Synthesis, crystal structure, and magnetic properties of RE$_3$Sb$_3$Mg$_2$O$_{14}$ (RE=La, Pr, Sm, Eu, Tb, Ho): new 2D Kagome materials

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Abstract

We present the crystal structures and magnetic properties of RE$_3$Sb$_3$Mg$_2$O$_{14}$ (La$_3$Sb$_3$Mg$_2$O$_{14}$, Pr$_3$Sb$_3$Mg$_2$O$_{14}$, Sm$_3$Sb$_3$Mg$_2$O$_{14}$, Eu$_3$Sb$_3$Mg$_2$O$_{14}$, Tb$_3$Sb$_3$Mg$_2$O$_{14}$, and Ho$_3$Sb$_3$Mg$_2$O$_{14}$), a family of novel materials based on a perfect geometry 2D rare earth Kagome lattice. Structure refinements were performed by the Rietveld method using X-ray diffraction data, indicating that the layered compounds are fully structurally ordered. The compounds crystallize in a rhombohedral supercell of the cubic pyrochlore structure, in the space group $R\bar{3}m$. As indicated by magnetic susceptibility measurements, they exhibit predominantly antiferromagnetic interactions between rare earth moments. Except for possibly Pr$_3$Sb$_3$Mg$_2$O$_{14}$ and Eu$_3$Sb$_3$Mg$_2$O$_{14}$, none of the compounds show any signs of magnetic ordering above 2 K.

This RE$_3$Sb$_3$Mg$_2$O$_{14}$ family of compounds is similar to that of RE$_3$Sb$_3$Zn$_2$O$_{14}$, except the series reported here features a fully ordered distribution of cations in both the nonmagnetic antimony and magnesium sites and the magnetic rare earth kagome sites. The compounds appear to be relatively defect-free and are therefore model systems for investigating magnetic frustration on an ideal 2D rare earth Kagome lattice.

Keywords: Rare earth; Kagome; Magnetic frustration; Pyrochlore
1. Introduction

With its network of corner-sharing triangles, the two-dimensional Kagome lattice is a model system for investigating geometric magnetic frustration. Two popular transition metal-based Kagome materials are Herbertsmithite, ZnCu$_3$(OH)$_6$Cl$_2$, and vesignieite, BaCu$_3$V$_2$O$_8$, which are also promising quantum spin liquid candidates.\textsuperscript{1,2} However, there has been a dearth of information related to rare earth Kagome materials. The langasites are one example, such as Pr$_3$Ga$_5$SiO$_{14}$ and Nd$_3$Ga$_5$SiO$_{14}$, but these structures possess “breathing” Kagome planes that are characterized by alternating larger and smaller rare earth triangles.\textsuperscript{3,4}

The 3D A$_2$B$_2$O$_7$ pyrochlore structure is another model for exploring geometric frustration. Pyrochlores with magnetic rare earth ions on the A site have been shown to exhibit exotic magnetic phenomena, such as the spin ices Dy$_2$Ti$_2$O$_7$ and Ho$_2$Ti$_2$O$_7$.\textsuperscript{5} In the pyrochlore structure, both the A and B ions form Kagome planes along [111] directions, connected by planes of A or B triangles to create a magnetic lattice of corner sharing tetrahedra. Many experiments have been conducted to selectively dope the pyrochlore structure with nonmagnetic ions in an ordered manner in an attempt to form a RE$^{3+}$-only Kagome lattice. This would enable the study of magnetic frustration on an intrinsic 2D rare earth Kagome. Unfortunately, such attempts have often resulted in defect structures.\textsuperscript{6}

Here we report the crystal structures and elementary magnetic properties of compounds in the RE$_3$Sb$_3$Mg$_2$O$_{14}$ family (RE=La, Pr, Sm, Eu, Tb, Ho), a series of new materials with a crystallographically ordered, ideal 2D Kagome lattice derived from partial ion substitution in the common cubic pyrochlore structure. This family is a variant of compounds originally reported with magnetic ions in place of the Mg$^{2+}$.\textsuperscript{7} The structure is similar to the A$_2$B$_2$O$_7$ pyrochlore, but is two-dimensional, with rare earth ions on an ideal Kagome lattice with MgRE$_3$ in the A sites and MgSb$_3$ in the B sites. This differs from the pyrochlore, which has magnetic ions connecting its Kagome planes (Figure 1). The magnetic properties of three compounds in this new family of materials (RE=Gd, Dy, Er), which all exhibit interesting magnetic ground states, including kagome spin ice, dipolar spin order, and the KT transition, have recently been reported.\textsuperscript{8} Just like the RE$_3$Sb$_2$Zn$_2$O$_{14}$ family of materials (RE=La, Pr, Nd, Sm, Eu, Gd), RE$_3$Sb$_3$Mg$_2$O$_{14}$ is fully layered with the rare earth ions in an ordered, symmetric Kagome array.\textsuperscript{9} While the Zn analogs have some local disorder due to the off-center displacement of one of the Zn$^{2+}$ ions, RE$_3$Sb$_3$Mg$_2$O$_{14}$ has a completely ordered distribution of cations. The perfect cation array and the
distinct rare earth Kagome lattice constructed by RE$^{3+}$ in RE$_3$Sb$_3$Mg$_2$O$_{14}$ make it an ideal model for exploring magnetic frustration in an intrinsic Kagome material. Here we describe the solid state chemistry and elementary magnetic properties of this family for a wide range of RE ions.

2. Experimental

Samples were synthesized by solid state reaction from La$_2$O$_3$, Pr$_6$O$_{11}$, Sm$_2$O$_3$, Eu$_2$O$_3$, Tb$_4$O$_7$, Ho$_2$O$_3$, Sb$_2$O$_3$, and Mg(OH)$_2$ in alumina crucibles. The rare earth oxides were first dried at 800 °C overnight. The stoichiometric mixtures were then thoroughly ground in an agate mortar and pestle and pre-reacted in air at 1000 °C for 15 hours. Following this, the mixtures were reacted in air at 1300 °C for 60 hours with repeated grindings.

The X-ray powder diffraction data were collected at room temperature using a Bruker D8 Advance Eco diffractometer with Cu Kα radiation ($\lambda$=1.5418 Å) and a Lynxeye detector. Structural refinements on RE$_3$Sb$_3$Mg$_2$O$_{14}$ were performed using the Rietveld method with the program Fullprof. The magnetic susceptibilities of RE$_3$Sb$_3$Mg$_2$O$_{14}$ were measured between 2 and 300 K in a Quantum Design Physical Properties Measurement System (PPMS) in an applied field of 5000 Oe. The magnetizations were linearly proportional to magnetic field for all temperatures above 2 K to fields of approximately 15,000 Oe in all materials; therefore, the magnetic susceptibility was defined as M/H at an intermediate field of H=5000 Oe.

3. Results and Discussion

3.1 Crystal Structure of RE$_3$Sb$_3$Mg$_2$O$_{14}$

The RE$_3$Sb$_3$Mg$_2$O$_{14}$ compounds studied here (RE=La, Pr, Sm, Eu, Tb, Ho) are all isostructural and crystallize in the rhombohedral space group R-3m in the hexagonal coordinate system. The structures were refined by placing Mg on the 3a and 3b sites and RE and Sb on the 9e and 9d sites. The oxygens were initially placed in the positions found in La$_3$Sb$_3$Zn$_2$O$_{14}$ as a guide. The Rietveld refinements proceeded smoothly, the results of which are summarized in Table 1. Figures 2 through 4 show the plots of the observed and calculated X-ray diffraction profiles for the final structural models. Some selected interatomic distances and angles are listed in Table 2.

Depicted in Figure 5 are the refined crystal structure of La$_3$Sb$_3$Mg$_2$O$_{14}$ (a) and its individual coordination polyhedra (b). Antimony is positioned in an octahedron of oxygen atoms.
with bond lengths of 1.94-2.00 Å. This SbO₆ octahedron is reasonably normal, with O-Sb-O bond angles of 90 ± 5°. Magnesium is also in octahedral coordination with a Mg1-O3 bond length of 2.13 Å, yet with O-Mg1-O bond angles that vary from 81.3 to 98.7°. The Mg2 site is 8-coordinated by two O1 oxygens with bond lengths of 1.94 Å and a puckered 6-membered ring of O2 oxygens with Mg2-O2 distances of 2.67 Å. Lanthanum is surrounded by eight oxygens in a distorted cube with three different rare earth-oxygen bond lengths: two short La-O1 bonds (2.39 Å), two long La-O2 bonds (2.64 Å), and four intermediate La-O3 bonds (2.54 Å).

As shown in Figure 6, the lattice parameters of RE₃Sb₃Mg₂O₁₄ decrease with decreasing ionic radius of the RE³⁺, as expected. The metal-oxygen distances are in general normal when compared to the sum of their ionic radii.¹⁰ While the RE-O bond distances become shorter from La (2.39-2.64 Å) to Ho (2.30-2.55 Å), the Sb-O and Mg1-O bond lengths are relatively constant, consistent with expectations. For example, for Ho₃Sb₃Mg₂O₁₄, the Sb-O2 (1.97 Å), Sb-O3 (1.94 Å), and Mg1-O3 (2.10 Å) bond lengths correspond well with those of La₃Sb₃Mg₂O₁₄ (2.00 Å, 1.94 Å, 2.13 Å). The O2-Sb-O2 bond angle changes slightly but systematically in going from La (86.3°) to Ho (83.4°). The Mg2-O bond lengths also change in a systematic manner throughout the series.

RE₃Sb₃Mg₂O₁₄ bears a strong resemblance to its parent cubic pyrochlore when considering the role that magnesium plays in the structure’s cation ordering. Mg²⁺ is present to fill in the non Kagome sites in both the RE³⁺ and Sb⁵⁺ planes, to form planes of MgRE₃ and MgSb₃ on what would be the A and B sites in an A₂B₂O₇ pyrochlore. The crystal structure presented in Figure 5a depicts the stacking of these MgRE₃ and MgSb₃ layers in the rhombohedral-on-hexagonal cell. From this perspective, RE₃Sb₃Mg₂O₁₄ can also be considered as (RE₀.₇₅Mg₀.₂₅)₂(Sb₀.₇₅Mg₀.₂₅)₂O₇, with the Mg and other ions ordered; this is essentially the pyrochlore structure with an ordered substitution of ¼ A³⁺ and B⁴⁺ ions. Examination of the x-ray diffraction patterns in Figures 2-4 reveals that the strongest reflection (222) of the cubic pyrochlore (20~30°) has split into two separate peaks in the current compounds, even qualitatively suggesting that the structures have complete Mg-Sb and Mg-RE ordering. It is also worthwhile to point out that the RE-RE separations in RE₃Sb₃Mg₂O₁₄ are very similar to those observed in the parent cubic pyrochlore. For instance, the interplane Pr-Pr distance in Pr₃Sb₃Mg₂O₁₄ is 3.72 Å, while that in Pr₂Zr₂O₇ is 3.78 Å.¹¹
3.2 Magnetic Properties

\( \text{Pr}_3\text{Sb}_3\text{Mg}_2\text{O}_{14} \)

The magnetic data for the compounds were fit to the Curie-Weiss law \( \chi = \chi_0 + \frac{C}{T-\theta_{CW}} \)

where \( \chi_0 \) is the temperature independent contribution to the susceptibility \( \chi \), \( C \) is the Curie Constant, and \( \theta_{CW} \) is the Weiss temperature. The effective moments were then obtained using \( \mu_{eff} \propto \frac{2.83\sqrt{C}}{2}. \) The magnetic susceptibility and inverse susceptibility of \( \text{Pr}_3\text{Sb}_3\text{Mg}_2\text{O}_{14} \) are shown in Figure 7. Data were fit to the Curie-Weiss law in the temperature range 150 to 300 K with a \( \chi_0 \) of 0.000005 emu Oe\(^{-1}\) mol Pr\(^{-1}\). This yielded an effective moment of 3.44 \( \mu_B \)/Pr and a Weiss temperature of \(-33.7\) K. A similar antiferromagnetic Curie-Weiss theta of \(-34.8\) K was reported for \( \text{Pr}_3\text{Sb}_3\text{Zn}_2\text{O}_{14} \). \( \mu_{eff} \) calculated for \( \text{Pr}^{3+} \) is slightly lower than the expected free ion value of 3.58 \( \mu_B \). As observed in other \( \text{Pr}^{3+} \)-containing oxides, such as \( \text{Pr}_3\text{Sb}_3\text{Zn}_2\text{O}_{14} \) (3.22 \( \mu_B \)/Pr), \( \text{Pr}_3\text{IrO}_7 \) (3.26 \( \mu_B \)/Pr), and \( \text{Pr}_{0.01}\text{U}_{0.99}\text{O}_2 \) (3.0 \( \mu_B \)/Pr), the observed moment of praseodymium is often reduced from the ideal due to its dependence on crystal field effects. \( \theta_{CW} \) indicates

This is a direct consequence of praseodymium’s excited state multiplets being located very close in energy to its ground state. \( \theta_{CW} \) indicates

The broad peak in the \( \chi(T) \) plot for \( \text{Pr}_3\text{Sb}_3\text{Mg}_2\text{O}_{14} \) at around 17 K suggests some type of magnetic ordering, but this has not yet been further investigated. The slight upswing in the susceptibility at low temperature is a consequence of the presence of either uncoupled spins or a magnetic impurity. The broad feature at around 17 K and the upturn at low temperatures were also observed in the \( \chi(T) \) for \( \text{Pr}_3\text{Sb}_3\text{Zn}_2\text{O}_{14} \). The H-dependent magnetization (M) plots of \( \text{Pr}_3\text{Sb}_3\text{Mg}_2\text{O}_{14} \) at 2 and 100 K are presented as insets to the susceptibility in Figure 7. At both high and low temperatures, the \( M(H) \) response is reversible and linear up to an applied field of \( \mu_0H=9\) T without any signs of saturation.

\( \text{Sm}_3\text{Sb}_3\text{Mg}_2\text{O}_{14} \)

As can be seen in the \( \chi(T) \) plot of \( \text{Sm}_3\text{Sb}_3\text{Mg}_2\text{O}_{14} \) in Figure 8, the high temperature susceptibility is characteristic of temperature-independent Van Vleck paramagnetism. This is common in many Sm-containing compounds, and arises from the first excited \( J=7/2 \) multiplet of \( \text{Sm}^{3+} \). Therefore, the Curie-Weiss law was fit at low temperature between 1.8 and 10 K, yielding a moment of 0.53 \( \mu_B \)/Sm and a Weiss temperature of \(-4.01\) K. The \( \theta_{CW} \) indicates
antiferromagnetic interactions between Sm moments. No \( \chi_0 \) was used in the fitting. Although the \( \mu_{\text{eff}} \) is low compared to the expected free ion value of 0.83 \( \mu_B/\text{Sm} \), it is similar to that of other reported Sm\(^{3+}\)-containing oxides, including Sm\(_3\)Sb\(_3\)Zn\(_2\)O\(_{14}\) (0.53 \( \mu_B/\text{Sm} \)) and Sm\(_2\)Zr\(_2\)O\(_7\) (0.50 \( \mu_B/\text{Sm} \)).\(^{16}\) Samarium’s large crystal field splitting of its lowest \( J=5/2 \) multiplet is likely related to the low moments observed for these compounds. The field-dependent magnetizations \( M(H) \) at 2 and 100 K provided in the inset to Figure 8 for Sm\(_3\)Sb\(_3\)Mg\(_2\)O\(_{14}\) are both linear and reversible with the field increasing and decreasing.

**Eu\(_3\)Sb\(_3\)Mg\(_2\)O\(_{14}\)**

The temperature dependent magnetic susceptibility of Eu\(_3\)Sb\(_3\)Mg\(_2\)O\(_{14}\) from 2 to 300 K is shown in Figure 9. As is typical for Eu\(^{3+}\) compounds, Eu\(_3\)Sb\(_3\)Mg\(_2\)O\(_{14}\)’s susceptibility exhibits Van Vleck paramagnetism at very high temperatures, increases with decreasing temperature, and then rapidly increases at around 2-10 K.\(^{12}\) Data were fit in the range 200-300 K with a \( \chi_0 \) of 0.001155 emu Oe\(^{-1}\) mol Eu\(^{-1}\), resulting in an effective moment of 3.54 \( \mu_B/\text{Eu} \) and \( \theta_{\text{CW}} \) of -100.1 K. The Weiss temperature is indicative of strong antiferromagnetic interactions and the effective moment is close to the observed value of 3.40-3.51 \( \mu_B/\text{Eu}^{3+} \).\(^{17}\) Similar to what was seen in the magnetic susceptibility of Eu\(_3\)Sb\(_3\)Zn\(_2\)O\(_{14}\), there may be a relationship between the interaction strength and the appearance of temperature independent paramagnetism; heat capacity or neutron diffraction measurements would conclusively determine whether magnetic ordering is present. The small peak at low temperature in the susceptibility is likely due to the presence of a magnetic impurity. This slight upturn has been observed in other Eu\(^{3+}\) oxides, including Eu\(_3\)Sb\(_3\)Zn\(_2\)O\(_{14}\), Eu\(_3\)MoO\(_7\), and Eu\(_2\)Ti\(_2\)O\(_7\).\(^{9,12,18}\) The magnetization at various applied fields for Eu\(_3\)Sb\(_3\)Mg\(_2\)O\(_{14}\) is shown in the inset to Figure 9. At both 2 and 100 K the \( M(H) \) plots are linear and reversible up to \( \mu_0H=9 \) T.

**Tb\(_3\)Sb\(_3\)Mg\(_2\)O\(_{14}\)**

The temperature dependence of magnetic susceptibility of Tb\(_3\)Sb\(_3\)Mg\(_2\)O\(_{14}\) is shown in Figure 10. \( \chi(T) \) was fit to the Curie-Weiss law from 150 to 300 K with a \( \chi_0 \) of 0.002 emu Oe\(^{-1}\) mol Tb\(^{-1}\). An effective magnetic moment of 9.67 \( \mu_B/\text{Tb} \) was obtained from the Curie-Weiss fit, which is close to the expected free ion value of 9.70 \( \mu_B/\text{Tb} \). A Weiss temperature of -8.86 K was extrapolated from the high temperature fit, which suggests the presence of antiferromagnetic
interactions between Tb$^{3+}$ spins. The field dependent magnetization plots of Tb$_3$Sb$_3$Mg$_2$O$_{14}$ at 2 and 100 K are displayed as insets to the magnetic susceptibility in Figure 10. At 100 K, the $M(H)$ plot is linear and reversible up to an applied field of $\mu_0 H = 9$ T. However, at 2 K, the response is nonlinear with the onset of saturation at roughly 5.8 $\mu_B$/Tb.

**Ho$_3$Sb$_3$Mg$_2$O$_{14}$**

Shown in Figure 11 are the magnetic susceptibility and inverse susceptibility for Ho$_3$Sb$_3$Mg$_2$O$_{14}$. Data were fit to the Curie Weiss law between 100 and 300 K with a $\chi_0$ of 0.0027 emu Oe$^{-1}$ mol Ho$^{-1}$. This yielded a moment of 10.60 $\mu_B$/Ho and a Weiss temperature of -13.7 K. The effective moment matches well with the expected free ion value of 10.60 $\mu_B$/Ho. The $\theta_{CW}$ is indicative of antiferromagnetic interactions. The $M(H)$ plots at 2 and 100 K are shown in the inset to Figure 11. The field dependent magnetization at 100 K is linear and reversible with the field increasing and decreasing. Conversely, the $M(H)$ plot at 2 K reveals a nonlinear response between magnetization and the applied field and saturation at roughly 5.6 $\mu_B$/Ho, a little more than half the value of the effective moment of Ho$^{3+}$ obtained from the Curie-Weiss fits. A saturation value of about half the effective moment in polycrystalline samples is typically attributed to powder averaging of Ising spins; this phenomenon has been observed in several holmium pyrochlores. Where overlapping, the results obtained here for all materials are in good agreement with the results reported by Dun et al.

4. Conclusions

We have synthesized several new compounds in the RE$_3$Sb$_3$Mg$_2$O$_{14}$ family (RE=La, Pr, Sm, Eu, Tb, Ho). Structural refinements indicate they are fully ordered and layered and crystallize in the space group $R-3m$ derived from the cubic pyrochlore structure. Magnetic property measurements show that the compounds display antiferromagnetic interactions, and no signs of magnetic ordering above 2 K except possibly the Pr and Eu cases. It is worthwhile to note that this structure type exhibits a wide range of chemical tolerance; Mg$^{2+}$ has already been substituted for Zn$^{2+}$, Co$^{2+}$, Mn$^{2+}$, and Ca$^{2+}$. The 3D pyrochlore analogs of these compounds have been shown to exhibit several exotic magnetic phenomena at low temperatures—from the spin ice behavior observed in Ho$_2$Ti$_2$O$_7$ and Ho$_2$Sn$_2$O$_7$, to the spin liquid phenomena reported in
Tb$_2$Ti$_2$O$_7$. Further characterization of these new Kagome compounds, especially at lower temperatures, could also potentially lead to novel and interesting magnetic phenomena.

**Acknowledgements**

All of this research was supported by the U.S. Department of Energy, Division of Basic Energy Sciences, Grant No. DE-FG02-08ER46544, through the Institute for Quantum Matter at Johns Hopkins University.
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### Table 1: Refinement Summary of RE$_3$Sb$_3$Mg$_3$O$_{14}$ @ 298 K

|          | La       | Pr       | Sm       | Eu       | Tb       | Ho       |
|----------|----------|----------|----------|----------|----------|----------|
| RE (9e)  | (½,0,0)  | (½,0,0)  | (½,0,0)  | (½,0,0)  | (½,0,0)  | (½,0,0)  |
| B (Å$^2$)| 2.64(4)  | 3.85(3)  | 3.64(3)  | 3.44(9)  | 2.87(2)  | 3.89(5)  |
| Mg1 (3a) | (0,0,0)  | (0,0,0)  | (0,0,0)  | (0,0,0)  | (0,0,0)  | (0,0,0)  |
| B (Å$^2$)| 2.00(8)  | 2.10(9)  | 2.89(2)  | 2.49(2)  | 1.00(1)  | 1.55(9)  |
| Mg2 (18g)| (0,0,½)  | (0,0,½)  | (0,0,½)  | (0,0,½)  | (0,0,½)  | (0,0,½)  |
| B (Å$^2$)| 3.15(7)  | 2.74(3)  | 2.66(8)  | 2.21(8)  | 1.43(1)  | 1.12(9)  |
| Sb (9d)  | (1/2,0,1/2)| (1/2,0,1/2)| (1/2,0,1/2)| (1/2,0,1/2)| (1/2,0,1/2)| (1/2,0,1/2)|
| B (Å$^2$)| 2.53(2)  | 3.56(8)  | 3.91(6)  | 3.08(6)  | 2.45(1)  | 2.90(7)  |
| O1 (6c)  | (0,0,z)  | (0,0,z)  | (0,0,z)  | (0,0,z)  | (0,0,z)  | (0,0,z)  |
| z        | 0.3903(1) | 0.3878(7)| 0.3873(4)| 0.3866(1)| 0.3866(1)| 0.3872(8)|
| B (Å$^2$)| 2.32(4)  | 2.26(1)  | 2.64(1)  | 3.60(1)  | 2.71(4)  | 2.90(8)  |
| O2 (18h) | (x,8,z)  | (x,8,z)  | (x,8,z)  | (x,8,z)  | (x,8,z)  | (x,8,z)  |
| x        | 0.5370(1) | 0.5361(4)| 0.5352(3)| 0.5346(8)| 0.5324(1)| 0.5324(9)|
| z        | 0.1471(9) | 0.1464(9)| 0.1462(6)| 0.1459(6)| 0.1456(1)| 0.1459(2)|
| B (Å$^2$)| 3.39(2)  | 3.29(8)  | 2.31(2)  | 3.26(7)  | 2.19(2)  | 2.60(8)  |
| O3 (18h) | (x,8,z)  | (x,8,z)  | (x,8,z)  | (x,8,z)  | (x,8,z)  | (x,8,z)  |
| x        | 0.1439(1) | 0.1451(6)| 0.1466(1)| 0.1471(1)| 0.1475(9)| 0.1477(1)|
| z        | -0.0581(7)| -0.0569(8)| -0.0559(1)| -0.0557(3)| -0.0545(4)| -0.0550(2)|
| B (Å$^2$)| 2.52(8)  | 3.96(9)  | 2.29(6)  | 3.61(7)  | 2.12(5)  | 2.76(9)  |
| a (Å)    | 7.50202(2)| 7.43870(7)| 7.38615(1)| 7.37237(2)| 7.33503(5)| 7.30440(9)|
| c (Å)    | 17.66983(2)| 17.58285(1)| 17.47037(1)| 17.42688(9)| 17.32900(6)| 17.25801(8)|
| $R_{wp}$ (%) | 12.9 | 17.6 | 18.2 | 15.2 | 19.1 | 19.0 | 11.4 | 16.9 | 18.5 | 15.8 | 17.7 | 17.7 | 2.79 | 3.20 | 3.05 | 2.25 | 3.07 | 3.85 |
Table 2: Selected bond distances (Å) and bond angles (°) for \(\text{RE}_3\text{Sb}_3\text{Mg}_2\text{O}_{14}\) (RE = La, Pr, Sm, Eu, Tb, Ho @ 298 K)

|       | La     | Pr     | Sm     | Eu     | Tb     | Ho     |
|-------|--------|--------|--------|--------|--------|--------|
| REO₈  |        |        |        |        |        |        |
| RE-O1 | 2.388(2)x2 | 2.351(7)x2 | 2.331(6)x2 | 2.321(9)x2 | 2.309(9)x2 | 2.304(9)x2 |
| RE-O2 | 2.644(8)x2 | 2.617(3)x2 | 2.594(6)x2 | 2.581(8)x2 | 2.556(3)x2 | 2.551(5)x2 |
| RE-O3 | 2.544(5)x2 | 2.507(9)x2 | 2.472(6)x2 | 2.463(7)x2 | 2.439(1)x2 | 2.431(4)x2 |
| Average RE-O | 2.530(7) | 2.496(1) | 2.468(1) | 2.457(6) | 2.436(3) | 2.430(1) |
| Intraplane RE-RE | 3.751(1) | 3.719(3) | 3.693(1) | 3.686(1) | 3.667(5) | 3.652(2) |
| Interplane RE-RE | 5.889(9) | 5.860(9) | 5.823(4) | 5.808(9) | 5.776(3) | 5.752(7) |
| SbO₆  |        |        |        |        |        |        |
| Sb-O2 | 2.00(1)x4 | 1.98(8)x4 | 1.97(9)x4 | 1.97(8)x4 | 1.97(9)x4 | 1.96(9)x4 |
| Sb-O3 | 1.93(9)x2 | 1.94(8)x2 | 1.95(2)x2 | 1.94(9)x2 | 1.95(8)x2 | 1.94(2)x2 |
| Average Sb-O | 1.97(9) | 1.97(5) | 1.97(1) | 1.96(9) | 1.97(2) | 1.96(1) |
| O2-Sb-O3 | 86.0(5)x4 | 85.2(5)x4 | 84.6(9)x4 | 84.4(2)x4 | 84.0(5)x4 | 84.1(9)x4 |
| O2-Sb-O2 | 93.9(5)x4 | 94.7(5)x4 | 95.3(2)x4 | 95.5(8)x4 | 95.9(5)x4 | 95.8(1)x4 |
| Average MgO₆ | 86.2(5)x2 | 85.7(8)x2 | 85.1(9)x2 | 84.8(7)x2 | 83.3(7)x2 | 83.3(6)x2 |
| Mg1-O3 | 2.13(3)x6 | 2.12(1)x6 | 2.11(4)x6 | 2.11(4)x6 | 2.09(9)x6 | 2.09(5)x6 |
| Mg2O₆ |        |        |        |        |        |        |
| Mg2-O1 | 2.13(8)x2 | 1.97(2)x2 | 1.96(8)x2 | 1.97(6)x2 | 1.96(5)x2 | 1.94(5)x2 |
| Mg2-O2 | 2.66(8)x6 | 2.63(6)x6 | 2.60(7)x6 | 2.59(6)x6 | 2.55(5)x6 | 2.54(4)x6 |
| Average Mg2-O | 2.48(6) | 2.47(1) | 2.44(7) | 2.44(1) | 2.40(7) | 2.39(4) |
Figure Captions

Figure 1
Ball and stick figures showing the connectivity of the rare earth atoms in the $A_2B_2O_7$ pyrochlore (left) and in the $RE_3Sb_3Mg_2O_{14}$ Kagome (right) along the [111] and [001] directions, respectively. The rare earth ions in $RE_3Sb_3Mg_2O_{14}$ make up discrete Kagome layers, while in $A_2B_2O_7$, a triangular layer of magnetic ions is positioned between the Kagome planes. The cubic and rhombohedral unit cells are drawn in the background of each model.

Figure 2
Rietveld refinement of $La_3Sb_3Mg_2O_{14}$ (upper panel) and $Pr_3Sb_3Mg_2O_{14}$ (lower panel) at room temperature using x-ray diffraction data. The experimental pattern is in red, the calculated pattern in black, and the difference plot in blue, showing the very good fit of the model to the data. The green marks indicate Bragg reflections.

Figure 3
Rietveld refinement of $Sm_3Sb_3Mg_2O_{14}$ (upper panel) and $Eu_3Sb_3Mg_2O_{14}$ (lower panel) at room temperature using x-ray diffraction data. The experimental pattern is in red, the calculated pattern in black, and the difference plot in blue, showing the very good fit of the model to the data. The green marks indicate Bragg reflections.

Figure 4
Rietveld refinement of $Tb_3Sb_3Mg_2O_{14}$ (upper panel) and $Ho_3Sb_3Mg_2O_{14}$ (lower panel) at room temperature using x-ray diffraction data. The experimental pattern is in red, the calculated pattern in black, and the difference plot in blue, showing the very good fit of the model to the data. The green marks indicate Bragg reflections.

Figure 5
A. The crystal structure of $La_3Sb_3Mg_2O_{14}$, depicting the stacking of $MgLa_3$ and $MgSb_3$ layers. The violet polyhedra represent $LaO_8$, the green polyhedra $SbO_6$, and the two pink polyhedra $Mg1O_6$ and $Mg2O_6$, respectively. B. The coordination polyhedra of
La$_3$Sb$_3$Mg$_2$O$_{14}$: La (upper left), Sb (lower left), Mg1 (upper right), and Mg2 (lower right). The different types of oxygen atoms are represented in different shades of blue.

**Figure 6**
The $a$ and $c$ lattice parameters for RE$_3$Sb$_3$Mg$_2$O$_{14}$ as a function of rare earth ionic radius. The purple and pink circles represent the $a$ and $c$ parameters, respectively. The standard deviations are smaller than the plotted points and so error bars are excluded from the figure.

**Figure 7**
The DC magnetic susceptibility and inverse susceptibility of Pr$_3$Sb$_3$Mg$_2$O$_{14}$ measured in an applied field of 5000 Oe. The Curie-Weiss fit is shown in black. The insets to the right of the MT plot show the magnetization as a function of applied field $M(H)$ at 2 K (upper panel) and 100 K (lower panel).

**Figure 8**
Temperature-dependent magnetic susceptibility of Sm$_3$Sb$_3$Mg$_2$O$_{14}$ measured in an applied field of 5000 Oe. The low temperature Curie-Weiss fit is shown in cyan. The insets to the right of the magnetic susceptibility plot display the field-dependent magnetizations at 2K and 100 K.

**Figure 9**
The DC magnetic susceptibility and reciprocal susceptibility of Eu$_3$Sb$_3$Mg$_2$O$_{14}$ measured in an applied field of 5000 Oe. The Curie-Weiss fit is shown in black. The plots in the upper and lower panels to the right of the MT graph show the field-dependent magnetizations at 2 and 100 K, respectively.

**Figure 10**
Temperature-dependent magnetic susceptibility of Tb$_3$Sb$_3$Mg$_2$O$_{14}$ measured in an applied field of 5000 Oe. The Curie-Weiss fit is shown in black. The insets display $M(H)$ plots of the compound at temperatures of 2 K (upper panel) and 100 K (lower panel).
Figure 11
Magnetic susceptibility and inverse susceptibility of Ho$_3$Sb$_3$Mg$_2$O$_{14}$ measured in an applied field of 5000 Oe. The Curie-Weiss fit is shown in light green. The panels to the right of the susceptibility plot show the field-dependent magnetizations at temperatures of 2 and 100 K.
Figures
Figure 1

$A_2B_2O_7$
Pyrochlore

$RE_3Sb_3Mg_2O_{14}$
Kagome
Figure 2

La$_3$Sb$_3$Mg$_2$O$_{14}$

$T = 298\; \text{K}$
$
\lambda = \text{Cu K}\alpha$

Intensity (arb. units)

Pr$_3$Sb$_3$Mg$_2$O$_{14}$

$T = 298\; \text{K}$
$
\lambda = \text{Cu K}\alpha$

Intensity (arb. units)
Figure 3

**Sm₃Sb₃Mg₂O₁₄**

- \( T = 298 \text{ K} \)
- \( \lambda = \text{Cu K}\alpha \)

**Eu₃Sb₃Mg₂O₁₄**

- \( T = 298 \text{ K} \)
- \( \lambda = \text{Cu K}\alpha \)
Figure 6
Figure 9

![Figure 9](image)

\( \chi - \chi_0 \) (emu Oe\(^{-1}\) mol Eu\(^{-1}\)) vs. Temperature (K)

\( \chi - \chi_0 \) (emu Oe\(^{-1}\)) vs. \( \mu_0 H \) (Oe)

\( M (\mu_B/\text{Eu}) \) vs. \( \mu_0 H \) (Oe)

\( T = 2 \) K

\( T = 100 \) K

Eu\(_3\)Sb\(_3\)Mg\(_2\)O\(_{14}\)

\( H = 5000 \) Oe

Figure 10

![Figure 10](image)

\( \chi - \chi_0 \) (emu Oe\(^{-1}\) mol Tb\(^{-1}\)) vs. Temperature (K)

\( \chi - \chi_0 \) (emu Oe\(^{-1}\)) vs. \( \mu_0 H \) (Oe)

\( M (\mu_B/\text{Tb}) \) vs. \( \mu_0 H \) (Oe)

\( T = 2 \) K

\( T = 100 \) K

Tb\(_3\)Sb\(_3\)Mg\(_2\)O\(_{14}\)

\( H = 5000 \) Oe
