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COMMUNICATION

Monoclinic LaGa$_{1-x}$Mn$_x$Ge$_2$O$_7$: A New Blue Chromophore Based on Mn^{3+} in Trigonal Bipyramidal Coordination with Longer Apical Bond Lengths

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New blue inorganic oxide materials LaGa$_{1-x}$Mn$_x$Ge$_2$O$_7$ are developed by a solid state reaction method. Substitution of Mn^{3+} in LaGaGe$_2$O$_7$ changes the color from white ($x = 0$) to blue ($x = 0.1 - 0.4$). The blue color is due to the absorption in the energy region of 1.7- 2.5 eV.

Behavior of d- electrons in the transition metals (TM) are of great significance in several phenomena that occurring in the TM oxides. Degeneracy of the d-orbital in the free transition metal ions in the oxides are energetically split due to the crystal field provided by the surrounding oxygen atoms. The extent of crystal field splitting strongly depends on the nature and co-ordination of the ligands.[1]Transitions between the d-states of the metal ions are of great influence on the optical property and these transitions determine the color. The color of a compound depends on the magnitude of crystal field splitting, which depends on the structure of the compound and d-orbital–ligand interaction.[2] In the case of ruby (red) and emerald (green) both contain Cr^{3+} in an octahedral environment provided by oxide ions.[3] But they possess different colors, for the reason that compositions of the host lattice are unlike with different Cr-O distances. Shorter Cr-O distances in ruby which increases the d orbital–ligand interactions and makes crystal field splitting relatively larger than that of emerald with longer Cr-O distances. At present, most commonly used inorganic blue pigments are cobalt blue (CoAl$_2$O$_4$), ultramarine blue (Na$_7$Al$_6$Si$_6$O$_{24}$S$_3$) and Prussian blue (Fe$_4$[Fe(CN)$_6$]$_3$). In cobalt blue the attribution of color is due to the spin allowed d-d transition of Co^{2+} in the tetrahedral coordination whereas in ultramarine blue it is based on the absorption in the S^{3-} radical anion, and in Prussian blue the color is associated with the inter valence charge transfer taking place from the Fe^{2+} to Fe^{3+} ion.[4,5] It is clear that the environment of the transition-metal ion, which is determined by the host lattice, considerably affects the optical properties of a compound. V, Cr, Mn, Fe, Co, Ni, and Cu are the most commonly used chromophores in pigment systems, which have incompletely filled d-orbitals.[3]

Subramanian et al. discovered new blue inorganic oxide materials with the introduction of Mn^{3+} in the trigonal bipyramidal (TBP) sites of hexagonal YInO$_3$, ScGaZnO$_4$, LuGaZnO$_4$ and LuGaZnO$_4$.[6,7] In addition to the individual ion and its oxidation state, absorption phenomena are markedly affected by the ionic environment. Recently a new blue chromophore Sr$_2$(Mg,Mn)Ge$_2$O$_{7+\delta}$ was synthesized which has a melilite type structure.[8] Crystal structure of Sr$_2$(Mg,Mn)Ge$_2$O$_{7+\delta}$ contains the rarely found Mn^{III}O$_5$ trigonal bipyramid and the GeO$_5$ square pyramid, this might result from the oxidation of Mn^{2+} ions due to uptake of an interstitial oxygen. In the case of hexagonal YIn$_{1-x}$Mn$_x$O$_3$ the origin of blue color is due to the d-d transition taking place from the Mn d'$_{(x^2-y^2, xy)}$→d'$_z^2$ state. Shorter Mn-O apical bond lengths play a key role in the d-d component of this transition and also favorable for the layered arrangements in hexagonal perovskites.[6] Recently reported a purple inorganic oxide material based on hexagonal perovskite YGaO$_3$ substituted with Mn^{3+} at the Ga^{3+} site.[9] The absorption spectrum of YGa$_{1-x}$Mn$_x$O$_3$ similar to the corresponding YIn$_{1-x}$Mn$_x$O$_3$ except that the lower energy band is assigned to transition from d'$_{(x^2-y^2, xy)}$→d'$_z^2$ blue shifted by about 0.3 - 0.5 eV. The blue shift in the absorption maxima is due to the slightly shorter Ga-O apical bond length in YGaO$_3$ compared to that of YInO$_3$. The shorter apical bonds in YGaO$_3$ produce more ligand field around the Mn^{3+}, thus increasing the energy separation between the e' & e'' and a'$_1$ orbitals. But in the case of YAl$_{1-x}$Mn$_x$O$_3$, the Al-O apical bonds are slightly shorter than that of Ga-O apical bonds. Here the absorption maxima formed around 2.5 eV and 3.5 eV. They proposed that such an apparently small differences in bond lengths of YAlO$_3$, YGaO$_3$ and YInO$_3$ host lattices produces a considerable change in the color of the Mn^{III}O$_5$ chromophore and they exhibited dark brown, purple and blue colors respectively. Also, this work shows that the color of the TBP co-ordianted Mn^{3+} could be tuned by altering the host material possessing different M–O apical bond lengths.[9] We inferred that the longer Mn-O apical bond lengths affect the crystal field stabilization around the Mn^{3+} in trigonal bipyramidal site. The crystal field splitting of Mn^{3+} in TBP

coordination shows that e' to a'$_1$ energy splitting, which is the lowest energy transition for a d^4 cation, depends sensitively on the apical M-O bond length.

Germanates of the type MRGe$_2$O$_7$ (M = Al^{3+}, Ga^{3+} or Fe^{3+} and R = rare earth ion) have been reported in the early 1980s which belongs to the monoclinic AlNdGe$_2$O$_7$ structure type with a space group of P2$_1$/c.[10] LaGaGe$_2$O$_7$ the rare-earth ions are separated by GaO$_5$ and Ge$_2$O$_7$ polyhedra and the oxygen coordination around rare-earth ion is in 9-fold. In the monoclinic unit cell of LaGaGe$_2$O$_7$ (Z = 4), four La^{3+}, four Ga^{3+}, eight Ge^{4+} and fourteen O^{2-} occupy the 4e positions of C$_1$ symmetry. These kinds of compounds are of great interest in laser crystal physics.[11] The luminescence study on these compounds provides much valuable information for optical applications, LaAlGe$_2$O$_7$ doped with Tb^{3+} and Tm^{3+} shows intense green and blue light emissions, respectively.[12,13] However no reference was found in the literature describing the optical studies of Mn^{3+} doped LaGaGe$_2$O$_7$ this work is just the first step. Recent times research efforts are being made to develop and explore cobalt free blue chromophores for environmentally benign pigments applications. However a few host structures having a Mn^{3+} ion in their geometry have been found so far. In this respect there is a growing need for finding out host structures incorporating Mn^{3+} in the trigonal bipyramid geometry. In the present investigation we prepared new blue pigment with the introduction of Mn^{3+} in the monoclinic host other than the hexagonal perovskites and we observed some changes in the absorption spectrum of Mn^{3+} in the TBP site from that observed in the hexagonal YIn$_{1-x}$Mn$_x$O$_3$.

Powder X-ray diffraction (XRD) patterns of LaGa$_{1-x}$Mn$_x$Ge$_2$O$_7$ indicate that the samples crystallize in monoclinic structure with a space group of P2$_1$/c (Figure S1). The doping of Mn^{3+} in the LaGa$_{1-x}$Mn$_x$Ge$_2$O$_7$ gives rise to a progressive increase in the lattice parameters up to 20 mol%. This expansion is due to the slightly increased ionic radii of Mn^{3+} (58 pm) compared to Ga^{3+} (55 pm). Above 20 mol % of the doping concentration of Mn^{3+}, lattice parameter decreases. This decrease is probably due to the oxidation of some Mn^{3+} into Mn^{4+} state. Variations in the lattice parameter and unit cell volume of LaGa$_{1-x}$Mn$_x$Ge$_2$O$_7$ (x = 0 - 0.4) are shown in Figure S2 in the supporting information. Crystal structure of LaGa$_{1-x}$Mn$_x$Ge$_2$O$_7$ was refined based on the experimental powder diffraction data by Rietveld analysis (Figure S3). In order to determine the quality of the final refinement reliability factors are defined to compare the difference between the observed pattern and calculated profile. The weighted profile reliability (Rwp) factor is the more valuable, for a complex phase (monoclinic to triclinic) a value <0.15 is good. The final reliability factors are Rwp = 13.91%, Rp= 10.82 % and GoF = 1.11. Lattice parameter data of all samples and the refinement results of LaGa$_{0.8}$Mn$_{0.2}$Ge$_2$O$_7$ are given in the supporting information Tables S1 & S2 respectively.

In ideal trigonal bipyramid the two apical bonds are identical, when different cations enter the bipyramids the two apical bonds are not identical and they have been classified into two categories. In Type I the three basal M-O bonds shorter than the two apical ones and the bipyramid shows not much distortion. In Type II one of the apical bonds is shorter and the other one longer than the three basal

ones: here the cation significantly off-centred from the basal plane, and pointing towards one of the corners.[14] Here the synthesized LaGa$_{1-x}$Mn$_x$Ge$_2$O$_7$ (x = 0.1 and 0.2) in which the two apical bonds are longer than the three basal M-O bonds, thus substitution of Mn^{3+} will not cause much distortion in the bipyramids. Above 20 mol% of the doping concentration, one of the apical bonds is longer and the other one is shorter than the three basal bonds, this may be due to the more distortion in the bipyramids. We calculate the bond valence sum of all the samples by using Pauling's BVS rule V$_{ij}$ =e$^{R0-Rij/B}$, where R$_0$ and R$_{ij}$ are expected and experimentally determined bond length between the atoms, B is a constant (0.37 Å).[15] and the value of R$_0$ (1.76 Å) for Mn-O. From this calculations we can see that the BVS of x = 0.3 and 0.4 are over bonded and have more deviation from the value of 3$^+$ oxidation state this may be due to the presence of Mn^{4+}. Mn-O bond lengths and BVS values are given in the Table S3 in the supporting information.
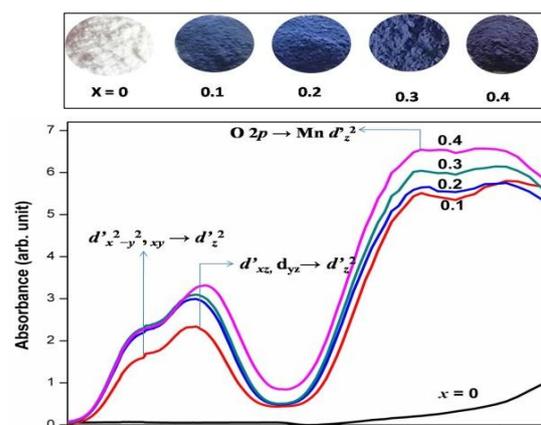

Figure 1. Colors and Absorbance spectra of LaGa$_{1-x}$Mn$_x$Ge$_2$O$_7$ (x = 0, 0.1, 0.2, 0.3 and 0.4)

To understand the origin of this blue color, we measured diffuse reflectance spectra using (Shimadzu UV-3600) UV-vis spectrometer. Coloring performance of Mn^{3+} bearing pigments very much depends on its co-ordination environment. Optical absorption spectra of the LaGa$_{1-x}$Mn$_x$Ge$_2$O$_7$ (x = 0 - 0.4) is shown in Figure 1. Band gap of undoped LaGaGe$_2$O$_7$ lies in the range of 3.3 eV. As we introduced the Mn^{3+} in the gallium site of LaGaGe$_2$O$_7$, two new absorption bands are observed in all doped samples. The D$_{3h}$ crystal-field symmetry of bipyramidal oxygen ions around the Mn^{3+} ion splits the Mn d levels into three components e" (d$_{xz}$, d$_{yz}$), e' (d$_{x^2-y^2}$, d$_{xy}$) and a'$_1$ (d$_z^2$)^{2}[16] in Figure 2. The e" orbitals directed away from the apical oxygens have the lowest energy, due to their small overlap with O$_{2p}$ orbitals. Next highest in energy e' orbitals strongly hybridize with O$_{2p}$ orbitals. Finally, the a'$_1$ orbital has the highest energy, the d$_z^2$ orbital remains empty in the ground state. Transitions to this unoccupied orbital will be of prime importance to the observed optical spectrum. The blue color of LaGa$_{1-x}$Mn$_x$Ge$_2$O$_7$ is mainly due to the absorption in the 1.7 - 2.5 eV energy region.[17] This absorption arises due to the symmetry-allowed optical transitions from d'$_{(x^2-y^2, xy)}$→d'$_z^2$ and d'$_{(xz, yz)}$→d'$_z^2$, (symmetry forbidden transition) and here the corresponding d-states hybridized with O$_{2p}$ orbital. Usually the absorption spectra of Mn^{3+} in TBP site will give an intense

absorption band in the 1.7 eV region and a weak one around 2.1 eV region.[17]

TBP site of $LaGa_{1-x}Mn_xGe_2O_7$ is in a distorted enviornment, there is a small splitting in the absorption band located at the 2 eV region of all samples; this is similar to what is appeared in the absorption spectra of $YIn_{1-x}Mn_xO_3$. An ideal TBP wiil not give such type of splitting in the 2 eV region, this kind of splitting has not been observed in the $ScGa_{1-x}Mn_xZnO_4$ in which the TBP possess full D_{3h} symmetry of an ideal one.[7] The absorption band located in the 3 - 4.5 eV region is due to the transition taking place from the $O_{2p} \rightarrow Mn$ d'$_z^2$ orbital.[18]
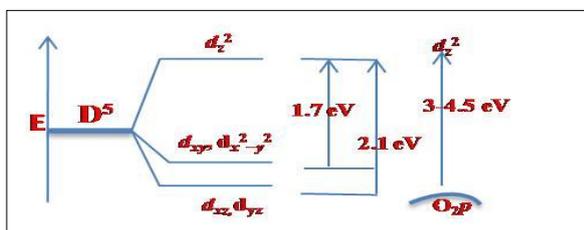
Figure 2. Crystalfield splitting of Mn^{3+} in TBP site of $LaGa_{1-x}Mn_xGe_2O_7$

But in our case the absorption spectra of $LaGa_{1-x}Mn_xGe_2O_7$ shows a weak intense band in the 1.7 eV region and a strong intense band in the 2.1 eV region. We inferred that the additional loss of intensity in the 1.7 eV region is due to the diminished hybridization strength of Mn d$_z^2$-orbitals with O_{2p} orbitals due to their longer Mn-O apical bond lengths (Figure 3).[19] We proposed that the increased intensity of absorbtion band arises from the d'$_{(xz, yz)} \rightarrow$d'$_z^2$ transition is due to the close proximity of spin allowed and spin forbidden transitions, these close proximity of the excited states lead to srong mixing through spin-orbit coupling. The mixing causes an increased intensity and bandwidth of the spin-forbidden transition.[20] Longer apical Mn–O bonds in $LaGa_{1-x}Mn_xGe_2O_7$ produces smaller ligand field around Mn^{3+}, thus decreasing the energy separation between the e' & e'' and a'$_1$ orbitals.

Figure 3. Effect of longer apical bond lengths in the intensity
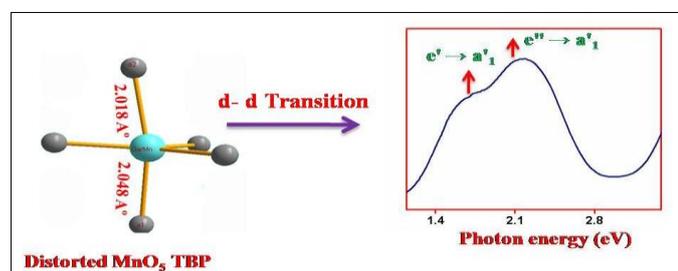
variation of symmetry allowed and forbbiden transitions.

Subramanian et al. pointed out the importance of Mn-O apical bonds in $YIn_{1-x}Mn_xO_3$, shorter Mn-O apical bonds favours effective hybridization with O_{2p} orbital, this will result in the origin of blue colour. In the present system $LaGa_{1-x}Mn_xGe_2O_7$ all the doped samples possess longer Mn-O apical bonds, this situation also favours the development of blue colour. The $L*a*b*$ values of $LaGa_{1-x}Mn_xGe_2O_7$ are given in Table S4 of the supporting information. Further the synthesized samples show more absorbance in the UV region with increasing the Mn concentration indicating as

promising UV absorbers. The homogeneous and crystalline nature of the sample can be observed from SEM photographs provided in the supporting information (Figure S4).

The temperature dependence of magnetic susceptibility $\chi(T)$ and its inverse $\chi^{-1}(T)$ measured in a field of 500 Oe is plotted in Figure S3 given in the supporting information. In order to analyse the Mn oxidation state in the $LaGa_{0.6}Mn_{0.4}Ge_2O_7$, $\chi(T)$ measurements were conducted. As can be seen from Figure S5, the χ^{-1} satisfactorily follows the Curie-Weiss law given by $\chi = C/(T - T_c)$. The observed value of μ_{eff} is 4.47 lower than that one would expect for a free Mn^{3+} ion (4.90). This lowering in the magnetic moment confirms the presence of Mn^{4+} along with Mn^{3+} in $LaGa_{1-x}Mn_xGe_2O_7$ ($x = 0.3$ & 0.4) which is in agreement with the lattice parameter variation.

In the present work we prepared new blue inorganic oxide material with the introduction of Mn^{3+} in the TBP site of monoclinic $LaGaGe_2O_7$ other than in the layered perovskites. In the absorption spectra of $LaGa_{1-x}Mn_xGe_2O_7$ ($x = 0.1$ to 0.4) two absorption bands are observed with the intensity of symmetry allowed transition (1.7 eV) diminished and the intensity of symmetry forbidden transition (2.1 eV) increased. We proposed that this effect is due to the presence of longer Mn-O apical bond length in $LaGa_{1-x}Mn_xGe_2O_7$ ($x = 0.1$ to 0.4).

Notes and references

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Table of Contents Graphic and Synopsis

Substitution of Mn^{3+} into the trigonal bipyramidal site of monoclinic $LaGaGe_2O_7$ produces blue color. Mn-O apical bond distances play a key role in the d-d transitions for exhibiting the color.