Inorganic Materials Exhibiting Nonlinear Optical Effects

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The investigation of the nonlinear interaction of light with matter and the resulting interactions between light waves has been an intriguing subject since the work of Franken et al. in 1961 [1]. It was then that the first nonlinear effect was observed in the form of second harmonic generation (SHG) in quartz using a beam from a Q-switched ruby laser. Consequently the media in which these nonlinear effects occurred also became a prime research concern [2,3].

Nonlinear optical effects arise through a nonlinear response of an individual molecule or unit cell of a solid to the fields of two or more light waves and thus violates the principle of superposition [4,5].

$$P_i^{\text{Nonlin.}} = \chi^{(2)}_{ijk} E_{jk} + \chi^{(3)}_{ijkl} E_{jkl} \cdots$$

These nonlinear effects are observed only when the incident radiation is very intense and thus the laser has been the optimal tool for studying and manipulating the nonlinearity of a variety of materials. In the case of SHG it is necessary to correlate crystal anisotropy with its birefringence and higher order nonlinearities of the polarization. In addition, the subtleties of phase matching to the material under study have to be considered to obtain a feel for the characteristics of the transmitted light.

Certain general criteria go into the assessment of a compound's viability as a nonlinear material. Lithium niobate ($LiNbO_3$) is a good model compound to introduce these criteria since it is well suited for nonlinear applications. Lithium niobate crystallizes in the space group R3c and is a uniaxial negatively birefringent crystal. It is a ferroelectric material with a Curie temperature 40 degrees below its melting point of 1253°C. $LiNbO_3$ displays unique electro-optical and nonlinear optical properties and its growth and physical properties have been discussed in a series of papers by Nassau et al. [6]. The indices of refraction have been measured by a number of workers. It has a transparency region from 0.35 to 4.5 μm and has a relatively large second order nonlinearity $X^{(2)}_{LiNbO_3} = 10X^{(2)}_{KDP}$. $LiNbO_3$ is relatively nonhygroscopic and is hard enough to be hand polished making it desirable from an applications viewpoint.

Large perfect single crystals that satisfy the strict optical requirements already discussed are very difficult to obtain. Fortunately there are now methods such as the Kurtz powder method and the electric field induced second harmonic generation (EFISH) method to examine the nonlinear properties of materials without having to grow the crystals and, in some cases, even if your molecule is symmetric [7,8]. With these methods in hand the expedition of molecular engineering for inorganic chemists is evident.

It has been found that the presence of low-lying charge-transfer (CT) states with large oscillatory strength is effective in enhancing the magnitude of the second order nonlinearities [9,10,11]. Many organometallics are known to possess low-lying CT excited states and so organometallic compounds are good candidates for exhibiting nonlinear polarizabilities [12,13]. This is the case

with some metal-pyridine and bipyridine complexes exhibiting SHG. The complexes $CF_3SO_3Re(bipy)(CO)_3$ and $Pt(bipy)Cl_4$ have SHG efficiencies of 1.7-2 and 1.2 times that of urea powder [14].

There are, however, several compounds that would prove to be interesting if it were not for the fact that they are SHG inactive due to their centrosymmetric space group. Recently a method in which inclusion into a host lattice imparts a polar director to the alignment of the molecular dipoles has been reported [15,16]. Inclusion hosts such as thiourea and clathrate hosts such as cyclodextrins are capable of forming guest-host complexes with a large variety of organometallic compounds.

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