Structural and Optical Properties of Sm$^{3+}$ Doped B-site Ba$_{0.5}$Rb$_{0.5}$LaTeO$_6$ Double Perovskites

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Abstract: A double perovskites Ba$_{0.5}$Rb$_{0.5}$LaTeO$_6$ and Ba$_{0.5}$Rb$_{0.5}$La$_{0.5}$Sm$_{0.5}$TeO$_6$ were synthesized by a solid-state reaction method. The structural properties were studied by using the X-Ray powder diffraction (XRD) and fourier transform infrared spectroscopy (FTIR). Structural analysis of XRD based on Rietveld refinement indicates that the Ba$_{0.5}$Rb$_{0.5}$LaTeO$_6$ and Ba$_{0.5}$Rb$_{0.5}$La$_{0.5}$Sm$_{0.5}$TeO$_6$ have cubic symmetry with space group Fm$ar{3}$m. The tolerance factor of the sample also decreases with Sm$^{3+}$ substitution. The value obtained from tolerance factor for Ba$_{0.5}$Rb$_{0.5}$LaTeO$_6$ and Ba$_{0.5}$Rb$_{0.5}$La$_{0.5}$Sm$_{0.5}$TeO$_6$ was 0.994 and 0.982 respectively. The optical properties were studied using the UV visible absorption spectroscopy (UV-vis). The Ba$_{0.5}$Rb$_{0.5}$LaTeO$_6$ and Ba$_{0.5}$Rb$_{0.5}$La$_{0.5}$Sm$_{0.5}$TeO$_6$ was assumed to be indirect band gap and the optical band gap obtained for Ba$_{0.5}$Rb$_{0.5}$LaTeO$_6$ and Ba$_{0.5}$Rb$_{0.5}$La$_{0.5}$Sm$_{0.5}$TeO$_6$ were 4.1 eV and 4.3 eV respectively.

Index Terms: double perovskites, optical properties, structural

1. INTRODUCTION

Double perovskite compounds with the general chemical formula AA'BB'O$_6$, where A, A' are alkali or rare-earth metals and B, B' are transition metals have been extensively studied in recent years [1],[2]. These compounds are important as they exhibit remarkable structural and physical properties which the most significant for the applications in spintronics applications, magnetoresistive and magneto-electric devices [3],[4],[5]. The chemical and physical properties of these compounds depends on the distortion in the structure, vacancies and modifications in composition and occupying the A and B sites cation ordering [6],[7].

The ideal structure of perovskite will form a network of B-O-B bonds because it consists of an array of corner sharing BO$_6$ octahedral at the body centered positions and the A cations at the corners with 12 fold coordination. Structural deformation results in the tilting of the BO$_6$/B'O$_6$ octahedra that affects the interactions along the B-O-B'-O-B paths. The unit cell of double perovskite is twice of the perovskite. Therefore, it has the same arrangement of 12 coordinate A sites and 6 coordinates B sites, but two cations are ordered on the B site [8]. The ideal double perovskite AA'BB'O$_6$ have a cubic symmetry as shown in Fig. [9].

In double perovskites, it is possible to doped at A-site or B-site but as reported by Aslam,H, since A-site mostly occupied by unusual-metals like transition metals that gives strong and magnetic interactions and technical applications. By controlling the size of the A and B-site cation, the crystal structures and physical properties of these materials can be effectively manipulated [10]. It was reported that the for Te-based compounds, SrLaLiTeO$_6$ and BaLaLiTeO$_6$ adopted tetragonal and monoclinic configuration respectively with both has tolerance factor lower than 1. This means that the larger size of Ba$^{2+}$, the structural will distorted and the structure would change due to different ionic radius of A-site [11].

Double perovskites with cations on the B-site show an enormous variety of intriguing electronic or optical properties. ABB'O$_6$ double perovskite can be ordered in octahedral sites and this ordering aided by huge difference in ionic radius and formal charge between B and B' cations [12],[13],[14]. Recently, Bayer reported tellurium-based double perovskites A$_2$MeTeO$_6$ compounds adopts the space group Fm$ar{3}$m, whereas the P$_2$/n monoclinic space group has been confirmed for CaLaLiTeO$_6$ and SrLaLiTeO$_6$ [15]. To the best of our knowledge, there are no reports on the structural and optical properties of Sm$^{3+}$ substitution at B'-site in half-doped rubidium, Ba$_{0.5}$Rb$_{0.5}$La$_{0.9}$Sm$_{0.1}$TeO$_6$. In the present study the crystal structure of Ba$_{0.5}$Rb$_{0.5}$LaTeO$_6$ and Ba$_{0.5}$Rb$_{0.5}$La$_{0.9}$Sm$_{0.1}$TeO$_6$ double perovskites was investigated using X-ray powder diffraction (XRD) and fourier transform infrared spectroscopy (FTIR) and optical properties are reported using UV visible absorption spectroscopy (UV-vis).
II. EXPERIMENT DETAILS

The polycrystalline $\text{Ba}_0.5\text{Rb}_0.5\text{LaTeO}_6$ and $\text{Ba}_0.5\text{Rb}_0.5\text{La}_0.9\text{Sm}_{0.1}\text{TeO}_6$ compound were synthesized by a solid state reaction method. Stoichiometric amounts of high purity (>99.9%) barium carbonate (BaCO$_3$), rubidium carbonate (Rb$_2$CO$_3$), lanthanum oxide (La$_2$O$_3$) and tellurium oxide (TeO$_2$) were mixed thoroughly with agate and mortar, ground for 2 hrs and calcined in air at 850 °C for 24 hr. The mixed oxide powders were reground and calcined at 900 °C for 24 hr. Final compounds were pressed into circular pellets and sintered in air at 950 °C for 24 hrs.

Phase identification of the $\text{Ba}_0.5\text{Rb}_0.5\text{LaTeO}_6$ and $\text{Ba}_0.5\text{Rb}_0.5\text{La}_0.9\text{Sm}_{0.1}\text{TeO}_6$ samples was performed by the X-ray powder diffraction (XRD) at room temperature. The XRD data were recorded using a PANalytical X’pert Pro X-ray diffractometer with CuK$\alpha$ radiation ($\lambda = 1.5406$ Å) in a scattering angle range 20° ≤ 2θ ≤ 80° and scan rate 0.02 °/s. Rietveld refinement and the structural analysis was carried out using GSAS program and EXPGUI interface [16,17] and visualized using VESTA program. Peak shape was modelled by pseudo-Voigt function refined together with cell parameter, scale factor, zero factor and background function. The IR reflectance spectra were recorded in FTIR-Raman Drift Nicolet 6700 equipment ranging from 400 to 1500 cm$^{-1}$ with a resolution of 1 cm$^{-1}$. The sample were mixed thoroughly with potassium bromide, KBr before the FT-IR characterization. Optical study performed by using Lambda 750, Perkin Elmer, Waltham, USA equipment for 2 to 5 h range.

III. RESULTS AND DISCUSSION

A. Structural Analysis

Fig. 2 shows the X-ray diffraction pattern of $\text{Ba}_0.5\text{Rb}_0.5\text{LaTeO}_6$ and $\text{Ba}_0.5\text{Rb}_0.5\text{La}_0.9\text{Sm}_{0.1}\text{TeO}_6$ where the presence of the sharp Bragg peaks signify the highly crystalline nature of the sample. There is no extra peak of the sample $\text{Ba}_0.5\text{Rb}_0.5\text{LaTeO}_6$, suggesting a pure single phase structure. The XRD indicates no structural change however some unknown impurity phase was detected for doped Sm$^{3+}$ with 0.1 concentrations and indicated by (*). The peaks of the XRD pattern of $\text{Ba}_0.5\text{Rb}_0.5\text{LaTeO}_6$ and $\text{Ba}_0.5\text{Rb}_0.5\text{La}_0.9\text{Sm}_{0.1}\text{TeO}_6$ were indexed in the cubic Fm\(\overline{3}\)m space group system using software GSAS and EXPGUI as reported in the JCPDS File No.01-070-4384 [18]. Refinement of all parameters are performed until convergence with the value of chi-square close to 1, which confirms the goodness of refinement. The Rietveld refinement are shown in Fig. 3. The determined lattice parameter obtained for of $\text{Ba}_0.5\text{Rb}_0.5\text{LaTeO}_6$: $a=b=c=8.578$ Å, $a=\beta=\gamma=90^\circ$ and unit cell volume, $V = 631.21$ Å$^3$ and for $\text{Ba}_0.5\text{Rb}_0.5\text{La}_0.9\text{Sm}_{0.1}\text{TeO}_6$: $a=b=c=8.574$ Å, $a=\beta=\gamma=90^\circ$ and unit cell volume, $V = 631.10$ Å$^3$, as reported by Tamraoui et al [19]. A decrease in lattice parameters might be due to the Sm substitutions at La-site as Sm has larger ionic radius compared to La. The structure of $\text{Ba}_0.5\text{Rb}_0.5\text{LaTeO}_6$ in Fig. 4 were obtained through VESTA software [20]. The similarities in the lattice parameter of $\text{Ba}_0.5\text{Rb}_0.5\text{LaTeO}_6$ and $\text{Ba}_0.5\text{Rb}_0.5\text{La}_0.9\text{Sm}_{0.1}\text{TeO}_6$ suggest that the compounds are isostructural. The polyhedral ordering of the La (4e) and Te (4b) cations and Ba/Rb is randomly distributed at (8c). The Te and La are in octahedral coordination and occupy B site with 100% rock salt type ordering. Rb ion is expected to occupy A site due to their large ionic radii. The result obtained matched the previous studies [21,22]. The values from the Rietveld analysis and metal-oxygen bond length are summarized in Table-I and Table-II.

Tolerance factor is a vital structural parameter which reflects the local distortion from the ideal perovskite structure, ABO$_3$. Tolerance factor calculated for $\text{Ba}_0.5\text{Rb}_0.5\text{LaTeO}_6$ and $\text{Ba}_0.5\text{Rb}_0.5\text{La}_0.9\text{Sm}_{0.1}\text{TeO}_6$ sample are 0.994 and 0.982 respectively. These values verify that the compounds are a cubic symmetry. The Goldschmidt tolerance factor is defined as [23]:

$$t = \frac{r_\text{A} + r_\text{O} - r_\text{B}}{\sqrt{2(r_\text{A} + r_\text{B})}}$$

Where $r_\text{A}$ is the average ionic radius at the A-site of the ABO$_3$ type compound, $r_\text{B}$ and $r_\text{O}$ are the ionic radii of the B-site and O-site respectively. The ionic radii used for the calculating tolerance factor are Ba$^{2+}$ = 1.61 Å, La$^{3+}$ = 1.36 Å, Rb$^{+}$ = 1.72 Å, Te$^{6+}$ = 0.56 Å and O$^{2-}$ = 1.35 Å [24].

The observed XRD pattern and obtained lattice parameters are very much similar and consistent with the reported ones [22]. The crystallite size (D) of the sample can broadly be determined by using peak broadening, scattering angle, wavelength, and optimized constant of diffraction peaks in Scherrer’s equation [25]. The crystallite size, D was calculated using the Scherrer equation,

$$D = \frac{K\lambda}{\beta\cos\theta}$$

where $K$ is constant with 0.94, $\lambda$ is wavelength of XRD which is 1.5405 Å and $\beta$ is full width at half maximum (FWHM) and $\theta$ is the angle of peak of XRD. The calculated value of crystallite size of $\text{Ba}_0.5\text{Rb}_0.5\text{LaTeO}_6$ and $\text{Ba}_0.5\text{Rb}_0.5\text{La}_0.9\text{Sm}_{0.1}\text{TeO}_6$ is $D = 54.98$ nm and 65.27 nm respectively.
Fig. 3: Rietveld refinement of X-ray diffraction pattern \( \text{Ba}_{0.5}\text{Rb}_{0.5}\text{LaTeO}_6 \). Blue solid lines are observed data, the solid red line is the calculated pattern, and the pink line is the difference. Tick marks indicate the allowed Bragg reflections for \( \text{Ba}_{0.5}\text{Rb}_{0.5}\text{LaTeO}_6 \).

Fig. 4: The crystallographic structure for \( \text{Ba}_{0.5}\text{Rb}_{0.5}\text{LaTeO}_6 \).

Green colored balls represent the Ba, pink colored balls represent the Rb, purple balls represent the La, orange balls represent the Sm and red colored balls represent the O.

Table I. Lattice parameters, unit cell volume, tolerance factor \((\tau)\), goodness of fit of \( \text{Ba}_{0.5}\text{Rb}_{0.5}\text{LaTeO}_6 \) and \( \text{Ba}_{0.5}\text{Rb}_{0.5}\text{La}_{0.9}\text{Sm}_{0.1}\text{TeO}_6 \) as obtained from Rietveld refinement

<table>
<thead>
<tr>
<th>Parameters</th>
<th>( \text{Ba}<em>{0.5}\text{Rb}</em>{0.5}\text{LaTeO}_6 )</th>
<th>( \text{Ba}<em>{0.5}\text{Rb}</em>{0.5}\text{La}<em>{0.9}\text{Sm}</em>{0.1}\text{TeO}_6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetry</td>
<td>Cubic</td>
<td>Cubic</td>
</tr>
<tr>
<td>Space Group</td>
<td>( \text{Fm-3} )</td>
<td>( \text{Fm-3} )</td>
</tr>
<tr>
<td>( a=b=c )</td>
<td>8.578(19)</td>
<td>8.574(24)</td>
</tr>
<tr>
<td>( \alpha=\beta=\gamma )</td>
<td>90.0</td>
<td>90.0</td>
</tr>
<tr>
<td>Unit cell volume (( V ))</td>
<td>631.21</td>
<td>631.10</td>
</tr>
<tr>
<td>Tolerance Factor (( \tau ))</td>
<td>0.994</td>
<td>0.982</td>
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</table>

Table II. Selected bond length and bond angle for the \( \text{Ba}_{0.5}\text{Rb}_{0.5}\text{LaTeO}_6 \) and \( \text{Ba}_{0.5}\text{Rb}_{0.5}\text{La}_{0.9}\text{Sm}_{0.1}\text{TeO}_6 \)

<table>
<thead>
<tr>
<th>Bond length (( \text{Å} )) and Bond Angles (( ^\circ ))</th>
<th>( \text{Ba}<em>{0.5}\text{Rb}</em>{0.5}\text{LaTeO}_6 )</th>
<th>( \text{Ba}<em>{0.5}\text{Rb}</em>{0.5}\text{La}<em>{0.9}\text{Sm}</em>{0.1}\text{TeO}_6 )</th>
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<tbody>
<tr>
<td>Te-O x 6</td>
<td>1.92 (3)</td>
<td>1.92(8)</td>
</tr>
<tr>
<td>La-O x 6</td>
<td>2.01(6)</td>
<td>2.10(4)</td>
</tr>
<tr>
<td>(Ba/Rb)-O x 12</td>
<td>3.02 (5)</td>
<td>2.89(8)</td>
</tr>
<tr>
<td>O-Te-O x 12</td>
<td>180</td>
<td>180</td>
</tr>
<tr>
<td>O-Te-O x 3</td>
<td>90</td>
<td>90</td>
</tr>
</tbody>
</table>

B. Fourier Transform Infrared Spectroscopy (FTIR)

Fig. 5 shows broad absorption band by using FTIR in range 800-1500 cm\(^{-1}\). The peaks of the samples at around 1422 and 1427 cm\(^{-1}\) might be due to vibrations of carbonate in \( \text{Ba}_{0.5}\text{Rb}_{0.5}\text{LaTeO}_6 \) and \( \text{Ba}_{0.5}\text{Rb}_{0.5}\text{La}_{0.9}\text{Sm}_{0.1}\text{TeO}_6 \) [26]. Another peak at around 1700 cm\(^{-1}\) might be due to presence of adsorbed moisture in KBr during the synthesis of the samples [27]. There is observable weak peak at 857 cm\(^{-1}\) which is due to external mode other than Te(Li)O\(_6\) octahedra [28],[29].
C. UV-vis Spectroscopy

The obtained spectra of diffuse reflectance measurements were performed in the wavelength of 200-1000 nm at room temperature as displayed by Fig. 6 for the Ba$_{0.5}$Rb$_{0.5}$LaTeO$_6$ and Ba$_{0.5}$Rb$_{0.5}$La$_{0.9}$Sm$_{0.1}$TeO$_6$. Both samples was assumed to be an indirect band gap. This is because the reflectance spectra have a gentle slope than what had been predicted for a direct transition [30]. As stated by Amrithakrishnan. B, the absorption of light includes the absorptive process of phonons also in the indirect transition [11]. In order to determine the optical band gap, the diffuse reflectance was converted into the Kubelka-Munk function given by

$$F(R) = \frac{(1-R)^2}{2R}$$

where \(R\) is the diffuse reflectance. For indirect allowed transition, the band gap \(E_g\) can be calculated using the equation

$$F(R)h\nu = (h\nu - E_g)^2$$  \hspace{1cm} (4)

The band gap was obtained from the x-intercept of the linear plot between (F(R) h\nu)$^{1/2}$ and h\nu . The optical band gap obtained for Ba$_{0.5}$Rb$_{0.5}$LaTeO$_6$ and Ba$_{0.5}$Rb$_{0.5}$La$_{0.9}$Sm$_{0.1}$TeO$_6$ were 4.1 eV and 4.3 eV respectively. It was illustrated in Fig. 7. The results of the UV-vis diffuse reflectance and the optical energy gap of the sample series indicate that they can be classified as wide band gap semiconductor materials. Further investigation on area such as gas sensor can be done due to having properties of semiconductor material.

IV. CONCLUSION

In conclusion, the structural and optical of Ba$_{0.5}$Rb$_{0.5}$LaTeO$_6$ and Ba$_{0.5}$Rb$_{0.5}$La$_{0.9}$Sm$_{0.1}$TeO$_6$ by using solid state method had been investigated using XRD, FTIR and UV-vis. Our results have shown that all samples have the cubic crystallographic structure and the unit cell volume decrease from 631.21 Å$^3$ to 631.10 Å$^3$ due to different ionic radii of the Sm$^{3+}$ and La$^{3+}$. The parameters obtained from UV vis spectroscopy indicate that the Ba$_{0.5}$Rb$_{0.5}$LaTeO$_6$ and Ba$_{0.5}$Rb$_{0.5}$La$_{0.9}$Sm$_{0.1}$TeO$_6$ was assumed to be an indirect band gap. The optical band gap obtained for Ba$_{0.5}$Rb$_{0.5}$LaTeO$_6$ and Ba$_{0.5}$Rb$_{0.5}$La$_{0.9}$Sm$_{0.1}$TeO$_6$ were 4.1 eV and 4.3 eV respectively. The substitutions of Sm$^{3+}$ has remarkable effects on the structural and optical of the system double perovskites.
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