Phase transitions and ferroelectricity in NaSb$_3$F$_{10}$

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Phase transitions and ferroelectricity in NaSb$_3$F$_{10}$

R. J. Christie,‡ P. K. Wu, P. Photinos and S. C. Abrahams*

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Atomic coordinate analysis allows materials with appropriate but previously unrecognized dielectric properties to be predicted as new ferroelectrics if their crystal structure is known. An earlier such prediction that NaSb$_3$F$_{10}$ is ferroelectric is confirmed herein without ambiguity. Its spontaneous polarization $P_s$ is found to exhibit reproducible dielectric hysteresis at room temperature, with $P_s' \sim 60 \mu$C m$^{-2}$, under the application of a field of 0.3 MV m$^{-1}$ or greater. The pyroelectric coefficient $\epsilon'_p = 17 (5)$ mC m$^{-2}$ K$^{-1}$ at 298 K. NaSb$_3$F$_{10}$ undergoes a phase transition at $T_C \approx 461$ K, on correction for thermal hysteresis, with entropy change $\Delta S = 5.7 (3)$ J mol$^{-1}$ K$^{-1}$. The colorless crystals melt at $T_m \approx 515$ K and decompose above $\approx 600$ K. The thermal hysteresis of $\approx 35$ K in $T_C$, on heating and cooling at 5–25 K min$^{-1}$, is typical of first-order phase transitions. The space group in ferroelectric phase III is $P\overline{6}_3$, and that in phase II is predicted to be $P\overline{6}_2\overline{2}$, a nonpolar supergroup of $P\overline{6}_3$; the supergroup expected in the prototypic nonferroic phase I is $P\overline{6}_3/mmc$. The space group of phase III is not a direct subgroup of phase I. The dielectric permittivity $\epsilon'$ at 1 kHz increases over an order of magnitude between 300 K and a major inflection at $T_C$, continuing to increase steadily thereafter to $T_m$.

1. Introduction

The structure of NaSb$_3$F$_{10}$, first prepared by Ducourant et al. (1975), was determined in space group $P\overline{6}_3$ by Fourcade et al. (1975); the final agreement factor was $R = 0.049$ based on least-squares refinement with 589 $F_{\text{meas}}$. Strongly distorted SbF$_5$$^E$ octahedra, where $E$ represents an Sb$^{\text{III}}$ lone electron pair, were reported as forming groups of three that share an equatorial F atom, leading to extended layers of [Sb$_3$F$_{10}$]$^n$ ions normal to the polar axis. Na$^+$ ions between layers occupy slightly distorted octahedra of F$^-$ ions. A view of the structure along the polar c axis, as reported, is shown in Fig. 1.

The small endothermal anomaly observed calorimetrically at $\approx 465$ K in NaSb$_3$F$_{10}$ was taken as the melting point by Charles & Gnanam (1994), who also reported discontinuities in electric conductivity ($\sigma$) at $\approx 385$ K for plots of log$\sigma$ versus $1/T$ along [100], and at $\approx 360$ K for plots along [001], with $\sigma \approx 8 \times 10^{-9}$ S m$^{-1}$ at $\approx 300$ K. They also found that the dielectric permittivity $\epsilon'$ at 1 kHz barely increased between 300 and $\approx 375$ K along either the a or the c axis as a function of frequency, with $\epsilon' \approx 27$ at 465 K. The corresponding inflection at 10 kHz was smaller and displaced $\approx 25$ K higher, becoming nearly indiscernible at 100 kHz.

The structural criteria for ferroelectricity were previously shown to be satisfied by the atomic arrangement in NaSb$_3$F$_{10}$ (Abrahams, 1990). Experimental confirmation of that crystallographic prediction is presented herein, together with a brief discussion of the phase transition and its related properties below the decomposition temperature.

2. Structure and ferroelectricity in NaSb$_3$F$_{10}$

2.1. Preparation of NaSb$_3$F$_{10}$

Evaporation of a 1:1 ratio of SbF$_3$ (Aldrich, 99.8%) and NaF (Alfa AESAR, 99.9995%), with 16.09 and 1.26 g.

Figure 1

Structure of NaSb$_3$F$_{10}$ phase III viewed along the polar c axis, after Fourcade et al. (1975), showing the F atoms in an irregular octahedral coordination about Na. Inclusion of the Sb lone electron pair results in a second irregular octahedron forming about the Sb atom. Prepared by use of ATOMS (Dowty, 2004).

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Table 1

Atomic x, y and modified z coordinates in NaSb$_3$F$_{10}$ (Fourcade et al., 1975), with hypothetical x', y' and z' coordinates and corresponding Δx, Δy and Δz displacements for a transition to space group P6$_0$22.

\[ a = 8.285 \text{ (3)}, \ c = 7.600 \text{ (3)}; \ Δx = (x - x')u; \ Δy = (y - y')u; \ Δz = (z - z')c \hat{A}, \text{ with } z' = z + 0.037 \text{ to satisfy } \sum z^* = \sum z'. \]

<table>
<thead>
<tr>
<th>Atom</th>
<th>P6$_0$</th>
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<tbody>
<tr>
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<td>6(c)</td>
<td>6(h)</td>
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<tr>
<td>Na</td>
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<tr>
<td>F4</td>
<td>2(b)</td>
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Wyckoff positions†

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<tbody>
<tr>
<td>x</td>
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</tr>
<tr>
<td>Sb</td>
<td>0.1163(1)</td>
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<tr>
<td>Na</td>
<td>0.204(1)</td>
</tr>
<tr>
<td>F11</td>
<td>0.111(1)</td>
</tr>
<tr>
<td>F2</td>
<td>0.055(1)</td>
</tr>
<tr>
<td>F4</td>
<td>0.12(1)</td>
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</table>

† Wyckoff positions In P6$_0$22 2(h) = (h/2,0,0); 2(d) = (0,1/2,h); 6(h) = 1/2 x, 2x, 1/2 x, x, 1/2 x, x; 12(i) = 1/2 (x, y, z, x, y, z; x, y, z, x, y, z; x, y, z, x, y, z; x, y, z, x, y, z; x, y, z, x, y, z; x, y, z, x, y, z; x, y, z, x, y, z; x, y, z, x, y, z; x, y, z, x, y, z; x, y, z, x, y, z; x, y, z, x, y, z). Note that F1 and F2 are independent in space group P6$_0$, both atoms occupying the same 12(i) location in supergroup P6$_0$22.

Table 2

Hypothetical x', y' and z' atomic coordinates for NaSb$_3$F$_{10}$ at ~460 K, as in Table 1, and x'', y'' and z'' coordinates assumed above ~480 K with atomic displacements to space group P6$_0$/mmc.

\[ a \approx 8.3, \ c \approx 7.6 \text{ Å}; \ Δx, Δy and Δz in Å, as in Table 1. \]

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<th>Wyckoff positions†</th>
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<tr>
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<td>F3</td>
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<td>0.504</td>
<td>1.009</td>
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</tr>
</tbody>
</table>

† Wyckoff positions In P6$_0$/mmc: 2(c) = (c/2,1/2,0); 2(d) = (d/2,1/2,0); 6(h) = 1/2 x, 2x, 1/2 x, x, 1/2 x, x; 2x, x, 1/2 x, -2x, 1/2 x, x; 12(k) = 1/2 (x, y, z, x, y, z; x, y, z, x, y, z; x, y, z, x, y, z; x, y, z, x, y, z; x, y, z, x, y, z; x, y, z, x, y, z; x, y, z, x, y, z; x, y, z, x, y, z; x, y, z, x, y, z; x, y, z, x, y, z; x, y, z, x, y, z; x, y, z, x, y, z). The F1 and F2 locations in supergroup P6$_0$/mmc uniquely retain locational variability.

respectively, dissolved in 50 ml of 40% aqueous HF using a polypropylene beaker at room temperature, led to the growth of colorless, transparent, strongly refractive NaSb$_3$F$_{10}$ crystals over a period of several days with maximum dimensions ca 5 × 5 × 2 mm. A small percentage of the crystals formed were opaque; most were structurally confirmed by powder X-ray diffraction to be single-phase NaSb$_3$F$_{10}$, with their observed patterns exhibiting no departures from or extra lines compared with that calculated on the basis of the Fourcade et al. (1975) crystal structure. All measurements were made on samples of confirmed NaSb$_3$F$_{10}$ composition, since a small percentage of Na$_3$Sb$_3$F$_{18}$ crystals with space group P2$_1$/n were also detected (see also §3.1).

2.2. Atomic displacements and phase transitions

The atomic coordinates reported by Fourcade et al. (1975) for NaSb$_3$F$_{10}$ in space group P6$_0$ at room temperature are shown in Table 1 to differ little from the atomic arrangement proposed in supergroup P6$_0$22. The largest polar displacement (Δz) for such a subgroup–supergroup phase transition is ~0.5 Å, with no ith atom displacement Δz$_i$ ≥ 0.83 Å. Table 2 shows that the atomic coordinates with P6$_0$22 symmetry in Table 1 are also related to a coordinate set with supergroup P6$_0$/mmc symmetry. A total displacement no greater than 0.26 Å by atoms F1 and F2 fulfills the latter supergroup symmetry. It may be noted that space group P6$_0$/mmc is not a subgroup of P6$_0$; although it is a supergroup of P6$_0$22. An NaSb$_3$F$_{10}$ phase transition from space group P6$_0$ to P6$_0$22 may hence be regarded as most likely, followed by an additional phase transition to P6$_0$/mmc under an additional but smaller energy input.

The nomenclature recommendations of Tolédano et al. (1998), applied to the phase transition sequence P6$_0$/mmc to P6$_0$22 to P6$_0$ in NaSb$_3$F$_{10}$, follow for subsequent use:

I | 575–465 K | P6$_0$/mmc (194) | Z = 2 | nonpolar | postulated prototypic structure.
II | 465–442 K | P6$_0$22 (182) | Z = 2 | nonpolar | postulated structure.
III | 442–300 K | P6$_0$ (173) | Z = 2 | ferroelectric | two variants.

2.3. Atomic displacements between phase III and the hypothetical nonpolar phase II

The largest polar displacement Δz$_i$ by an Sb atom, the central ith atom as noted below, in NaSb$_3$F$_{10}$ phase III to the

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1 Where Δz$_i$ = [(x$_i$ - x$^*_i$)$^2$ + (y$_i$ - y$^*_i$)$^2$ + (z$_i$ - z$^*_i$)$^2$]$^{1/2}$ in a hexagonal setting.

2 Initial use of the full nomenclature with all six fields is recommended, with subsequent reference to an individual phase by only the two leading fields. The lowest temperature to which phase III remains stable is undetermined.
corresponding location in phase II is $\Delta z_i \simeq 0.28 \text{ Å}$ (see Table 1). With all thermal or static $\Delta z_i$ atomic displacements significantly smaller than $\Delta z(F)$, the structural criteria for ferroelectricity are fully satisfied (cf. Abrahams, 1990). The relationship between $\Delta z_i$ and the Curie temperature $T_C$ is given by equation (1):

$$T_C = \left(\kappa/2k\right)(\Delta z_i)^2 K,$$

(1)

where $\kappa = 5.52 (25) \times 10^4 \text{ kPa}$ is a force constant, $k$ is Boltzmann’s constant, $\kappa/2k = 2.00 (9) \times 10^4 \text{ K}^{-2}$ and $\Delta z_i$ is the largest polar displacement by the central $i$th cation (Abrahams et al., 1968). The displacement $\Delta z_i$ provides a reliable estimate of $T_C$ for oxygen or fluorine octahedral structures, as for example $T_C^{\exp} = 325–335 \text{ K}$ versus $T_C^{\text{calc}} = 343 \text{ K}$ in the case of octahedral Cu(OH)$_2$ (Abrahams et al., 1995).

The substantial difference between $\Delta z_{\text{Sb}} \simeq 0.15 \text{ Å}$ as given by equation (1) and the experimental value of 0.28 Å in Table 1 is attributed to the atomic environment about Sb, in which a normal octahedral atomic coordination is replaced by three F atoms at distances $d_{\text{Sb}–F} \simeq 1.96 \text{ Å}$, two at $d_{\text{Sb}–F} \simeq 2.50 \text{ Å}$ and a lone electron pair; residual uncertainties in the structure are additional likely contributors to the apparent increase in $\Delta z_{\text{Sb}}$ value. We are grateful to an anonymous referee for pointing out the potential value of reinvestigating the NaSb$_3$F$_{10}$ crystal structure by careful neutron diffraction analysis.

3. Calorimetric, gravimetric and dielectric measurements of NaSb$_3$F$_{10}$

3.1. Calorimetry

Calorimetric measurement, using a Perkin–Elmer Differential Scanning Calorimeter Model DSC-7, reveals a thermal hysteresis-corrected phase transition at $\sim 461 \text{ K}$ with entropy change $\Delta S = 5.7 (3) \text{ J mol}^{-1} \text{ K}^{-1}$, followed by a second endotherm at $\sim 515 \text{ K}$ with $\Delta S \simeq 70 \text{ J mol}^{-1} \text{ K}^{-1}$, and decomposition above $\sim 600 \text{ K}$. The phase transition (see Fig. 2) is identifiable with the Curie temperature $T_C$. The second endotherm is identifiable with $T_m$ (melting), as verified by the observable shape change in crystalline samples heated above $\sim 515 \text{ K}$. The entropy change at $T_C$, with endotherm width $\sim 7.5 \text{ K}$ at half-height, gives $\Delta S$ close to $R \ln 2$ (i.e. $5.76 \text{ J mol}^{-1} \text{ K}^{-1}$); at $T_m$, $\Delta S = 66 (20) \text{ J mol}^{-1} \text{ K}^{-1}$. $T_C$ undergoes a thermal hysteresis of $\sim 35 \text{ K}$ at $25 \text{ K min}^{-1}$, a value that remains nearly constant at heating or cooling rates as low as $1 \text{ K min}^{-1}$. The phase transition exotherm on cooling is broad in some crystals but more often resolves into two peaks as in Fig. 2, each about half the width at half-height of the endotherm on heating, as expected by the successive space-group transitions noted in §2.2. The endotherm at $T_C$ is consistent with two peaks that overlap as a result of the greater heat content released in the transition from phase III to II than in the transition from phase II to I. The magnitude of the thermal hysteresis is typical of first-order phase transitions, with the variability in $T_{\text{m,exp}}$ attributable to possible changes in stored crystals. It is noted that the value obtained by Charles & Gnanam (1994) for $T_c$ (see §1), originally identified as $T_m$, is otherwise in good agreement with the present report.

A second phase, with composition Na$_3$Sb$_5$F$_{18}$ and structure reported in space group $P2_1/n$ by Fourcade et al. (1983), was identified among a number of opaque crystals that sometimes form together with NaSb$_3$F$_{10}$ (see §2.1); the optimum conditions for the growth of NaSb$_3$F$_{10}$ crystals have not been exhaustively investigated. Both compositions contain distorted five-coordinated Sb$^{5+}$ and octahedrally coordinated Na$^+$ ions. The unit-cell dimensions of Na$_3$Sb$_5$F$_{18}$ were re-determined by Weakley (2001) as $a = 5.4568 (11)$, $b = 24.0837 (13)$ and $c = 12.1191 (7) \text{ Å}$.

3.2. Thermogravimetry

No variation in the mass of $\sim 25 \text{ mg}$ NaSb$_3$F$_{10}$ samples was observed at temperatures below $\sim 600 \text{ K}$ on heating from 300 to $870 \text{ K}$ in a Perkin–Elmer Pyris 1 thermogravimetric analyzer. Mass loss begins above $\sim 600 \text{ K}$, indicating thermal stability in NaSb$_3$F$_{10}$ from ambient temperature to $\sim 80 \text{ K}$ above $T_m$.

3.3. Dielectric constant

The dielectric constant or relative dielectric permittivity $\varepsilon'(\text{NaSb}_3\text{F}_{10}) = C_i/C_0$, where $C_0$ is the capacitance of an empty cell and $C_i$ is that of the cell and sample. Measurements were made with a Stanford Research Systems SR720 LCR meter under PC control. Samples were pressed, under $\sim 1 \text{ GPa}$, into 13 mm-diameter 1.1 mm-thickness disks. Both major faces were coated with flexible silver ink (Englehard-CLAL, now Technitol Inc.), leaving a bare frame. Heating the disk from 350 to $550 \text{ K}$, under PC control in a CM Model 1706 Furnace, results in $\varepsilon'$ increasing nearly an order of magnitude at $1 \text{ kHz}$ before reaching a plateau at $T_C \simeq 465 \text{ K}$ (see Fig. 3), following a correction for the thermal gradient of $\sim 30 \text{ K}$ in the furnace between sample and thermocouple. Smaller increases occur at 10 and $100 \text{ kHz}$, with a plateau again forming above $T_C$. Permittivity values above $T_C$ remain high and are presumed to be due to electrochemical effects at the electrodes.

![Figure 2](image)

Figure 2

Differential scanning calorimetry temperature dependence between 453 and 493 K, for heating and cooling at $25 \text{ K min}^{-1}$. 

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[2] Thermal uncertainties are sample dependent; caloricometric results at melting and decomposition are not shown.
3.4. Dielectric hysteresis and spontaneous polarization

The dielectric hysteresis was determined on a disk of polycrystalline NaSb$_3$F$_{10}$, prepared as in §3.3, by use of a modified Sawyer & Tower (1930) circuit (see Singh et al., 1996), modified further by means of a BK Precision 4011A 5 MHz function generator with a TREK 677B HV supply/amplifier for the applied field. An oscilloscope measured the polarization through a 1000:1 Caddock Electronics Inc. THU10 voltage divider network. The resulting hysteresis loops were displayed as a function of $E_x$ versus $E_y$ voltages in the xy mode of a Tektronix TDS 220 Digital Oscilloscope with GPIB interface to a PC; the minimum field required to reverse the polarization sense was 0.3 MV m$^{-1}$. Import from the oscilloscope provides a graphical display of the hysteresis, as presented in Fig. 4.

The spontaneous polarization in Fig. 4 was calibrated by comparison with the value similarly obtained by measuring a ceramic disk of BaTiO$_3$, giving $P_s$(BaTiO$_3$) = 0.08 C m$^{-2}$; the single-crystal value in BaTiO$_3$ along [001] is 0.26 C m$^{-2}$ (Mitsui & Nakamura, 1981), hence $P_s \simeq 60 \mu$C m$^{-2}$ for NaSb$_3$F$_{10}$.

3.5. Pyroelectric coefficient

A poled disk, similar to that used in §3.3 for measuring $\varepsilon'$, was mounted on a microscope slide and heated rapidly from ~300 to ~325 K. The temperature difference $\Delta T$ was determined by means of a thermocouple in contact with the disk, using a Fluke Model 45 multimeter/80 TK module. The voltage thereby produced in a 4.7 $\mu$F capacitor connected across the disk on heating, as measured by a Keithley 6517 electrometer, integrates the charge $\Delta P$ generated and leads to $(p) = \Delta P/\Delta T = 17 (5) \mu$C m$^{-2}$ K$^{-1}$. The pyroelectric coefficients of relatively few materials with hexagonal symmetry have been reported; among them are $p_3 = 140 (10) \mu$C m$^{-2}$ K$^{-1}$ for Ba(NO$_2$)$_2$H$_2$O, space group $P6_3$, and $p_3 = 9 (2) \mu$C m$^{-2}$ K$^{-1}$ for Cs$_2$S$_2$O$_6$, space group $P6_3mc$ (Liminga et al., 1980). The present value for NaSb$_3$F$_{10}$ falls well within this 9–140 $\mu$C m$^{-2}$ K$^{-1}$ range.

4. Discussion

4.1. Ferroelectricity in NaSb$_3$F$_{10}$

The 1990 prediction that NaSb$_3$F$_{10}$ is a new ferroelectric led to its preparation, confirmation of a previously reported phase transition at $T_C \simeq 461$ K and experimental validation of the prediction. The observed entropy change of 5.7 J mol$^{-1}$ K$^{-1}$ in the transparent crystals is close to $R \ln 2$, indicative of a phase transition in which the number of structural degrees of freedom changes by a factor of 2, a result congruent with reversible polarization below and a nonpolar atomic arrangement above $T_C$. The two closely spaced exotherms observed in the opaque crystals are generally replaced by a single exotherm in the transparent crystals. The endotherm width at half-height in Fig. 1 is notably wider than that of either individual exotherm; a doubled endotherm has not yet been observed. Further investigation is required for full clarification of the thermodynamics of this phase transition and of the conditions required for single-phase formation. The 25–35 K thermal hysteresis observed at scan rates of 10–25 K s$^{-1}$ is typical of weak first-order phase transitions. Reduction of the scan rate to 1 K s$^{-1}$ does not strongly reduce the thermal hysteresis at $T_C$.

The ~60 $\mu$C m$^{-2}$ value for $P_s$ in NaSb$_3$F$_{10}$ determined in §3.4 is about four orders of magnitude smaller than that in many oxides, such as PbTiO$_3$, with $P_s \simeq 0.76$ C m$^{-2}$ (Kuprianov et al., 1983). However, the 4.7 $\mu$C m$^{-2}$ value reported for the (NH$_4$)$_2$SO$_4$-type ferroelectric RbLiSO$_4$ by Yamaguchi & Sawada (1980), and the 5 $\mu$C m$^{-2}$ for K$_2$Co$_2$(SO$_4$)$_3$, reported by Yamada et al. (1980), are representative of many materials with smaller $P_s$.

4.2. Fluorine octahedra ferroelectrics

Complex ferroelectric octahedral fluorides such as NaSb$_3$F$_{10}$ are not uncommon. Six other fluorine octahedral families reported to exhibit ferroelectricity, in addition to another four containing both octahedral oxygen and fluorine, were reviewed by Abrahams & Ravez (1992). The pyroelectric coefficient magnitudes in the BaMF$_6$ family with $M = \text{Mg, Co}$, $\text{Mg, Co}$

\[ P_t \] magnitudes given above follow SI terminology; the common use of mixed units such as 10$^{-2}$ C m$^{-2}$ does not.

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Ni and Zn are high, ranging from $6.7 \times 10^4$ μC m$^{-2}$ K$^{-1}$; each material remains pyroelectric until melting as a ‘frozen’ ferroelectric. Members of the $ABF_5$ family with $A = \text{Sr}$ and $B = \text{Al}, \text{Cr}$ and Ga, as well as those with $A = \text{Ba}$ and $B = \text{Ti}, \text{V}$ and Fe, are ferroelectric, although $P_s$ values have not been reported because the conductances are as high as $10^{-8}$ Ω$^{-1}$.

It is noted that all reported dielectric and calorimetric $T_c$ magnitudes for these materials satisfactorily match the values predicted on the basis of equation (1). Other octahedral complex fluorides investigated structurally include $\text{Sr}_3\text{Fe}_2\text{F}_{12}$, $\text{Pb}_5\text{Cr}_3\text{F}_{19}$, $\text{K}_3\text{MoO}_3\text{F}_3$, $\text{Ba}_3\text{TiO}_3\text{F}_2$, $\text{Pb}_3\text{W}_3\text{O}_9\text{F}_{10}$ and $\text{NaSbF}_3\text{F}_{10}$, with $\text{NaSbF}_4$, $\text{NaSb}_2\text{F}_7$, $\text{NaSbF}_5$ and $\text{NaSb}_2\text{F}_{15}$ also known; phase transitions in several of these materials have been reported, but not the associated structure–property relations.

5. Conclusions

The structural prediction that $\text{NaSb}_3\text{F}_{10}$ is a new ferroelectric has been confirmed. The spontaneous polarization $P_s \approx 60$ μC m$^{-2}$ at ambience, with a phase transition at $\sim 461$ K to the expected space group $P6_3/mmc$, followed by another at slightly higher temperature to $P6_3/mmc$. The potential of several fluorine octahedral families for dielectric and other possible application invites further investigation.

Contributions to this and related studies formed part of the requirements in their senior undergraduate year for the Southern Oregon University degree of BS for M. P. Aguirre, M. Andrus, M. Bauer, C. S. Gallagher, J. E. Matthews, C. R. Murata, Y. T. Tan and W. V. Raveane. We warmly thank Dr T. J. R. Weakley for his X-ray examination of several single crystals of $\text{NaSb}_3\text{F}_{10}$. Support of this research by the National Science Foundation (grant No. DMR-0137323) is gratefully acknowledged.

References