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Linear and Nonlinear Optical Properties of Na_2SbF_5

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The macroscopic (crystal) hyperpolarizability (d_{123}) of orthorhombic Na_2SbF_5 is found to be 2.8×10^{-10} esu. This corresponds to a microscopic (bond) hyperpolarizability for the Sb–F bonds and Sb lone pair of approximately three quarters of that found for iodine–oxygen (I–O) bonds.

Introduction

The need for nonlinear optical materials which are not subject to optical damage (*1*) has led us to investigate the highly ionic fluorides since one would expect higher breakdown voltages in these less polarizable crystals (2). The observation that the threshold for optical damage, i.e. (the optical power necessary to ionize electrons in a solid) is intimately related to polarizability has been extensively studied and is reasonably well understood (1). Fluorides are also inherently more transparent than oxides. It is also felt that the small optical anisotropy (linear birefringence) found in ionic compounds might be increased[1] by concentrating on that subclass of metal fluorides which contain steriochemically active lone pairs (*3*) (see Fig. 1). To this end we have characterized the system Na_2SbF_5.

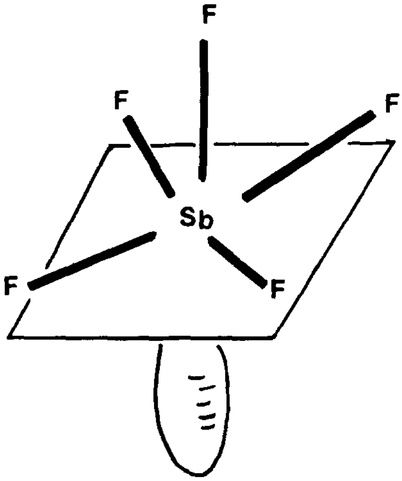

FIG. 1. Antimony pentafluoride $[SbF_5\text{ (lone pair)}]^{2-}$ octahedron showing the four coplanar fluorines which are displaced from the basal plane of the idealized octahedron by ~12° due to the repulsion of the lone pair.

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[1] The so called phase-matchability criterion ($\Delta n \geq$ dispersion) is a necessary device characteristic.

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TABLE I

CRYSTALLOGRAPHIC AND INDEX OF REFRACTION RESULTS FOR Na_2SbF_5[a]

	Group $P2_12_12_1$	
a_0	5.45 Å	
b_0	11.23 Å	
c_0	8.08 Å	
z	4 formula units/unit cell	
	0.53 μm	1.06 μm
n_x	1.474	1.449
n_y	1.479	1.467
n_z	1.438	1.426

[a] $(x, y, z) \leftrightarrows (a, b, c) \leftrightarrows (1, 2, 3)$; (crystallographic (X-ray) results are taken from Ref. (*4*).

TABLE II

NONLINEAR OPTICAL RESULTS FOR Na_2SbF_5, SHOWING THE OBSERVED COEFFICIENTS (d's) AND THEIR RESPECTIVE COHERENCE LENGTHS (l's)[a]

d_{123}	2.9×10^{-10} esu
$\frac{1}{2}(d_{231} + d_{312})$	2.6×10^{-10} esu
l_{123}	9.4 μm
$l_{231,312}$	26.2 μm

[a] Estimated errors in (d, l) are ± (20, 5)%, respectively. Coefficients were measured relative to $d_{111}(SiO_2)$ and converted to an absolute scale via (*8*) $d_{111}(SiO_2) = 1.2 \times 10^{-9}$ esu

Experimental Results and Discussion

Water white crystals of sodium pentafluoroantimonate(III) were grown in two stages: first, a batch of seed material was prepared from an aqueous solution containing SbF_3 and a large excess of NaF; second, growth of the nuclei to the desired dimensions (~6 mm on a side) was carried out by evaporation of the solvent from a saturated hydrofluoric acid solution held at constant temperature (30°C). Na_2SbF_5 crystallizes in symmetry $P2_12_12_1$ with four molecules per unit cell (*4*), the dimensions of which are shown in Table I. The indices of refraction, also shown in Table I, were obtained from a best fit to both Abbe refractometer results as well as the coherence length measurements shown in Table II. Assuming Kleinman symmetry (*5*), the three nonlinear coefficients (*6*) for point group 222 are reduced to one, i.e., ($d_{123} = d_{231}$ d_{312}). These coefficients, shown in Table II, were measured relative to d_{111} of quartz with a Q-switched Nd–YAG laser, operating at 1.06 μm. Experimental details of the non-linear optical measurements are given elsewhere (*7*, *8*). The components of the nonlinear polarization ($P^{2\omega}$) at the second harmonic in terms of the E fields at the fundamental wavelength (E^{ω}) are given by (*9*)

$$P^{2\omega} = \begin{pmatrix} 0 & 0 & 0 & d_{123} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{231} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{312} \end{pmatrix} \begin{bmatrix} (E_x^{\omega})^2 \\ (E_y^{\omega})^2 \\ (E_z^{\omega})^2 \\ 2F_y^{\omega}E_z^{\omega} \\ 2E_x^{\omega}E_z^{\omega} \\ 2E_x^{\omega}E_y^{\omega} \end{bmatrix} . \quad (1)$$

The crystal was cut in the form of a small wedge (Fig. 2), the propagation direction being along 011. Coupling to d_{123} was accomplished by alignment of the fundamental polarization perpendicular to x since

$$P_x^{2\omega} = 2d_{123}E_y^{\omega}E_z^{\omega}. \quad (2)$$

Hence the harmonic is polarized along the x axis. The determination of the average of the other two coefficients was accomplished by polarizing the fundamental at 45° to x since

$$P_y^{2\omega} + P_z^{2\omega} = 2d_{231}E_x^{\omega}E_z^{\omega} + 2d_{312}E_x^{\omega}E_y^{\omega}. \quad (3)$$

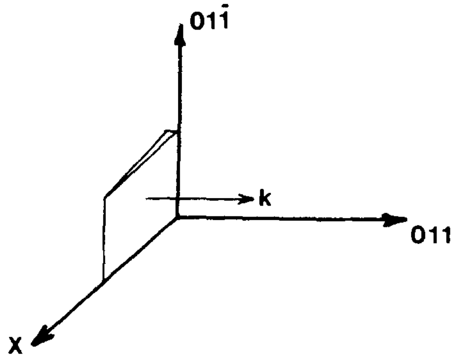

FIG. 2. Na_2SbF_5 wedge configuration used for coupling to d_{123} and $\frac{1}{2}(d_{123} + d_{312})$.

Coefficient	Fundamental polarization	Harmonic polarization
d_{123}	$\perp x$	$\parallel x$
$\frac{1}{2}(d_{213} + d_{312})$	45° to x	$\perp x$

Hence the harmonic is now polarized perpendicular to the x axis. The results, which are shown in Table II, are in good agreement, viz., $d_{123} = \frac{1}{2}(d_{231} + d_{312})$.

The percentage transmission vs wavelength is shown in Fig. 3. While Na_2SbF_5 is phase matchable for $\lambda \stackrel{\sim}{>} 0.65\ \mu m$, its small nonlinear susceptibility tends to preclude the materials device utility.

Since antimony and iodine belong to the same period, i.e., ($5s^25p^3$ vs $5s^25p^5$, respectively) one can assume reasonable similarities in their hyperpolarizabilities, viz., ($\beta_{Sb} \stackrel{\sim}{<} \beta_I$). Therefore one can estimate the measured coefficient of Na_2SbF_5 from known microscopic values of the iodine polarizabilities. The basis of the calculation is given by

$$d_{ijk} = (1/V) G_{il} G_{jm} G_{kn} \beta_{lmn}, \tag{4}$$

where the matrix $[G]$ represents the 3 × 3 of direction cosines which transforms our microscopic (bond) coordinate system into our macroscopic (crystal) coordinate system and V represents the volume of the unit cell. Hence for d_{123} one has

$$d_{123} = (1/V) G_{1l} G_{2m} G_{3n} \beta_{lmn}. \tag{5}$$

Assuming a bond of symmetry $C_{\infty V}$, the form of β is reduced to the following two independent elements $\beta_{333} \equiv \beta^{\parallel}$ and $\beta_{311} = \beta_{113} = \beta_{131} = \beta_{322} = \beta_{223} = \beta_{232} \equiv \beta^{\perp}$. Substituting these various elements into Eq. (5) and recalling that G is an orthonormal matrix, one finds

$$d_{123} = (1/V) G_{13} G_{23} G_{33} (\beta^{\parallel} - 3\beta^{\perp}), \tag{6}$$

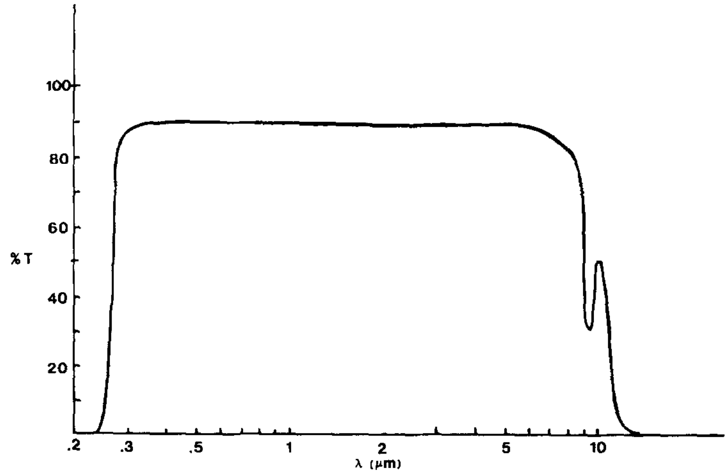

FIG. 3. Percentage transmission vs wavelength for Na_2SbF_5. Sample thickness ~1 mm. Data are uncorrected for surface reflections and taken with an unpolarized beam.

where the three elements of G (13, 23, 33) represent the direction cosines of a bond with respect to the crystal x, y, z axes, respectively, viz.,

$$G_{13} = \cos \theta_x \equiv l, \tag{7}$$

$$G_{23} = \cos \theta_y = m, \tag{8}$$

$$G_{33} = \cos \theta_z \equiv n. \tag{9}$$

Hence the sum over all 24 bonds in the unit cell is given by

$$d_{123} = \frac{1}{V} \sum_{i=1}^{i=24} l_i m_i n_i (\beta_i^{\parallel} - 3\beta_i^{\perp}), \tag{10}$$

20 of which are Sb–F bonds ($\beta_{\mathrm{Sb-F}}$) and 4 of which are Sb lone pairs (β_{LP}). We assume that $\beta_{\mathrm{Sb-F}} \sim \beta_{\mathrm{LP}}$ as found (7) in other systems. Using the recent structural result of Fourcade and co-workers (*4*), one finds

$$d_{123} = 1/V(0.33)\,(\beta^{\parallel} - 3\beta^{\perp}), \tag{11}$$

where $V = 5 \times 10^{-22}$ cm^3. Using the hyperpolarizability values of $(\beta^{\parallel}, \beta^{\perp}) = (3.6, 1) \times 10^{-30}$ esu as found in the several iodates (7), one finds

$$d_{123}\ (\text{calculated}) = 4 \times 10^{-10}\ \text{esu},$$

which is quite close to, and expectedly larger than, our measured value of $\sim 3 \times 10^{-10}$ esu.

In summary, we have shown that the macroscopic (crystal) hyperpolarizability (d_{123}) of Na_2SbF_5 is $\sim 3 \times 10^{-10}$ esu, and that this corresponds to a microscopic (bond) hyperpolarizability for the Sb–F bonds and Sb lone pair of approximately three quarters of that found for iodine–oxygen (I–O) bonds. It is unfortunate that the geometrical factor for point symmetry 222 includes the septor (*10*) $(\beta^{\parallel} - 3\beta^{\perp})$ since $\beta^{\parallel} \sim 3\beta^{\perp}$. In polar structures, where the vector $(\beta^{\parallel} + 2\beta^{\perp})$ can be seen, one might thus expect larger macroscopic susceptibilities.[2]

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[2] The terms septor and vector describe two of the irreducible components of the third rank β tensor. In this particular case (nonpolar group 222) only one irreducible term is present and this is the septor, given by $\beta^{\parallel} - 3\beta^{\perp}$. In certain polar groups such as 4 and 4 mm, one finds not only the septor $(\beta^{\parallel} - 3\beta^{\perp})$ but also a vector term given by $\beta^{\parallel} + 2\beta^{\perp}$. Details of the irreducible components approach to nonlinear optical tensors can be found in the early paper by Jerphagnon (*11*).

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