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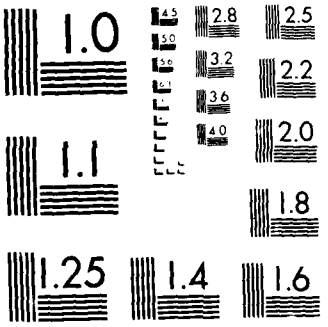

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INCLUSION TUNING OF NON-LINEAR OPTICAL MATERIALS: SWITCHING THE SHG OF P-NITROANILINE AND 2-METHYL-P-NITROANILINE WITH MOLECULAR SIEVE HOSTS.

by

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ABSTRACT

A study of the relative intensities of second harmonic generation (SHG) in sorbate complexes of p-nitroaniline (NA) and 2-methyl-p-nitroaniline (MNA) in molecular sieve hosts is presented. An SHG signal ten times larger than that of any previously reported organic or organometallic inclusion complex is observed. NA in ALPO-5 complexes have a maximum SHG of 630 at 13 wt. % NA. Pure NA has no SHG signal. With MNA in ALPO-5 (13 wt. %) the SHG signal is equal to that of the ALPO-5 host. X-ray powder diffraction was used to characterize the inclusion nanocomposites. The ability to switch on and enhance SHG in NA and switch off SHG in MNA is ascribed to sorbate-host and sorbate-sorbate alignment interactions.

(Aniline, nitro radical

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Inclusion of a guest species into a host framework can be used in a combinatorial or synergistic mode to create non linear optic properties which are dramatically different from those of either host or guest independently. Molecular dipolar alignment has been observed in organic and organometallic host-guest chemistry where, for example, p-nitroaniline (NA, SHG=0 due to its centrosymmetric crystal structure) in β-cyclodextrin has an SHG=64 x quartz.[1] Inclusion chemistry can also be used to modify wave mixing and wave guide characteristics as illustrated by the use of ion exchange in the potassium titanyl phosphate (KTP) family.[2]

These observations and the fact that non-linear optical properties are particularly sensitive to structural variations[3,4], suggest that inclusion chemistry can be used as a means for achieving fine control, through careful synthetic choices, of a variety of non-linear optical effects. This paper gives the first report of the use of inorganic hosts and organic guests to form non-linear optic materials. An SHG signal ten times larger than that of any previously reported organic or organometallic inclusion complex is observed.

Second harmonic generation (SHG) requires noncentrosymmetric structural features[3,5] which can be imposed on a sorbate by an acentric host or created by sorbate-host interactions. Many zeolites have ideal pore dimensions for the ordering or alignment of aromatic sorbates such as NA, and some have acentric structures. NA and 2-methyl-p-nitroaniline (MNA, SHG=375[6]), which have similar second order molecular hyperpolarizabilities,[7,8] were introduced into a variety of acentric and centrosymmetric zeolite hosts by a vapor-phase loading method.[9] Loading levels are easily varied by this method up to a maximum at which pore-filling occurs. The guest molecules are

strongly adsorbed. Heating to 100°C under dynamic vacuum does not result in appreciable weight loss below the pore-filling level specific to each host-guest pair. The samples have a uniform bright yellow or yellow-orange color which pales slightly as the loading is lowered. Exposure to ambient air does not cause displacement of adsorbed organic from the molecular sieve pores according to X-ray powder diffraction pattern, which shows peaks due to the organic only when the pore capacity of the zeolite is exceeded.

NA in zeolites Y, Omega and Mordenite[10] shows no SHG[11]. These are all centrosymmetric molecular sieves[12]. The Figure on the left hand axis shows the SHG results for NA in ALPO-5[10], an acentric (space group P6cc) molecular sieve with a neutral framework composed of alternating AlO_4 and PO_4 tetrahedra linked by oxygen bridges forming an array of one-dimensional 12-ring channels[13]. The SHG is near zero up to 3 wt. % loading, then rapidly increases to a maximum of 630 at 13 wt. % NA. This maximum is ten times larger than for any NA-organic host complex. SHG intensity tapers off at higher loadings due to dilution with external NA. Changes in unit cell volume with loading, determined from indexed x-ray powder patterns, are shown on the right hand axis of the Figure. There is a steady increase in unit cell volume up to the loading level where maximum SHG is observed followed by a flattening off thereafter. This shows that the NA is within the pores and that the maximum SHG signal occurs when the pores are full.

Figure

In contrast, MNA in ALPO-5 shows nearly complete loss of SHG on

inclusion. A 13 wt. % MNA sample shows SHG of 0.66. Only at higher loadings, when MNA is outside the pores of the zeolite as shown by X-ray powder diffraction, does the SHG increase. 23 wt. % MNA in ALPO-5 has an SHG of 2500. In all other respects (color, stability, unit cell volume increase with loading) the NA and MNA samples are very similar.

ALPO-5 thus switches NA on and MNA off. This is a dramatic demonstration of how inclusion can influence non-linear optical properties. It is clear that subtle size, shape and symmetry effects are at play. The extra size of the methyl group in MNA must restrict its orientation in the AlPO-5 channels in ways which prohibit the required bulk dipolar alignment. These restrictions must be missing for NA. The acentric structure of ALPO-5 is an important factor in switching on the SHG of NA since the centrosymmetric hosts did not have the same effect.

A more thorough look at loading levels, other sorbate-host combinations including other acentric hosts, and further structural characterization is underway.

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(6) Powder intensity reported in ref. 5. Matching of coherence length and particle size can give a much larger SHG intensity (> 5000).

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(9) The desired portions of pre-dried molecular sieve and NA or MNA (purified by vacuum sublimation followed by recrystallization from 95% ethanol) are placed in an ampoule connected to a vacuum stopcock. This step is done in a dry atmosphere. The ampoule is evacuated, closed off and heated to 100°C for 16 hours.

(10) Sample kindly provided by Union Carbide Corporation.

(11) SHG measurements were made as described by J.P. Dougherty and S. K. Kurtz, J. Appl. Cryst., 1976, 9, 145-158. The values quoted are in reference to quartz samples.

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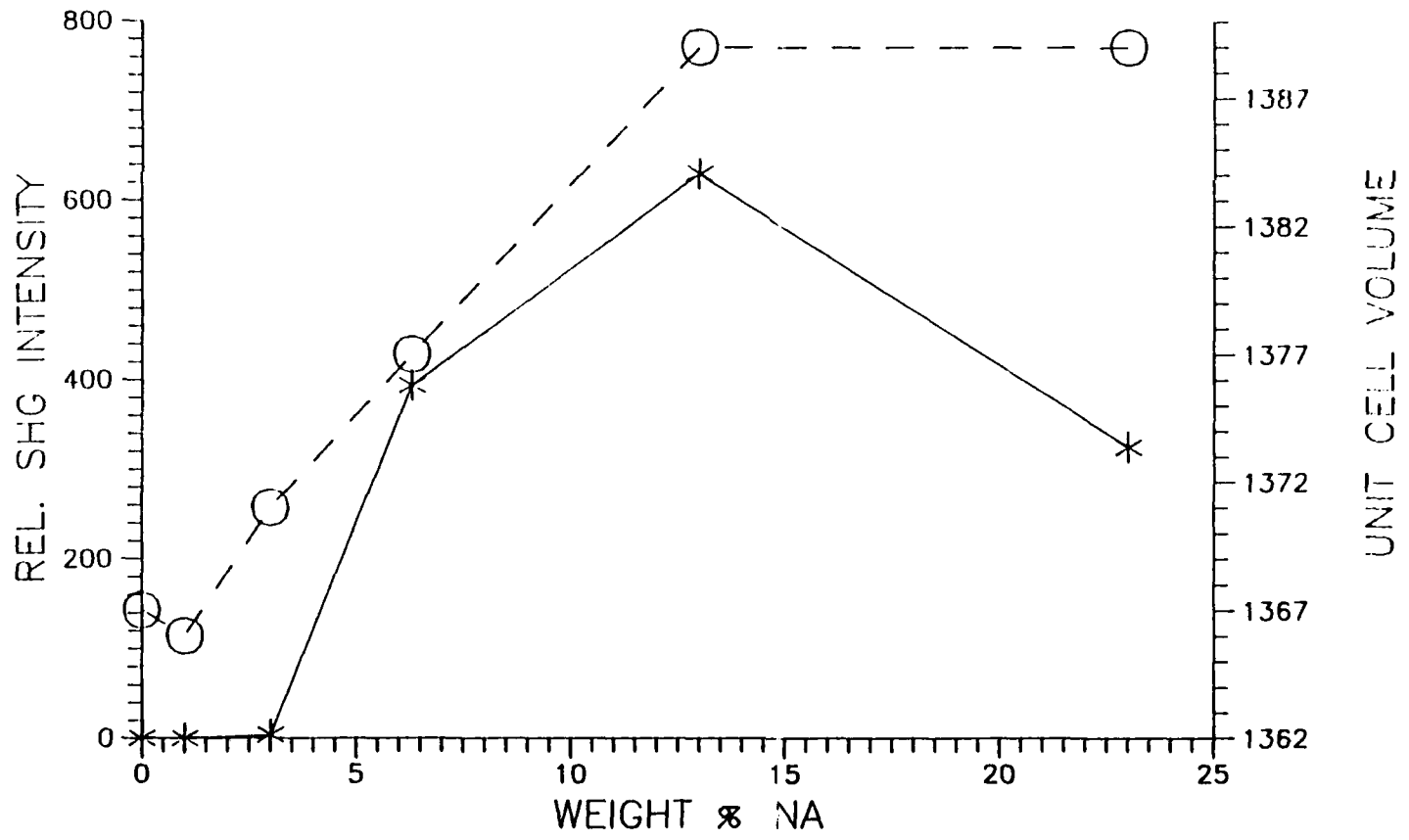
FIGURE CAPTION

p-Nitroaniline in ALPO-5. Loading level (weight % NA) versus SHG intensity relative to quartz (solid line, *) and unit cell volume in $Å^3$ (dashed line, O).

FIGURE


800
600
400
200
0
REL. SHG INTENSITY
0
5
10
15
20
25
WEIGHT % NA
1387
1382
1377
1372
1367
1362
UNIT CELL VOLUME

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