Signature of Oxide-Ion Conduction in Alkaline-Earth-Metal-Doped Y$_3$GaO$_6$

Pragati Singh, Raghvendra Pandey,* Tadeusz Miruszewski, Kacper Dzierzgowski, Aleksandra Mielewczyk-Gryn, and Prabhakar Singh*

ABSTRACT: We have studied alkaline-earth-metal-doped Y$_3$GaO$_6$ as a new family of oxide-ion conductor. Solid solutions of Y$_3$GaO$_6$ and 2% -Ca$^{2+}$, -Sr$^{2+}$, and -Ba$^{2+}$-doped Y$_3$GaO$_6$, i.e., Y$_{(3-0.06)}$M$_{0.06}$GaO$_6$-δ (M = Ca$^{2+}$, Sr$^{2+}$, and Ba$^{2+}$), were prepared via a conventional solid-state reaction route. X-ray Rietveld refined diffractions of all the compositions showed the formation of an orthorhombic structure having the Cmc2$_1$ space group. Scanning electron microscopy (SEM) images revealed that the substitution of alkaline-earth metal ions promotes grain growth. Aliovalent doping of Ca$^{2+}$, Sr$^{2+}$, and Ba$^{2+}$ enhanced the conductivity by increasing the oxygen vacancy concentration. However, among all of the studied dopants, 2% Ca$^{2+}$-doped Y$_3$GaO$_6$ was found to be more effective in increasing the ionic conductivity as ionic radii mismatch is minimum for Y$^{3+}$/Ca$^{2+}$. The total conductivity of 2% Ca-doped Y$_3$GaO$_6$ composition calculated using the complex impedance plot was found to be ∼0.14 × 10$^{-3}$ S cm$^{-1}$ at 700 °C, which is comparable to many other reported solid electrolytes at the same temperature, making it a potential candidate for future electrolyte material for solid oxide fuel cells (SOFCs). Total electrical conductivity measurement as a function of oxygen partial pressure suggests dominating oxide-ion conduction in a wide range of oxygen partial pressure (ca. 10$^{-20}$–10$^{-4}$ atm). The oxygen-ion transport is attributed to the presence of oxygen vacancies that arise from doping and conducting oxide-ion layers of one, two-, or three-dimensional channels within the crystal structure. The oxide-ion migration pathways were analyzed by the bond valence site (BVS) approach. Photoluminescence analysis, dilatometry, Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscopy studies were also performed to verify the experimental findings.

INTRODUCTION

A mismatch in the demand and supply of energy to the world’s requirement compels the world to look for some alternative sources of energy, which can efficiently produce electricity. Fuel cells, especially solid oxide fuel cells (SOFCs), have received considerable attention because of its higher energy conversion efficiency.1−3 In SOFC, a very good oxide-ion conduction is needed for its electrolyte part; besides electrolytes, oxygen-ion conductors have received considerable attention due to their wide applications in various electrochemical devices such as gas sensors, electrolyzer cells, catalysts, and separation membranes. Oxide-ion conductors are generally used as a solid electrolyte in solid oxide fuel cells.4−6 A variety of diverse structured families such as fluorite structured,7,8 perovskite structured,9−12 scheelite type,13 mellite-based structured,14,15 apatite structured,16,17 pyrochlore,18,19 layered perovskite,20−23 double perovskite,24−26 Ruddlesden−Popper,27−32 aurivillius phase,33,34 brownmillerites,35,36 hexagonal perovskite derivatives,37−46 and BaNdInO$_4$-based oxides38−40 are well reported and investigated for oxide-ion conduction. But still, a lot of studies are being conducted for the discovery of new families of oxide-ion conductors that may have sufficient ionic conductivity in intermediate- or lower-temperature range (300−700 °C). A recent report using first-principles calculations predicted that the Ln$_3$GaO$_6$ (Ln = La, Nd, Gd, Tb, Ho, Dy, Er, or Lu) system might be a good oxide-ion-conducting system.44 However, earlier, a few experimental studies on some derivatives of these species have also been carried out by researchers. Purohit et al. had reported the Nd$_3$GaO$_6$-based system as a new family of oxide-ion conductor.45 They tested Ca$^{2+}$ and Sr$^{2+}$ as dopants at Nd site and found an enhancement in the conductivity by more than 3 orders of magnitude. A recent study was also carried out on the synthesis and electrical properties of alkali-earth-substituted Gd$_3$GaO$_6$ oxide-ion and proton conductors,46 and it shows a total oxide-ion conductivity at 800 °C, $\sigma_{800\text{°C}} = 1 \times 10^{-2}$ S cm$^{-1}$, for the highest substitution level of Ca$^{2+}$. In the
present study, we have tried to investigate the electrochemical properties of undoped and doped \( \text{Y}_3\text{GaO}_6 \) systems, which is analogous to \( \text{Gd}_3\text{GaO}_6 \) oxide-ion and proton conductors. Till now, apart from structural studies, only a few optical studies like luminescence behavior of tri-yttrium gallate \((\text{Y}_3\text{GaO}_6)\) are reported.47,48 Here, we have explored the potential of doped \( \text{Y}_3\text{GaO}_6 \) as an oxide-ion-conducting material. To the best of our knowledge, this is the first study on oxide-ion conduction in alkaline-earth-metal-doped \( \text{Y}_3\text{GaO}_6 \). There are four compounds that can be formed with \( \text{Y}_2\text{O}_3 - \text{Ga}_2\text{O}_3 \) pseudo-binary systems, viz., \( \text{YGaO}_3 \), \( \text{Y}_3\text{Ga}_5\text{O}_{12} \), \( \text{Y}_4\text{Ga}_2\text{O}_9 \), and \( \text{Y}_3\text{GaO}_6 \). Of these, tri-yttrium gallate \((\text{Y}_3\text{GaO}_6)\) is a comparatively less studied system. \( \text{Y}_3\text{GaO}_6 \) crystallizes in the orthorhombic structure with space group \( \text{Cmc}_2_1 \). This structure contains 12-Y (eight Y ions occupy 8\text{b} and four Y ions occupy 4\text{a} Wycko site), 4-Ga, and 24-O atoms in a unit cell,48 which are made up with two edge-sharing of \( \text{YO}_7 \) pentagonal bipyramids polyhedra, making a three-dimensional (3D) framework and with a \( \text{GaO}_4 \) tetrahedron. It means that the \( \text{Y}^{3+} \) cations are localized in two different asymmetrical sites of sevenfold coordination, and \( \text{Ga}^{3+} \) is in distorted oxygen tetrahedral (Figure 1).48

\( \text{Ga}^{3+} \) is bonded to four \( \text{O}^{2-} \) atoms to form \( \text{GaO}_4 \) tetrahedra that share a corner−corner with one \( \text{YO}_7 \) pentagonal bipyramid and an edge−edge with one \( \text{YO}_7 \) pentagonal bipyramid. Usually, the aliovalent substitution increases the oxygen vacancies to maintain the electrical neutrality of the material. Several reports are available on the enhancement of the conductivity by aliovalent substitution.50 Here, divalent ions such as \( \text{Ca}^{2+} \), \( \text{Sr}^{2+} \), and \( \text{Ba}^{2+} \) are doped on the A-site (i.e., Y-site) and their effect on the bulk electrical conductivity is studied. The purpose of this study is to explore alkaline-earth-metal-doped \( \text{Y}_3\text{GaO}_6 \) as an oxide-ion-conducting material and also to identify a suitable dopant for achieving enhanced conductivity. Hereafter, the undoped \( \text{Y}_3\text{GaO}_6 \) and 2\%−\( \text{Ca}^{2+} \), −\( \text{Sr}^{2+} \), and −\( \text{Ba}^{2+} \)-doped \( \text{Y}_3\text{GaO}_6 \) are abbreviated as \( \text{YGO} \), \( \text{YCGO} \), \( \text{YSGO} \), and \( \text{YBGO} \), respectively.

**RESULTS AND DISCUSSION**

**Structural Analysis.** Comparative X-ray diffraction (XRD) patterns of the \( \text{YGO} \), \( \text{YCGO} \), \( \text{YSGO} \), and \( \text{YBGO} \) samples in the \( 2\theta \sim 10−120^\circ \) region are shown in Figure 2a. All of the diffraction peaks are found to be phase-pure and indexed according to the noncentrosymmetric orthorhombic symmetry with space group \( \text{Cmc}_2_1 \). The X-ray diffraction patterns of all of the compositions match with the standard ICSD file no. 155086. The polyhedral representation of the \( \text{YGO} \) system is shown in Figure 2b representing a similar crystal structure as earlier reported in the literature.50 The Rietveld refinements were carried out using FullProf software taking pseudo-Voigt peak profile (Figure 3).51 The atomic coordinates were allowed to vary free of constraints, and the values obtained in each stage were used as a starting parameter for further refinements. The occupancy factor for all of the elements was kept fixed to their nominal value. The values of lattice...
parameters calculated from refinement are listed in Table 1. The ions Y, Ga, and O atoms were found to be 7, 4, and 4, respectively, in the YGO system. After divalent doping on the Y\(^{3+}\) site, there is a slight increase in the volume as Ca\(^{2+}\) (1.20 Å), Sr\(^{2+}\) (1.35 Å), and Ba\(^{2+}\) (1.52 Å) have larger cell volume compared to Y\(^{3+}\) (1.10 Å).\(^{53,54}\) It is easier to introduce lesser amount of Ca into the Y\(_2\)GaO\(_6\) lattice without causing a major lattice distortion. As the doping level of Ca further increases, a secondary phase of Y\(_2\)O\(_3\) corresponding to JCPDF no. 89−5591 is found to evolve (shown in Figure S1, Supporting Information). This indicates that the solid solubility limit of the divalent atom is only ca. 2−3%. However, for the other substituent as Sr\(^{2+}\) and Ba\(^{2+}\), it is expected that the dissolution limit is less at the Y-site, and also, they will create much distortion in the lattice in compared to Ca\(^{2+}\) because of larger mismatch of ionic radii between the host and dopants ions.

**Bond Valence Energy-Based Approach for Identification of Migration Pathways.** The bond valence model is an imperative approach to evaluate the chemical credibility of inorganic crystal structures. This model is based on the bond valence sum (BVS) rule from the Pauling's electrostatic valence concept, which expresses that the sum of all bond valences linked to an atom almost equals the absolute value of its oxidation state. According to this approach, the sum of bond valences, \(S_i\), about any ion, \(i\), is equal to its valence, \(V_i\) (i.e., the formal oxidation state)

\[
V_i = \sum_j S_{ij}
\]

(1)

where the sum runs over all adjacent atoms \(j\) of the atom \(i\). The bond valence \(S_{ij}\) can be considered as a measure of the electrostatic flux between a cation and an anion. It is directly related to the strength of the bond and is correlated inversely with bond length. It can be estimated by the following relation

\[
S_{ij} = \exp\left(\frac{R_{ij} - R_j}{B}\right)
\]

(2)

where \(R_i\) and \(B\) are constant parameters and \(R_{ij}\) is the interatomic distance between atoms \(i\) and \(j\). For many bonds, \(B\) is approximated to 0.37. The bond valence approach is also used to explain the structural distortions from the ideal three-dimensional crystal structure by calculating the global instability index parameter.\(^{53,54}\) The energy barriers obtained by the BVS analysis are only relative to and not as accurate as the ones obtained by more sophisticated computational methods. To explore a new family of oxide-ion conductor, we examined the bond valence energy (BVE) landscapes (BVELs) of O\(^{2−}\) ions diffusion in a few yttrium-containing oxide materials.\(^{55,56}\) Using the BVE approach, the BV-based energy barrier for Y\(_3\)GaO\(_6\) was found to ~0.54 eV along the c-axis of the crystal structure. Hence, due to the less energy barrier compared to other Y-containing oxide systems, this system was taken for further study. The migration pathways in the BVE calculations were constructed with linearly interpolated images between the fully relaxed starting and ending structures. The energy barrier for oxygen migration is calculated as \(E_\text{b} = E_{\text{max}} - E_{\text{min}}\), where \(E_{\text{max}}\) and \(E_{\text{min}}\) are the highest and lowest energies along the migration pathway, respectively (Figure S2). Figure 4a shows the schematic bond valence energy (BVE) landscape for the migration of single oxygen ion inside the crystal lattice. (b) Crystal structure, including migration isosurface of 2.7 eV in Y\(_3\)GaO\(_6\). The yellow color represents the isosurface. Connection of yellow isosurface represents the possible oxide-ion migration path. The dotted red lines are shown for the aid of visualization.
This can also be visualized in Figure S3 and also confirmed with Figure S4 of reaction coordinates (Supporting Information).

**Conductivity Analysis.** The complex impedance plot of all of the studied samples at 600 °C is shown in Figure 6a. The YGO and YBGO samples were found to exhibit a single depressed semicircular arc, whereas the YCGO and YSGO samples exhibit two semicircular arcs. No apparent electrode response is observed for any of the samples due to the grain boundary contribution (inset of Figure 6a, b). The capacitance related to all contributions is calculated according to the following relation: \( \omega = \frac{1}{R C^t} \), where \( \omega \) is the relaxation frequency, \( R \) is the resistance, and \( C \) is indicative of bulk capacitive response. The capacitance values of bulk and grain boundary at 600 °C are listed in Table 2. The lower value of constant phase element (CPE) in the higher-frequency range is indicative of bulk material, and the higher capacitance value in the lower-frequency range is because of the grain boundary contribution.

Table 2. Value of Grain, Grain Boundary Capacitance, Total Conductivity at 600 °C, and Activation Energy of Studied Compositions

| composition | \( C_b \) (F) | \( C_{gb} \) (F) | \( \sigma_{total} \) (S cm\(^{-1}\)) at 600 °C | activation energy (eV) |
|-------------|--------------|----------------|---------------------------------|------------------------|
| YGO         | 0.24 \times 10^{-12} | 0.11 \times 10^{-9} | 0.953 \times 10^{-7} | 1.361 |
| YCGO        | 1.62 \times 10^{-10} | 4.14 \times 10^{-6} | 0.572 \times 10^{-4} | 0.686 |
| YSGO        | 3.66 \times 10^{-12} | 8.70 \times 10^{-6} | 0.180 \times 10^{-4} | 0.918 |
| YBGO        | 0.19 \times 10^{-10} | 0.29 \times 10^{-9} | 0.122 \times 10^{-6} | 0.973 |

constant phase element (CPE) in the higher-frequency range is indicative of bulk material, and the higher capacitance value in the lower-frequency range is because of the grain boundary contribution.

The resistances of bulk and grain boundary are calculated from the intercept of the corresponding arc on the real axis (\( Z' \)). The total resistance of the electrolyte is given by: \( R_t = R_b + R_{gb} \), where \( R_b \) is the bulk resistance and \( R_{gb} \) is the grain boundary resistance. Further, this total resistance of the electrolyte was used to obtain the total conductivity using the
formula $\sigma_t = \frac{d}{A R_t}$, where $\sigma_t$ is the total conductivity, $R_t$ is the total resistance, $d$ is the thickness, and $A$ is the area of the pellet. The temperature dependence of total conductivity of all of the samples is shown in Figure 6c. It is remarkable that the conductivity increases significantly for the Ca$^{2+}$ and Sr$^{2+}$ dopants, while it decreases for the Ba$^{2+}$ dopant. Figure 6c depicts the Arrhenius representation of the conductivity data. The activation energy ($E_a$) is estimated for the studied compositions using the Arrhenius equation

$$
\sigma T = \sigma_0 \exp \left( -\frac{E_a}{k_B T} \right)
$$

where $\sigma_0$ is the preexponential factor, $k_B$ is the Boltzmann constant, and $E_a$ is the activation energy. The activation energy has been calculated by the slope of the Arrhenius plot, which is in good agreement with a few other earlier reported prominent anionic conductors, indicating the formation of vacancies and ionic charge carriers. The activation energy ($E_a$) is equal to the sum of the vacancy formation energy ($E_f$) and the migration barrier ($E_m$). The $E_m$ value depends on the local atomic arrangement of the system. In this study, $E_m$ obtained from the BVE approach, is the minimum for YCGO composition among all of the doped compositions. Hence, the activation energy is minimum for the YCGO sample. The bulk conductivity of 2% Ca-doped sample (YCGO) was found to be a maximum due to the minimal mismatch of ionic radii to the host atom and the comparatively less dissociation energy in the Ca–O bond (Table S2). The highest solubility limit in Y$_{1.99}$Ca$_{0.06}$GaO$_{6.65}$ can be attributed to the smallest size mismatch for Ca$^{2+}$, $|r$(Ca$^{2+}) - r$(Y$^{3+})| < |r$(Sr$^{2+}) - r$(Y$^{3+})| < |r$(Ba$^{2+}) - r$(Y$^{3+})| = 0.06 < 0.19 < 0.21$ Å. Here, $r$(A) denotes the ionic radius of A$^{2+}$ cation. This leads to less activation energy of migration in the YCGO sample compared to others. At higher temperatures, the no. of vacancies will be dissociated; hence, the ionic conductivity is directly related to the formation of oxygen vacancies.

**Effect of Dopant Size on Oxygen Partial Pressure Dependent Conductivity.** For fixed valency substitution and a fixed number of vacancies, conductivity depends on the dopant size. The total conductivity variation against the ratio of dopant radii and host radii is shown in Figure 7a. The maximum conductivity is obtained for Ca$^{2+}$ doping with $r$$_{Ca^{2+}}$/ $r$$_{Y^{3+}}$ ~ 1.09. These types of optimum values are observed in many other ionic conductors such as NdGaO$_3$, LaAlO$_3$, BaGdInO$_3$, La$_{0.53}$Sr$_{0.47}$SiO$_{2.6}$ and Na$_{0.5}$Ba$_{0.5}$TiO$_{3}$, respectively. It is believed that the maximum conductivity appears for $r$$_{dopant}$/ $r$$_{host}$ ~ 1.05 in the perovskite- and brownmillerite-type structure.

The comparable size of dopant and host minimizes the local strain in the lattice and assists the migration of oxygen ions (shown in Supporting Information Figure S5). The total conductivity as a function of oxygen partial pressure at 700 and 800 °C is shown in Figure 8. The flat region at a lower partial pressure in all of the studied samples is attributed to predominant ionic contribution and the positive slope of the curve at $p_{O_2}$ > 10$^{-4}$ atm, showing p-type conduction with a predominant hole conductivity. The extent of ionic contribution is changing with substitution and temperature. As the hole and electron concentrations increase rapidly with the increase in temperature, the mobility of oxide ion decreases. The process of hole formation can be described by the equation

$$
V_{O}^{••} + \frac{1}{2} O_2 = O_{O}^{••} + 2h^+
$$

Thus, the total conductivity will be given by

$$
\sigma_{total} = \sigma_p \sim V_{O}^{••} P(O_2)^{1/6}
$$

where $V_{O}^{••}$ is nearly constant and the slope of log $\sigma$ vs log $p_{O_2}$ is ~1/6 in the higher-pressure region. In the lower-$p_{O_2}$ region (<10$^{-4}$ atm), the concentration of oxygen vacancies is higher than the concentration of holes and electron, and the total conductivity is given by

$$
\sigma_{total} = \sigma_{v_{O}^{••}} = \text{constant}
$$

Since Y$^{3+}$, Ga$^{3+}$, Ca$^{2+}$, Sr$^{2+}$, and Ba$^{2+}$ are neither prone to oxidation nor reduction, we can expect the conductivity to remain constant at a lower partial pressure. Further, as the mobilities of cationic species such as Y$^{3+}$, Ga$^{3+}$, Ca$^{2+}$, Sr$^{2+}$, and Ba$^{2+}$ are negligible, we can conclude that the conductivity is mainly because of oxide ions in the given range of oxygen partial pressures. The variation of ionic conductivity with dopant size at 700 °C is shown in Figure 7b.

**UV–Vis Analysis.** Figure 9 depicts the band gap variation of the studied composition. The band gap of the studied compositions was calculated using Tauc’s relation, represented by the relation:

$$
\alpha h\nu = A(h\nu - E_g)^n
$$

where $A$ is a constant, $h\nu$ is the energy, $\alpha$ is the absorption coefficient, $E_g$ is the band gap, and $n$ is the probability transition rate; $n = 1/2$ for direct transition and $n = 2$ for indirect transition. The observed direct band gap of pure YGO is found to be 5.49 eV, and its value is found to decrease with the divalent doping. This decrease in band gap results in an increase in the oxygen vacancies formed by the charge

![Figure 7](https://example.com/figure7.png)

Figure 7. Dependence of (a) total conductivity and (b) oxide-ion conductivity on the dopant ionic radii at 700 °C.

![Figure 8](https://example.com/figure8.png)

Figure 8. Oxygen partial pressure dependence of the total electrical conductivity of the YGO, YCGO, and YSGO samples at (a) 700 and (b) 800 °C, respectively. It suggests the dominant oxide-ion-type conduction in the pressure range of 10$^{-4}$–10$^{-20}$ atm.

![Figure 9](https://example.com/figure9.png)

Figure 9. Band gap analysis of the studied composition.
compensation mechanism. Among all of the doped compositions, Ca²⁺ has the lowest solution energy on Y³⁺ for creating oxygen defects. So, the number of defects formed will be maximum for Ca²⁺. This type of behavior is observed in NdBaInO₄.4³

Further, these results are also evident from the photoluminescence (PL) analysis (discussed in detail in the Supporting Information). The room-temperature photoluminescence spectra of the YGO, YCGO, and YSGO samples are shown in Figure S6. All of the compositions exhibit a broad and strong peak at ∼420 nm. The PL spectra could be used to describe the charge carrier trapping, transfer, and electron–hole pair interaction. The emission band located at ∼420 nm is mainly due to the formation of defects associated with the divalent dopant. The photoluminescence intensity also varies according to the surface oxygen vacancies and defects.6⁸ Usually, lower PL intensity corresponds to higher conductivity because of the lower recombination rate and effective charge carrier separation.6⁸ Its intensity is found to decrease with the dopant, with a minima for Ca doping. This suggests that the vacancy concentration is maximum for Ca doping.

Fourier Transform Infrared (FTIR) Analysis. Fourier transform infrared spectroscopy is used to get information about the chemical bond and structure of the material. The bands are formed by bending and stretching of vibrations. The FTIR spectra of the undoped and Ca²⁺-, Sr²⁺-, and Ba²⁺-doped YGO samples are shown in Figure 10. The characteristic peak around 3400 cm⁻¹ is assigned to the stretching vibrations of O–H associated with the hydroxyl group.6⁹ The peak around 1600 cm⁻¹ is attributed to the H–O–H bending vibration. As the synthesized compositions do not contain any O–H molecule-based precursor and the XRD of the samples also do not show any impure phases, we can conclude that the OH peak observed in the spectrum is because of the moisture adsorbed on the powder sample during measurements. To further confirm this, we have added the thermogravimetric analysis (TGA) measurement of YSGO in the Supporting Information (Figure S7). A strong band at 526–694 cm⁻¹ is attributed to the stretching of the Y–O vibrations,⁷⁰ and the band originated at 450, and 627 cm⁻¹ is assigned to Ga–O vibrations, probably due to the formation of metal oxide bond. However, a slight decrease in the magnitude and peak broadening is observed after doping with alkali-earth metal, mainly because of the increase in the defects and distortion caused by dopant ion in the host lattice.⁷¹ The Ca–O peak around 300–400 cm⁻¹ is not observed in the band. The presence of a band around 2350 cm⁻¹ in the YCGO sample can be attributed to the Ca–O bond.⁷² The peak around 870 cm⁻¹ present in the YSGO sample is assigned to the Sr–O bond, and the kink around 860 cm⁻¹ is assigned to the Ba–O bond.⁷³

Scanning Electron Microscopy (SEM) Analysis. The SEM images of the fractured cross section of the YGO, YCGO, and YSGO samples are shown in Figure 11. Irregular and agglomerated grains for the YGO sample are attributed to poor sinterability of the material. However, micrographs of the alkaline-earth-metal-doped YGO samples show quite dense and polygonal morphology with low porosity. The densification of the doped samples indicates the improvement in the sinterability after doping. Grains become more connected after doping, and the effective number of grain boundaries increases. Energy-dispersive X-ray (EDX) mapping of the YGO, YCGO, and YSGO samples (see Figure S8) confirms the presence of all of the constituent elements in the matrix. The average grain size is calculated using ImageJ software. Grain size is observed to increase with the doping of alkaline-earth metal ions. The
density of all of the sample was calculated using the Archimedes principle. The density is found to increase with the alkaline earth doping, as summarized in Table 1. The increase in density is correlated with the increase in grain size, as observed in the SEM micrographs of the sample.

**Thermal Expansion Study.** The variation of thermal expansion of pure YGO, and Ca\(^{2+}\) and Sr\(^{2+}\)-doped YGO is shown in Figure 12. No appreciable difference is observed in the heating and cooling curves. All of the samples show a linear change with temperature. This trend also indicates the absence of any kind of structural change in the studied temperature range. Thermal expansion coefficient (TEC) can be obtained using the following relation

\[
\alpha_T = \frac{\Delta L}{L \Delta T}
\]

where \(\alpha_T\) denotes the value of thermal expansion coefficient (TEC), \(L\) is the length of sample, \(\Delta L\) is the change in length, and \(\Delta T\) is the change in temperature.\(^7\)

The TEC values of all of the samples are approximately the same. This indicates that the introduction of 2% Ca\(^{2+}\) and Sr\(^{2+}\) does not change the TEC value. Its TEC values are close to lightly doped La\(_{1-x}\)Sr\(_x\)MnO\(_3\), so it will exhibit better thermal compatibility with the LaMnO\(_3\) family cathode materials. The obtained TEC values (mentioned in Table 3) are also corroborated with the TEC values of many manganite- and nickelate-based cathode materials, as reported in the literature.\(^8\)

## EXPERIMENTAL SECTION

**Sample Preparation.** Polycrystalline samples of Y\(_2\)GaO\(_4\) and 2% Ca\(^{2+}\), Sr\(^{2+}\), and Ba\(^{2+}\)-doped Y\(_2\)GaO\(_4\) were prepared via the solid-state reaction route. The Y\(_2\)O\(_3\) (Otto, 99.99%), CaCO\(_3\) (Alfa Aesar, 99.5%), SrCO\(_3\) (Loba Chemie, 99.9%), and BaCO\(_3\) (Alfa Aesar, 99.9%) were preheated at 300 °C for 5 h and weighed in a stoichiometric amount. The raw powders were then mixed in a mortar thoroughly using acetone as a mixing media. After grinding, the powder was calcined at 900 °C for 12 h in air. Then, the calcined powders were mixed with 2% poly(vinyl alcohol) and uniaxially pressed into pellets by applying a load of \(\sim\)1 × 10\(^5\) MPa. The samples were then sintered at 1200 °C for 24 h and at 1350 °C for 6 h in air.

**Characterizations.** The structural study was done by a Rigaku Miniflex-II desktop X-ray diffractometer with Cu K\(_\alpha\) radiation in the 2θ range of 10°–120° and at a scan rate of 5° min\(^{-1}\). The bulk density was calculated using the Archimedes density measurement kit (DENVER SI-234). Surface morphology and composition analysis of polished samples were carried out using SEM (EVO-scanning electron microscope MA15/18). Impedance measurement was carried out on a sintered pellet in an ambient atmosphere via a Wayne Kerr 6500P series LCR meter using a two-probe method. Data were collected in the temperature range of 400–700 °C using platinum paste as the electrode. The total conductivity as a function of oxygen partial pressure was measured by a conventional DC-2W method using a Keysight 34970A precise digital multimeter.

![Figure 12. Thermal expansion curves of YGO, YCGO, and YSGO compositions from room temperature to 1000 °C.](https://dx.doi.org/10.1021/acsomega.0c03433)

### Table 3. TEC Values of the Measured Samples between Room Temperature and 1000 °C

| compositions | thermal expansion coefficient, \(\alpha_T \times 10^{-4} (\text{K}^{-1})\) |
|-------------|--------------------------------------------------|
| YGO         | 10.7                                             |
| YCGO        | 10.7                                             |
| YSGO        | 10.5                                             |
| YBGO        | –                                                |

### CONCLUSIONS

Doping of a small amount of alkaline-earth metal ion has a remarkable effect on the properties of Y\(_2\)GaO\(_4\). Partially replacing the Y by 2% Ca\(^{2+}\) or Sr\(^{2+}\) improves the bulk conductivity by more than 3 orders without any alteration in the conduction mechanism. However, the doping of Ba\(^{2+}\) did not significantly enhance the conductivity. Higher electrical conductivity with the Ca\(^{2+}\) doping is attributed to the oxygen vacancies and the formation of migration channels only. Doping of alkaline-earth metals in Y\(_2\)GaO\(_4\) results in an increase in the conductivity and decrease in the band gap. Despite higher polarizability and lower bond strength of Sr\(^{2+}\) with O, Ca\(^{2+}\) doping was found to be more effective and efficient than Sr\(^{2+}\). This is attributed to the optimum dopant size mismatch with the host ion as it produces minimum strain in the crystal lattice. The microstructures show an increase in grain size and densification after doping of alkaline-earth metals. This is due to the lower melting points of Ca\(^{2+}\), Sr\(^{2+}\), and Ba\(^{2+}\) compared to that of Y\(^{3+}\). The bond valence energy-based approach was employed to screen and identify the ionic migration pathways in the crystal structure of the investigated compositions. The oxygen partial pressure dependence of the total electrical conductivity (\(pO_2\)) study at 700 and 800 °C confirms that the material is an oxide ionic conductor in a wide range of partial pressure (ca. 10\(^{-20}\)–10\(^{-14}\) atm). Furthermore, this system has the potential to improve its ionic conductivity on further optimizing dopant and synthesis method. The other structural, microstructural (SEM), thermal (TEC, TGA), and optical characterizations (PL, UV, FTIR) also support the XRD, BVE, and electrical behavior and are correlated with the experimental findings. Thus, this study explores a new family of anionic conductors that in the future may be used in electrochemical device applications.

![Image of Table 3](https://dx.doi.org/10.1021/acsomega.0c03433)
with data acquisition mode. The measurements were done in a temperature range of 650–800 °C. To introduce the proper atmosphere to the measurement cell, a gas mixer was used. The atmospheres were changed from pure and dry argon to dry oxygen, and the step was 0.1 atm. During the measurements, the samples were held at the final temperature to see the constant value of recorded resistance, which indicated the thermodynamic equilibrium between the sample and gas. This procedure was repeated in every temperature and atmosphere. UV–visible absorption spectra in the wavelength range of 200–1000 nm were recorded using a JASCO V-770 UV–vis spectrometer. Room-temperature photoluminescence measurement was done using a photoluminescence spectrometer (Fluorolog Horiba Scientific) employing an excitation wavelength of 260 nm. Fourier transform infrared spectra were recorded using a Nicolet iS THERMO Electron Scientific Instruments LLC in the wavenumber range of 400–4000 cm⁻¹ using KBr media. Thermogravimetric analysis of the sample was done in a nitrogen atmosphere using a Netzsch Jupiter449 F1 (Burlington, MA) with a gas flow rate of 100 mL min⁻¹. Thermal expansion of bulk sample in the temperature range of 50–1000 °C was studied using a Netzsch DIL 420 PC/4 dilatometer with a constant cooling and heating rate of 2 °C min⁻¹ in airflow. The thermal expansion coefficient is calculated by linear fitting the elongation vs temperature function.

**Bond Valence Energy Calculations.** To inspect the oxide-ion diffusion path and migration barrier in the crystal structure, we have done bond valence-based energy calculations using SoftBV program. The room-temperature X-ray Rietveld refined crystallographic information file parameters were used for the bond valence energy calculations, and the BVE landscape and crystal structure were drawn using Vesta software. The spatial resolution in the calculation was set to 0.1 Å. The energy barriers for oxide-ion migration were estimated using the BVE landscape.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03433.

X-ray diffractograms of the Ca-doped-YGO samples at room temperature, bond valence energy landscape for oxide-ion migration viewed along the c axis with various isosurfaces and energy barrier histogram, oxygen-ion diffusion migration pathways, BVEL showing migration along the faces and edges of the GO₄ tetrahedra and the YO₆ pentagonal bipyramid, Rietveld refined crystallographic information file parameters, intrinsic strain calculated using the Williamson–Hall analysis, bonding strength with the oxygen of divalent A-site dopant, room-temperature photoluminescence analysis, thermogravimetric analysis of the YSGO sample, and EDX mapping. (PDF)

### AUTHOR INFORMATION

**Corresponding Authors**

Raghvendra Pandey — Department of Physics, A.R.S.D. College, University of Delhi, New Delhi 110021, India; orcid.org/0000-0002-7061-0352; Email: raghvendra@arisd.du.ac.in

Prabhakar Singh — Department of Physics, Indian Institute of Technology (Banaras Hindu University), Varanasi 221005, India; orcid.org/0000-0001-5104-0131; Email: psingh.app@iitbhu.ac.in

**Authors**

Pragati Singh — Department of Physics, Indian Institute of Technology (Banaras Hindu University), Varanasi 221005, India

Tadeusz Miruszewski — Faculty of Applied Physics and Mathematics, and Advanced Materials Centre, Gdańsk University of Technology, 80-233 Gdańsk, Poland

Kacper Dziergowski — Faculty of Applied Physics and Mathematics, and Advanced Materials Centre, Gdańsk University of Technology, 80-233 Gdańsk, Poland

Aleksandra Mieleczewczyk-Gryn — Faculty of Applied Physics and Mathematics, and Advanced Materials Centre, Gdańsk University of Technology, 80-233 Gdańsk, Poland;

orcid.org/0000-0001-6795-3840

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c03433

**Notes**

The authors declare no competing financial interest.

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Conductors.

Nihon Kessho Gakkaishi

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