Powder Second Harmonic Generation Efficiencies of Saccharide Materials

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Saccharide materials are potential candidates for frequency conversion applications. In addition to being chiral, which ensures crystallization in a space group necessary for three-wave mixing processes, they generally possess useful physical and optical properties. We have examined the powder second harmonic generation efficiencies of both saturated saccharides and sugars with simple polar π-functionalities. Powder efficiencies of up to 5 times that of sucrose were observed for simple saturated sugars, whereas values of 18 times sucrose (or 0.45 × urea) were observed for unsaturated saccharide derivatives. We have noted that for both classes of material, there is a tendency for more efficient nonlinear compounds to reside in a monoclinic rather than an orthorhombic space group. We have also noted that there appears to be a correlation between the phase-matching potential and the crystal symmetry. In addition, two promising saccharide materials have been identified for frequency conversion applications, based on their powder second-harmonic generation efficiencies, their phase-matching capabilities, and their UV transparency.

Introduction

Second-order nonlinear optical materials[1] capable of efficient frequency conversion of infrared laser radiation to visible or ultraviolet wavelengths are of interest for applications such as optical communication, laser remote sensing, optical disk data storage, laser-driven fusion, and medical and spectroscopic lasers. The basic requirements for a nonlinear optical crystal to be successfully utilized in frequency conversion are a nonzero nonlinear optical coefficient, transparency at all wavelengths involved, efficient transfer of energy between the optical waves propagating through the crystal and good physical (low vapor pressure, large Mohs hardness) and optical (large optical damage threshold, large birefringence, low dispersion) properties.

At present, commercially available nonlinear optical crystals are predominantly inorganic, e.g., potassium niobate,[2] lithium niobate,[3] potassium dihydrogen phosphate (KDP)[4] and β-barium borate.[5] It has long been known[6] that organic molecular single crystals often possess nonlinear optical responses which far surpass those of their inorganic counterparts. However, the increase in nonlinearity is often accompanied by a decrease in the ultraviolet/visible transparency of the material, the so-called nonlinearity-transparency tradeoff.[7] Thus, some researchers[8] have been led to examine classes of organic materials, such as amino acids and their salts, that exhibit the maximum short-wavelength transparency and that still have potential to meet the other essential requirements[9] for use in frequency conversion. Saccharides are another class of biologically derived organic material that have potential to play a role in optical frequency conversion. They exhibit extremely good UV transparency and offer a combination of attractive properties for three-wave mixing processes, e.g., chirality (a single enantiomer of a chiral molecule must crystallize in a noncentrosymmetric manner, thus causing some of the nonlinear optical coefficients to be nonzero), large birefringence and low dispersion (permitting the possibility of phase-matched nonlinear optical applications). To date, one of the major drawbacks to organic materials becoming commercial nonlinear optical devices has been the lack of quality and/or size of the bulk crystals. Strong growth anisotropy caused by specific solvent–solute interactions has precluded the development of some of the most promising materials into large crystals. Even if adequate sized specimens of reasonable quality are obtained, the samples are often soft and cannot be cut and polished using standard optical techniques. Saccharides being polyhy-

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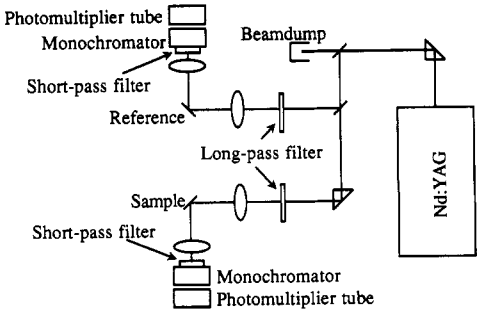

Figure 1. Apparatus for the determination of the SHG efficiency of powders.

droxylic compounds are generally capable of multidirectional hydrogen bonding and this may explain why many saccharide materials are known to grow from solution to relatively large sizes.[10] Additionally, because of their capability for extensive hydrogen bonding in the solid state, saccharides are generally higher melting and harder[11] than van der Waals bonded organic crystals of comparable molecular weight, thus allowing fabrication of optical components using standard techniques.

Although saccharides appear to be potential candidates for laser frequency conversion devices, only a few of these materials have previously been examined.[10-12] One aim of this work was to examine a wide range of available mono-, di-, and trisaccharides, as well as saccharides derivatized with small unsaturated groups. This work presents an assessment of the second harmonic generation (SHG) efficiencies of crystalline saccharides in powder form.

Experimental Section

The full optical characterization of any crystalline nonlinear optical material requires reasonably large single crystals of good optical quality. The single crystals once grown must be precisely cut and polished in a prescribed orientation. The time required for growth, cutting, and polishing of one crystal slab can be considerable, and thus this approach to screening the large number of available saccharide materials is clearly impractical. To overcome these problems, Kurtz and Perry[13] devised an experimental technique which allowed a quick and efficient way of screening candidate materials. This method requires the nonlinear optical material in microcrystalline powder form, which is usually readily available.

The apparatus used to determine the powder SHG efficiency of saccharide materials is shown in Figure 1. The 1064-nm output of a Q-swtiched Nd:YAG laser, operating with a repetition rate of 10 Hz, was attenuated by a beam splitter, with the majority of the beam energy being collected by a beam-dump. The attenuated beam was split to form a reference and sample channel. Long-wavelength-pass filters were used to eliminate visible radiation emitted by the laser flashlamps. The beam was focused onto the reference (lithium niobate) and sample powders respectively. The power density at the sample/reference was approximately 0.2 MW/cm^2. The scattered second harmonic radiation was separated from the fundamental using short-pass filters and a monochromator and was detected by a photomultiplier tube, whose output was amplified and integrated with 10-ns gate widths. The signal from the lithium niobate reference channel was used to normalize the signal from the sample channel in order to minimize the effect of shot-to-shot laser intensity fluctuations. The possibility of spurious scattered light and two-photon fluorescence[14] adding to the signal at the wavelength of the second harmonic radiation was eliminated by scanning the bandwidth of the detected radiation using the monochromators (a very narrow bandwidth being indicative of SHG).

The samples used were microcrystalline powders, obtained by grinding, held between two glass cover slides, with the sample thickness (0.5 mm) kept constant in all experiments. The powders were not immersed in index-matching fluid. The broad distribution of particle sizes ranged from about 40 to 120 μm. The powder SHG efficiency of all tested materials was compared to that of sucrose, which has a relatively modest nonlinearity compared to conventional frequency doublers.[11,12] All materials tested were obtained commercially from Sigma Chemical Co.

The precision of the measurements was estimated, based on the variations observed between different samples of the same material, at approximately 25%. It was assumed that the magnitude and direction of the scattered radiation did not fluctuate from sample to sample since refractive index variations between the saccharide samples was small (typically, n = 1.49–1.59 for saccharides). In addition, the geometry used created strong "hemispheric" backscattering of nearly uniform angular intensity distribution, with a large attenuation of both fundamental and harmonic beams in the forward direction, ensuring that the fraction of scattered radiation detected was constant for all samples.

Results and Discussion

(A) Theoretical Dependence of SHG Intensity on Particle Size. Kurtz and Perry[13] have shown that for non-phase-matchable materials, the intensity of the generated second harmonic radiation, $I^{2\omega}$, is given by

$$I^{2\omega} \propto (d_{ijk}{}^2) l_c{}^2/r \tag{1}$$

where r is the average powder grain size, (d_{ijk}) is the angular average of the second-order polarizability tensor and l_c is the average coherence length. For phase-matchable materials

$$I^{2\omega} \propto (d_{\text{eff}}{}^2) \sin(\theta_m)/\beta \tag{2}$$

where (d_{eff}) is the effective nonlinear coefficient for phase-matched second harmonic generation, θ_m is the phase-matching angle, and β is given by

$$\beta = (\omega n_\omega/c) \sin \rho \tag{3}$$

where ω is the angular frequency of the fundamental wave, c is the speed of light, n_ω is the fundamental refractive index and ρ is the angle between the sphere and ellipse index surfaces (ρ is commonly referred to as the walk-off angle). Equations 1 and 2 are valid only when the average powder grain size is much greater than the characteristic interaction length for SHG.[13,15] For saccharides, a mean grain size of approximately 100 μm meets this requirement.[15] For an average powder grain size much less than the characteristic SHG interaction length, the second harmonic intensity for both phase-matchable and non-phase-matchable materials is directly proportional to the average grain size, i.e.

$$I^{2\omega} \propto (d^2)r \tag{4}$$

where d^2 is $d_{ijk}{}^2$ for non-phase-matchable or $d_{\text{eff}}{}^2$ for phase-matchable materials.

The dependence of $I^{2\omega}$ on the powder grain size is illustrated in Figure 2 for phase-matchable and non-phase-

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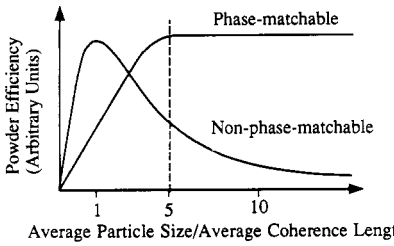


Figure 2. Particle size dependence on $I^{2\omega}$ for phase-matchable and non-phase-matchable materials. Adapted from ref 13.

matchable materials.[13] The salient feature of Figure 2 is that for grain sizes much greater than the average SHG interaction length (to the right of the vertical dashed line), $I^{2\omega}$ for phase-matchable materials is independent of the grain size (eq 2) whereas $I^{2\omega}$ for non-phase-matchable materials varies inversely with grain size (eq 1). It is this behavior which allows phase-matchable and non-phase-matchable materials to be identified by powder SHG measurements. It should be noted that preferential alignment on packing of the particles can lead to an incorrect assignment of the material phase matchability, as based on particle size dependent intensity measurements. This shall be discussed further in section F.

(B) Powder SHG Efficiencies of Saturated Saccharides. The powder SHG efficiencies of simple saccharides are given in Table I, together with other saturated saccharide-based materials, i.e., those possessing no π-functionality. These include sugar alcohols, deoxysugars, anhydro-sugars, methyl ethers (glycosides) and amino sugars. The distribution of powder SHG values for this class of material suggests a limit to $I^{2\omega}$ of approximately 5 × sucrose (0.125 × urea or 1 × KDP). Despite the modest nonlinearity displayed by the saturated sugars, the vast majority of the sugars displayed easily measurable powder SHG efficiencies, consistent with the guarantee of noncentrosymmetry provided by their chirality. Materials whose powder SHG efficiency could not be differentiated from the background noise level (0.01 × sucrose) are assigned a powder SHG efficiency of <0.01. It should be noted that materials with no anomeric designation may be assumed to be anomeric mixtures, e.g., maltose in Table I. The SHG efficiency of compounds examined by Rosker and Tang[10] are in good agreement with those in Table I.

Saturated saccharides with SHG efficiencies comparable to or greater than sucrose are all of monoclinic crystal symmetries, where known. Also, where tested, these materials were phase-matchable, as will be discussed in section F. On the other hand, materials with SHG efficiencies much less than that of sucrose were mostly non-phase-matchable, where tested, and orthorhombic, where known. The variation in SHG efficiencies among the phase-matchable materials is probably due to variations in d coefficients as a result of differences in crystal packing and/or molecular nonlinearity. For the non-phase-matchable materials tested, the mean coherence lengths were all comparable, around 20 μm. Therefore, the variation in SHG efficiencies for the non-phase-matchable materials also reflects differences in d coefficients. The structure of saturated sugars which possessed a powder SHG efficiency larger than sucrose are presented in Figure 3.

The molecular second-order nonlinearity in saturated sugars is probably dominated by the contribution of the high-energy n $\rightarrow$ σ^* electronic transition involving the

Table I. Powder SHG Efficiencies of Various Saturated Sugars[a]

monosaccharides	symmetry	$I^{2\omega}/I^{2\omega}$(sucrose)
D-altrose	U	2.10
D-mannoheptulose	M	0.80
D-lyxose	O	0.50
β-D-glucose	O	0.40
β-L-allose	O	0.30
α-D-xylose	O	0.20
α-L-xylose	O	0.20
D-ribose	U	0.15
L-sorbose	O	0.10
D-arabinose	O	0.08
α-D-talose	O	0.08
D-galactose	O	0.05
β-D-fructose	O	0.02
D-mannose	O	0.02
di- and oligosaccharides	**symmetry**	$I^{2\omega}/I^{2\omega}$(sucrose)
maltose	O,M	1.10
sucrose	M	1.00
β-lactose	M	0.95
cellobiose	M	0.90
α-lactose monohydrate	M	0.65
palatinose	U	0.10
maltotetraose	U	0.10
melezitose	O	0.07
melibiose monohydrate	O	0.05
stachyose tetrahydrate	U	0.03
raffinose	O	0.03
maltopentaose	U	0.02
turanose	O	0.02
trehalose dihydrate	O	0.01
maltotriose	U	<0.01
sugar alcohols	**symmetry**	$I^{2\omega}/I^{2\omega}$(sucrose)
D-arabitol	U	1.90
D-mannitol	O	0.20
D-xylitol	O	0.10
D-sorbitol	O	0.05
adonitol	U	0.01
maltitol	O	0.01
galactitol	U	<0.01
glycosides	**symmetry**	$I^{2\omega}/I^{2\omega}$(sucrose)
methyl-α-D-glucoside	O	0.19
methyl-α-D-xyloside	M	0.07
3-*O*-methyl-D-glucose	O	0.05
methyl-β-D-galactoside	O	0.02
deoxy sugars	**symmetry**	$I^{2\omega}/I^{2\omega}$(sucrose)
2-deoxy-D-galactose	M	3.90
2-deoxy-D-glucose	U	1.35
6-chloro-6-deoxy-α-glucose	U	1.20
α-L-rhamnose monohydrate	M	0.70
α-L-fucose	O	0.30
6-fluoro-6-deoxygalactose	U	0.30
2-deoxy-D-ribohexopyranose	U	0.15
3-fluoro-3-deoxyglucose	U	0.07
1,6-anhydro-β-D-glucose	O	0.04
2-deoxy-D-ribose	O	0.01
6-fluoro-6-deoxyglucose	U	0.01
amino sugars	**symmetry**	$I^{2\omega}/I^{2\omega}$(sucrose)
1-D-galactosylamine	M	2.40
1-D-lyxosylamine	U	1.30
D-glucosamine sulfate	U	0.85
D-mannosamine HCl	U	0.20
1-fucosylamine	U	0.20
D-mannosamine	U	0.12
D-glucosamine HCl	M	0.10
D-galactosamine HCl	O	0.08

[a] Key to symmetry abbreviations: O, orthorhombic; H, hexagonal; M, monoclinic; U, undetermined. Background noise level = 0.01 × sucrose.

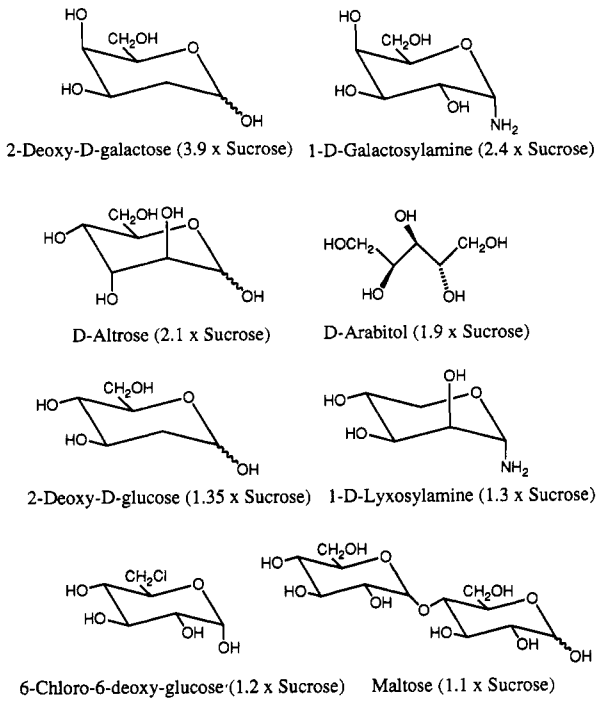


Figure 3. Saturated sugars with a powder SHG efficiency larger than sucrose.

oxygen lone pairs and the C–O σ bond. For these relatively localized transitions, the molecular nonlinearity can be considered to be a vectorial sum of contributions from the individual C–O bonds. Because of the typically similar number of oppositely projected axial and equatorial C–O bonds in the closed ring saccharides, there is likely to be significant cancellation in the net projection in any given direction. Thus, the nonlinearity of saturated saccharide crystals would be expected to be low, even if the crystal packing were optimal, consistent with the trend observed.

(C) Powder SHG Efficiencies of Saccharide Phosphates and Sulfates. Many saccharides occur naturally as anionic phosphate derivatives. The utility of various inorganic phosphates such as potassium dihydrogen phosphate and ammonium dihydrogen phosphate[16] led us to investigate this family of compounds. Twenty five salts of sugar phosphates and the related sulfates were tested for their second harmonic generation efficiency (Table II).

In general, these compounds did not exhibit an increased nonlinear optical response compared to that of purely saturated sugars. The largest SHG powder efficiencies were obtained with α-D-glucose-6-phosphate (1.2 × sucrose) and the dipotassium and disodium salts of α-D-glucose-1-phosphate (1.7 and 1.3 × sucrose, respectively). The structures of these three compounds are presented in Figure 4. The majority of sugar phosphate salts crystallize from aqueous media in highly hydrated form and many are hygroscopic, so that they have poor stability with respect to atmospheric humidity, which may limit their practical value. Lower crystallinity and water adsorption are probably reflected in the low SHG efficiencies associated with some of the materials in this class of sugars.

(D) Powder SHG Efficiencies of Saccharides with Simple Polar π-Substituents. Another class of natural sugar derivatives are those with simple polar π-functionalities. This includes the naturally occurring sugar acids, which may exist as a variety of acid salts or as lactones through intramolecular cyclic ester formation. Chemically related, are sugars possessing amido functions, either from amides of the sugar acids, e.g., α-glucuronamide, or from the acetylation of amino sugars, e.g., *N*-acetyl-D-glucosamine. The powder SHG efficiencies of these unsaturated compounds are given in Table III.

Although there exists a wide spread in the range of powder SHG efficiencies, the upper values are now clearly larger than for the saturated sugars (Table I). The structures of some unsaturated molecules which have a powder SHG efficiency surpassing that of sucrose are presented in Figure 5.

D-Isoascorbic acid and L-ascorbic acid displayed large powder SHG efficiencies (11 × sucrose and 2.2 × sucrose, respectively). These molecules have an extended π-system with a C=C bond conjugated with a lactone functionality. However, the reduced UV transparency (λ_{max} = 264 nm for D-isoascorbic acid and 256 nm for L-ascorbic acid compared to 192 nm for *N*-acetyl-D-glucosamine) may limit their applicability to UV generation. Several simple lactones had $I^{2\omega} \gg$ sucrose, notably D-glucurono-6,3-lactone (10 × sucrose). Comparable $I^{2\omega}$ values were found among the *N*-acetylated amino sugars and amides, the most promising material being *N*-acetyl-D-glucosamine (6.1

Table II. Powder SHG Efficiencies of Various Sugar Phosphates and Sulfates

compound	sym-metry	$I^{2\omega}/I^{2\omega}$ (sucrose)
α-D-glucose 1-phosphate dipotassium salt dihydrate	M	1.70
α-D-glucose 1-phosphate disodium salt tetrahydrate	M	1.30
α-D-glucose-6-phosphate	U	1.20
α-D-glucose-6-phosphate barium salt hydrate	M	0.50
glucose-6-sulfate sodium salt	U	0.30
α-mannose-1-phosphate	U	0.20
D-galactose-1-phosphate	U	0.13
α-D-galactose-1-phosphate	U	0.11
α-galactopyranosyl-1-phosphate	U	0.11
D-glucose-1,6-diphosphate	U	0.10
α-D-mannose-6-phosphate barium salt	U	0.10
D-fructose-1,6-diphosphate calcium salt	U	0.08
α-D-glucose-6-phosphate disodium salt hydrate	M	0.05
D-glucosamine-6-phosphate sodium salt	U	0.05
α-fucose-1-phosphate	U	0.04
galactose-6-phosphate	U	0.03
galactose-6-sulfate	U	0.03
mannose-6-phosphate	U	0.03
D-glucosamine-6-phosphate	U	0.03
D-glucosamine-3-sulfate free acid	U	0.02
D-fructose-1-phosphate barium salt	U	0.02
D-galactose-6-phosphate barium salt	U	0.01
D-glucosamine-6-phosphate barium salt	U	0.01
D-glucosamine-6-sulfate	U	<0.01
D-glucosamine-2-sulfate sodium salt	U	<0.01

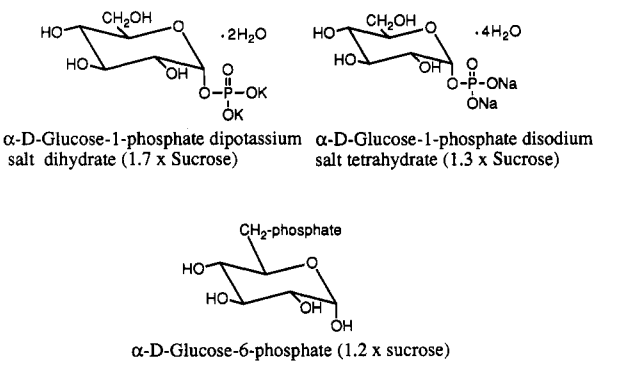


Figure 4. Sugar phosphates with a powder SHG efficiency larger than sucrose.

(16) Zernike, F. *J. Opt. Soc. Am. B* **1964**, *54*(10), 1215–1220.

Table III. Powder SHG Efficiencies of Various Unsaturated Sugars

N-acetylated amino sugars, amides	symmetry	$I^{2\omega}/I^{2\omega}$ (sucrose)
N-acetyl-D-glucosamine	M	6.10
α-D-glucuronamide	M	2.60
N-acetyl-D-galactosamine	M	1.90
N-acetyl-β-D-neuraminic acid	M	0.90
N-acetyl-β-D-mannosamine	O	0.75
N,N'-diacetyl-α-chitobiosamine	O	0.55
N-acetyl-α-glucosamine-1-phosphate	U	0.25
N,N,N-triacetylchitotriosamine	U	0.22
N-acetyl-α-galactosamine-1-phosphate Na	U	0.06
N-acetyl-glucosamine-6-phosphate	U	0.03

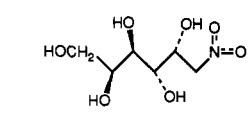
acids and salts	symmetry	$I^{2\omega}/I^{2\omega}$(sucrose)
D-isoascorbic acid	M	11.0
sodium D-glucuronate	M	4.50
calcium D-galactonate	M	3.10
sodium D-glucoheptonate	M	3.00
sodium D-gluconate	M	3.00
L-ascorbic acid	M	2.20
barium D-glucuronate	U	1.90
lithium L-lactate	U	1.80
potassium D-gluconate	M	1.40
5,6-isopropylidene ascorbic acid	U	0.70
magnesium D-glucoheptonate	U	0.60
D-glucuronic acid	U	0.50
zinc D-glucoheptonate	U	0.44
α-D-galacturonic acid	U	0.20
calcium saccharate	O	0.09
zinc L-lactate	U	0.06
calcium D-glucoheptonate	U	0.02
calcium L-lactate	U	0.01
calcium xylonate	U	<0.01
lactobionic acid	U	<0.01

nitro sugars	symmetry	$I^{2\omega}/I^{2\omega}$(sucrose)
1-deoxy-1-nitro-D-mannitol	H	18.0
1-deoxy-1-nitro-D-glucitol	U	9.00
1-deoxy-1-nitro-D-allitol	U	0.25
1-deoxy-1-nitro-D-altritol	U	0.20

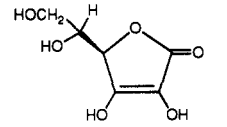
lactones	sym-metry	$I^{2\omega}/I^{2\omega}$ (sucrose)
D-glucurono-6,3-lactone	M	10.0
D-saccharic acid 1,4-lactone	M	3.50
D-erythronic acid γ-lactone	U	2.50
D-saccharic acid 6,3-lactone	U	2.10
α,β-glucooctanoic acid γ-lactone	U	1.60
1,2-isopropylidene-α-D-glucurono-6,3-lactone	M	0.80
L-mannoheptonic-γ-lactone	U	0.60
D-galactono-1,4-lactone	O	0.32
pantolactone	U	0.31
D-ribono-1,4-lactone	O	0.30
D-glucono-1,5-lactone	O	0.18
L-glucono-1,4-lactone	O	0.16
D-mannuronic acid 6,3-lactone	U	0.12
L-mannono-1,4-lactone	U	0.08
D-glucoheptono-1,4-lactone	U	0.02

× sucrose). In addition to the above series of compounds, several straight-chain sugars with terminal nitro (NO_2) groups were tested and two members, 1-deoxy-1-nitro-D-mannitol (18 × sucrose) and 1-deoxy-1-nitro-D-glucitol (9 × sucrose), were found to have significant powder SHG efficiencies.

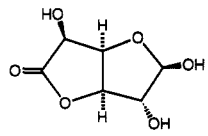
Nearly all of the simple π-substituted sugars that exhibited $I^{2\omega}$ values greater than sucrose were monoclinic crystals, where known. Again, as for the saturated sugars, most of these were phase-matchable (section F), where tested. For these phase-matchable materials the variation in $I^{2\omega}$ values is probably due to differences in d coefficients. Clearly, the nonlinearities of saccharides substituted with simple polar π-substituents are enhanced relative to the



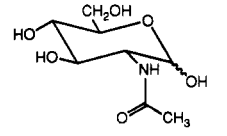
1-Deoxy-1-nitro-D-mannitol (18 x Sucrose)



D-Isoascorbic acid (11 x Sucrose)



D-Glucurono-6,3-lactone (10 x Sucrose)



N-Acetyl-D-glucosamine (6.1 x Sucrose)

Figure 5. Unsaturated sugars with a powder SHG efficiency much larger than sucrose.

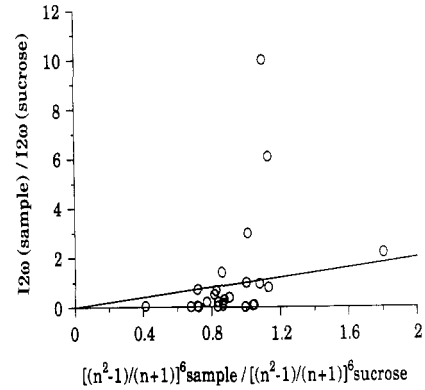


Figure 6. Powder SHG efficiency as a function of the linear susceptibility for saturated and π-substituted sugars. The solid line represents the relationship predicted by Miller.[17]

saturated sugars. Miller[17] has shown that the second-order nonlinear optical response is directly porportional to the materials linear susceptibility. Kurtz and Perry[13] noted that this dependence manifests itself on the powder SHG efficiency in the following way:

$$I^{2\omega} \propto \left[\frac{n^2-1}{n+1}\right]^6 \quad (5)$$

where n is the refractive index of the sample. Refractive indexes (at 589 nm) of some of the materials in Tables I–III have been reported by Winchell.[18] Figure 6 shows the observed powder SHG efficiency versus the calculated values of $[(n^2-1)/(n+1)]^6_{\text{sample}}/[(n^2-1)/(n+1)]^6_{\text{sucrose}}$ for these materials. The solid line in Figure 6 represents the predicted[17] powder SHG efficiency (relative to sucrose), according to eq 5. The observed SHG efficiencies are highly scattered relative to the theoretical line with all saturated sugars in Figure 6 on or below this line and all unsaturated sugars on or above this line. The increased powder SHG efficiencies of π-substituted sugars relative to saturated sugars can not then be adequately explained just by a simple increase in their linear susceptibilities and we conclude that the larger powder SHG efficiencies for these π-substituted sugars are likely due to enhanced molecular nonlinearities.

(E) Powder SHG Efficiencies of Miscellaneous Sugar Derivatives. A number of other miscellaneous sugar derivatives, including sugar esters (acetates and

(17) Miller, R. C. *Appl. Phys. Lett.* **1964**, *5*(1), 17–19.
(18) Winchell, A. N. *The Optical Properties of Organic Compounds*; Wisconsin Press: Madison, 1943. Refractive indices for D-glucurono-6,3-lactone and N-acetyl-D-glucosamine were measured by Laura Davis (unpublished results).

Table IV. Powder SHG Efficiencies of Various Unsaturated Sugars

acetates	symmetry	$I^{2\omega}/I^{2\omega}$(sucrose)
β-D-xylose 1,2,3,4-tetraacetate	M	1.50
β-D-ribose 1,2,3,5-tetraacetate	O	0.30
α-glucose pentaacetate	U	0.18
β-lactose octaacetate	U	0.18
α,β-galactose pentaacetate	U	0.17
mannose pentaacetate	U	0.11
maltose octaacetate	O	0.08
β-glucose pentaacetate	O	0.05
α-D-fucose 1,2,3,4-tetraacetate	U	0.03
trehalose octaacetate	U	0.02
D-raffinose undecaacetate	U	<0.01

aromatic glycosides etc	symmetry	$I^{2\omega}/I^{2\omega}$(sucrose)
phenyl-β-D-galactoside	U	2.30
phenyl-β-D-glucoside	O	0.90
α-D-glucose pentabenzoate	U	0.05
salicin	O	0.03

benzoates) and phenyl glycosides, were tested. The results in Table IV indicate that no enhancement of the nonlinearity is realized for a sugar containing multiple ester (O—C=O) groups. In fact, it appears that the average SHG efficiencies for the multiple ester substituted sugars are lower than those for the singly substituted sugars. This observation is consistent with the notion that there may exist significant cancellation of the individual group contributions from multiple axial and equatorial sites.

(F) Relationship between the Saccharide Molecular/Crystal Structure and the Observed Nonlinearities. In addition to molecular composition factors which affect the first molecular hyperpolarizability, β, the powder efficiencies will also be influenced by molecular packing arrangements. X-ray structure determinations,[19] performed on approximately 75 of the compounds tested in the survey, revealed that the vast majority of sugars crystallize in one of two space-groups: monoclinic $P2_1$ and orthorhombic $P2_12_12_1$. As stated previously, sugars, being chiral, must pack in one of the 21 noncentrosymmetric space groups. However, the majority of these are unavailable since they contain mirror or glide planes, the result being that sugars crystallize mainly in two different symmetry classes, 2 or 222, with space-groups $P2_1$ and $P2_12_12_1$ predominant. Analysis of the powder SHG efficiencies as a function of crystal symmetry reveals a propensity for higher efficiencies in monoclinic versus orthorhombic saccharide crystals, for both saturated (Figure 7A) and π-substituted sugars (Figure 7B). Velsko *et al.* have previously reported a similar observation for chiral amino acid salts.[8,20] This observation may be a result of the lower number of nonzero d coefficients (which are potentially phase matchable) for the higher symmetry materials. Furthermore, Zyss and Oudar[21] have stated that materials in the orthorhombic point-group 222 may be nonoptimized for utilization of the molecular nonlinearity because of cancellations due to symmetry (for four molecules per unit cell, two are inactive for any nonlinear optical d_{ijk} coefficient).

It was shown earlier that the powder SHG intensity is dependent on (1) the nonlinearity of the material (the

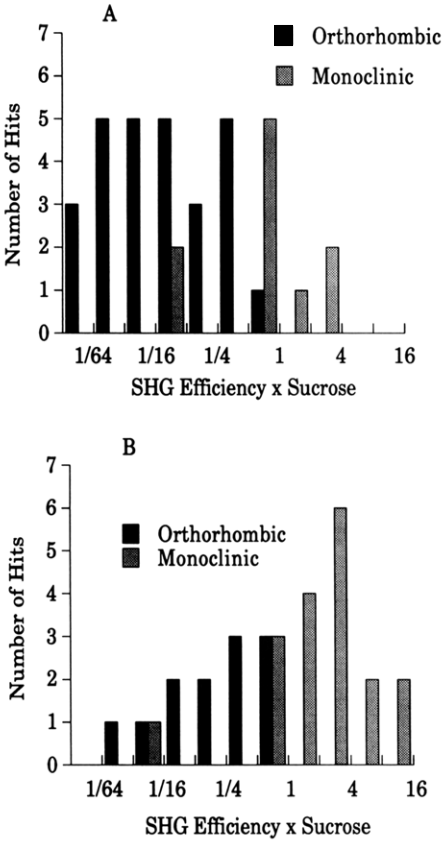


Figure 7. (A) Distribution of $I^{2\omega}$ versus crystal symmetry for saturated sugars. (B) Distribution of $I^{2\omega}$ versus crystal symmetry for π-substituted sugars.

values of the d coefficients), (2) whether the material is phase matchable, and (3) the mean particle size of the powder. The dependence of $I^{2\omega}$ on the particle size was measured on approximately 30 saccharide compounds by making up samples which had been screened through filters of differing mesh size. For each compound, a set of samples was prepared with particle sizes <10, <15, <20, <25, <35, and <100 μm. The values of $I^{2\omega}$ obtained indicated that our general procedures were consistent with the ungraded compounds in Tables I–IV having particle sizes in the range 40–120 μm. The results of the particle size dependence analysis are given in Table V where there is a noticeable correlation between $I^{2\omega}$ and the phase-matching character. All sugars that were tested with $I^{2\omega}$ > sucrose displayed phase-matching character (Figure 8). Additionally, we note that there is a correlation between monoclinic symmetry and phase-matchability. Thus, phase-matching appears to be playing a significant role in the magnitude of the powder SHG efficiencies.

It was noted earlier that one caveat associated with predicting the phase-matchability of materials from particle size dependent intensity measurements was that preferential orientation of the particles, due for example to nonspherical particle shape, may lead to a sampling of a nonuniform distribution of nonlinear optical coefficients. This could result in an increasing or decreasing SHG intensity with increasing particle size and preferential ordering, leading to an incorrect assignment of the material phase-matchability. Five compounds assigned as being phase-matchable in Table V were examined as single crystals and the phase matchability of each was confirmed. Hence for these materials at least, the relationship between

(19) Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146–153. Symmetry assignments for calcium D-galactonate, sodium D-glucoheptonate, and 1-deoxy-1-nitro-D-mannitol courtesy of I. D. Williams and N. J. Taylor (unpublished results).

(20) Velsko, S. P.; Davis, L. E.; Wang, F.; Eimerl, D. *Proc. SPIE* **1988**, *971*, 113–117.

(21) Zyss, J.; Oudar, J. L. *Phys. Rev. A* **1982**, *26*(4), 2028–2048.

Table V. Phase-Matchability As Assessed by the Dependence of $I^{2\omega}$ on Particle Size at 1064 nm[a]

compound	symmetry	$I^{2\omega}/I^{2\omega}$(sucrose)	PM
1-deoxy-1-nitro-D-mannitol	H	18.0	Y
D-isoascorbic acid	M	11.0	Y
D-glucurono-6,3-lactone	M	10.0	Y
N-acetyl-D-glucosamine	M	6.10	Y
sodium D-glucuronate	M	4.50	Y
2-deoxy-D-galactose	M	3.90	Y
calcium D-galactonate	M	3.10	Y
sodium D-glucoheptonate	M	3.00	Y
α-D-glucuronamide	M	2.60	Y
1-D-galactosylamine	M	2.40	Y
L-ascorbic acid	M	2.20	Y
D-arabitol	U	1.90	Y
sucrose	M	1.00	Y
β-lactose	M	0.95	Y
D-galactono-1,4-lactone	O	0.32	Y
cellobiose	M	0.90	PY
α-L-fucose	O	0.30	I
D-glucono-1,5-lactone	O	0.18	I
D-xylitol	O	0.10	I
L-sorbose	O	0.10	PN
D-glucosamine HCl	M	0.10	PN
D-arabinose	O	0.08	PN
α-L-rhamnose	M	0.70	N
salicin	O	0.03	N
raffinose	O	0.03	N
trehalose dihydrate	O	0.01	N

[a] Key to phase-matching abbreviations: Y, phase-matchable; N, non-phase-matchable; PY, probably phase-matchable; PN, probably non-phase-matchable; I, inconclusive.

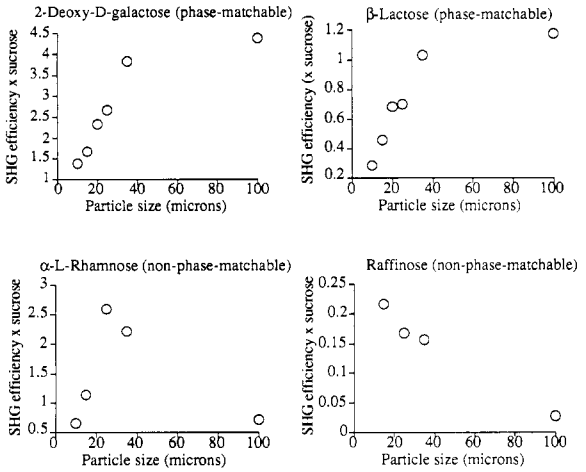


Figure 8. Particle size dependence on $I^{2\omega}$ for representative phase-matchable and non-phase-matchable materials.

intensity, monoclinic symmetry and phase matchability still holds.

(G) UV-Transparency of Saccharides with High Powder SHG Efficiencies. We have identified six saccharide materials with effective nonlinearities greater than or equal to that of KDP (≳5 × sucrose). Electronic absorption spectra were recorded for saturated solutions of some of these materials in water. The wavelength corresponding to the onset of optical absorption (absorption edge) is presented in Table VI, with the value for sucrose given for comparison. Given the 30–50-nm bathochromic shift in the absorption edge in going from solution to the solid-state, all but two (1-deoxy-1-nitro-D-mannitol and D-isoascorbic acid) of the saccharides in Table VI are potential candidates for frequency doubling and tripling the 1064 nm output of a Nd:YAG laser. For this reason, we have concentrated our attention on D-glucurono-6,3-lactone and *N*-acetyl-D-glucosamine. Single crystal specimens of both of these materials have been grown and their characterization will be reported in a forthcoming paper.

Table VI. UV Transparency of Saccharide Materials with a Large Powder Efficiency

compound	absorption edge, nm	$I^{2\omega}/I^{2\omega}$(sucrose)
1-deoxy-1-nitro-D-mannitol	250	18.00
D-isoascorbic acid	300	11.00
D-glucurono-6,3-lactone	240	10.00
N-acetyl-D-glucosamine	230	6.10
sodium D-glucuronate	220	4.50
2-deoxy-D-galactose	220	3.90
sucrose	200	1.00

Conclusions

The present survey of approximately 150 saccharide compounds has led to the identification of six materials with effective nonlinearities greater than or equal to that of KDP. From this survey two materials have been selected for single crystal studies. Saccharide compounds that possess a powder SHG efficiency comparable to or greater than sucrose will in general be both monoclinic and phase matchable. Since phase matching is of vital importance in frequency conversion applications, it appears that the search for phase-matchable saccharide derivatives possessing a relatively large optical nonlinearity will, in general, be more successful with monoclinic saccharides substituted with small polar π-bonding functionalities.

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