Effect of magnesium on the XPS and Raman spectra of \((\text{Ba}_{0.5}\text{Sr}_{0.5})(\text{Al}_{0.2-x}\text{Mg}_x\text{Fe}_{0.8})\text{O}_{3-\xi}\) \((x \leq 0.2)\)

Shivendra Kumar Jaiswal*, Vijay Kumar Kashyap and Jitendra Kumar**

*Department of Physics, National Institute of Technology Patna, Bihar, India; **Department of Materials Science and Metallurgical Engineering, UIET, CSJM University, Kanpur, India; *Materials Science Programme, Indian Institute of Kanpur, India

**ABSTRACT**

The perovskite-type cubic oxides have found useful applications in catalysis, solid oxide fuel cells, gas sensors, and membrane technology. XPS and Raman studies of a recently developed \((\text{Ba}_{0.5}\text{Sr}_{0.5})(\text{Al}_{0.2}\text{Mg},\text{Fe}_{0.8})\text{O}_{3-\xi}\) \((x = 0–0.2)\) oxygen-permeable system are reported here. The effect of magnesium is shown to alter the relative amounts of Fe\(^{3+}\), Fe\(^{4+}\), and oxygen species via Fe \((2p_{3/2}\) and \(2p_{1/2}\)) and O \(1s\) signals. Besides, it causes a surge in oxygen vacancies, an increase in Fe\(^{3+}\) ions, a decline in B - O bond strength \((B = \text{Al}/\text{Mg}/\text{Fe})\), and a rise in anion flow. The O1s signals at \(~528.5\) and \(~531.0\) eV correspond to surface oxide and adsorbed \(\text{O}_2^+\), \(\text{O}^–\), or \(\text{O}^0\) species, respectively. Raman spectra offer evidence for symmetric \(\text{Al}_{12}\) stretching, oxygen vacancies, distorted \(\text{BO}_6\) octahedra, A-O stretching vibration modes \((A = \text{Ba}, \text{Sr})\), and bending B-O linkages. A good correlation is advanced between the XPS and Raman results, in con"
information. A Thermo-electron X-ray diffractometer (model ARL X’TRA) was employed for phase analysis. The molecular vibrational spectra having sensitivity to local structure and chemistry were obtained using a Raman microscope (Renishaw model Invia) at the excitation wavelength of 1064 nm (YAG laser); resolution being 0.3 cm⁻¹ (FWHM). To explore the electronic states of species, the X-ray photoelectron spectra (sample area 100 μm x 100 μm) were recorded with a PHI 5000 VersaProbe (Model Ulvac) using an Al Kα (hν = 1486.6 eV) at the pressure of ~ 6.7 × 10⁻⁸ Pa. The signal was gathered at the take-off angle of 45° to get a contribution from the sub-surface region. The high-resolution (step 125 meV) spectra of species were obtained inappropriate energy regimes. Carbon 1s peak at 284.6 eV (with the precision of 0.1–0.2 eV) was used as a reference for deducing the binding energy (BE) accurately. The data accumulation time interval was fixed at 3 – 60 min and an Origin 8.5 software was utilized for fitting of each peak assuming the Gaussian/Lorentzian distribution(s).

3. Results and discussion

(Ba₀.₅Sr₀.₅)(Al₀.₂₋ₓMgₓFe₀.₈)O₃₋ₓ (0 ≤ x ≤ 0.2) powder samples exhibit a perovskite-type cubic structure with lattice parameter 3.953–3.978 Å ± 0.002 Å (Fig S1 supplementary information). XPS data contain information about the oxidation state(s) of species as well as local charge transfer related effects in the material [31]. The electronic/bonding states and local chemical environment around oxygen are examined through XPS studies to understand the anion vacancy formation with magnesium insertion (x ≤ 0.2) at Al³⁺ sites in (Ba₀.₅Sr₀.₅)(Al₀.₂₋ₓMgₓFe₀.₈)O₃₋ₓ. The carbon C 1s peak at 284.6 eV is used as a standard for calibration of XPS data. X-ray photoelectron (XP) spectra of (Ba₀.₅Sr₀.₅)(Al₀.₂₋ₓMgₓFe₀.₈)O₃₋ₓ (0 ≤ x ≤ 0.2) having contributions from Ba 3d, Sr 3d, Al 2p, Mg 1s, Fe 2p, and oxygen (O 1s) levels shown in Figure 1 appear nearly similar for all the powder samples. For instance, the Ba 3d doublet is invariably observed in the energy range of 775–800 eV with FWHM of ~ 1.5–1.7 eV (Figure 2(a)). But the peaks shift slightly toward higher energy and show progressive broadening with magnesium insertion, i.e. from ~794.79 and 779.54 eV for x = 0 to ~ 794.92 and 779.67 eV for x = 0.20, indicative thereby increasing distortion. The presence of two peak maxima at ~ 779 and ~ 795 eV also gives the signature of the perovskite structure [31,32]. Figure 2(b) depicts the XPS scans of Ba 3d₃/₂ and Ba 3d₅/₂ peaks at respective binding energies (marked) in different compositions. The peak is deconvoluted into two with centers around 779 eV and 777 eV in the case of Ba 3d₅/₂. The exact position, width, and percentage area of each fitting peak for both the cases are summarized in Table 1. Notice that the (%) peak area decreases at ~779.5 eV but increases at ~ 777.5 eV with a rise in magnesium content. These correspond to barium lying on the surface and in subsurface regions, respectively. The figures suggest

![Figure 1](image-url). XPS survey spectra of (Ba₀.₅Sr₀.₅)(Al₀.₂₋ₓMgₓFe₀.₈)O₃₋ₓ (x = 0, 0.05, 0.10, 0.20) powder samples indicating peaks belonging to different elements. Carbon 1s peak, taken as standard, is also shown.
depletion of barium at the surface with increased magnesium content. Further, the presence of both the peaks points toward relaxed states for Ba-species [31–35]. The Sr 3d signal appears as a doublet due to spin-orbit coupling of 3d_{3/2} and 3d_{5/2} levels; their binding energies (BE) being ~133 and ~135 eV, respectively (Figure 3). These peaks shift marginally toward lower energy with magnesium insertion, i.e. from 133.42 and 134.92 eV for \( x = 0 \) to 133.04 and 134.79 eV for \( x = 0.20 \). On examining closely, a hump is observed at the lower energy side (~131.67 eV) in the spectrum of composition \( x = 0.20 \). The above binding energy values match well with the Sr^{2+} ion data observed before in the perovskite-type cubic oxides [33,34,36]. The Sr 3d and Ba 3d XPS data support XRD findings, which conform to occupancy of barium and strontium at A-sites in ABO_{3-\delta} cubic structure [30]. Figure 4 depicts the XP spectra of (Ba_{0.5}Sr_{0.5})(Al_{0.2}xMg_{x}Fe_{0.8})O_{3-\delta} samples for aluminum (Al 2p) and magnesium (Mg 1s).

Figure 2. XPS spectra of (Ba_{0.5}Sr_{0.5})(Al_{0.2}xMg_{x}Fe_{0.8})O_{3-\delta} (x = 0, 0.05, 0.10, 0.15, 0.20) showing (a) Ba 3d_{3/2} and 3d_{5/2} levels and (b) their deconvoluted fitting curves for the composition (x) = 0.05, 0.10, 0.20.
The XP spectra of Fe 2p level in (Ba0.5Sr0.5)(Al0.2xMg0.8xFe0.23)O3-ε (x = 0.05, 0.10, 0.20) samples are shown in Figure 5. The spin-orbit splitting gives rise to doublets for 2p3/2 and 2p1/2 levels. Their Gaussian fitting have four peaks. While the main ones at ~710.2 and ~712.8 eV correspond to Fe3+ (2p3/2) and Fe4+ (2p3/2), respectively, others at ~723.3 and ~725.6 eV resemble with Fe5+ (2p1/2) and Fe6+ (2p1/2), respectively. Thus, iron ions exist in two oxidation states (namely, 3+ and 4+) in (Ba0.5Sr0.5)(Al0.2xMg0.8xFe0.23)O3-ε (x = 0–0.2) samples. Their origin lies with electrostatic interaction, spin-orbit coupling between 2p core hole and unpaired 3d electron of photoionized cation, and crystal field effect [37–40]. The relative amounts of Fe3+ and Fe4+ ions are deduced from respective areas of the fitting curves and summarized in Table 2. Clearly, there is decrease of Fe4+ ions and increase of Fe3+ species with rise in magnesium content (x), both occupying B-sites in ABO3-ε structure. It essentially means that magnesium substitution induces some Fe4+ → Fe3+ conversion with added anion vacancies and consumption of electron released by oxygen desorption as molecule. These findings are consistent and in agreement with the Mössbauer data, revealing upsurge of Fe3+ ion concentration in (Ba0.5 Sr0.5)(Al0.2xMg0.8xFe0.23)O3-ε (0 ≤ x ≤ 0.2) [30].

The high-resolution XP spectrum of O 1s level presented in Figure 6 is fitted with two Gaussian peaks at ~528.5 and ~531.0 eV (say, for x = 0), ascribed to surface oxide, and adsorbed (O2−, O2−, or O−) species, respectively (Table 3) [41]. The lower binding energy (LBE) peak at 528.5 eV with FWHM of ~1.4 eV corresponds to B – O linkages (B = Fe/Mg/Al), whereas the higher binding energy (HBE) signal at ~531 eV is attributed to A – O bonds (A = Ba, Sr) associated with adsorbed oxygen [31,36,41–45]. The growth of LBE peak area suggests increase in B – O linkages at the surface with rise in magnesium content. A weak B–O bond is expected to release extra oxygen, increasing thereby the anion vacancies. This scenario provides more open space in the structure and facilitates the anion movement – leading to higher ionic conductivity, as found earlier [30,31,41–45].

### Table 1. XPS parameters of Ba 3d5/2 and Ba 3d3/2 levels in (Ba0.5Sr0.5)(Al0.2xMg0.8xFe0.23)O3-ε (x = 0.05, 0.10, 0.20).

| Composition (x) | Position (eV) Ba 3d5/2 | FWHF (eV) | Position (eV) Ba 3d3/2 | FWHF (eV) | Ascribed (%) to Area |
|-----------------|-----------------------|-----------|-----------------------|-----------|----------------------|
| 0.05            | 794.8                 | 1.51      | 779.5                 | 1.50      | Surface 98           |
| 0.10            | 792.5                 | 0.72      | 777.4                 | 0.71      | # 02                 |
| 0.20            | 795.1                 | 1.52      | 779.6                 | 1.50      | Surface 90           |

# - Sub-surface

![Figure 3](x = 0)

![Figure 3](x = 0.05)

![Figure 3](x = 0.10)

![Figure 3](x = 0.15)

![Figure 3](x = 0.20)

Figure 3. XPS spectra of (Ba0.5Sr0.5)(Al0.2xMg0.8xFe0.23)O3-ε (x = 0–0.20) showing Sr 3d3/2 and Sr 3d5/2 levels.
Structural symmetry of oxides can be evaluated by Raman spectroscopy because of its sensitivity to local chemistry and coordination [46]. Figure 7(a) displays a few typical Raman spectra of \((\text{Ba}_{0.5}\text{Sr}_{0.5})(\text{Al}_{0.2-x}\text{Mg}_x\text{Fe}_{0.8})\text{O}_3\xi\) (\(x = 0–0.20\)) powder samples in the wavenumber range of 300–900 cm\(^{-1}\). Interestingly, the main peak having Raman shift (> 600 cm\(^{-1}\)) moves toward higher wavenumber with increasing magnesium content \((x)\); notice that the Mg\(^{2+}\) ion is lighter and has less positive charge than Al\(^{3+}\). Also, a shoulder in the Raman band observed in the sample of composition \(x = 0.20\) indicates splitting of the signal into two peaks centered around 540 and 680 cm\(^{-1}\) (Figure 7(b)). A band with Raman shift in the range of 600–700 cm\(^{-1}\) corresponds to a totally symmetric \(A_{1g}\) stretching mode of BO\(_6\) self-distorted octahedra (or in-phase stretching breathing mode of oxygen in close vicinity of B-ion). The band near 680 cm\(^{-1}\) provides evidence for oxygen vacancies too [46,47]. These characteristics possibly arise due to local distortion of the crystal symmetry [32,48]. Generally, the anti-stretching (\(E_g\)) mode is two-fold \((E_g^1\) and \(E_g^2\)) whereas that of bending \(F_{2g}^i\) is three-fold \((i = 1,2,3)\) degenerate and represent octahedra tilting as well as Ba\(^{2+}\)/Sr\(^{2+}\) translation. Both \(E_g\) and \(F_{2g}\) modes exhibit Raman shift in the range of 500–600 cm\(^{-1}\). Thus, the split peak at 540 cm\(^{-1}\) arises due to octahedral tilting and/or Sr/Ba-ion translation induced by the creation of extra anion vacancies in the vicinity. The orthorhombic distortion of BO\(_6\) octahedra displays a total of 24 Raman active modes involving rotation, anti-stretching, bending, and stretching effects [49–51]. The oxygen vibrates along M-O-M’
bonds, where M and M’ stand for metal ions of different size and oxidation states. The relative size of M and M’ ions (Mg$^{2+}$, Al$^{3+}$, Fe$^{3+}$, Fe$^{4+}$) alters the stiffness of bonds and hence the frequency of vibration. Also, the occupation of Mg$^{2+}$ ion at Al$^{3+}$ site in (Ba$_{0.5}$ Sr$_{0.5}$)(Al$_{0.2-x}$Mg$_x$Fe$_{0.8}$)O$_{3-ξ}$ affects oxygen vacancies in the neighborhood and, in turn, modifies the local symmetry. As a result, some variation in the B-O stretching occurs, leading to different vibration modes. This change is revealed by peak shifting and splitting. It further suggests that Mg$^{2+}$ addition brings in the distortion of octahedra as well as enhancement in the oxygen vacancies (or non-stoichiometry parameter, ξ). With increase occurring in lattice parameter.

Figure 5. Typical XPS spectra (open circles) and fitted curves of (Ba$_{0.5}$Sr$_{0.5}$)(Al$_{0.2-x}$Mg$_x$Fe$_{0.8}$)O$_{3-ξ}$ (x = 0.10, 0.15, 0.20) compounds showing individual contributions of Fe$^{3+}$ and Fe$^{4+}$ species.
and anion vacancy concentration in (Ba$_{0.5}$Sr$_{0.5}$)(Al$_{0.2-x}$Mg$_x$Fe$_{0.8}$)O$_{3-\delta}$ with rise in magnesium content ($x$), the perovskite-type cubic structure becomes more open, facilitates charge carrier movement, and leads to a high ionic conductivity. The weak band observed with Raman shift of 405 cm$^{-1}$ corresponds to internal $F_{2g}$ (or $v_5$) mode caused by bending of B – O linkages (B = Mg, Al, Fe) belonging to the distorted BO$_6$ octahedra. The corresponding Raman shift usually lies in the range of 305–420 cm$^{-1}$ depending on the nature of B – ions $[52,53]$. Generally, A-O (A = Ba, Sr) linkage modes fall in the low-frequency range (80–281 cm$^{-1}$). But peaks which appear below 200 cm$^{-1}$ only are attributed to stretching vibrations $[32,47,54]$. Notice that the bands observed in the composition of $x = 0.20$ correspond to Raman shift of ~ 122, 165, 405, 540, and 680 cm$^{-1}$. These can be associated with A-O stretching vibrations (122, 165 cm$^{-1}$), bending of B-O linkages (405 cm$^{-1}$), and BO$_6$ symmetric A$_{1g}$

| Composition ($x$) | Oxidation state | Binding energy (eV) | Peak area |
|-------------------|-----------------|---------------------|-----------|
|                   |                 | $2p_{1/2}$ | $2p_{3/2}$ | (%)  |
| 0.05              | Fe$^{3+}$       | 709.91     | 723.32    | 77   |
|                   | Fe$^{4+}$       | 712.82     | 725.62    | 23   |
| 0.10              | Fe$^{3+}$       | 710.41     | 723.42    | 80   |
|                   | Fe$^{4+}$       | 712.76     | 725.57    | 20   |
| 0.15              | Fe$^{3+}$       | 710.02     | 723.56    | 82   |
|                   | Fe$^{4+}$       | 712.25     | 725.52    | 18   |
| 0.20              | Fe$^{3+}$       | 709.88     | 723.68    | 85   |
|                   | Fe$^{4+}$       | 711.48     | 725.46    | 15   |

Figure 6. XPS spectra of O1s for (Ba$_{0.5}$Sr$_{0.5}$)(Al$_{0.2-x}$Mg$_x$Fe$_{0.8}$)O$_{3-\delta}$ ($x = 0, 0.05, 0.10, 0.15, 0.20$) with Gaussian fitting using two peaks in each case. The peaks with higher and lower binding energies are attributed to adsorbed oxygen species and surface oxide, respectively.
stretching, octahedra tilting and/or A-O translation, and oxygen vacancies (540, 680 cm\(^{-1}\)).

Magnesium in \((\text{Ba}_{0.5}\text{Sr}_{0.5})(\text{Al}_{0.2-x}\text{Mg}_x\text{Fe}_{0.8})\text{O}_3-\xi (0 \leq x \leq 0.2)\) compounds (a) expands the ABO\(_3\) cubic cell \((a = 3.953–3.978 \text{ Å})\) due to its size being larger than the substituted Al\(^{3+}\) \((r_{\text{Mg}^{2+}} = 0.72 \text{ Å}, r_{\text{Al}^{3+}} = 0.585 \text{ Å})\), (b) creates additional anion vacancies with oxygen desorption as \(\text{O}^2- \rightarrow \frac{1}{2} \text{O}_2 + e^-\), (c) induces \(\text{Fe}^{4+} \rightarrow \text{Fe}^{3+}\) conversion following \(\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}\), (d) increases the electrical conductivity, and (e) weakens the metal-oxygen bond. These characteristics are consistent and well supported by XPS data and Raman spectra discussed above, evident in Mossbauer studies reported before [30], and responsible for improving the oxygen permeability \((J_{O2})\) of the membrane (thickness ~ 1 mm) to ~ 4.05–4.51 ml/cm\(^2\) min at 1000 °C (measurement details given briefly in the supplementary information). The process involves (i) a reaction \(\text{O}_2 (\text{Air}) + 4e^- \rightarrow 2\text{O}^2-\) at preferential sites on the front surface, (ii) migration of \(\text{O}^2-\) ions via anion vacancies and due to pressure difference across the membrane, and (iii) liberation of oxygen as a molecule with release of associated electrons at the exit surface. The electrons then travel back to the front surface as such or by hopping via \(\text{Fe}^{3+} - \text{O} - \text{Fe}^{4+}\) framework for continuation/recycle of the process. The enhancement in \((J_{O2})\) with Mg\(^{2+}\) content results due to enlarged unit cell, increased

| Composition \((x)\) | Binding energy position (eV) | Attribute |
|-----------------|-----------------------------|-----------|
| 0               | 528.5, 531.0                | Surface oxide, Adsorbed species |
| 0.05            | 528.54, 531.0               | Surface oxide, Adsorbed species |
| 0.10            | 528.56, 531.02              | Surface oxide, Adsorbed species |
| 0.20            | 528.59, 531.05              | Surface oxide, Adsorbed species |

**Figure 7.** (a) Room temperature Raman spectra of \((\text{Ba}_{0.5}\text{Sr}_{0.5})(\text{Al}_{0.2-x}\text{Mg}_x\text{Fe}_{0.8})\text{O}_3-\xi (x = 0, 0.10, 0.15, 0.20)\) in the wave number range of 110–900 cm\(^{-1}\) and (b) deconvoluted fitting curves covering span of 500–850 cm\(^{-1}\) (associated with oxygen vacancies) having peaks at 540 and 680 cm\(^{-1}\) for the composition \(x = 0.20\).
4. Conclusions

Magnetite in (Ba$_{0.5}$Sr$_{0.5}$)(Al$_{0.2}$Mg$_{0.2}$)O$_{3-\delta}$ (x = 0–0.2) brings distortion in oxygen octahedra, creates additional oxygen vacancies, weakens the B-O (B = Al, Mg, Fe) bonds in perovskite ABO$_{3-\delta}$ cubic structure, and induces some Fe$^{4+}$ → Fe$^{3+}$ conversion. These features accompanied by unit cell enlargement provide phase stability and significant improvement in the oxygen permeation in the system.

Disclosure statement

No potential conflict of interest was reported by the authors.

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