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La_2MgGeO_6: a novel Ge based perovskite synthesised under ambient pressure

Mark Swaffer,[a] Peter R. Slater,*[a] Richard K. B. Gover,[b] Tadaaki Matsumura,[c] Ryoji Kanno[c] and Takashi Kamiyama[d]

[a] *Department of Chemistry, University of Surrey, Guildford, Surrey, UK GU2 7XH.*
E-mail: p.slater@surrey.ac.uk; Fax: +44 (0)1483 686851; Tel: +44 (0)1483 686847
[b] *School of Chemistry, University of Durham, Science Laboratories, South Road, Durham, UK DH1 3LE*
[c] *Department of Electronic Chemistry, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-Ku, Yokohama, 226-8502, Japan*
[d] *Neutron Science Laboratory, Institute of Materials Structure Science, High Energy Accelerator Research Organization, 1-1, Oho, Tsukuba, Ibaraki 305-0801, Japan*

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In this communication we report the synthesis and structural characterisation of the new perovskite phase La_2MgGeO_6, which is the first example of a Ge based perovskite phase synthesised at ambient pressure.

Materials with the perovskite structure have attracted considerable interest, due to the fact that they can exhibit a wide range of technologically important properties, *e.g.* superconductivity, colossal magnetoresistance, oxide ion conductivity, proton conductivity and ferroelectricity. In addition perovskite phases account for a large part of the Earth′s lower mantle. In this latter case, the phases concerned are Si based high pressure polymorphs, such as $MgSiO_3$.[1] Because of the interest in the nature of the Earth′s mantle, there has been a lot of interest in the synthesis and structures of these phases. Such synthesis is not facile requiring high temperature and very high pressure. Germanium based perovskites, *e.g.* $CaGeO_3$ and $SrGeO_3$, have therefore also attracted significant attention as structural analogs of the silicate materials. However even these phases require high pressure synthesis, albeit lower than for the corresponding silicates.[2–5] We have been investigating Ge based compounds, and during studies of phases in the La–Mg–Ge–O system, we have discovered a new perovskite type phase, La_2MgGeO_6, which is reported here. Significantly this phase is to our knowledge the first example of a Ge based perovskite phase that can be prepared under ambient pressure.

The synthesis of this phase was performed as follows: high purity La_2O_3, MgO and GeO_2 were weighed out in the correct ratio to give the stoichiometry La_2MgGeO_6, and ground together for 15 minutes. The resultant mixture was then heated to 1350 °C for 14 h. The sample was then reground and reheated to 1400 °C for a further 14 h. Phase purity was examined using powder X-ray diffraction (Seifert 3003TT X-ray diffractometer). For the structural determination a 2 g sample was prepared, and time of flight neutron powder diffraction data were collected on the Vega Diffractometer, located at the KENS neutron source, Japan. Structure refinement was performed by the Rietveld method using the program RIETAN 2001-T.[6]A single phase sample according to X-ray diffraction was obtained for the composition La_2MgGeO_6. The pattern could be indexed on a hexagonal cell, $a \approx 5.51$, $c \approx 13.33$ Å. Structural refinement was attempted with a range of space groups, the best fit being observed for the space group $R3$, which allows for the possibility of ordering of the Mg and Ge in the small cation sites of the perovskite structure. Refinement using this space group gave a good fit to the data and indicated an ordered arrangement of Mg and Ge. The refined data is shown in Table 1, with selected bond distances in Table 2. Refinement of site occupancies gave values that did not deviate significantly from 1.0, and so in the final refinement, the occupancies were fixed at 1.0.

Table 1 Refined structural parameters for La_2MgGeO_6

Atom	Site	*x*	*y*	*z*	B/Å^2	Site Occ.
La1	3a	0	0	0.248(3)	0.31(6)	1.0
La2	3a	0	0	0.752(2)	0.19(6)	1.0
Mg	3a	0	0	0	0.1(1)	1.0
Ge	3a	0	0	0.503(3)	0.2(1)	1.0
O1	9b	0.119(2)	0.354(2)	0.089(2)	0.5(2)	1.0
O2	9b	0.112(2)	0.789(2)	0.578(2)	0.3(2)	1.0

Space group $R3$, $a = 5.5125$ (1), $c = 13.3295(2)$ Å; $R_{wp} = 7.03\%$, $R_p = 4.94\%$, $R_e = 2.97\%$, $R_I = 2.17\%$.

Table 2 Selected bond distances for La_2MgGeO_6

Bond	Bond distance/Å
La1–O1	2.73 (3) (× 3)
	2.78 (3) (× 3)
La1–O2	3.03 (3) (× 3)
	2.48 (3) (× 3)
La2–O1	3.08 (2) (× 3)
	2.44 (2) (× 3)
La2–O2	2.80 (2) (× 3)
	2.70 (2) (× 3)
Ge–O1	1.87 (3) (× 3)
Ge–O2	1.86 (3) (× 3)
Mg–O1	2.09 (2) (× 3)
Mg–O2	2.04 (2) (× 3)

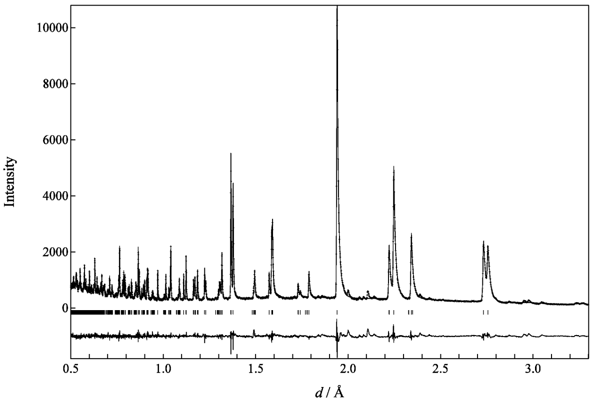

Fig. 1 Observed, calculated and difference neutron diffraction profiles for La_2MgGeO_6.

The neutron diffraction profiles are shown in Fig. 1. The anisotropy of the peak shapes is associated with the characteristics of the moderator at the KENS neutron source. The small

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impurity peaks are due to MgO and an apatite-type phase $(La/Mg)_{10-x}Ge_6O_{26+y}$, which were present in the larger sample prepared for the structural study. XRD studies of the evolution of this phase with temperature have shown that this latter apatite-type phase tends to form initially at lower temperatures, and then reacts together with the MgO at higher temperatures (1400 °C) to give La_2MgGeO_6.

The structure determined for La_2MgGeO_6 is shown in Fig. 2, where the ordering of Mg and Ge in the small cation sites can be seen. Each Mg is surrounded by six Ge and *vice versa*. This results in different bond lengths around the Mg and Ge sites, with shorter bond lengths for the latter. Both Mg and Ge are six-coordinate, although there is some distortion away from the ideal octahedral geometry. In addition there is some tilting of the octahedra, as seen in a number of perovskites. Bond strength sum calculations were performed for the Mg, Ge and La sites, and are consistent with the values expected for these ions (La1 2.8+, La2 3.0+, Mg 2.2+, Ge 4.4+).[7,8]

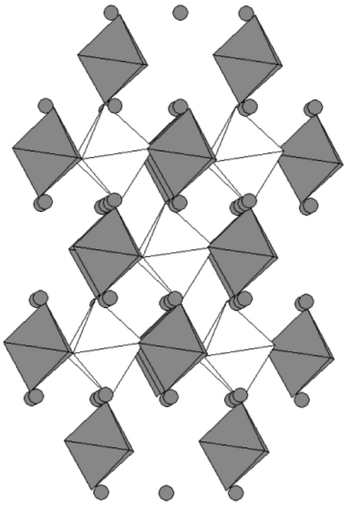

Fig. 2 Structure of La_2MgGeO_6 showing ordering of Mg and Ge in the small cation sites (light octahedra = MgO_6, dark octahedra = GeO_6, spheres = La).

As stated this is a rare example of a Ge based perovskite, and to our knowledge, the first that has been synthesised under ambient pressure. The lack of Ge containing perovskites may be explained by the small size of the Ge^{4+} ion and its general preference for tetrahedral geometry. It is presumably the presence of the larger Mg around each Ge that helps stabilise the structure in this case, and this therefore represents a strategy for the design of other Ge based or even Si based perovskites.

Further studies were therefore performed to try to prepare other related Ge containing perovskites. Attempts to replace Mg by Zn or Cu were unsuccessful with no sign of a perovskite phase being formed. In contrast, replacing Mg by Ni was possible to give La_2NiGeO_6, although small apatite-type impurities were observed. In order to obtain single phase samples according to XRD it was found to be necessary to increase the Ni:Ge ratio slightly, a composition of $La_2Ni_{1.1}Ge_{0.9}O_{6-x}$ being single phase. As before, the pattern could be indexed on a hexagonal cell, $a = 5.518(2)$, $c = 13.258(5)$ Å. Attempts were also made to vary the rare earth size, however this was unsuccessful with no sign of a perovskite phase being formed in the case of Nd_2MgGeO_6.

In conclusion we have prepared a new Ge containing perovskite La_2MgGeO_6 as well as an analogue with Ni in place of Mg. Significantly this phase can be prepared at ambient pressure unlike previously reported Ge based perovskites, and gives a stable example of octahedral Ge in a perovskite system. Such compounds are of interest to both solid state chemists and Earth scientists.

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Notes and references

1 A. E. Ringwood, *Geochim. Cosmochim. Acta*, 1991, **55**, 2083.
2 Y. Shimizu, Y. Syono and S. Akimoto, *High Temp.–High Pressure*, 1970, **2**, 113.
3 S. Sasaki, C. T. Prewitt and R. C. Liebermann, *Am. Mineral.*, 1983, **68**, 1189.
4 JCPDS 35-1399.
5 JCPDS 24-1158.
6 T. Ohta, F. Izumi, K. Oikawa and T. Kamiyama, *Physica B (Amsterdam)*, 1997, **234–236**, 1093.
7 I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B*, 1985, **41**, 244.
8 N. E. Brese and M. O′Keefe, *Acta Crystallogr. Sect. B*, 1991, **47**, 192.