A phosphor emitting at wavelengths greater than 650 nm is not an efficient red photon generator for use in general illumination. This is because the spectrum of such phosphors will make a poor match with the human eye response (luminosity response function) resulting in low brightness even when the quantum efficiency of the phosphor is high. However, the far-red (FR) region (700–740 nm) of the spectrum generated by the deep red emitting phosphors has significant implications for plants. An important family of plant photoreceptors are the phytochromes (PHYs) that sense and signal changes in the red (660–730 nm) and the far-red (725–735 nm) ratios in a given spectrum. Exposure of the plant to red light produces the biologically active PHY photoisomer (Pr) while reversion to the inactive form (Pfr) occurs under FR light. They act as rapid and reversible molecular switches that can be used to control a wide variety of plant characteristics. The balance of red to FR light is critical in nature and controlled environment agriculture as it regulates processes ranging from seed germination, height, leaf expansion, branching, plant immunity, circadian rhythm, leaf chlorophyll concentration to freezing tolerance. Additionally, FR light plays a role in photosynthesis. The two photosystems (PSI and PSII) work electrochemically in series to generate the chemical energy required by the plant for growth and development. They absorb different regions of the spectrum with the quantum yields for PSI being greatest < 680 nm and is greatest between 680 nm and 720 nm for PSII. In short, phosphors emitting wavelengths between 700–740 nm can be used to induce or inhibit photomorphogenesis (light mediated plant characteristics). The resulting emission spectrum is in the deep red because of the Mn<sup>4+</sup> emission transition. Which per the literature reveals that the 4A<sub>2g</sub> emission transition is determined by octahedral site distortion. The greater is the site distortion, the lower is the Mn-O covalent interaction and the higher is the energy of the 2E<sub>g</sub>→4A<sub>2g</sub> emission transition. The work provides guidelines for the development of deep red emitting phosphors for agricultural (horticultural) applications.

The compounds La<sub>2</sub>MgTiO<sub>6</sub>, La<sub>2</sub>MgGeO<sub>6</sub>, La<sub>2</sub>LiTaO<sub>6</sub>, La<sub>2</sub>MgSiO<sub>4</sub>, LaAlO<sub>3</sub>, LaGaO<sub>3</sub>, GdAlO<sub>3</sub>, CaAl<sub>2</sub>O<sub>4</sub>, SrTiO<sub>3</sub>, Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub> and Ca<sub>4</sub>ZrO<sub>3</sub> have been reported in the literature for their emission in red wavelengths. For these perovskite-based phosphors we investigated the optical properties of Mn<sup>4+</sup> and the higher is the energy of the 2E<sub>g</sub>→4A<sub>2g</sub> emission transition. The work provides guidelines for the development of deep red emitting phosphors for agricultural (horticultural) applications.

The optical properties of Mn<sup>4+</sup> (3d<sup>3</sup>) in the double perovskites, La<sub>2</sub>LiSbO<sub>6</sub> and La<sub>2</sub>MgTiO<sub>6</sub>, are investigated. The Mn<sup>4+</sup> energy levels are calculated using the exchange charge model of crystal-field theory and compared with the experimental spectroscopic data. A comparative study of the optical properties of Mn<sup>4+</sup> in the perovskite structure shows that energy of the 2E<sub>g</sub>→4A<sub>2g</sub> emission transition is determined by octahedral site distortion. The greater is the site distortion, the lower is the Mn-O covalent interaction and the higher is the energy of the 2E<sub>g</sub>→4A<sub>2g</sub> emission transition. The work provides guidelines for the development of deep red emitting phosphors for agricultural (horticultural) applications.

The compound La<sub>2</sub>Li(Sb<sub>0.998</sub>Mn<sub>0.002</sub>)O<sub>6</sub> was synthesized by a conventional solid-state reaction technique. Prior to its use as the starting compound that crystallize in the perovskite structure. Examples include Gd<sub>2</sub>MgTiO<sub>6</sub>, Ba<sub>2</sub>LaNbO<sub>6</sub>, NaLaMgTeO<sub>4</sub>, CaZrO<sub>3</sub>, LaAlO<sub>3</sub>, LaGaO<sub>3</sub>, GdAlO<sub>3</sub>, Ca<sub>2</sub>SiO<sub>4</sub>, YbAlO<sub>3</sub> and SrTiO<sub>3</sub>. The goal of our program is to develop a set of guidelines for tuning the wavelength of the 2E<sub>g</sub>→4A<sub>2g</sub> emission transition, which per the Tanabe-Sugano diagram for d<sup>4</sup> ions, depends chiefly on the “Mn<sup>4+</sup>−ligand” bonding covalence. Analysis of data presented in the archival literature reveals that the 2E<sub>g</sub>→4A<sub>2g</sub> transition energy changes little in fluoride compounds and varies greatly in oxides. This is because variation in covalence is smaller in fluorides than in oxides. Recently, we have presented how the “Mn<sup>4+</sup>−ligand” covalent mixing is influenced by connectivity of the octahedral moieties and deviation of O-Mn-O bond angle from the ideal value of 90° in oxides. We examined cases where the octahedral groups share corners (as in the ABO<sub>3</sub> and A<sub>2</sub>B B′ O<sub>6</sub> perovskites) or edges and faces as in α-LiAlO<sub>2</sub>, Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub> and CaAl<sub>2</sub>O<sub>4</sub>. It was concluded that a highly symmetrical octahedral moiety increases “Mn<sup>4+</sup>−ligand” bonding covalence. The resulting emission spectrum is in the deep red because of the lowering of the 2E<sub>g</sub>→4A<sub>2g</sub> emission transition energy. Thus, a strategy for generating deep red photons in the perovskite structure for plant growth is to substitute Mn<sup>4+</sup> in sites with near ideal O<sub>6</sub> symmetry that maximizes “Mn<sup>4+</sup>−ligand” bonding covalence. This can be achieved by choosing a perovskite lattice in which the corner linked octahedral groups with equal M-L bond lengths and O-M-O bond angles that do not deviate from the ideal values.

In this paper, we report the synthesis and spectroscopic properties of the double perovskite La<sub>2</sub>LiSbO<sub>6</sub> activated with Mn<sup>4+</sup>. For comparative purposes, we also evaluate the spectroscopic data of the double perovskite La<sub>2</sub>MgTiO<sub>6</sub>:Mn<sup>4+</sup>, which has been reported in the literature. For both compounds, the energy position of the Mn<sup>4+</sup> emission wavelength with structural peculiarities that control the covalence of “Mn<sup>4+</sup>−ligand” bonding.
material, La$_2$O$_3$ (Alfa Aesar, 99.99%) was heated to 1000°C under nitrogen atmosphere. An excess (50 mole% over the stoichiometric proportion) of the starting material Li$_2$CO$_3$ (Alfa Aesar, 99.998%) was added to compensate for any loss of lithium occurring because of the high vapor pressure at high temperatures during synthesis. These starting materials were blended with Sb$_2$O$_3$ (Alfa Aesar, 99.9%) and Mn$_2$O$_3$ (Aldrich 99.999%) and heated in air at 700°C for one hour. The resulted powder was ball milled and heated to 1000°C for 10 h to form the final product.

Luminescence measurements were performed as previously described. The spectra were corrected for the wavelength dependent variations in the Xe-lamp intensity and the photomultiplier response.

Crystal Structure of La$_2$LiSbO$_6$ and La$_2$MgTiO$_6$ and Method of Calculations

Structural studies on La$_2$LiSbO$_6$ are presented in References 25,26. The compound crystallizes in the P2$_1$/C space group (No. 14) with two formula units per unit cell. The lattice constants are (in Å): $a = 5.6226$, $b = 5.7199$, $c = 7.9689$, $\beta = 89.796^\circ$.

In Reference 6, the XRD pattern of La$_2$MgTiO$_6$ indexed on a cubic cell. However, the monoclinic P2$_1$/n space group is better suited to explain the diffraction pattern of this perovskite. For our analysis, the data presented in Reference 27 where the XRD pattern is indexed on a monoclinic cell is used. The double perovskite crystallizes in the P2$_1$/c space group (No. 14) with four formula units per unit cell. The lattice constants are (in Å): $a = 5.5467$, $b = 5.5616$, $c = 7.8426$, $\beta = 89.959^\circ$.

In these perovskites, the Mn$^{4+}$ ions substitute for the six-fold coordinated Sb$^{5+}$ and Ti$^{4+}$ ions, respectively. Obviously, in La$_2$LiSbO$_6$ charge-compensation is required when Mn$^{4+}$ replaces Sb$^{5+}$ in the lattice. The La$^{3+}$ ions in both cases are eight-fold coordinated, and the Li$^+$, Mg$^{2+}$ ions are six-fold coordinated (Figure 1). Enlarged views of the TiO$_6$ and SbO$_6$ octahedral complexes along with bond lengths and bond angles are shown in Fig. 2.

Details pertaining to the calculations of the Mn$^{4+}$ energy level by the exchange charge mode of crystal field theory has been presented before. The reliability and vitality of the ECM is confirmed by its success in calculating the energy level of the transition metal and rare earth ions, and references therein. In the following we will only provide the results of our calculations that are relevant to the interpretation of the La$_2$LiSbO$_6$:Mn$^{4+}$ and La$_2$MgTiO$_6$:Mn$^{4+}$ experimental spectra.

Results and Discussion

X-ray diffraction pattern of La$_2$Li(Sb$_{0.998}$Mn$_{0.002}$)O$_6$.—Apart from very weak lines which were identified as being caused by the minor phase of Li$_3$SbO$_4$, the X-ray diffraction pattern of the La$_2$Li(Sb$_{0.998}$Mn$_{0.002}$)O$_6$ product indicated a single-phase material with monoclinic symmetry.

Figure 1. One unit cells of La$_2$LiSbO$_6$ (left) and La$_2$MgTiO$_6$ (right). Drawn with VESTA. The octahedral coordination of the Sb and Ti ions and chemical bonds around La ions are shown.

Figure 2. Enlarged views of the SbO$_6$ (left) and TiO$_6$ (right) complexes in La$_2$LiSbO$_6$ and La$_2$MgTiO$_6$. Drawn with VESTA. The chemical bond lengths (in Å) are shown. All characteristic angles (in °) are listed below for each complex. SbO$_6$: 1-Sb1-4, 2-Sb1-5, 3-Sb1-6 – 180; 1-Sb1-2, -3, -5, -6: 89.97, 89.28, 90.03, 90.72, correspondingly; 2-Sb1-3, -4, -6: 91.94, 90.03, 88.06; 3-Sb1-4, -5: 90.72, 88.06; 4-Sb1-5, -6: 89.97, 89.28; 5-Sb1-6: 91.94. TiO$_6$: 1-Ti1-4, 2-Ti1-5, 3-Ti1-6 -180; 1-Ti1-2, -3, -5, -6: 86.74, 89.42, 93.26, 90.58, correspondingly; 2-Ti1-3, -4, -6: 94.91, 93.26, 85.09; 3-Ti1-4, -5: 90.58, 85.09; 4-Ti1-5, -6: 86.74, 89.42; 5-Ti1-6: 94.91.
cm was necessary because the overlap of O$_2^+$ appear on the high frequency side of the ZPL.\( \nu \) moiety:

- Excitation bands at 706 nm (14 164 cm$^{-1}$) correspond with the O$_2^+$
- Bands at 706 nm (14 164 cm$^{-1}$) is assigned to the host lattice absorption.
- Excitation bands at 31 nm (13 717 cm$^{-1}$) and 422 cm$^{-1}$
- The excitation spectrum was decomposed into a sum of Gaussian
- \( \nu \) transitions, respectively.
- The excitonic spectrum was decomposed into a sum of Gaussian

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\begin{table}[h]
\centering
\begin{tabular}{ccc}
\hline
\textbf{La$_2$LiSbO$_6$} & \textbf{La$_2$MgTiO$_6$} \\
\hline
$B_1^2$ & 172 & 3452 \\
$B_2^1$ & 618 & 4661 \\
$B_2^3$ & 725 & 1025 \\
$B_2^3$ & -1856 & -5901 \\
$B_2^3$ & 1486 & 4982 \\
$B_{3}^3$ & -16646 & 12081 \\
$B_{4}^3$ & -14195 & -5572 \\
$B_{1}^3$ & 1833 & -3387 \\
$B_{1}^3$ & -5643 & -4341 \\
$B_{1}^3$ & 4002 & 3958 \\
$B_{2}^3$ & -24188 & 21633 \\
$B_{2}^3$ & 2360 & 352 \\
$B_{3}^3$ & -23385 & 24765 \\
$B_{4}^3$ & -19400 & -23641 \\
$B$ & 750 & 700 \\
$C$ & 2953 & 3136 \\
\hline
\end{tabular}
\caption{The crystal field (Stevens normalization) and Racah parameters (all in cm$^{-1}$) for Mn$^{4+}$ ions in La$_2$LiSbO$_6$ and La$_2$MgTiO$_6$.}
\end{table}

Results of energy level calculations.—The octahedral moieties in both La$_2$LiSbO$_6$ and La$_2$MgTiO$_6$ deviate considerably from the ideal $O_h$ group. As exhibited in Fig. 2, both octahedral clusters are characterized by the presence of three pairs of different interatomic distances. Further, the characteristic octahedral bond angles are also deviating from the ideal values. Therefore, all orbitally degenerated energy levels of the Mn$^{4+}$ ion in such clusters will be split.

The crystal structural data were used to calculate the non-zero parameters of crystal field, which are listed in Table I. The values of the Racah parameters $B$ and $C$, which were chosen from the best agreement with experimental data, are also given in Table I. We should point out that the value of the second Racah parameter $C$ is found from adjusting the calculated position of the $2E_g$ (2G) state to its experimental value determined from the emission spectrum. Thus, it is imperative to correctly identify the energy position of the $2E_g$ $\rightarrow$ $A_{2g}$ zero phonon transition.

The crystal field splitting of all 8 LS terms of the Mn$^{4+}$ ion was calculated by diagonalizing the crystal field Hamiltonian with all crystal field parameters. The lowest calculated energy levels, which are located in the spectral range corresponding to the experimental excitation/emission spectra, are listed in Table II. The low symmetry of the crystal lattice sites is confirmed by a complete removal of the orbital degeneracy of the triplet and doublet states. There is good agreement between these calculated energy levels and corresponding experimental spectra (Fig. 3). Note that the splitting of the orbital triplets in La$_2$MgTiO$_6$ is greater than in La$_2$LiSbO$_6$, which indicates considerably lower crystal field symmetry in the former case.

Influence of MnO$_6$ distortions on the energy of the $^2E_g$ state in double perovskites.—In this section, we present a comparative study of the spectroscopic properties of Mn$^{4+}$ ion in double perovskite compounds with the formulation $A_2BB_0$ $O_6$ (Table III). The study establishes a relationship between the energy position of the $^2E_g$ state and octahedral site distortion. The greater is the octahedral distortion,
the smaller is the overlap between the Mn and O wave functions and higher is the energy position of the \( \text{2E} \) state.

In Table III compares the values for the Racah parameters \( B \) and \( C \), peak emission energy of the \( \text{2E} \rightarrow \text{4A} \) transition and the value of the non-dimensional quantity \( \beta_1 = \sqrt{\left( \frac{\text{E}_1}{\text{E}_{\text{zero}}^*} \right)^2 + \left( \frac{\text{E}_2}{\text{E}_{\text{zero}}^*} \right)^2} \), (the subscript ‘0’ refers to the values of the Racah parameters of the free ion) for \( \text{Mn}^{4+} \) in three double perovskites and in \( \text{SrTiO}_3 \). The function \( \beta_1 \) was introduced by Brik and Srivastava\(^{16} \) in the spectroscopy of \( d^3 \) ions to connect the energy of the \( \text{2E} \rightarrow \text{4A} \) transition with the Racah parameters \( B \) and \( C \).

In an ideal octahedral moiety, all six bonds are equal. Out of 15 characteristic angles of an octahedron, three are 180° and twelve are 90°. There are two ways in which the octahedral moiety of the perovskite lattice can distort: varying M-O interatomic distances and the O-M-O bond angle deviating from the ideal 90° value.

The data in Table III are arranged in the order of decreasing octahedral site distortion. Agreement between the calculated and experimental results was shown to be good. Our study shows that octahedral site distortions decreases Mn-O covalent interaction which increases the energy of the \( \text{2E} \) state. We, therefore, conclude that the development of deep red emitting phosphors for plant growth application in the perovskite based materials requires minimization of the octahedral site distortion. This results in stronger Mn-O covalent bond interaction which decreases the energy of the \( \text{Mn}^{4+} \) \( \text{2E} \rightarrow \text{4A} \), zero phonon transition.

### Acknowledgments

M. G. Brik thanks the supports from the Recruitment Program of High-end Foreign Experts (grant No. GDW20145200225), the Program for the Foreign Experts offered by Chongqing University of Posts and Telecommunications, Ministry of Education and Research of Estonia, Project PUT430, and European Regional Development Fund (TK141).

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