddlesden-popper perovskites for optoelectronics. Adv Mater 2018, 30: 1703487.

[47] Spanopoulos I, Hadar I, Ke WJ, et al. Uniaxial expansion of the 2D Ruddlesden-Popper perovskite family for improved environmental stability. J Am Chem Soc 2019, 141: 5518–5534.

[48] Ganguly P, Rao CNR. Crystal chemistry and magnetic properties of layered metal oxides possessing the K2NiF4 or related structures. J Solid State Chem 1984, 53: 193–216.

[49] Rao CNR, Ganguly P, Singh KK, et al. A comparative study of the magnetic and electrical properties of perovskite oxides and the corresponding two-dimensional oxides of K2NiF4 structure. J Solid State Chem 1988, 72: 14–23.

[50] Rao CNR. Trends in Chemistry of Materials. World Scientific, 2008.

[51] Bednorz JG, Müller KA. Possible high Tc superconductivity in the Ba-La-Cu-O system. Z. Physik B - Condensed Matter 1986, 64: 189–193.

[52] Chrones A, Vokv RV, Goulatis IL, et al. Oxygen transport in perovskite and related oxides: A brief review. J Alloys Compd 2010, 494: 190–195.

[53] Lee D, Lee H. Controlling oxygen mobility in Ruddlesden-Popper oxides. Materials 2017, 10: 368.

[54] Chen BH. Introduction of a tolerance factor for the Nd2CuO4(T)-type structure. J Solid State Chem 1996, 125: 63–66.

[55] Mazo GN, Mamaev YA, Galin MZ, et al. Structural and transport properties of the layered cuprate Pr2CuO4. Inorg Mater 2011, 47: 1218–1226.

[56] Wilhelm H, Cros C, Reny E, et al. Pressure-induced structural phase transitions in Ln0.75Nd0.25CuO4 for Ln=La (0.6≤x≤2) and Ln=Pr (x=0). J Solid State Chem 2000, 151: 231–240.

[57] Goldschmidt VM. Die gesetze der krystallochemie. Naturwissenschaften 1926, 14: 477–485.

[58] Rodriguez-Carvajal J, Fernandez-Diaz MT, Martinez JL. Neutron diffraction study on structural and magnetic properties of La2NiO4. J Phys: Condens Matter 1991, 3: 3215–3234.

[59] Shannon RD. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Cryst 1976, A32: 751–767.

[60] Allanyon C, Rodriguez-Carvajal J, Fernandez-Diaz MT, et al. Crystal structure of the high temperature phase of oxidised Pr2NiO4.10. Z Phys B - Condensed Matter 1996, 100: 85–90.

[61] Rice DE, Buttrey DJ. An X-ray diffraction study of the oxygen content phase diagram of La2NiO4. J Solid State Chem 1993, 105: 197–210.

[62] Allancon C, Gonthiervassal A, Bascat J, et al. Influence of oxygen on structural transitions in Pr2NiO4. Solid State Ionics 1994, 74: 239–248.

[63] Flura A, Dru S, Nicollet C, et al. Chemical and structural changes in Ln2NiO4+δ (Ln=La, Pr or Nd) lanthanide nickelates as a function of oxygen partial pressure at high temperature. J Solid State Chem 2015, 228: 189–198.

[64] Kröger FA, Vink HJ. Relations between the concentrations of imperfections in crystalline solids. Solid State Phys 1956, 3: 307–435.

[65] Zhao H, Li Q, Sun LP. Ln2MO4 cathode materials for solid oxide fuel cells. Sci China Chem 2011, 54: 898–910.

[66] Choisnet J, Mouron P, Crespin M, et al. Molecular dynamics study of oxygen diffusion in Pr2NiO4. J Chem Phys 2010, 12: 6834–6836.

[67] Kieda N. Nonstoichiometry and electrical properties of La2CuO4 and La2(Cu,Ni)O4. Solid State Ionics 1991, 49: 85–88.

[68] Bieringer M. Topotactic solid-state metal hydride reductions of Sr2MnO4. Inorg Chem 2015, 54: 4249–4256.

[69] Broux T, Bahout M, Hernandez O, et al. Reduction of Sr2MnO4 investigated by high temperature in situ neutron powder diffraction under hydrogen flow. Inorg Chem 2013, 52: 1009–1017.

[70] Sun LP, Li Q, Zhao H, et al. Preparation and electrochemical properties of Sr-doped Nd3NiO4 cathode materials for intermediate-temperature solid oxide fuel cells. J Power Sources 2008, 183: 43–48.
of \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta} \): Oxygen nonstoichiometry and thermodynamic stability. *J Solid State Chem* 1997, **131**, 150–159.

[75] Khandale AP, Bhoga SS, Kumar RV. Effect of Ni doping on structural, electrical and electrochemical properties of \( \text{Nd}_{1.8}\text{Ce}_{0.2}\text{Cu}_{1-x}\text{Ni}_x\text{O}_4 \)-mixed ionic–electronic conductor. *Solid State Ionics* 2013, **238**, 1–6.

[76] Khandale AP, Bansod MG, Bhoga SS. Improved electrical and electrochemical performance of co-doped \( \text{Nd}_{1.8}\text{Sr}_{0.2}\text{Ni}_{0.3}\text{Cu}_{0.1}\text{O}_{4+x} \). *Solid State Ionics* 2015, **276**, 127–135.

[77] Khandale AP, Bhoga SS. Electrochemical performance of \( \text{Nd}_{1.8}\text{Sr}_{0.2}\text{CuO}_{4+\delta} \)-mixed–ionic–electronic conductor for intermediate solid oxide fuel cells. *Solid State Ionics* 2011, **182**, 82–90.

[78] Rao CNR, Buttery DJ, Otuka N, et al. Crystal structure and semiconductor-metal transition of the quasi-two-dimensional transition metal oxide, \( \text{La}_2\text{NiO}_4 \). *J Solid State Chem* 1984, **51**, 266–269.

[79] Skinner SJ, Kilner JA. Oxygen diffusion and surface exchange in \( \text{La}_{2-x}\text{Sr}_x\text{NiO}_4 \). *Solid State Ionics* 2000, **135**, 709–712.

[80] Nikonov AV, Kuterbekov KA, Bekmyzra K, et al. A brief review of conductivity and thermal expansion of perovskite-related oxides for SOFC cathode. *Eurasian J Phys Funct Mater* 2018, **2**, 274–292.

[81] Wilk P. Structural and electrical properties of \( \text{Li}_{0.95}\text{Ni}_{0.05}\text{O}_2 \). *Solid State Ionics* 2003, **157**, 109–114.

[82] Cleave AR, Kilner JA, Skinner SJ, et al. Atomicistic computer simulation of oxygen ion conduction mechanisms in \( \text{La}_2\text{NiO}_4 \). *Solid State Ionics* 2008, **179**, 823–826.

[83] Norimatsu W, Koyama Y. Evolution of orthorhombic domain structures during the tetragonal-to-orthorhombic phase transition in the layered perovskite \( \text{Sr}_2\text{La}_0\text{MnO}_4 \). *Phys Rev B* 2006, **74**, 085113.

[84] McCabe EE, Greaves C. Synthesis and structural and magnetic characterization of mixed manganese–copper \( n=1 \) Ruddlesden–Popper phases. *Chem Mater* 2006, **18**, 5774–5781.

[85] Negri B, Leoni M, Hassen RB. Synthesis, structural and electrical characterizations of \( \text{LaSrC}_{0.6}\text{Al}_{0.4}\text{O}_{3-\delta} \). *Mater Renew Sustain Energy* 2017, **6**, 22.

[86] Paolone A, Giura P, Calvani P, et al. Charge-localization effects in the infrared transmittance of layered perovskites. *Phys B: Condens Mater* 1998, **244**, 33–40.

[87] Midouni A, Houchati MI, Othman WB, et al. Influence of nickel doping on oxygen–ionic conductivity of the \( n=1 \) Ruddlesden–Popper phases \( \text{La}_{1.8}\text{Ce}_{0.2}\text{Cu}_{1-x}\text{Ni}_x\text{O}_{4-\delta} \) \( (\delta=0.0905) \). *J Solid State Chem* 2016, **240**, 101–108.

[88] Opila EJ, Fuller HL, Wuessch BJ, et al. Oxygen tracer diffusion in \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta} \) single crystals. *J Am Ceram Soc* 1993, **76**, 2363–2369.

[89] Bochkov DM, Kharton VV, Kovalevsky AV, et al. Oxygen permeability of \( \text{La}_2\text{Cu}(_{0.75}\text{Co}_{0.25})\text{O}_{4-\delta} \) solid solutions. *Solid State Ionics* 1999, **120**, 281–288.

[90] Kharton VV, Viskup AP, Naumovich EN, et al. Oxygen ion transport in \( \text{La}_2\text{NiO}_4 \)-based ceramics. *J Mater Chem* 1999, **9**, 2623–2629.

[91] Chrono A, Yildiz B, Tarancón A, et al. Oxygen diffusion in solid oxide fuel cell cathode and electrolyte materials: Mechanistic insights from atomistic simulations. *Energy Environ Sci* 2011, **4**, 2774–2789.

[92] Mazo GN, Savvin SN. The molecular dynamics study of oxygen mobility in \( \text{La}_2\text{Sr}_x\text{CuO}_{4-\delta} \). *Solid State Ionics* 2004, **175**, 371–374.

[93] Savvin SN, Mazo GN, Ivanov-Schitz AK. Simulation of ion transport in layered cuprates \( \text{La}_2\text{Sr}_x\text{CuO}_{4-\delta} \). *Crystallogr Rep* 2008, **53**, 291–301.

[94] Chrono A, Parfitt D, Kilner JA, et al. Anisotropic oxygen diffusion in tetragonal \( \text{La}_2\text{NiO}_{4-\delta} \). Molecular dynamics calculations. *J Mater Chem* 2010, **20**, 266–270.

[95] Sayers R, de Souza RA, Kilner JA, et al. Low temperature diffusion and oxygen stoichiometry in lanthanum nickelate. *Solid State Ionics* 2010, **181**, 386–391.

[96] Shirhani-Faradonbeh H, Paydar MH. Electrical behavior of the Ruddlesden–Popper phase, \( \text{Nd}_{0.9}\text{La}_{0.1}\text{Ni}_{0.75}\text{Cu}_{0.25}\text{O}_4 \) (NLNC) and NLNC–\( x \) wt % \( \text{Sm}_2\text{Cu}_{0.75}\text{O}_{1.9} \) (SDC) \( (x=10, 30 \) and 50), as intermediate-temperature solid oxide fuel cathode. *Ceram Int* 2018, **44**, 1971–1977.

[97] Li SL, Tu HY, Li F, et al. Investigation of \( \text{Nd}_{1.8}\text{Sr}_{0.2}\text{Mn}_x\text{O}_{4-x} \) \((M=Ni, Co, Cu, Fe, and Mn)\) cathodes for intermediate-temperature solid oxide fuel cell. *J Alloys Compd* 2017, **694**, 17–23.

[98] Wang YP, Xu Q, Huang DP, et al. Diagnosis on improved electrocatalytic activity of \( \text{La}_2\text{NiO}_{3-x}\text{Cu}_x\text{O}_4 \) electrodes towards oxygen reduction reaction. *Appl Surf Sci* 2017, **423**, 995–1002.

[99] Zheng K, Świerczek K. Evaluation of \( \text{La}_2\text{NiO}_{3-x}\text{Cu}_x\text{O}_4 \) and \( \text{Pr}_2\text{NiO}_{3-x}\text{Cu}_x\text{O}_4 \) Ruddlesden-popper-type layered oxides as cathode materials for solid oxide fuel cells. *Mater Res Bull* 2016, **84**, 259–266.

[100] Wang YP, Xu Q, Huang DP, et al. Survey on electrochemical properties of \( \text{La}_{2-x}\text{Sr}_x\text{NiO}_{4-\delta} \) \((x=0.2 \) and 0.8, \( \delta=0 \)) cathodes related with structural stability under cathodic polarization conditions. *Int J Hydrogen Energy* 2017, **42**, 6290–6302.

[101] Zhang X, Zhang LF, Meng JL, et al. Highly enhanced electrochemical property by Mg-doping \( \text{La}_2\text{Ni}_{1-x}\text{Mg}_x\text{O}_{4-\delta} \) \((x=0.0, 0.02, 0.05 \) and 0.10) cathodes for intermediate-temperature solid oxide fuel cells. *Int J Hydrogen Energy* 2017, **42**, 29498–29510.

[102] Bhoga SS, Khandale AP, Pahune BS. Investigation on \( \text{Pr}_{2-x}\text{Sr}_x\text{NiO}_{4-\delta} \) \((x=0.3–1.0)\) cathode materials for intermediate temperature solid oxide fuel cell. *Solid State Ionics* 2014, **262**, 340–344.

[103] Bansod MB, Khandale AP, Kumar RV, et al. Crystal structure, electrical and electrochemical properties of Cu co-doped \( \text{Pr}_{1.3}\text{Sr}_{0.7}\text{NiO}_{4-\delta} \) mixed ionic-electronic conductors (MIECs). *Int J Hydrogen Energy* 2018, **43**, 373–384.

[104] Chaudhari VN, Khandale AP, Bhoga SS. An investigation on strontium doped \( \text{Sm}_2\text{NiO}_{4-\delta} \) cathode for intermediate temperature solid oxide fuel cells. *J Power Sources* 2014, **248**, 647–654.
of Ln$_2$CuO$_4$ (Ln: La, Pr, Nd) oxides as cathode materials
Zheng K, Gorzkowska-Sobaś A, Świerczek K. Evaluation State Commun 2015, 66: 381–386.

Dielectric permittivity in AFe$_{1/2}$B$_{1/2}$O$_3$ nonferroelectric layered perovskite electrode material for IT-SOFCs. Zhou J, Chen G, Wu K, Mazo GN, Kazakov SM, Kolchina LM, Conductivity of A$_{2-\delta}$B$_{1/2}$O$_3$ for IT-SOFC applications. Sinclair DC, Adams TB, Morrison FD, et al. CaCu$_3$Ti$_4$O$_{12}$. Nonintrinsic origin of the colossal dielectric constants in transition-metal oxides.

Iguchi E, Mochizuki S. Electric conduction and dielectric properties of NdBaInO$_4$ by Sr doping. Fujii K, Shiraiwa M, Esaki Y, et al. Structural, microstructural and dielectric studies in multiferroic LaSrNiO$_{4.8}$ prepared by mechanical milling method. J Alloys Compd 2016, 662: 467–474.

Chouket A, Optasanu V, Bidault O, et al. Dielectric relaxation and polaronic hopping in Mn-substituted LaSrNiO$_4$ nickelates prepared by mechanical milling method. J Alloys Compd 2016, 688: 163–172.

Wang J, Liu G, Jia BW, et al. Giant dielectric response and polaronic hopping in Al-substituted A$_{2}$Sr$_{3}$Ti$_{3}$O$_{4}$ (A=La, Nd) ceramics. Ceram Int 2014, 40: 5583–5590.

Song CL, Wu YJ, Liu XQ, et al. Dielectric properties of La$_{1.75}$Ba$_{0.25}$NiO$_{4}$ ceramics prepared by spark plasma sintering. J Alloys Compd 2010, 490: 605–608.

Shi CY, Hu ZB, Hao YM. Structural, magnetic and dielectric properties of La$_{3-x}$Ca$_{x}$NiO$_{4}$ (x = 0, 0.1, 0.2, 0.3). J Alloys Compd 2011, 509: 1333–1337.

Krohns S, Lunkenheimer P, Kant C, et al. Colossal dielectric constant up to gigahertz at room temperature. Appl Phys Lett 2009, 94: 122903.

Liu G, Liu XQ, Chen XM. Contribution of oxygen vacancies to the giant dielectric response in Sm$_{1-x}$Sr$_x$NiO$_{4+\delta}$ ceramics. Appl Phys A 2014, 116: 1421–1427.

Thongbai P, Yamwong T, Maensiri S. Microstructure and modified giant dielectric response in Ga-doped La$_{1.5}$Sr$_{0.5}$NiO$_{4}$ ceramics. Mater Lett 2012, 82: 244–247.

Chupakhina TI, Melnikova NV, Gyrdasova ОI. Synthesis, structural characteristics and dielectric properties of a new K$_2$NiF$_4$-type phase Sr$_3$Mn$_{0.5}$Ti$_{3.5}$O$_{12}$. J Alloys Compd 2016, 670: 105–112.

Mira J, Castro-Couceiro A, Sánchez-Andújar M, et al. High dielectric constant in charge-ordered Ca$_{1.75}$Pr$_{0.25}$MnO$_3$. J Phys D: Appl Phys 2006, 39: 1192–1196.

Ren GR, Zhu JY, Li L, et al. SrLa(R$_{0.5}$Ti$_{0.5}$)O$_4$ (R = Mg, Zn) microwave dielectric ceramics with complex K$_2$NiF$_4$-type layered perovskite structure. J Am Ceram Soc 2017, 100: 2582–2589.

Xiao Y, Chen XM, Liu XQ. Stability and microwave dielectric characteristics of Ca$_{1-x}$Sr$_x$LaAlO$_4$ ceramics. J Electroceram 2008, 21: 154–159.

Liu B, Yi L, Liu XQ, et al. Structure and microwave dielectric properties of SrSmAlO$_4$–SrTiO$_3$ solid solutions. J Electroceram 2015, 34: 114–121.

Mao MM, Fan XC, Chen XM. Effect of A-site ionic radius on the structure and microwave dielectric
characteristics of Sr_{1−x}Sm_{x}Al_{1−y}Ti_{2}O_{4} ceramics. Int J Appl Ceram Technol 2010, 7: E156–E162.

[138] Zhang C, Yi L, Li L, et al. Structure and microwave dielectric characteristics of solid solutions in SrNdAlO_{3}−Sr_{2}TiO_{3} system. Int J Appl Ceram Technol 2013, 10: E70–E76.

[139] Yuan HX, Chen XM, Mao MM. Structure and microwave dielectric characteristics of Ca_{1−x}Nd_{x}Al_{1−y}Ti_{2}O_{4} ceramics. J Am Ceram Soc 2009, 92: 2286–2290.

[140] Mao MM, Liu XQ, Chen XM. Structural evolution and its effects on dielectric loss in Sr_{1−x}Sm_{x}Al_{1−y}Ti_{2}O_{4} microwave dielectric ceramics. J Am Ceram Soc 2011, 94: 2506–2511.

[141] Luo Y, Zhang J, Yue ZX, et al. Improvement in microwave dielectric properties of Sr_{2}TiO_{3} ceramics through post-annealing treatment. J Electroceram 2018, 41: 67–72.

[142] Liu B, Li L, Liu XQ, et al. Sr_{n}Ti_{2}O_{3n+1} (n = 1, 2) microwave dielectric ceramics with medium dielectric constant and ultra-low dielectric loss. J Am Ceram Soc 2017, 100: 496–500.

[143] Balachandran PV, Puggioni D, Rondinelli JM. Crystal-chemistry guidelines for noncentrosymmetric A_{2}B_{2}O_{7} ruddlesden–popper oxides. Inorg Chem 2014, 53: 336–348.

[144] Benedek NA, Mulder AT, Fennie CJ. Polar octahedral rotations: A path to new multifunctional materials. J Solid State Chem 2012, 195: 11–20.

[145] Mulder AT, Benedek NA, Rondinelli JM, et al. Turning ABO_{3} antiferroelectrics into ferroelectrics: Design rules for practical rotation-driven ferroelectricity in double perovskites and A_{2}B_{2}O_{7} ruddlesden-popper compounds. Adv Funct Mater 2013, 23: 4810–4820.

[146] Xiao Y, Chen XM, Liu XQ. Microstructures and microwave dielectric characteristics of CaRaAlO_{3} (R=Nd, Sm, Y) ceramics with tetragonal K_{2}NiF_{4} structure. J Am Ceram Soc 2005, 87: 2143–2146.

[147] Liu XQ, Chen XM. Microwave dielectric characteristics of SrLaGaO_{4} and SrNdGaO_{4} ceramics. J Eur Ceram Soc 2006, 26: 1969–1971.

[148] Monika DL, Nagabhushana H, Nagabhushana BM, et al. One pot auto-ignition based synthesis of novel Sr_{3}CeO_{3}Ho^{3+} nanophosphor for photoluminescent applications. J Alloys Compd 2015, 648: 1051–1059.

[149] Srinivas M, Tamboli S, Dhoble SJ. VUV-UV photoluminescence properties of Ce^{3+} doped Ca_{2}SnO_{4} phosphor for PDP application. Optik 2017, 145: 202–208.

[150] Yamashita T, Ueda K. Blue photoluminescence in Ti-doped alkaline-earth stannates. J Solid State Chem 2007, 180: 1410–1413.

[151] Shi MM, Zhang DY, Chang CK. Dy^{3+}:Ca_{2}SnO_{4}, a new yellow phosphor with afterglow behavior. J Alloys Compd 2015, 639: 168–172.

[152] Lei BF, Zhang HR, Mai WJ, et al. Luminescent properties of orange-emitting long-lasting phosphorescence phosphor Ca_{2}SnO_{4}Sm^{3+}. Solid State Sci 2011, 13: 525–528.

[153] Lei BF, Yue S, Zhang YZ, et al. Luminescence properties of Sr_{2}SnO_{3}:Sm^{3+} afterglow phosphor. Chinese Phys Lett 2010, 27: 037201.

[154] Yang HM, Shi JX, Gong ML. A new luminescent material, Sr_{2}SnO_{3}:Eu^{3+}. J Alloys Compd 2006, 415: 213–215.

[155] Kamimura S, Yamada H, Xu CN. Purple phosphochromism in Sr_{2}SnO_{3}:Eu^{3+} with layered perovskite-related structure. Appl Phys Lett 2013, 102: 031110.

[156] Khadraoui Z, Horchani-Naifer K, Ferhi M, et al. Electronic structure and optical properties of TbPO_{4}: rare earth ions. Sci Technol Adv Mater 2009, 10: 496–500.

[157] Ye X, Chen XY, Zhang XQ, et al. Improvement in microwave dielectric loss in Sr_{1−x}Sm_{x}Al_{1−y}Ti_{2}O_{4} microwave dielectric ceramics. J Am Ceram Soc 2011, 94: 2506–2511.

[158] Zhang J, Yue ZX, Li ZL, et al. Preparation and luminescence properties of Dy^{3+}, Li^{+} doped CaMoO_{4} phosphor. J Rare Earth 2011, 29: 540–543.

[159] Li HF, Jia YL, Sun WZ, et al. Novel energy transfer mechanism in single-phase-color-tunable Sr_{2}CeO_{4}:Eu^{3+} phosphors for WLEDs. Opt Mater 2014, 36: 1883–1889.

[160] Guan L, Jia GQ, Yang BZ, et al. Synthesis and optical properties of Dy^{3+}, Li^{+} doped CaMoO_{4} phosphor. J Rare Earth 2011, 29: 540–543.

[161] Du QQ, Zhou GJ, Zhou J, et al. Enhanced luminescence of novel Y_{2}Zr_{2}O_{7}:Dy^{3+} phosphors by Li^{+} co-doping. J Alloys Compd 2013, 552: 152–156.

[162] Balakrishniah R, Yi SS, Jang K, et al. Enhanced luminescence properties of YBO_{3}:Eu^{3+} phosphors by Li-doping. Mater Res Bull 2011, 46: 621–626.

[163] Zhang LX, Jiu HF, Fu YH, et al. Preparation and photoluminescence enhancement of Li^{3+} and Eu^{3+} co-doped YPO_{4} hollow microspheres. J Rare Earth 2013, 31: 449–455.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made.

The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.