Melilite-type blue chromophores based on Mn$^{3+}$ in a trigonal-bipyramidal coordination induced by interstitial oxygen†

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A new, earth-abundant, environmentally benign, and stable inorganic blue chromophore series Sr$_2$(Mg$_{1-x}$Mn$_x$)Ge$_2$O$_{7+x}$ has been prepared and characterized by X-ray absorption spectroscopy, synchrotron X-ray diffraction, and ab initio total energy calculation. As the content of Mn in the compound was increased, the color changed from white (for $x = 0.0$) to sky blue, deep blue, and finally black body color (for $x = 1.0$). Sr$_2$MgGe$_2$O$_7$ has the melilite-type structure comprising Mg(2+)O$_4$ and GeO$_4$ tetrahedra. On the other hand, it was found that the Mn ion in Sr$_2$(Mg$_{1-x}$Mn$_x$)Ge$_2$O$_{7+x}$ is mainly trivalent and that the additional oxygen atom infiltrates into the lattice to compensate for the excess positive charge. The additional oxygen atom occupies an interstitial site, leading to the formation of Mn(3+)O$_5$ trigonal bipyramid and Ge(4+)O$_5$ square pyramid. As the driving force for the Mn(3+)O$_5$ formation, the tendency for improving the lattice coherency between BO$_4$–B‘O$_4$ and AO$_6$ layers in the melilite A$_2$B'B'O$_7$ is suggested.

1 Introduction

Rich blue pigments, which are used for art and decorative purposes, were rare and expensive before the industrial revolution. Owing to significant efforts to find low-cost blue pigments, several useful synthetic materials that are blue in color, such as Prussian blue (Fe$_4$(Fe(CN)$_3$)$_3$·xH$_2$O) associated with the intercalation charge transfer from Fe$^{2+}$ to Fe$^{3+}$, French ultramarine (Na$_3$AlSi$_6$O$_{18}$S$_3$) based on the absorption in thiosindan anion S$_2$$^-$, Cobalt blue (CoAl$_2$O$_4$) and Cerulean blue (CoO·nSnO$_2$) attributed to the allowed d-d transition in the Co$^{2+}$ ion, have been developed since the 18th century. Even though these materials exhibit good color properties and relatively low costs – they are typically less expensive than the natural gemstone lapis lazuli – their toxicity or insufficient durability continue to be issues. Recently, the synthesis of chromophore oxides including a Mn$^{3+}$ ion in the trigonal-bipyramidal coordination was reported as a new route for developing earth-abundant, environmentally benign, and stable inorganic blue pigments. The blue color originates from green/red-range absorption by a symmetry-allowed optical transition between Mn 3d$^4$–y$^2$xy and Mn 3d$^5$ states in the coordination. Their color hue can be finely tuned by the types and compositions of the hosts. However, few host structures having a Mn$^{3+}$ ion in their geometry have been found so far. Most of them have hexagonal YInO$_3$–YbFe$_2$O$_4$, and LuFeO$_3$(ZnO)$_2$-type structures, where Mn$^{3+}$ is partially substituted in the In$^{3+}$ or Fe$^{3+}$ sites. This is primarily due to the instability of five coordinated Mn$^{3+}$ ions in the trigonal-bipyramidal geometry. In this study, we synthesized a new blue chromophore, Sr$_3$(Mg,Mn)Ge$_2$O$_{7+x}$, which has a melilite-related structure. It has been known that the melilite-type compounds with a general formula Sr$_2$MGe$_2$O$_7$ (M = Mg, Zn, Co, Mn) consist of M$^{2+}$ and Ge$^{4+}$ in tetrahedral coordinations without excess oxygen for more than 30 years. On the basis of X-ray absorption spectroscopy measurements, synchrotron X-ray diffraction analysis, and ab initio total energy calculation, however, we revealed the existence of an Mn$^{3+}$ ion in a trigonal-bipyramidal coordination and Ge$^{4+}$ in a square-pyramidal coordination induced by the infiltrated oxygen interstitial in Sr$_2$(Mg,Mn)Ge$_2$O$_{7+x}$. It was expected that Mn$^{3+}$ ions substituted in MgO$_4$ tetrahedral sites have a trigonal-bipyramidal coordination, since other hosts for blue chromophores based on Mn$^{3+}$ ions have originally trivalent trigonal-bipyramidal sites, such as In(3+)O$_5$, Ga(3+)O$_5$, Fe(3+)O$_5$, etc. It
is suggested that the five coordinations around \( \text{Mn}^{3+} \) and \( \text{Ge}^{4+} \) ions might result from the oxidation of \( \text{Mn}^{2+} \) ions owing to the uptake of an additional oxygen atom.

2 Experimental section

\( \text{Sr}_2(\text{Mg}_{1-x}\text{Mn}_x)\text{Ge}_2\text{O}_7 \) \( (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, \text{and} \ 1.0) \) were prepared using solid-state reaction. Stoichiometric amounts of \( \text{SrCO}_3 \) \( \text{(Aldrich, 99.99\%)} \), \( \text{MgO} \) \( \text{(Aldrich, 99.99\%)} \), \( \text{MnCO}_3 \) \( \text{(Aldrich, 99.99\%)} \), and \( \text{GeO}_2 \) \( \text{(Kojundo, 99.99\%)} \) were homogeneously mixed. The mixtures were fired at 1250 °C for 6 h under ambient conditions. Optical absorption of the resultant was measured with a UV-VIS absorption spectroscope with an integrating sphere (Hitachi U-3310). Phase information was obtained by using a normal X-ray diffraction with \( \lambda = 1.540562 \text{ Å} \) (XRD, Phillips X'Pert Pro, Target Cu K\( \alpha \), 40 kV, 40 mA).

Synchrotron X-ray powder diffraction experiments were performed using a multiple detector system installed at the 8C2 beamline of the Pohang Light Source, Pohang Accelerator Laboratory in Korea. A monochromatic 1.549 Å X-ray beam was used. Diffraction data were collected over the 2\( \theta \) range of 10–130° with a step of 0.005° in asymmetric flat-specimen reflection geometry with a fixed angle of 7.0° at room temperature. Rietveld refinement was carried out using the Rietan-2000 package.\(^{12} \) Whole-pattern fitting based on the maximum entropy method (MEM) was carried out using the computer program PRIMA47 with 160 \( \times \) 160 \( \times \) 100 pixels. VESTA (ver. 3.0.3) was used to draw the electron density maps from the MEM analysis.

The X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra at the Mn K-edge were recorded in transmission mode with a wiggler 17C1 beamline at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. XANES spectra at Mn L\( _2,3 \)-edges and the O K-edge were recorded in transmission mode with a wiggler 17C1 beamline at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. XANES spectra at Mn L\( _2,3 \)-edges and the O K-edge were obtained at the BL20A beamline in total electron yield (TEY) mode.

The first-principles calculations based on the density functional theory (DFT)\(^{13} \) were performed using Vienna Ab initio Simulation Package (VASP) code to estimate the density of states.\(^{14,15} \) The plane-wave cutoff energy was chosen to be 400 eV and the k-points were sampled on \( 4 \times 4 \times 6 \) uniform grids. The exchange–correlation interactions between electrons were described by generalized gradient approximation (GGA),\(^{16} \) and the projector-augmented wave (PAW) potentials\(^{14,15} \) were used to describe the ion–electron interactions. The conjugate gradient method for geometry optimization was used. The optimization procedure was truncated when the residual forces for the relaxed atoms were less than 0.01 eV Å\(^{-1} \).

3 Results and discussion

The Mn-substituted melilite-type \( \text{Sr}_2\text{MgGe}_2\text{O}_7 \) exhibited blue color, as shown in Fig. 1(a). As the amount of Mn substituted in the compound was increased, the color changed from white to sky blue, blue, and then deep blue. In its final composition, \( \text{Sr}_2\text{MnGe}_2\text{O}_7 \) shows black body color. Fig. 1(b) shows the optical absorption spectra of \( \text{Sr}_2(\text{Mg}_{1-x}\text{Mn}_x)\text{Ge}_2\text{O}_7 \) \( (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, \text{and} \ 1.0) \). The optical bandgap of \( \text{Sr}_2\text{MgGe}_2\text{O}_7 \) without Mn was estimated to be 5.6 eV, and two absorption bands appeared in the energy range of 1.6–2.8 eV and 3.5–6.0 eV by the Mn substitution. The blue hue of the compound was attributed to absorption in the visible light range, i.e., absorption at 1.6–2.8 eV. As the Mn concentration was increased, the relative absorption intensities increased and so did the widths of the two bands. This change is manifested in the form of changes in the color which increased in vividness and depth and ultimately became black (Fig. 1(a)).

The structural change induced by the substitution of Mg with Mn was checked using X-ray diffraction (XRD) analysis (Fig. S1†). The overall crystallographic structure with a \( \text{P4}_2/m \) space group was maintained for all Mn concentrations. This meant that Mn was incorporated into the \( \text{MgO}_4 \) tetrahedron site in the \( \text{Sr}_2\text{MgGe}_2\text{O}_7 \) structure. In the case of the successful substitution of \( \text{Mn}^{2+} \) for \( \text{Mg}^{2+} \), one can expect a gradual increase in the volume of the unit cell due to the fact that the \( \text{Mn}^{2+} \) ion (80 pm) is 13% larger than the \( \text{Mg}^{2+} \) ion (71 pm).\(^{17} \) However, in reality, the cell volume decreased with an increase in the Mn concentration as shown in Fig. 2. Shrinkage along the \( a \)-axis was more dominant than the expansion along the \( c \)-axis. Hence, the decrease in the unit cell volume implied that the substitution would be more complex change than \( \text{Mg}^{2+} \) ions merely be replaced by \( \text{Mn}^{2+} \) at the site.

In general, the d–d transition of a high spin \( \text{Mn}^{2+} \) (d\(^5\)) ion in a tetrahedral coordination does not result in such a strong optical absorption. This is due to the spin-forbidden character of the transition.\(^{18} \) In addition, the absorption attributable to the charge transfer from the O 2p level to the Mn 3d level does not occur in the visible-light range. Hence, the \( 2+ \) oxidation state of Mn was investigated more closely. Fig. 3(a) shows the L-edge X-ray absorption near-edge structure (XANES) spectra of Mn originating from an electric dipole-allowed 2p → 3d transition in \( \text{Sr}_2(\text{Mg}_{1-x}\text{Mn}_x)\text{Ge}_2\text{O}_7 \) and \( \text{Sr}_2\text{MnGe}_2\text{O}_7 \).
MnO(2+), Mn2O3(3+), and MnO2(4+) were used as the reference samples. L3-absorption edges of two samples show the linear combination of the L 3-edges of MnO(2+) and Mn2O3(3+) (Fig. S2†), and the relative intensity of the characteristic peak of MnO(2+) is smaller in Sr2MnGe2O7 than in Sr2(Mg0.7Mn0.3)Ge2O7. That is, the Mn ions in both samples have mixed oxidation states of 2+/3+, and the oxidation state of Mn in Sr2MnGe2O7 is closer to 3+ than in Sr2(Mg0.6Mn0.4)Ge2O7. The mixed oxidation states of Mn are noticed from the positions of the Mn K-edge (1s → 4p) at around 6550 eV (Fig. 3(b)) and the characteristic pre-peak shoulder in the O K-edge (1s → 2p) at around 531 eV (Fig. 3(c)) as well. The average oxidation states of Sr2(Mg0.6Mn0.4)Ge2O7 and Sr2MnGe2O7 were quantitatively estimated from a linear dependence of Mn K-edge positions on the formal Mn valences from the reference samples, and were found to be 2.54 and 2.62, respectively (inset of Fig. 3(b)).21 The edge positions were determined from the first inflection point of the XANES spectra. As can be seen from the extended X-ray absorption fine structure (EXAFS) spectra (Fig. 3(d)), the average bond distances between the Mn and O atoms in Sr2(Mg0.6Mn0.4)Ge2O7 and Sr2MnGe2O7 (153 pm) were smaller than those in the case of Sr3MnGe2O8 (184 pm) composed of only Mn2+ ions. This result also supported the conclusion that the oxidation state of Mn is mixed and close to 3+. Therefore, it would be reasonable to assume that the blue color was the result of absorption by Mn3+, rather than by Mn2+ which is optically inert to visible light.

When Mn3+ ions are present in the melilite-type structure, there should be concomitant deviations in the known structure. This is due to the following two reasons. First, to compensate for the excess positive charge caused by the presence of a Mn3+ ion at a Mg2+ site (MnMg), either other cation vacancies (V//Sr or V//=Ge) or an additional anion (O//i) should be formed. Second, Mn3+ ions (d4) in a tetrahedral coordination are energetically unfavorable owing to the Jahn–Teller distortion and, to our knowledge, have never been reported previously.22 To reduce the energy of the system, the coordination around the Mn3+ ions should have a distribution different from that around Mn2+ ions. The Rietveld refinement of the synchrotron XRD patterns on the basis of the known structure model9 gave extremely high

![Fig. 2](a) Unit cell volumes and (b) lattice parameters of Sr2(Mg1−xMnx)Ge2O7 (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0) powders.

![Fig. 3](a) Mn L-edge, (b) Mn K-edge, and (c) O K-edge XANES, and (d) Fourier transformed EXAFS spectra of Sr2(Mg0.6Mn0.4)Ge2O7 and Sr2MnGe2O7. MnO(2+), Mn3O4(2.67+), Mn2O3(3+), and MnO2(4+) were used as the reference samples for the XANES spectra, and Sr3MnGe2O8(2+) for the EXAFS spectra. The inset in (b) is the oxidation state determination of Sr2(Mg0.6Mn0.4)Ge2O7 and Sr2MnGe2O7 (vacant red circles) using the Mn K-edge shift of the reference Mn compounds (vacant black squares).
values of the displacement parameters of the Mn and O ions (Table S1†). This suggested that the actual structure might be slightly perturbed from the reference model around the Mn and O ions. From the electron mapping performed via an entropy maximum method (MEM)-based analysis, we could detect the trace of an additional oxygen (O4) atom around (0.35, 0.42, and 0.19) as shown in Fig. 4. However, the refinement simply including an O4 atom at the 8f site in the unit cell also did not reduce the large displacement parameters despite the slight improvement of reliability factors from \(R_wpp = 10.06, R_p = 7.75,\) and \(S = 1.15\) to \(R_wpp = 9.31, R_p = 7.18,\) and \(S = 1.07\) (Table S2†).

The complex split of atomic positions induced by partial occupancy of the interstitial atoms could not be clearly refined, because the atomic displacement is reflected just in the broadening of diffraction peaks without the distinct peak separation. Accordingly, we could not help estimating only the average position of component atoms with considerable inaccuracy. Nevertheless, it is noteworthy that the interstitial O4 plausibly positioned just in the octahedral sites. Integrated intensities of the pre-edge peaks from \(\text{Sr}_2(\text{Mg}_{0.6}\text{Mn}_{0.4})\text{Ge}_2\text{O}_7, \text{Sr}_2\text{MnGe}_2\text{O}_7,\) and \(\text{MnFe}_2\text{O}_4\), as a reference, with 85% Mn2+ in tetrahedral sites and 15% Mn2+ in octahedral sites. Integrated intensities of the pre-edge peaks from \(\text{Sr}_2(\text{Mg}_{0.6}\text{Mn}_{0.4})\text{Ge}_2\text{O}_7, \text{Sr}_2\text{MnGe}_2\text{O}_7,\) and \(\text{MnFe}_2\text{O}_4\), as a reference, with 85% Mn2+ in tetrahedral sites and 15% Mn2+ in octahedral sites. Integrated intensities of the pre-edge peaks from \(\text{Sr}_2(\text{Mg}_{0.6}\text{Mn}_{0.4})\text{Ge}_2\text{O}_7, \text{Sr}_2\text{MnGe}_2\text{O}_7,\) and \(\text{MnFe}_2\text{O}_4\), as a reference, with 85% Mn2+ in tetrahedral sites and 15% Mn2+ in octahedral sites.

Fig. 5 Pre-edge peaks from \(\text{Sr}_2(\text{Mg}_{0.6}\text{Mn}_{0.4})\text{Ge}_2\text{O}_7, \text{Sr}_2\text{MnGe}_2\text{O}_7,\) and \(\text{MnFe}_2\text{O}_4\) with a tetrahedral coordination around the Mn2+ ion. Baselines for estimating the integrated intensities are also plotted as dashed lines.

\[
\Delta E(O_i) = E_{\text{tot}}(O_i) - E_{\text{tot}}^0 - \mu_O,
\]

where \(E_{\text{tot}}(O_i)\) and \(E_{\text{tot}}^0\) are the total energies of the supercells with \((\text{Sr}_2\text{MnGe}_2\text{O}_{7.5})\) and without interstitial oxygen \(O_i\) respectively, and \(\mu_O\) is the chemical potential of O calculated on the basis of the O2 molecule. Using the calculated values of \(E_{\text{tot}}(O_i), E_{\text{tot}}^0,\) and \(\mu_O\), which were \(-172.27\) eV, \(-164.78\) eV, and \(-4.93\) eV, respectively, the energy of formation of an interstitial oxygen atom was found to be \(-2.56\) eV. The inclusion of the additional oxygen atom reduces the total energy of the system, i.e. \(\text{Sr}_2\text{MnGe}_2\text{O}_{7.5}\) is energetically more stable than \(\text{Sr}_2\text{MnGe}_2\text{O}_7\). The calculated crystal structures of \(\text{Sr}_2\text{MnGe}_2\text{O}_7\) and \(\text{Sr}_2\text{MnGe}_2\text{O}_{7.5}\) are shown in Fig. 6(a) and (b). (The atomic positions and selected bond distances of \(\text{Sr}_2\text{MnGe}_2\text{O}_{7.5}\) are listed in Tables S3 and S4† respectively.) The location of the interstitial oxygen atom (0.53, 0.29, and 0.78) is consistent with that estimated through the MEM and the refinement of the synchrotron XRD patterns as (0.58, 0.34, and 0.82). The interstitial atom between MnO4 and GeO4 pushes the adjacent oxygen atoms and transforms the corner-shared MnO4–GeO5–MnO4 unit into the edge-shared MnO4–GeO5–MnO5 unit as shown in Fig. 6(c) and (d). All the MnO4...
tetrahedrons and one-fourth of the GeO$_4$ tetrahedrons in the
unit cell of Sr$_2$MnGe$_2$O$_7$ are transformed into MnO$_3$ distorted-
trigonal bipyramids and GeO$_2$ square pyramids by the addition
of one oxygen atom. Inclusion of an interstitial oxygen has been
reported in the Ga-based melilite structure La$_{1+x}$Sr$_{1-x}$Ga$_2$O$_7$/$x/2$
(LSG) to compensate for the excess charge from the La/Sr ratio
by Kuang et al.$^{28}$ They expected that the flexibility of the Ga$_2$O$_4$
 tetrahedron at the 4e site with a non-bridging terminal oxygen
might be the key condition for the interstitial binding. However,
in Sr$_2$(Mg,Mn)Ge$_2$O$_7$ the interstitial O$_3$ is shared by MnO$_4$ at
the 2a site as well as by GeO$_3$ at the 4e site. Non-bridging
terminal oxygen might not be a critical factor for the interstitial
uptake in Sr$_2$(Mg,Mn)Ge$_2$O$_7^+$
Though Sr$_2$MnGe$_2$O$_7$ also exhibited antiferromagnetic ordering,
show an optical transition in the d orbitals (Fig. 7(b)). Even
the Mn ions had fully occupied 3d orbitals and thus cannot
be attributed to the intrinsic property of Sr$_2$MnGe$_2$O$_7.5$
attributable to the intrinsic property of Sr$_2$MnGe$_2$O$_7.5$
rather than to the experimental error in the measurement.

On the basis of the optical absorption spectra of the melilite-
type A$_2$(B,Mn)B$_2$O$_7$ compounds with various A, B, and B$'$ ions,
such as (Sr$_{0.8}$Ca$_{0.2}$)$_2$(Mg$_{0.8}$Mn$_{0.2}$)Ge$_2$O$_7$, (Sr$_{0.8}$Ca$_{0.2}$)$_2$(Mg$_{0.8}$Mn$_{0.2}$)$_2$
Ge$_2$O$_7$, Sr$_2$(Mg$_{0.8}$Mn$_{0.2}$)Ge$_2$O$_7$, Ba$_2$(Mg$_{0.8}$Mn$_{0.2}$)Ge$_2$O$_7$,
Sr$_2$(Zn$_{0.8}$Mn$_{0.2}$)Ge$_2$O$_7$, Sr$_2$(Mg$_{0.8}$Mn$_{0.4}$)Ge$_2$O$_7$, and Sr$_2$(Mg$_{0.6}$Mn$_{0.4}$)Si$_2$O$_7$ as shown in Fig. 8 we could gain insight into
the conditions for the occurrence of a Mn$^{3+}$ ion in the melilite
structure including a Mn atom. Among the various melilites,
only Ba$_2$(Mg$_{0.8}$Mn$_{0.2}$)Ge$_2$O$_7$ and Sr(Mg$_{0.8}$Mn$_{0.4}$)Si$_2$O$_7$ in which
the A cation is larger than Sr and the B$'$ cation is smaller than Ge,
respectively, are not blue in color. This result suggests that
the oxidation states of Mn in these melilites depend on the sizes
of the component ions in the melilites, since their colorless
appearance results from Mn$^{2+}$ and not from Mn$^{3+}$. On the basis
of this observation, we propose the following condition for the
occurrence of a Mn$^{3+}$ ion in Sr$_2$MnGe$_2$O$_7$.5. The A$_2$BB$'$O$_7$-type
melilite structure consists of two layers: the AO$_8$-connected
layer and the BO$_4$-B$'$O$_4$-connected layer. Because the two layers
shares an oxygen atom, the horizontal size of a unit block in the BO$_4$–
B$'$O$_4$ layer should be comparable to that of a unit block in the AO$_8$
layer, as is the case in heteroepitaxial bilayers. If the mismatch
in the sizes of the unit blocks of the two layers is too large, the
melilite structure would be energetically unstable. This can be
expressed as the scheme shown in Fig. S6.$^{†}$ In Sr$_2$Mn(2+)-Ge$_2$O$_7$,
the Mn(2+)-O$_4$-Ge$_4$O$_7$ layer might be too large to be matched to the
SrO$_8$ layer, because a Mn$^{2+}$ ion (80 pm) is 12.6% larger than a
Mg$^{2+}$ ion (71 pm) in stable Sr$_2$MgGe$_2$O$_7$. However, if the Mn$^{2+}$
ion is oxidized to the smaller Mn$^{3+}$ ion (72 pm in the five coordina-
tion), the discrepancy between the two layers would decrease,
and the total energy of the system could be reduced. This is
shown schematically in Fig. 9. On the other hand, the BaO$_4$
layer in Ba$_2$(Mg$_{0.8}$Mn$_{0.2}$)Ge$_2$O$_7$ is larger than the SrO$_8$ layer (Ba$^{2+}$: 156
pm, Sr$^{2+}$: 140 pm) and large enough to be matched to the Mn(2+)-
O$_4$-Ge$_4$O$_7$ layer. In addition, the Mn(2+)-O$_4$-Si$_2$O$_7$ layer in
Sr$_2$(Mg$_{0.8}$Mn$_{0.4}$)Si$_2$O$_7$ is smaller than the Mn(2+)-O$_4$-Ge$_4$O$_7$ layer
Fig. 7 Calculated partial density of states for Mn1 3d and Mn2 3d in (a)
Sr$_2$MnGe$_2$O$_7$ and (b) Sr$_2$MnGe$_2$O$_7$. The Fermi level is set to zero.

Fig. 8 Absorption spectra of the melilite A$_2$(B,Mn)B$_2$O$_7$ with the various A, B,
and B$'$ ions such as (Sr$_{0.8}$Ca$_{0.2}$)$_2$(Mg$_{0.8}$Mn$_{0.2}$)Ge$_2$O$_7$, (Sr$_{0.8}$Ca$_{0.2}$)$_2$(Mg$_{0.8}$Mn$_{0.2}$)$_2$
Ge$_2$O$_7$, Sr$_2$(Mg$_{0.8}$Mn$_{0.2}$)Ge$_2$O$_7$, Ba$_2$(Mg$_{0.8}$Mn$_{0.2}$)Ge$_2$O$_7$,
Sr$_2$(Zn$_{0.8}$Mn$_{0.2}$)Ge$_2$O$_7$, Sr$_2$(Mg$_{0.8}$Mn$_{0.4}$)Ge$_2$O$_7$, and Sr$_2$(Mg$_{0.6}$Mn$_{0.4}$)Si$_2$O$_7$. This report was based on the
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basis of the results of X-ray absorption spectroscopy, synchrotron radiation has a melilite-type structure, was found to have Mn(3+)O5 trigonal bipyramid and GeO5 stretches for controlling the coordinations or the valence states of transition metal ions. The analysis performed in the study suggest that such a layered-structure could be determined on the basis of the degree of mismatch in the sizes of the AO8 and BO4 layers in the structures. It should be noted here that not all the Mn ions in Sr2(Mg,Mn)Ge2O7+ need to be of the Mn3+ type, and that this is the case only if coherency between the AO8 and BO4 layers is attained. The result that the mixed valence states of the Mn ions in Sr2(Mg0.6Mn0.4)Ge2O7+ and Sr2MnGe2O7+ are 2.54 and 2.62 can be attributed to this reason.

4 Conclusions

In summary, the blue chromophore Sr2(Mg,Mn)Ge2O7+ which has a melilite-type structure, was firstly synthesized. On the basis of the results of X-ray absorption spectroscopy, synchrotron X-ray diffraction analysis, and ab initio calculations, it was found that the crystal structure of Sr2(Mg,Mn)Ge2O7+ includes the rarely found Mn(3+)O5 trigonal bipyramid and the GeO5 square pyramid, which were both induced by an interstitial oxygen atom. The blue color of the chromophore results from the d-d electronic transition in Mn3+(d4), which has a trigonal-bipyramidal coordination. We proposed that the formation of Mn(3+)O5 might be the result of the tendency to decrease the mismatch between the sizes of the Mn(2+)O4-GeO4 and SrO8 layers in the layered melilite Sr2(Mg,Mn)Ge2O7+. The results of the analysis performed in the study suggest that such a layered-melilite structure, which has various isomorphs, could be used for controlling the coordinations or the valence states of transition metal ions.

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