inorganic compounds

Monoclinic superstructure of SrMgF$_4$ with perovskite-type slabs

Nobuo Ishizawa,[a]* **Katsumi Suda,**[a] **Barbara E. Etschmann,**[a] **Takashi Oya**[a]† **and Nobuhiro Kodama**[b]

[a]Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama 226, Japan, and [b]Department of Materials Science and Engineering, Akita University, Akita 010-8502, Japan
Correspondence e-mail: nishizaw@n.cc.titech.ac.jp

Crystals of Ce-doped SrMgF$_4$, strontium magnesium tetrafluoride, have been found to have a monoclinic $P2_1$ structure with doubled a and tripled c cell lengths compared with the orthorhombic $Cmcm$ structure previously reported in the literature. The perovskite-type slabs, composed of corner-sharing MgF$_6$ octahedra and Sr atoms, are stacked along the b axis. The six crystallographically independent MgF$_6$ octahedra are rotated so as to provide long periodicities along **a** and **c**. The coordination numbers and bond distances around the six crystallographically independent Sr atoms are slightly different in each case. In the superstructure, the Sr atoms lie on local mirror planes which are thought to originate at the high-temperature phase transition.

Comment

Crystals of the (Sr,Ba)MgF$_4$ solid solution have attracted attention as host materials for optical applications (Banks *et al.*, 1980; Yamaga *et al.*, 2000). The room-temperature structure of the end member, SrMgF$_4$, was reported to have orthorhombic symmetry in the space group $Cmcm$, with a = 3.917 (2), b = 14.451 (8) and c = 5.637 (3) Å, determined by powder diffraction (Banks *et al.*, 1982). In the present study, however, it was found that the Ce-doped SrMgF$_4$ crystal has a monoclinic superstructure with doubled a and tripled c cell lengths with respect to the $Cmcm$ unit cell.

The structure of SrMgF$_4$ projected along **c**, **a** and **b*** is shown in Figs. 1, 2 and 3, respectively. The first setting, with a unique c axis, was used to match the 2_1 axis with those in the $Cmcm$ and $Cmc2_1$ modifications. The structure is essentially regarded as the end member (n = 2) of the homologous series $A_nB_nX_{3n+2}$ with perovskite-type slabs (Ishizawa *et al.*, 1975), where A is an alkaline, alkali earth or rare earth element, B is a metal element with octahedral coordination and X is oxygen or a halogen. The perovskite-type slab is composed of corner-

sharing MgF$_6$ octahedra and Sr atoms, and is extended infinitely along **a** and **c**. Neighbouring slabs are shifted by **a**/4, corresponding to half the height of an octahedron, as shown in Fig. 1. The rotation of MgF$_6$ octahedra projected along **a**, as shown in Fig. 2, closely resembles those reported for the $Cmc2_1$ modifications of BaZnF$_4$ (von Schnering & Bleckmann, 1968), BaMgF$_4$ (Gingl, 1997) and Ba$_{1-x}$Sr$_x$MgF$_4$, with x = 0.27 and 0.55 (Kubel *et al.*, 1997).

Although the six octahedra, Mg1F$_6$–Mg6F$_6$, are crystallographically independent, they have approximately the same shape. The octahedral rotation occurs in a complicated manner, as shown in Fig. 3. The rotation can be split into three orthogonal components about the a, b* and c axes. All octahedra are rotated by 15–20° about **a**. Mg1F$_6$ and Mg4F$_6$ are rotated approximately 8° about **b***, while the rotation for the other MgF$_6$ octahedra is negligible about **b***. Conversely, the rotation about **c** is negligible for Mg1F$_6$ and Mg4F$_6$, and approximately 8° for the other MgF$_6$ octahedra. The complexity of the octahedral rotation results in the formation of a relatively large unit cell with tripled c and doubled a cell lengths.

Although there are no constraints among the positional parameters of the six independent Sr atoms, they align almost on a plane perpendicular to **a**, as shown in Figs. 1 and 3. The Mg1F$_6$ and Mg4F$_6$, Mg2F$_6$ and Mg5F$_6$, and Mg3F$_6$ and Mg6F$_6$ octahedra pairs are related by a pseudo-mirror plane formed by the Sr atoms. Since the neighbouring slabs are shifted by half the height of an MgF$_6$ octahedron, these mirrors are local symmetries effective only within every other slab. Such local mirrors in perovskite-type slabs also exist in the monoclinic
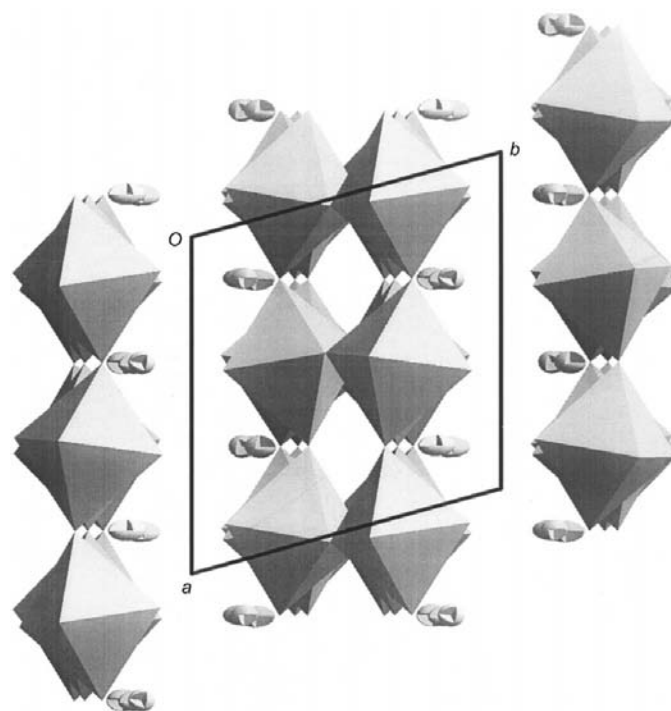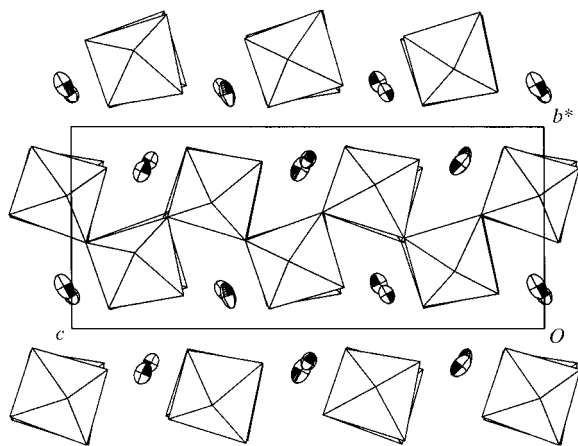

Figure 1
A polyhedral view of SrMgF$_4$ projected along **c**. Displacement ellipsoids for Sr atoms are drawn at the 97% probability level.

† On leave from Tokai University, Hiratsuka, Kanagawa 259-1292, Japan.

modifications of $La_2Ti_2O_7$ (Gasperin, 1975) and $Ca_2Nb_2O_7$ (Ishizawa *et al.*, 1980), which are $n = 4$ members of the $A_nB_nX_{3n+2}$ series. The phase transition in $BaMgF_4$ at 1082 K (Bingyi & Banks, 1982) could be the origin of such local mirror symmetries, as is the case for $La_2Ti_2O_7$ (Ishizawa *et al.*, 1982).

It is appropriate to assume that the prototype structure of $BaMgF_4$ has orthorhombic *Cmcm* symmetry with unit-cell vectors $\mathbf{a}_0 = \frac{1}{2}\mathbf{a}$, $\mathbf{b}_0 = \frac{1}{2}\mathbf{a} + 2\mathbf{b}$ and $\mathbf{c}_0 = \frac{1}{3}\mathbf{c}$. However, the *Cmcm* structure of $SrMgF_4$ determined at room temperature by powder diffraction (Banks *et al.*, 1982) contains some geometrical problems. In particular, the Mg atoms are shifted, somewhat unusually, from the centre of each coordination octahedron, resulting in a range of Mg—F bond distances, *i.e.* 1.71 Å × 2, 1.92 Å × 2 and 2.04 Å × 2. The 1.71 Å distances are rather short for MgF_6 octahedra, as the effective ionic radius is 1.3 Å for F^- and 0.72 Å for Mg^{2+} (Shannon, 1976). No such problem was observed in the present study; all Mg—F distances in the six independent MgF_6 octahedra fall within the range 1.91–2.04 Å.

As shown in Fig. 3, the Sr atoms are shifted onto the pseudo-mirror planes to fit in the space formed by the six MgF_6 octahedra of a slab and one MgF_6 of a neighbouring slab. The Ce dopant supposedly replaces Sr, as the ionic radius of Ce is much closer to Sr than Mg. Therefore, the modulation of the coordination geometry around various Sr sites becomes important for understanding the optical properties of Ce-doped $SrMgF_4$. If we count F atoms with Sr—F distances less than the shortest Sr—Mg distance, there are eight F atoms around Sr1 at distances in the range 2.46–2.80 Å, and three more in the range 2.98–3.36 Å. There is a gap of 0.18 Å between these two groups of bond distances. The coordination number of Sr1 may thus be expressed as 8+3. In a similar way, there are seven F (2.45–2.65 Å) plus three F (2.95–3.16 Å) around Sr2, nine F (2.39–2.70 Å) around Sr3, nine F (2.45–2.71 Å) around Sr4, seven F (2.37–2.73 Å) plus three F (3.00–3.38 Å) around Sr5 and ten F (2.43–2.93 Å) around Sr6.

Figure 2
A polyhedral view of $SrMgF_4$ along **a**. Displacement ellipsoids for Sr atoms are drawn at the 97% probability level. The two crystallographically independent octahedra fall at nearly the same positions in the projection along **a**.

Regarding the coordination of Sr3, Sr4 and Sr6, there is no distinct gap in bond distances similar to that seen for Sr1, Sr2 and Sr5.
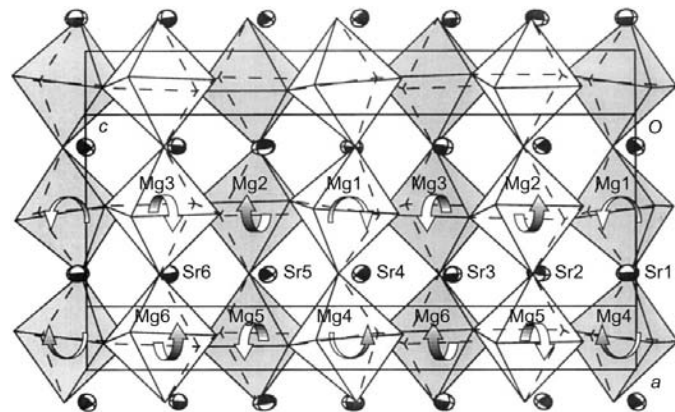
Figure 3
A polyhedral view of $SrMgF_4$ projected along $\mathbf{b}^*$. Displacement ellipsoids for Sr atoms are drawn at the 97% probability level. Arrows show the directions of rotation of the MgF_6 octahedra.

Experimental

Ce-doped $SrMgF_4$ crystals were grown by the Bridgman method (Bridgman, 1925). The starting $4N$ grade powders were mixed together in a CeF_3:SrF_3:MgF_2 ratio of 0.005:0.995:1. This mixture was placed in a carbon crucible which was heated in a resistance furnace under an argon atmosphere. A colourless single crystal of about 18 mm diameter and 30 mm length was grown by displacing the crucible vertically at a speed of 0.07 mm h^{-1}. The atomic ratio of Sr to Ce was determined by X-ray fluorescence spectrometry to be 0.9994:0.0006. Since the concentration of Ce was considered to be negligible, a stoichiometric composition of $SrMgF_4$ was assumed for the structure analysis.

Crystal data

$SrMgF_4$	$D_x = 3.907$ Mg m^{-3}
$M_r = 187.92$	Mo $K\alpha$ radiation
Monoclinic, $P112_1$	Cell parameters from 87 446
$a = 7.8249\ (8)$ Å	reflections
$b = 7.4930\ (7)$ Å	$\theta = -30$ to $70°$
$c = 16.9248\ (17)$ Å	$\mu = 16.99$ mm^{-1}
$\gamma = 105.041\ (11)°$	$T = 298$ K
$V = 958.34\ (17)$ Å^3	Irregular, colourless
$Z = 12$	$0.30 \times 0.20 \times 0.15$ mm

Data collection

Rigaku R-AXIS RAPID Imaging Plate diffractometer	7537 independent reflections
	4369 reflections with $I > 3\sigma(I)$
ω scans	$R_{int} = 0.073$
Absorption correction: Gaussian (*RAPID AUTO*; Rigaku, 1999)	$\theta_{max} = 45.3°$
	$h = -13 \rightarrow 15$
$T_{min} = 0.020$, $T_{max} = 0.257$	$k = -14 \rightarrow 11$
58 521 measured reflections	$l = -33 \rightarrow 33$

Refinement

Refinement on F	$\Delta\rho_{max} = 2.00$ e Å^{-3}
$R = 0.044$	$\Delta\rho_{min} = -1.85$ e Å^{-3}
$wR = 0.037$	Extinction correction: Zachariasen
$S = 3.14$	(1968)
4130 reflections	Extinction coefficient: $2.35\ (6) \times 10^3$
326 parameters	Absolute structure: Flack (1983)
$(\Delta/\sigma)_{max} < 0.001$	Flack parameter = 0.097 (8)

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Table 1
Selected bond lengths (Å).

Mg1—F2	1.931 (5)	Mg4—F13	1.921 (5)
Mg1—F10	1.950 (5)	Mg4—F14^{ii}	1.946 (5)
Mg1—F1	1.978 (5)	Mg4—F10^{ii}	1.973 (5)
Mg1—F22	1.980 (5)	Mg4—F22	1.999 (6)
Mg1—F4	1.985 (5)	Mg4—F16^{iii}	2.012 (5)
Mg1—F3	1.994 (5)	Mg4—F15	2.028 (5)
Mg2—F4^{i}	1.929 (5)	Mg5—F16^{ii}	1.934 (4)
Mg2—F5	1.959 (5)	Mg5—F17	1.981 (5)
Mg2—F11	1.969 (4)	Mg5—F11	1.989 (5)
Mg2—F23	1.999 (4)	Mg5—F19^{ii}	1.990 (5)
Mg2—F6	2.010 (5)	Mg5—F18	2.004 (5)
Mg2—F7	2.041 (5)	Mg5—F23^{ii}	2.013 (5)
Mg3—F8	1.910 (5)	Mg6—F19	1.934 (5)
Mg3—F7	1.966 (4)	Mg6—F20	1.987 (5)
Mg3—F24	1.981 (5)	Mg6—F12^{iv}	1.989 (4)
Mg3—F12	1.987 (5)	Mg6—F24	1.989 (5)
Mg3—F2	2.011 (5)	Mg6—F21	2.000 (5)
Mg3—F9	2.025 (5)	Mg6—F14	2.040 (5)

Symmetry codes: (i) $1-x, 1-y, z-\frac{1}{2}$; (ii) $x-1, y, z$; (iii) $1-x, 1-y, \frac{1}{2}+z$; (iv) $1+x, y, z$.

Since there were virtually no significant reflections at 2θ higher than 90°, all data in this region were eliminated. Equivalent reflections were merged using *Xtal*3.4 (Hall *et al.*, 1995). Friedel pairs were considered as separate reflections for the merge. In all, 4369 independent Friedel pairs with $I > 3\sigma(I)$ and $R_{int} = 0.073$ were used for the structure determination and the refinement procedure. The z coordinate of Sr4 was fixed at $\frac{1}{2}$ to define the origin.

Data collection: *RAPID AUTO* (Rigaku, 1999); cell refinement: *RAPID AUTO*; data reduction: *RAPID AUTO*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *CRYLSQ* in *Xtal*3.4 (Hall *et al.*, 1995); molecular graphics: *ATOMS* (Dowty, 1999); software used to prepare material for publication: *BONDLA* and *CIFIO* in *Xtal*3.4.

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