SYNTHESIS AND PHYSICAL PROPERTIES OF THE NEW DOUBLE PEROVSKITE $X_2\text{AlVO}_6$ ($X=$Ca, Sr & Ba)

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ABSTRACT
Three members of the double perovskite materials $X_2\text{AlVO}_6$ ($X=$ Ca, Sr and Ba) were synthesis by solid state interaction method. Crystal structure, optical and dielectrical properties calculations of these double perovskite materials were described. X- Ray Diffraction (XRD), Fourier Transform Infra Red (FTIR), Ultra Violet visible (UV), and Impedance spectroscopies were used as analytical techniques. XRD measurements showed that these materials are crystallize in orthorhombic double perovskite structures with (Pnma) space group. Unit cell parameters, atomic positions, crystalline size and site occupations were calculated by standared Rietveld method through the Fullprof program. Lattice parameters were $a=b=5.4798$ Å and $c=7.7621$ Å for $\text{Ca}_2\text{AlVO}_6$, $a=b=5.5518$ Å and $c=7.8695$Å for $\text{Sr}_2\text{AlVO}_6$ and $a=b=5.5759$ Å and $c=7.89380$ Å for $\text{Ba}_2\text{AlVO}_6$. The energy gap were calculated for $\text{Ca}_2\text{AlVO}_6$, $\text{Sr}_2\text{AlVO}_6$ and $\text{Ba}_2\text{AlVO}_6$, and found to be 4.16eV, 4.79eV and 4.87eV respectively.

KEY WORDS: Double perovskite, energy gap, Impedance, space group, XRD.

INTRODUCTION
In the recent past, a high attention was focus on perovskite type compounds which show a large diversity of interesting electrical, optical and magnetic functional properties outcome their compositional and structural variety. As the previous studies, many compounds that belong to this group have been synthesized. The perovskites formula is $\text{ABO}_3$, where A and B might be almost any metal or semimetal from the periodic table\(^{[1-3]}\). The general chemical formula of double perovskite oxides expressed as $\text{A}_2\text{BB'}\text{O}_6$, where A is Ca, Sr and Ba. The B site is occupied by first row of 3d magnetic element in the perodic table, where the B’ site is occupied by the 4d nonmagnetic elements, with O atom located in between forming alternate $\text{BO}_6$ octahedral and B-O-B bonds. The wide range of double perovskite material is due to alteration at the magnetic and non–magnetic of B and B’ elements as well as the A-site cations\(^{[4, 5]}\). In particular, the compositions $\text{A}_2\text{BMO}_6$, where B = Fe, Mn, Cr are magnetic ions are currently studied for their potentiality as magnetoresistive systems and thermoelectrics\(^{[6]}\). The synthesis and structural properties of new Dy$_2$MgTiO$_6$ and Gd$_2$MgTiO$_6$ perovskite-like material was performed. These materials crystallize in monoclinic double perovskites with P2/n space group that showed by Rietveld analyses. These double perovskite compounds had semiconducting behavior, which showed by Density of states results, with energy gap between 0.6 eV and 0.73 eV and effective magnetic moment of 13.9 $\mu_B$ and 10.1 $\mu_B$ for Dy$_2$MgTiO$_6$ and Gd$_2$MgTiO$_6$, consecutively, which are majority due to the f-orbitals of the rare earth cations\(^{[7]}\). $\text{ALaFeTiO}_6$ (A= Ba, Sr and Ca) double perovskite oxides of chemical mode had been done by following the precursor method, and the structural analysis of $\text{BaLaFeTiO}_6$ is cubic and consistency with it’s tolerance factor\(^{[8]}\). La$_{1-x}$K$_x$MnO$_3$ perovskites ($x=0.1, 0.125$ and $0.150$) had prepared by solid-state reaction method, rhombohedral-distorted structure showed by the Rietveld refinements of X-ray diffraction patterns\(^{[9]}\). Spin-reorientation situation of YFe$_{1-x}$Mn$_x$O$_3$ ($x=0.0, 0.2$) perovskite had showed and corroborated by magnetic properties and Mossbauer spectroscopy. The spin-reorientation transition temperature (TSR) increment when the N’eel temperature (TN) decrement with increasing x, under the weakening of the exchange interaction between Fe ions. They shown occurrence of spin-reorientation relative to crystal axes from the Mossbauer spectra of YFe$_{1-x}$Mn$_x$O$_3$ ($x=0.1, 0.2$)\(^{[10]}\). Solid-state technique was used to synthesized $\text{Ce}_2\text{CeNbO}_6$ double perovskite oxide. The orthorhombic perovskite structure, the electrical and optical properties of this materail had studied, all the peak that refer to the double perovskite structure bonds showed in small hump. The frequency- dependent electrical data were analyzed in the framework of conductivity and electric modulus formalisms. Frequency dependent imaginary electric modulus (M”) subjected to an Arrhenius law\(^{[11]}\). The $\text{Sr}_2\text{CaW}_x\text{Mo}_{1-x}\text{O}_6$ double perovskite series have been synthesized by solid–state reaction. The self- activated host material emit strong blue lights at round 435 and 468 nm upon the excitation of near –UV at about 290nm due to W-O charge transfer transition. The hosts show weak orange–red emission by excitation of 400nm due to Mo-charge transfer transition\(^{[12]}\). The aim of this work is to synthesize new samples of double provskite oxides by solid state interaction method. In addition, the structural, optical and
Properties of the new double perovskite $X_2\text{AlVO}_6$ (X=Ca, Sr & Ba)

**MATERIALS & METHODS**

The new samples of double proviskite oxides synthesized by solid state interaction method by different treatments to get single phase for the samples. The samples prepared by mixing stoichiometric amounts of $\text{Al}_2\text{O}_3$, $\text{V}_2\text{O}_5$ with (CaCO$_3$, SrCO$_3$ and BaCO$_3$) all from Alfa Acer of purity 99.9% were used to prepare the $X_2\text{AlVO}_6$ Where X are (Ca or Sr or Ba). The mixtures of compounds ground in agate mortar with the addition of acetone then heated in air, after put in crucibles initially at 800°C during 12 hours four times, pellet in around shape and heated in 1200°C three times permeated every time grinding with the addition of acetone, the ratio of all amounts calculated by the fowling equations:

$$\frac{2\text{CaCO}_3}{2\text{SrCO}_3} \quad \frac{1}{2} \frac{\text{Al}_2\text{O}_2}{2\text{BaCO}_3} \quad \rightarrow \quad X_2\text{AlVO}_6 + \text{CO}_2 \uparrow$$ (1)

X-ray diffraction (XRD) used is a Bruker - axs D8- Focus X-ray diffractometer. The data were collected for the 29 range 20° – 80° at step size of 0.02 and count time of 5s. The collected data are then fed to fullprof suite for determination of the lattice parameters, space group, atom’s positions and crystalline size by scherrer equation.

$$D = \frac{0.944}{\beta_{1/2} \cos \theta}$$ (2)

A Fourier transform infrared (FTIR) spectrum was recorded in transmittance mode at room temperature between 400 and 2000 cm$^{-1}$ with a Fourier transform infrared spectrometer (Satellite FTIR 5000) in the wavelength range of 400 to 4000 cm$^{-1}$ [15]. The UV-visible absorption spectrum was obtained by an automatic recording single beam spectrophotometer type UV Mini 1240 manufactured by Shimadzu company–Japan and coming with serial number A10934081718SM. HCl was used as a reference for 100% absorbance, after that the Energy Gap was measured for all samples [16].

The LCR Meter used to study the dielectric properties; both flat surfaces of pellets were electrode with fine silver paint and were kept at 1200°C for 12 h prior to conducting the experiment impedance of the sample measured as a function of frequency (10 Hz- 1MHz) at room temperature. The resistivity, conductivity and dielectric constant were calculated at $\omega = 100$ Hz [17].

**RESULTS & DISCUSSION**

**X-ray diffraction (XRD) analysis**

Figure (1) shows the room temperature XRD pattern of $\text{Ca}_2\text{AlVO}_6$, $\text{Sr}_2\text{AlVO}_6$ and $\text{Ba}_2\text{AlVO}_6$ respectively. All reflection peaks of the X-ray profile and lattice parameters determined with full proof program, they had orthorhombic crystal structure with (Pnma) space group. The XRD results have been fitted by standard Rietveld method using the Fullprof suite and Figure (2) shows the case of $\text{Ba}_2\text{AlVO}_6$. Elena-Adriana Perianu [1] studied Preparation and Dielectric Spectroscopy Characterization of $\text{A}_3\text{MnMoO}_6$ (A = Ca, Sr and Ba) Double Perovskites and they found that the size of cation X seems to be relevant to the structural distortions. In our case the tolerance factor increases with the size of cation X: with increasing of the ionic radius in the series $r_{\text{Ca}^{2+}} < r_{\text{Sr}^{2+}} < r_{\text{Ba}^{2+}}$, the tolerance factor increases from t = 0.9064 (for compound with Ca$^{2+}$) at t = 0.9584 (for compound with Sr$^{2+}$) and at t = 1.0160 (for compound with Ba$^{2+}$) [1]. The size of cation X seems to be relevant to the structural distortions. In our case the tolerance factor increases with the size of the cation X: with increasing of the ionic radius in the series $r_{\text{Ca}^{2+}} < r_{\text{Sr}^{2+}} < r_{\text{Ba}^{2+}}$, the tolerance factor T = $r_{\text{X}^{2+}} + r_{\text{O}^{2-}} / r_{\text{Ca}^{2+}} + r_{\text{O}^{2-}}$ increases from T=0.9926 (for compound with Ca$^{2+}$) at T= 1.0496 (for compound with Sr$^{2+}$) and at T= 1.1127 (for compound with Ba$^{2+}$), and the crystalline size increases with the size of the cation X: with increasing of the ionic radius in the series $r_{\text{Ca}^{2+}} < r_{\text{Sr}^{2+}} < r_{\text{Ba}^{2+}}$, the crystalline size increases from D = 61.61nm (for compound with Ca$^{2+}$ at D = 69.83nm (for compound with Sr$^{2+}$) and at D = 76.38nm (for compound with Ba$^{2+}$). The obtained lattice parameters and atoms position listed in Table (1), crystalline size calculated by scherrer equation [19]. Figure (3) show the relation between crystalline size and Tolerance factor with ionic radius of X-site, and the crystalline size and tolerance factor are list in table (2).

**FTIR – UV visible** spectroscopy analysis

The two major absorptions peaks are explicitly split, probably as an effect of the orthorhombic distortion of the unit cell. The strong high-energy band centered at about 640 cm$^{-1}$ can surely be assigned to the anti-symmetric stretching mode of the (Al–O$_6$) and (V–O$_6$) octahedra, due to the higher charge of this cation. Another interesting point appear by this spectra is the presence of the high intensity band at 825 cm$^{-1}$ which can eventually be assigned to the symmetric stretching vibration of these octahedra as explained in figure (4). The positions of these bands suggests relatively long (Al–O$_6$) and (V–O$_6$) bonds [18]. All the peaks in the spectrum are assigned small hump at approximately 1645 cm$^{-1}$ which is due to the presence of adsorbed moisture in KBr during the synthesis of all samples [20]. The peak around 1400 cm$^{-1}$ likely corresponds to overtones of the substantial vibrations in $X_2\text{AlVO}_6$ where X= (Ca, Sr and Ba), Chandrahas Bharti,T.P. Sinha showed that in another study [21]. Figure (5) shows the FTIR spectrum of $X_2\text{AlVO}_6$ where (X= Ca,Sr and Ba). All the peaks in the spectra are the characteristics of the material.
TABLE 1: The lattice parameter and atoms position, of the samples

<table>
<thead>
<tr>
<th>Element</th>
<th>Coordinate</th>
<th>Ca$_2$AlVO$_6$</th>
<th>Sr$_2$AlVO$_6$</th>
<th>Ba$_2$AlVO$_6$</th>
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<td>Ca/Sr/Ba$_2$</td>
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</table>

$\alpha = \beta = \gamma = 90^\circ$

$a$ A$_0$ = 5.4798

$b$ A$_0$ = 5.4798

$c$ A$_0$ = 7.7642

TABLE 2: Tolerance factor and crystalline size (nm) of all samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>T (Tolerance Factor)</th>
<th>D (Crystalline size)(nm)</th>
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<tr>
<td>Ca$_2$AlVO$_6$</td>
<td>0.9064</td>
<td>61.61</td>
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<td>Sr$_2$AlVO$_6$</td>
<td>0.9584</td>
<td>69.83</td>
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<td>Ba$_2$AlVO$_6$</td>
<td>1.0160</td>
<td>76.38</td>
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TABLE 3: the wave length and band gap energy list of all samples

<table>
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<th>Samples</th>
<th>($\lambda$)nm</th>
<th>band gap energy (eV)</th>
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<td>Ca$_2$AlVO$_6$</td>
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<td>Sr$_2$AlVO$_6$</td>
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<td>Ba$_2$AlVO$_6$</td>
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TABLE 4: Dielectric Impedance parameters (and dielectric constant at $\omega = 100$ Hz) at room temperature

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<th>Sample</th>
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<th>$Z''$</th>
<th>$Z'$(M$\Omega$)</th>
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<th>$\sigma$'(M$\Omega$.m)</th>
<th>$\varepsilon'$</th>
</tr>
</thead>
<tbody>
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<td>Ca$_2$AlVO$_6$</td>
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<td>5.0x10$^8$</td>
<td>1641</td>
<td>6.24x10$^5$</td>
<td>1.6x10$^6$</td>
<td>1.1x10$^9$</td>
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<tr>
<td>Sr$_2$AlVO$_6$</td>
<td>2.1x10$^8$</td>
<td>3.4x10$^8$</td>
<td>407</td>
<td>2.38x10$^5$</td>
<td>4.2x10$^6$</td>
<td>9.3x10$^9$</td>
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<tr>
<td>Ba$_2$AlVO$_6$</td>
<td>1.2x10$^8$</td>
<td>2.3x10$^8$</td>
<td>123</td>
<td>1.59x10$^5$</td>
<td>6.3x10$^6$</td>
<td>5.9x10$^9$</td>
</tr>
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</table>
Properties of the new double perovskite $X_2AlVO_6$ ($X$=Ca, Sr & Ba)

**FIGURE 1:** The room temperature XRD pattern of Ca$_2$AlVO$_6$, Sr$_2$AlVO$_6$ and Ba$_2$AlVO$_6$ samples

**FIGURE 2:** The XRD diffractograms of the Ba$_2$AlVO$_6$ sample

**FIGURE 3:** Relation between crystalline size and Tolerance Factor ionic with radius of X-site
Figure (6) shows the absorption spectrum of samples that dispersed in hydrochloric acid solution. The mean exciton absorption was found at Convergent values. The intensity of absorption is high, this is due to the high concentration of solution. The relation between the absorption and wavelength shows for the samples, and by using Tauc plot method the energy gap were calculated for Ca$_2$AlVO$_6$, Sr$_2$AlVO$_6$ and Ba$_2$AlVO$_6$, and found to be 4.16eV, 4.79eV and 4.87eV respectivily \cite{22}.

$$\alpha h\nu = A(h\nu - E_g)^n$$  \hspace{1cm} (3)

Where $E_g$ the band gap, constant A is different for different transitions, (h$\nu$) is energy of photon and n value is respectively 1/2 and 2 for direct and indirect transition, Figure (7) refer to the Tauc plot of Ba$_2$AlVO$_6$ case, the wavelength and band gap energy were listed for the samples in table (3).
Impedance spectroscopy analysis

In order to understand the dynamics of the mobile ions (dielectric relaxation) in $X_2\text{AlVO}_6$ where ($X=\text{Ca}, \text{Sr}$, and $\text{Ba}$), the complex plane impedance ($z^*=z'-z''$) plots for $X_2\text{AlVO}_6$ where ($X=\text{Ca}, \text{Sr}$, and $\text{Ba}$) at room temperature are shown in fig.4 using cole cole plot. Complex plane impedance spectra can be seen as semicircles along frequencies and their center are depressed to below the real impedance axes, figure (8) expresses the complex plane impedance spectra $\text{Ba}_2\text{AlVO}_6$ case.

The samples have similar represented from relation between $|Z|$ against the applied frequency. Figure (9) is graph of $|Z|$ against the applied frequency shows that for $\text{Ba}_2\text{AlVO}_6$ case a higher values of $|Z|$ with a long value of low frequency and vice-versa, that mean the dielectric constant was found at lower frequency and this refer to insulator behavior. The dielectric constant, impedance, resistivity and conductivity were calculated for all samples for $X_2\text{AlVO}_6$ where ($X=\text{Ca}, \text{Sr}$, and $\text{Ba}$) at room temperature, the positive dielectric constants might be attributed to insulator materials. Table (4) shows dielectric impedance parameters (and dielectric constant at $\omega = 100$ Hz) at room temperature.

![Graph 7](image1.png)

**FIGURE 7:** Give the plot of $(\chi hv)^2$ in term of band gap for $\text{Ba}_2\text{AlVO}_6$ double perovskite

![Graph 8](image2.png)

**FIGURE 8:** (Cole Cole plot) complex plane impedance spectra for $\text{Ba}_2\text{AlVO}_6$ sample

![Graph 9](image3.png)

**FIGURE 9:** Graphs of $|Z|$ against the applied frequency for $\text{Ba}_2\text{AlVO}_6$ sample.
CONCLUSION
The X-site substitutions of $X_2$AlVO$_6$ where (x = Ca, Sr and Ba) were achieved successfully using solid reaction method. XRD proved that the structure is orthorhombic with (pnnm) space group and crystalline size was found to be 61.61, 69.83 and 76.38 nm. FTIR showed numbers of peaks and were assigned to double perovskite structure. UV studied and the energy band gap found to be in the range 4.1eV to 4.8 eV. Dielectric constants takes the positives values which are indicate that the samples possess an insulators behavior.

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REFERENCES