

ment of any new microscopy. In addition, it is very easy to adapt it to different types of sample environments like ultra high vacuum, low temperatures, high magnetic field, etc. which are nontrivial in other types of high resolution microscopy. There is yet another aspect to this new form of microscopy. A number of different probes can be used for scanning giving different 'views' of the same subject. This is the origin of the general name of Scanning Probe Microscopy. Sometimes even the same probe can be used to do more than one type of microscopy by tuning to different points of the conductance curve. For instance, if one takes a constant current scan of a surface one gets the topography but if it is a surface of a superconductor kept in a magnetic field and one scans by keeping the maximum of the tunneling conductance constant one would get the flux lattice!

In addition to microscopy, there are two other extremely important applications of this new area. First, it can do scanning spectroscopy of the surface using electrons with energy typically within an eV with very high resolution (much better than 0.1 meV). Second, it can measure properties (like mechanical and electrical properties) at a nanometer level. In particular one can mention recent works on studies of friction at nanometer level. Third, one can do modification of surface (like nanoindentation) and create atomic level structures. In my opinion, while microscopy will be a popular tool mainly with non-physicists the last mentioned applications will be popular with physicists and even with a section of engineers.

In our country this is a field which has just started. Given the importance of the field more groups will enter the field. It is definitely desirable that proper funding is given to this area. In particular, given the very high price of the equipment it is good if groups are encouraged to build their own equipment which can be done at a fraction of the cost of imported equipment. In addition, it is also correct that many times a physics type experiment needs features which are not available in commercial instruments. For this reason it is strongly

advisable that the groups willing to build their apparatus should be given preference.

It will be good to sketch briefly the published works from India in this field. Most of the published works are essentially room temperature imaging of oxide superconductor surfaces, C_{60} and other exotic objects like carbon nanotubes etc. These works are all based on imported STMs. These groups have also done some spectroscopic studies. In particular, regarding metallicity of small particles, interesting information had been obtained from these investigations.

The low temperature investigation was done from one group only. This is a home made microscope. The emphasis of this work is on spectroscopy and studies on small junctions. Significantly new results were obtained from these investigations.

From the above it is clear that this area is very weak in this country and a good deal of investment will be needed to promote the area. It is an interesting as well as an important area with potential for first rate, basic as well as applied science. This should get reflected in the scientific planning of national laboratories as well as of the academic institutions. Particularly since this is becoming an area of its own it will be desirable to appoint people who have specific training in these areas and prior exposure. This is important because it will nucleate new activities and will cut down amateurism which invariably comes about when an area is new and there is shortage of trained manpower.

One particular sub-field of this area which will have tremendous technological fall-out is the use of STM in nanofabrication. There is no awareness of this in the country amongst the managers of high technology. However, in a decade's time we may rise up to find that a high price has to be paid for a technology which could have been developed at a fraction of the cost. It is therefore strongly felt that steps be initiated to start activities in this direction. It may need some level of infrastructural development and financial investment but will definitely pay off in the long run.

Crystals for nonlinear optical applications

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The advent of high field density light sources coupled with the recent advances in the materials technology has led to rapid progress in the field of nonlinear optics. This article deals briefly with the materials development that has taken place all over the world during the last forty odd years and reviews the present status of this activity in our country.

In its long history, optics, until the advent of lasers remained linear. The tenets of linear optics are based on the assumption, which provides the linear dependence of polarization wave generated in the medium on the interacting electromagnetic field. However, when the radiation field is large, the induced polarization would become nonlinear and its dependence on the radiation

field is represented by,

$$P = \epsilon_0(\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \dots) \quad (1)$$

An immediate consequence of this is the generation of fields at frequencies different from that of the incident radiation. To be more specific, the quadratic term in E of equation (1) yields a component at twice the fundamental frequency. Similarly, the cubic term in the above equation yields a component at thrice the fundamental frequency. The two examples cited above are referred to as optical second and third harmonic generations respectively. In addition, there are other exotic effects such as parametric oscillation, rectification, optical phase conjugation, etc. which manifest at high optical fields. However, frequency conversion is the most studied NLO process and is particularly important in device applications.

Materials perspectives

Ever since the first demonstration of second harmonic generation in quartz¹, progress in nonlinear optics has always been dictated by the availability of better and newer materials. The conversion efficiency of the second harmonic generation process is given by²

$$\eta_{\text{SHG}} = \frac{P_{2\omega}}{P_{\omega}} = 2 \left(\frac{\mu}{\epsilon_0} \right)^{3/2} \frac{\omega^2 d^2 l^2}{n^3} \frac{\sin^2(\Delta k l / 2)}{(\Delta k l / 2)^2} \frac{P_{\omega}}{A} \quad (2)$$

Here d is the effective nonlinear optical coefficient and k is the wave vector. For a given material and for a given frequency (ω), the conversion efficiency is dependent on the square of the interaction length l , hence it is imperative that large crystals are needed. As a result of the interference from the input fundamental polarization wave and the driven harmonic polarization wave, the maximum usable length of the crystal is limited to a few microns. However, this problem could be circumvented by decreasing Δk to zero, technically known as phase matching. The quotient d^2/n^3 is called the figure of merit for SHG. This is a material-limited parameter, often meriting the first consideration, in the search of newer materials. In a chosen material and a selected interaction geometry, conversion efficiency can be further enhanced by increasing the power density (P_{ω}/A) of the input beam. This can be physically achieved by focusing the beam into the crystal, increasing the power densities to the tolerance limit, called the damage threshold. In addition to the above parameters, a few other physical properties of the crystals need be considered. For example, the chosen material should have large transparency window, high melting point, mechanical stability and chemical inertness. There are very few materials which

satisfy most of these requirements. Hence the search for new materials seems to be unending. Though other forms of materials, like thin films, polymers, etc., are also currently being explored, the discussion herein is limited to single crystals.

In the initial stages, the materials explored for nonlinear optical applications had always been inorganic. Many inorganic crystals are well studied in terms of their physical properties. For example, high temperature oxide materials are well studied for diverse applications in terms of piezoelectricity, ferroelectricity, pyroelectricity and electrooptics. Hence when search for new materials began in NLO, scientists often trusted their intuition, screened the known materials and were fairly successful. Some of the most useful crystals discovered are LiNbO₃, KNbO₃, potassium dihydrogen phosphate (KDP) and its analogues, potassium titanyl phosphate and its analogues, beta barium borate, etc. Indeed most of the commercial frequency doublers used presently are all made of these inorganic materials. Table 1 summarizes the present status of these materials, comparing all the device-related parameters. However, in as early as 1969, Bergman *et al.*³, have indicated that inorganic materials have only $\approx 20\%$ probability of acentricity. Hence, in search of newer materials with higher nonlinearity, inorganics stand a poor chance and the advances have been limited in the past two decades.

Organic compounds are often formed by weak van der Waals and hydrogen bonds and hence possess high degree of delocalization. Thus, they are expected to be optically more nonlinear than their inorganic counterparts. Some of the advantages of organic materials include, the ease of varied synthesis, scope for altering the properties by functional substitutions, inherently high nonlinearity, high damage resistance, etc. The prototype organic NLO material contains one or more delocalized bonds, typically a ring structure like benzene. When substituted with donor and acceptor at the para position, (e.g. *p*-nitroaniline) they have large induced dipole moments under the influence of electromagnetic fields. However such structures, when packed as crystals tend to be mostly centrosymmetric, thus leading to vanishing dipole moment. A suitable addition at another site as in the case of 3-methyl 4-nitroaniline can ensure a macroscopically non-vanishing dipole moment for the donor-acceptor substituted systems. The above example typifies the strategy of molecular engineering towards achieving efficient nonlinear materials⁴. Table 2 gives the list of well developed organic NLO materials and their physical properties. However, there has been little progress in fabricating devices out of these molecular crystals. These crystals have several unfavourable physical parameters. For example, most of these molecular materials have poor transparency and small transparency windows. Consequently, the generated harmonic wave

Table 1. Some physico-chemical properties of inorganic NLO materials

| Material | LiNbO ₃ | KD*P | LiIO ₃ | BBO | KTP | LBO | KNbO ₃ |
|--|----------------------------------|----------------------------------|----------------------------------|----------------------------------|--|--|--|
| Point group | 3 m | 42 m | 6 m | 3 m | mm2 | mm2 | mm2 |
| Transparency | 350-5000 | 180-1800 | 340-4000 | 198-2600 | 350-4500 | 160-2300 | 400-5500 |
| Refractive index (at 1064 nm) | $n_o = 2.2322$ $n_e = 2.1560$ | $n_o = 1.4931$ $n_e = 1.4582$ | $n_o = 1.8567$ $n_e = 1.7168$ | $n_o = 1.6551$ $n_e = 1.5425$ | $n_x = 1.5737$ $n_y = 1.7395$ $n_z = 1.8305$ | $n_x = 1.5649$ $n_y = 1.5907$ $n_z = 1.6052$ | $n_x = 2.1194$ $n_y = 2.2195$ $n_z = 2.2576$ |
| d_{eff} (pm/V) | 5.1 | 0.35 | 1.8 | 1.6 | 3.2 | 0.85 | 13 |
| Threshold power (MW) | 0.70 | 30 | 66 | 13 | 0.029 | NA | NA |
| Damage threshold (GW/cm ²) | 0.3 (10 nsec) | 5 (1 nsec) | 1 (0.1 nsec) | 23 (14 nsec) | 9-20 (1 nsec) | 1-4 (12 nsec) | 1 (10 nsec) |

NA, Not available.

Table 2. Some physico-chemical properties of organic NLO materials

| Material | MNA | POM | DAN | MMONS | MBANP | MAP |
|---|---|---|-----------------------------------|--|-------------------------|--|
| Point group | mm2 | 222 | 2 | mm2 | 2 | 2 |
| Melting point (°C) | 114 | 136 | 166 | NA | 84 | 80.9 |
| Transparency (nm) | 480-2000 | 500-1700 | 485-270 | 510-2100 | NA | 500-2500 |
| Refractive indices | $n_x = 1.800$ $n_y = 1.600$ $n_z = ?$ | 1.663 1.829 1.625 | 1.517 1.636 1.843 | 1.530 1.630 1.961 | 1.650 1.714 1.688 | 1.507 1.59 1.843 |
| Nonlinear coefficient ($\times 10^{-9}$ esu) | $d_{11} = 60$ $d_{12} = 90$ | $d_{14} = 23$ $d_{25} = 23$ $d_{36} = 23$ | $d_{22} = 12.4$ $d_{23} = 119$ | $d_{24} = 55$ $d_{32} = 41$ $d_{33} = 184$ | $d_{22} = 8.3$ | $d_{21} = 40$ $d_{22} = 44$ $d_{23} = 8.8$ |
| Damage threshold (GW/cm ²) | 0.2 | 2 | 5 | NA | 1 | 3 |

NA, Not available.

gets absorbed in the crystal, leading to poor efficiency. Also, organic NLO materials are inherently poor in mechanical hardness, have low melting points and poor chemical inertness. Owing to the high polar nature of the molecules they often tend to crystallize as long needles or thin platelets.

The inherent limitation on the maximum attainable nonlinearity in inorganic materials and the moderate success in growing device grade organic single crystals, have made scientists to adopt newer strategies. The obvious one was to develop hybrid inorganic-organic materials with little trade off in their respective advantages. This new class of materials has come to be known as the semiorganics⁵. One approach to high efficiency, optical quality organic-based NLO materials in this class is to form compounds in which a polarizable organic molecule is stoichiometrically bonded to an inorganic host. A typical case is the formation of inorganic salts of chiral organic molecules (classified as Type I). L-arginine phosphate monohydrate (LAP) is an example of this class. The choice of organic molecules to form salts is plenty. For example tartarates, oxalates and aminoacid salts are predominantly NLO active. An alternative approach is to form metal coordination com-

plexes of organic materials (Type II). The choices for ligands in type II are unlimited. In fact, the organic part need not be noncentrosymmetric. This is typified by the example of thiourea, which forms excellent complexes, with Zn, Cd and Hg. Thiourea is more polarizable than urea, because of the presence of large sulphur atoms and the hydrogen bonds in NH₂ ensure the lack of centre of inversion, in many thiourea complexes. The other popular choices for ligands in type II are, allylthiourea, guanidium and dithiocarbamate.

An added advantage of this class of materials is that they have moderate nonresonant $\chi^{(3)}$ which can be resonantly enhanced by doping with metals that can absorb in the operable wavelength. For example, ZTS has a $\chi^{(3)}$ value of 0.1 times that of CS₂ which can be enhanced to 1.5 times CS₂ by doping it with Co at 10 ppm level⁵. Table 3 gives a list of some of the semiorganic compounds and their physical properties.

National scenario

In the preceding section we had briefly dealt with the materials development for non-linear optical applications

Table 3. Some physico-chemical properties of semiorganic NLO materials

| Material | dLAP | BTCC | ZTS | ATCC | ATMB | TSCCB |
|--|---|---|---|--|---|--|
| Point group | 2 | mm2 | mm2 | 3m | 3m | m |
| Melting point (°C) | 130 | 185 | > 200 | 101 | 138 | 230 |
| Transparency (nm) | 250–1300 | 300–2000 | 300–2000 | 300–1500 | 330–1500 | 330–1420 |
| Refractive indices at 1064 nm | $n_x = 1.49769$ $n_y = 1.5595$ $n_z = 1.5686$ | $n_x = 1.6097$ $n_y = 1.7902$ $n_z = 1.8600$ | $n_x = 1.6306$ $n_y = 1.6936$ $n_z = 1.6984$ | $n_o = 1.6996$ $n_e = 1.6400$ | $n_o = 1.7046$ $n_e = 1.6341$ | $n_x = 1.7200$ $n_y = 1.7180$ $n_z = 1.8120$ |
| Nonlinear susceptibility ($\times 10^{-9}$ esu) | $d_{14} = 0.22$ $d_{16} = 0.48$ $d_{22} = 0.68$ | $d_{31} = 2.75$ $d_{32} = 0.2$ $d_{33} = 2.7$ | $d_{31} = 0.31$ $d_{32} = 0.35$ $d_{33} = 0.23$ | $d_{31} = 1.5$ $d_{22} = 0.7$ $d_{33} = 1.9$ | $d_{31} = 0.27$ $d_{22} = 8.2$ $d_{33} = 2.7$ | $d_{11} = 0.5$ $d_{13} = 0.3$ $d_{15} = 2.8$ |
| d_{eff} (pm/V) | 0.98 | 1.65 | 0.13 | NA | NA | 0.9 |
| Damage threshold (GW/cm ²) | 13.0 | NA | NA | 0.32 | NA | NA |

NA, Not available.

(with special emphasis on frequency conversion) that had taken place world over, during the past 40-odd years. In this section we dwell on the national status in this important field.

Though the crystal growth activity has been going on in this country for quite some time now, its impact on our scientific endeavour is rather meagre. In a recent status report on the research and developmental activity in laser-related materials written for DST, it is stated that 'the country has lagged behind in the area of materials as a whole and laser-related optical materials are no exception'.⁶ The report has listed materials developed/being developed in the country and the organization undertaking such developmental work. While the list may not be truly exhaustive, it definitely gives an indication as to how much effort is being put-in in this challenging area. It is very clear that relatively only a few institutions in India have undertaken developmental work to grow well established nonlinear crystals. Consequently, such crystals are not easily available to other users in the country. It may be pointed out here that, while there are about 70 institutions and over 1000 people engaged in crystal growth research in China⁷, the corresponding figures in India may be only around 10–15 and 100 respectively. This is not an encouraging situation. Certainly this is an area which needs to be given major thrust both in terms of finance and man power.

Crystal growth has become a high technology area which can be carried out only with adequate infrastructural facility and sufficient man power. It is quite a labour intensive programme and there cannot be quick results here. Only a sustained effort for long duration can give any tangible results. One way of achieving this is to identify certain centres as national facility for growing and characterizing crystals, each centre specializing in certain class of crystals. Such centres should be provided with sustained financial and organizational support and they in turn should be able to meet the requirement of scientists working in the country. Then only Indian crystal growth activity would be able to make definite impact and the Indian crystal growers would be recognized among the international crystal growth community.

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