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Structurally ferroelectric $SrMgF_4$

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The crystal structure of 0.06% Ce-doped $SrMgF_4$, strontium magnesium tetrafluoride, reported by Ishizawa *et al.* [(2001), *Acta Cryst.* C**57**, 784–786] is shown to satisfy the structural criteria for ferroelectricity and to have a predicted Curie temperature $T_c \simeq 1450$ K. The estimated spontaneous polarization $P_s \simeq 11 \times 10^{-2}$ C m^{-2} is consistent with classification as a two-dimensional ferroelectric in which minor Δx and major Δy, Δz atomic coordinate component displacements are required for ferroelectric switching.

1. Introduction

All members of the BaMF$_4$ family (M = Mg, Mn, Fe, Co, Ni and Zn) were reported by Eibschütz *et al.* (1969) to exhibit ferroelectricity, each with a spontaneous polarization (P_s) between ~7 and 10 × 10^{-2} C m^{-2};[1] Keve *et al.* (1969, 1970) determined the structure of the family members M = Mn and Co. The structures of $BaMgF_4$, $BaFeF_4$, $BaNiF_4$ and $BaZnF_4$, isostructural with $BaMnF_4$ and $BaCoF_4$, were subsequently determined by Gingl (1997), Averdunk & Hoppe (1988), Cox *et al.* (1970), von Schnering & Bleckmann (1968) and Lapasset *et al.* (1996), respectively. The recent redetermination of the structure of $SrMgF_4$ by Ishizawa *et al.* (2001) raised the possibility, by analogy with the $BaMF_4$ family, that it also might be ferroelectric, although it crystallizes in space group $P112_1$, whereas $BaMgF_4$ forms in space group $A2_1am$($Cmc2_1$). $SrMgF_4$ was first prepared by Banks *et al.* (1980) who identified it as orthorhombic, with lattice constants comparable to those of $BaMnF_4$. A negative test for second harmonic generation led them to suggest the space group *Amam*; they also showed that solid solutions with ~1% $EuMgF_4$ were photoluminescent. Apart from Banks *et al.*'s (1980) observation that $SrMgF_4$ melts incongruently at ~1175 K and Bingyi & Banks (1982) report of a solid-state transformation in the SrF_2–MgF_2 binary system at 1080 (10) K, no additional physical measurements were found in the literature other than spectroscopic, on rare-earth doped $SrMgF_4$, *e.g.* Wu & Shi (1995, 1996) and Sun *et al.* (1995). Ishizawa *et al.* (2001) have now shown that $SrMgF_4$ forms a monoclinic superstructure of the earlier orthorhombic arrangement. Analysis of the monoclinic coordinates obtained thereby shows that they fully satisfy the structural criteria for ferroelectricity.

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[1] Units inconsistent with the SI, but in customary use for spontaneous polarization magnitudes.

Table 1
Atomic coordinates of $SrMgF_4$ at 298 K in space group $P112_1$ (Ishizawa *et al.*, 2001), hypothetical $x'y'z'$ coordinates in supergroup $P112_1/m$, atomic displacements (Δx, Δy, Δz) in Å at the phase transition and thermal/static ($u_{\rm iso}$) displacement in Å at 298 K.

a = 7.8249 (8), b = 7.4930 (7), c = 16.9248 (17) Å, γ = 105.041 (11)°. $z^* = z - 0.270842$; $\Delta x = (x - x')a$, $\Delta y = (y - y')b$, $\Delta z = (z^* - z')c$.

	Wyckoff position $P112_1$, $P112_1/m$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	$u_{\rm iso}$
Sr1	2(*a*), 2(*e*)†	0.18015 (12)	0.2084 (2)	0.24503 (7)	0.18015	0.2084	1/4	0	0	−0.084	0.12 (2)
Sr2	2(*a*)	0.33110 (9)	0.8164 (2)	0.40647 (9)	0.32531	0.79732	0.41321	0.045	0.143	−0.114	0.11 (2)
	4(*f*)										
Sr6	2(*a*)	0.31952 (8)	0.7783 (1)	0.08005 (7)	0.32531	0.7973	0.08679	−0.045	−0.143	−0.114	0.11(2)
Sr3	2(*a*)	0.83449 (8)	0.8308 (1)	0.06336 (8)	0.83480	0.8336	0.08204	−0.002	−0.022	−0.316	0.09 (2)
	4(*f*)										
Sr5	2(*a*)	0.83511 (9)	0.8365 (2)	0.39929 (8)	0.83480	0.8336	0.41797	0.002	0.022	−0.316	0.11 (2)
Sr4	2(*a*), 2(*e*)	0.66509 (10)	0.1619 (1)	0.22916	0.66509	0.1619	1/4	0	0	−0.353	0.09 (2)
Mg1	2(*a*), 2(*e*)	0.5423 (3)	0.6592 (4)	0.2521 (2)	0.5423	0.6592	1/4	0	0	0.036	0.09 (3)
Mg2	2(*a*)	0.5403 (3)	0.6683 (3)	−0.0801 (2)	0.5418	0.6693	−0.0823	−0.012	−0.007	0.037	0.09 (3)
	4(*f*)										
Mg3	2(*a*)	0.4568 (3)	0.3296 (3)	0.0845 (2)	0.4582	0.3307	0.0823	−0.012	−0.008	0.037	0.08 (3)
Mg4	2(*a*), 2(*e*)	0.0379 (3)	0.6634 (4)	0.2520 (2)	0.0379	0.6634	1/4	0	0	0.034	0.09 (3)
Mg5	2(*a*)	0.0432 (3)	0.6633 (3)	−0.0804 (2)	0.0427	0.6672	−0.0834	−0.005	−0.029	0.050	0.08 (3)
	4(*f*)										
Mg6	2(*a*)	0.9579 (3)	0.3290 (3)	0.0863 (2)	0.9573	0.3328	0.0834	−0.005	−0.028	0.050	0.08 (3)
F1	2(*a*)	0.5964 (5)	0.8285 (6)	0.1606 (3)	0.5935	0.8591	0.1720	0.023	−0.229	−0.193	0.11 (4)
	4(*f*)										
F3	2(*a*)	0.5905 (6)	0.8897 (5)	0.3166 (3)	0.5935	0.8591	0.3280	−0.023	0.229	−0.193	0.12 (4)
F2	2(*a*)	0.5008 (6)	0.4286 (5)	0.1952 (3)	0.4879	0.4903	0.1684	0.101	−0.462	0.454	0.11 (4)
	4(*f*)										
F4	2(*a*)	0.4749 (6)	0.5519 (5)	0.3585 (3)	0.4879	0.4903	0.3316	−0.101	0.462	0.455	0.14 (4)
F5	2(*a*)	0.5656 (6)	0.8222 (6)	−0.1750 (3)	0.5954	0.8644	−0.1614	−0.233	−0.317	−0.230	0.12 (4)
	4(*f*)										
F9	2(*a*)	0.3749 (5)	0.0934 (5)	0.1478 (3)	0.4046	0.1356	0.1614	−0.232	−0.317	−0.230	0.11 (4)
F6	2(*a*)	0.5779 (6)	0.8994 (5)	−0.0147 (3)	0.5833	0.8479	−0.0002	−0.042	0.386	−0.246	0.11 (4)
	4(*f*)										
F8	2(*a*)	0.4114 (6)	0.2036 (6)	−0.0144 (3)	0.4167	0.1521	0.0002	−0.041	0.386	−0.246	0.13 (4)
F7	2(*a*), 2(*d*)	0.5463 (5)	0.5698 (5)	0.0320 (2)	1/2	1/2	0	0.362	0.523	0.542	0.11 (4)
F10	2(*a*), 2(*e*)	0.7898 (5)	0.6663 (7)	0.2710 (3)	0.7898	0.6663	1/4	0	0	0.355	0.11 (4)
F11	2(*a*)	0.2826 (5)	0.6224 (6)	−0.0666 (3)	0.2932	0.6676	−0.0772	−0.084	−0.339	0.179	0.13 (4)
	4(*f*)										
F24	2(*a*)	0.6963 (5)	0.2872 (6)	0.0878 (3)	0.7068	0.3324	0.0772	−0.083	−0.339	0.179	0.13 (4)
F12	2(*a*)	0.2190 (5)	0.3753 (6)	0.0962 (3)	0.2076	0.3296	0.0889	0.090	0.343	0.124	0.13 (4)
	4(*f*)										
F23	2(*a*)	0.8038 (5)	0.7162 (6)	−0.0815 (3)	0.7924	0.6704	−0.0889	0.090	0.343	0.125	0.12 (4)
F13	2(*a*)	0.0584 (5)	0.7965 (6)	0.1540 (3)	0.0839	0.8507	0.1707	−0.201	−0.406	−0.282	0.12 (4)
	4(*f*)										
F15	2(*a*)	0.1094 (5)	0.9048 (5)	0.3127 (3)	0.0839	0.8507	0.3293	0.201	0.406	−0.282	0.11 (4)
F14	2(*a*)	0.9613 (6)	−0.5748 (5)	0.1992 (3)	1.0040	−0.5050	0.1686	0.334	−0.523	0.518	0.12 (4)
	4(*f*)										
F16	2(*a*)	0.9534 (5)	0.4351 (5)	−0.1379 (3)	0.9960	0.5050	−0.1686	−0.333	−0.524	0.519	0.12 (4)
F17	2(*a*)	0.0965 (5)	0.8283 (5)	−0.1736 (3)	0.0860	0.8645	−0.1624	0.083	−0.271	−0.190	0.10 (4)
	4(*f*)										
F21	2(*a*)	0.9246 (5)	0.0993 (5)	0.1512 (3)	0.9140	0.1355	0.1624	0.084	−0.271	−0.190	0.09 (4)
F18	2(*a*)	0.1196 (6)	0.8921 (5)	−0.0143 (3)	0.0961	0.8654	−0.0036	0.185	0.200	−0.181	0.11 (4)
	4(*f*)										
F20	2(*a*)	0.9274 (6)	0.1613 (6)	−0.0071 (3)	0.9039	0.1346	0.0036	0.185	0.200	−0.181	0.11 (4)
F19	2(*a*), 2(*b*)	0.9808 (5)	0.5533 (5)	0.0262 (3)	0	1/2	0	−0.151	0.399	0.443	0.12 (4)
F22	2(*a*), 2(*e*)	0.2901 (6)	0.6563 (7)	0.2393 (3)	0.2901	0.6563	1/4	0	0	−0.181	0.13 (4)

† Equivalent 2(*a*) positions in space group $P112_1$, x, y, z; $\bar{x}, \bar{y}, \frac{1}{2} + z$. In $P112_1/m$ for 4(*f*), x, y, z; $\bar{x}, \bar{y}, \frac{1}{2} + z$; $\bar{x}, \bar{y}, \bar{z}$; $x, y, \frac{1}{2} - z$. For 2(*e*), $x, y, \frac{1}{4}$; $\bar{x}, \bar{y}, \frac{3}{4}$; for 2(*d*), $\frac{1}{2}, \frac{1}{2}, 0$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; and for 2(*b*), $0, \frac{1}{2}, 0$; $0, \frac{1}{2}, \frac{1}{2}$.

2. Atomic coordinates, structural criteria for ferroelectricity and predicted Curie temperature of $SrMgF_4$

The unusual displacement of all Mg atoms from the centers of their F-atom octahedra in $SrMgF_4$ resulting from the proposed space group *Amam* led Ishizawa *et al.* (2001) to redetermine the atomic arrangement. Refinement of 326 parameters in space group $P112_1$ was undertaken using 4130 independent absorption- and extinction-corrected Friedel pairs measured at 298 K with $I > 3\sigma(I)$; 239 reflections were excluded. The composition of the Ce-doped Bridgman-grown crystal, Sr:Ce = 0.9994:0.0006, was assumed equivalent to stoichiometric in the structure analysis. The final values of $R = 0.044$, $wR = 0.037$ are given for the *xyz* atomic coordinates presented in Table 1, in which an origin shift of −0.27084 has been applied along the polar axis. This shift minimizes the total $\Sigma\Delta z$, see below, for a transition to a prototype structure with the supergroup assumed to be $P112_1/m$. Alternative supergroups may be possible, but are not expected to change the present conclusions significantly; experimental investigation at higher temperatures would be appropriate. Table 1 additionally gives the set of $x'y'z'$ coordinates in the prototype structure derived from the xyz values under the requirement of conformity with the symmetry of Wyckoff positions 4(*f*), 2(*e*), 2(*d*) or 2(*b*) in space group $P112_1/m$, also the corresponding $x - x' = \Delta x$, $y - y' = \Delta y$, $z - z' = \Delta z$ axial displacements. Table 1 shows that no atom in space group $P112_1$ is any further than $\Delta x = 0.36$, $\Delta y = 0.52$ or $\Delta z = 0.54$ Å from locations that fulfill the symmetry of space group $P112_1/m$ in the predicted phase I.

The Δz magnitudes in Table 1 fully satisfy the structural criteria for ferroelectricity (Abrahams, 2000), namely:

(*a*) that the *i*th atom forming the shortest and least-ionic bonds in the unit cell (Mg in the case of $SrMgF_4$) undergoes no polar displacement $\Delta z_l \gtrsim 1$ Å between the location reported at $x_iy_iz_i$ and that at which the resulting spontaneous polarization P_s vanishes, and

(*b*) that the largest Δz_i exceeds ∼0.1 Å or the r.m.s. thermal or static displacement u of that *i*th atom.

$SrMgF_4$ is hence confidently predicted to be a new ferroelectric crystal.

The Curie temperature T_c of a ferroelectric with known crystal structure may also be predicted if the *i*th atom therein occupies an octahedron of O or F atoms, as in the present case. Abrahams *et al.* (1968) have shown, for such structures, that

$$T_c = (\kappa/2k)(\Delta z_i)^2 \text{ K}, \qquad (1)$$

where the force constant $\kappa \simeq 5.52$ kPa, k is Boltzmann's constant, Δz_i is the largest displacement along the polar c axis by the *i*th atom defined above and $\kappa/2k = 2.00\,(9) \times 10^4$ K Å^{-2}.

The six independent MgF_6 octahedra in $SrMgF_4$ phase II may be seen in Table 1 to undergo displacement at the transition to phase I by forming three symmetry-related pairs of octahedra. The Mg1 and Mg4 pair occupies the mirror plane at $z = \frac{1}{4}$, the Mg2, Mg3 and Mg5, Mg6 pairs in Table 1 becoming related by an inversion center. However, symmetry equivalents of Mg3 and Mg6 in Table 1 are also related to Mg2 and Mg5 by the mirror plane at $z = \frac{1}{4}$. Four F atoms occupy Wyckoff symmetry positions 2(*b*), 2(*d*) or 2(*e*) above T_c, the remaining 20 F atoms occuping the 4(*f*) general positions.

It is noteworthy that four of the six *i*th atoms in $SrMgF_4$ have variable polar coordinates *above* T_c. In consequence, the uncertainty in Δz_i is propagated to that in the predicted magnitude of T_c. By contrast, each *i*th atom in a ferroelectric with symmetry higher than monoclinic generally undergoes displacement to *special* positions at or above T_c. In the case of ferroelectric $YMnO_3$ in space group $P6_3cm$, for example, $z'(\text{Y1}) \rightarrow \frac{1}{2}$, $z'(\text{Y2}) \rightarrow 0$ and $z'(\text{Mn}) \rightarrow \frac{1}{4}$ as $T \rightarrow T_c$ (Abrahams, 2001); no further uncertainty beyond that in the polar coordinates and the constant in (1) is thereby introduced in the resulting Δz or T_c magnitudes in the case of higher symmetry ferroelectrics.

The most reliable measure of uncertainty in Δz_i for $SrMgF_4$ would be a comparison of the z' coordinates in Table 1 with an accurate experimental determination above T_c; direct measurement of T_c would also allow an estimate of uncertainty. In the absence of such measurement, however, differences between Mg2, Mg3, Mg5 and Mg6 z coordinates may provide substitute indicators of uncertainty. Assuming these four Mg atoms have a common $z' = \pm 0.0828$ above T_c (see Table 1) leads to $\sigma\langle\Delta z_i(\text{Mg})\rangle = 0.052$ Å; if the Mg atoms were to form independent pairs with $z' = \pm 0.0823$ and ± 0.0834, then the mean uncertainty would be reduced to ∼0.04 Å. The polar coordinates of the Mg atoms are, however, not necessarily confined to these alternatives. The uncertainty in Δz_i may hence differ strongly from either estimate.

Denoting octahedra by their Mg^{2+} ions, the centers of the F^- ion charge in Mg1(oct)–Mg6(oct) are located, respectively, at $z' = 0.2569\,(2)$, $-0.0746\,(2)$, $0.0908\,(3)$, $0.2564\,(3)$, $-0.0746\,(2)$ and $0.0923\,(2)$. Each charge center is displaced further from the paraelectric position, corresponding to the $z'(\text{Mg})$ coordinates in Table 1, than the central Mg^{2+} ion and with the same sense. The effective displacement $\Delta z_i(Mg^{2+})$ is thus given by the octahedral displacement which ranges from 0.108 Å for Mg4(oct) to 0.150 Å for Mg6(oct). The Curie temperature in (1) necessarily corresponds to the largest Δz_i, hence T_c for $SrMgF_4$ is predicted to be 450 K with an uncertainty that may range between 370 and 270 K.

An anomaly at 1080 (10) K was observed by Bingyi & Banks (1982) for all compositions in the binary system $Sr_xMg_{1-x}F_4$ from $x = 0.15$ to 0.975. SrF_2 is cubic with $a = 5.794$ Å, MgF_2 is tetragonal with $a = 4.628$ and $c = 3.045$ Å, both structures differing considerably from that of $SrMgF_4$. Careful calorimetric and dielectric study of stoichiometric $SrMgF_4$ is necessary to determine if the variable-composition solid-state transformation noted is related to T_c.

3. Atomic displacement dimensionality and spontaneous polarization

The atomic displacements undergone by members of the ferroelectric $BaCoF_4$ family in the course of polarization reversal are strictly two-dimensional, all atoms in phase II (space group $A2_1am$) occupying a mirror symmetry plane (Keve *et al.*, 1970); the hypothetical phase I with $T_c >$ m.p. is expected to have the space group *Amam*. The corresponding atomic displacements to the paraelectric state in $SrMgF_4$ are substantial in all three dimensions, with the maximum value ∼0.55 Å, see Table 1; they are, however, far from isotropic with average magnitudes 0.09, 0.23 and 0.23 Å along the *a*, *b* and *c* axes, respectively.

Ferroelectrics generally exhibit the highest P_s values, in the range ∼10 to 70 × 10^{-2} C m^{-2}, for materials with atomic displacements under polarization reversal that are primarily one-dimensional. Intermediate magnitudes of P_s, ranging from ∼3 to 10 × 10^{-2} C m^{-2}, correspond to atomic displacements that are primarily two-dimensional under ferroelectric switching; ferroelectrics with displacements of comparable magnitude in each dimension have the lowest magnitudes with $P_s \lesssim 3 \times 10^{-2}\,\mathrm{C\,m^{-2}}$ (Abrahams & Keve, 1971).

The magnitude and sense of P_s in $\mathrm{SrMgF_4}$ may be derived from (2), using the atomic coordinates in Table 1 and a point charge model

$$P_s = (e/V)\Sigma Z_j \Delta z_j. \qquad (2)$$

Summation over volume V for one unit cell containing j ions of charge Z_j (2+ for Sr and for Mg, 1− for F) displaced by Δz_j from the paraelectric arrangement, see Table 1, gives $P_s = 10.6\,(6) \times 10^{-2}\,\mathrm{C\,m^{-2}}$. This value is consistent with the distribution of atomic displacements in Table 1, both magnitude and dimensionality agreeing with the classification of $\mathrm{SrMgF_4}$ as, primarily, a two-dimensional ferroelectric.

The strong polar properties of $\mathrm{SrMgF_4}$ noted herein, together with the possibility of growing single crystals as large as the samples with ~18 mm diameter and 30 mm length reported by Ishizawa *et al.* (2001), offer the potential for use in a variety of pyroelectric, piezoelectric and nonlinear optical applications.

4. Phase transition nomenclature for $\mathrm{SrMgF_4}$

The recommended nomenclature of Tolédano *et al.* (1998) for the hypothetical prototype phase I and predicted ferroelectric phase II of $\mathrm{SrMgF_4}$, based on the results above, follows.

I	>450 (350) K	$P112_1/m$ (11)	$Z = 12$	Nonferroic	Hypothetical prototype phase
II	<450 (350) K	$P112_1$ (4)	$Z = 12$	Predicted ferroelectric	2 variants

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In the paper by Abrahams (2002) *Acta Cryst.* (2002), B**58**, 34–37 two errors were printed. First, in the abstract the Curie temperature was incorrectly given as 1450 K. The correct value is 450 K. The second error occurs in section (*a*) of p. 36. The polar displacement expression is currently given as $\Delta z_l \simeq 1$ Å. The correct expression should be $\Delta z_i \simeq 1$ Å.

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