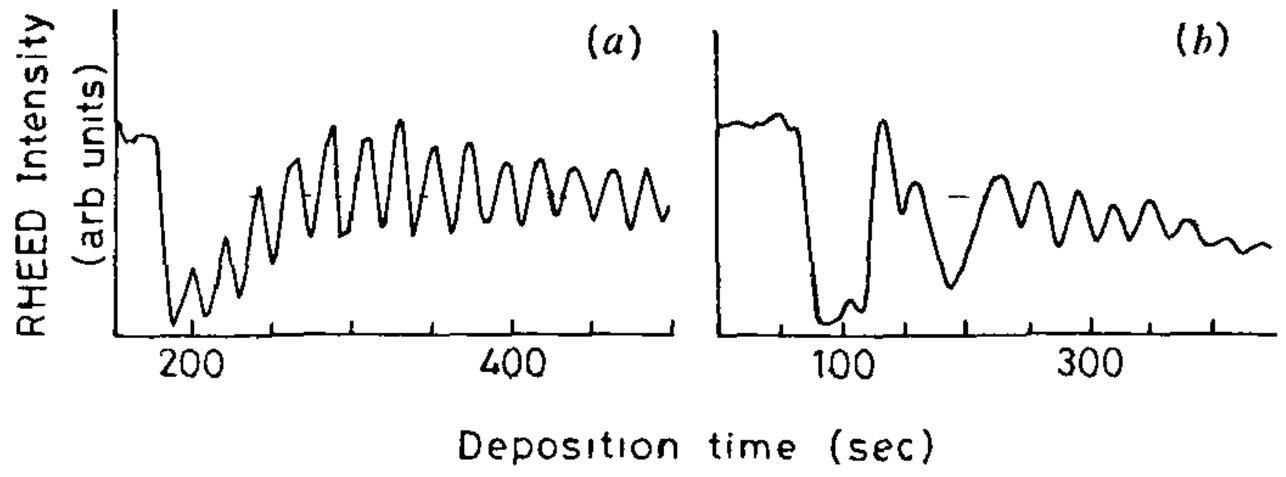


**Figure 2.** RHEED oscillations (0.4 nm) observed during the epitaxial growth of (*a*) $SrTiO_3$ (0 0 1) and (*b*) $BaCuO_2$ (0 0 1) on $SrTiO_3$ (0 0 1). Growth units are $SrO/TiO_2$, respectively (after Kawai *et al.*[5]).

possibility of growing novel or even unknown oxides layer by layer. It should be possible to fabricate a variety of hybrid devices and stacked unit cells or layers of perovskites which have good lattice matching with oxide substrates besides Si. For example, layered cuprate superconductors can be constructed or modified by depositing two-dimensional lattices (or layers) of different compositions chosen appropriately. In Figure 1, we show layered lattice structures related to perovskite oxides and high-$T_c$ cuprates. The quality of such lattices is established by RHEED, RBS, STM, AFM and other techniques. A typical example of atomically controlled epitaxy of oxides is provided by $BaCuO_2$, which is a layered cuprate[5]. In Figure 2, RHEED oscillations obtained in the growth of such oxide layers are shown.

The wide range of properties of oxide systems certainly seems attractive compared to the $Si/SiO_2$ system, where the oxide can only provide it insulating characteristic. Valence control and impurity doping, readily accomplished in the case of Si, should be possible in oxides as well. In the short term, however, it should be possible to fabricate superconductor–insulator-superconductor (SIS) tunnel junctions exhibiting clear I–V hysteresis above 77 K. Such an SIS junction would be useful in switching devices which are expected to work faster than conventional transistors. It should be noted that there has already been success in fabricating simple devices using superconducting films or grain boundary and step edge junctions[6,7]. The use of oxides in combination with Si has also several possible applications in integrated devices. Clearly, there is much to be done in exploring oxides for electronic applications and in designing oxide superlattices with unexplored quantum functions. We have to find ways of doping, controlling valency and attaining the right carrier mobilities as well as in designing the right structures.

The importance of oxide electronics has been recognized widely in Japan, where there is considerable investment in this area. A large number of chemists, physicists and engineers are working on the various aspects of metal oxides, starting from synthesis and characterization to device applications. The Japanese consider oxides as electronic materials of the 21st century. In Tokyo Institute of Technology alone, a dozen or more professors work in this area. It is highly desirable that strong interdisciplinary groups in this country are encouraged and supported to work on various aspects of oxides.

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# Noncentrosymmetric monolayers from centrosymmetric molecules – A fresh approach to materials for frequency doubling

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The age we live in is often called the 'electronic age'. Some recent developments in physics, chemistry, materials science and engineering, however, indicate that a 'photonic era' is not too far in the future, when the role of electrons in information technology will be played much more efficiently by photons. Signs of the transition can already be seen, e.g. in fibre-optic communication systems utilizing electrooptic devices; many believe that all-photonic devices will soon appear. These devices for light transmission, processing and storage would be based on a variety of nonlinear optical (NLO) phenomena. The nonlinearity refers to the second- and higher-order terms in electric field ($E$) in the expres-

sion for the bulk electric polarization ($P$) of a medium $\chi^{(1)}$ refers to the linear electric susceptibility:

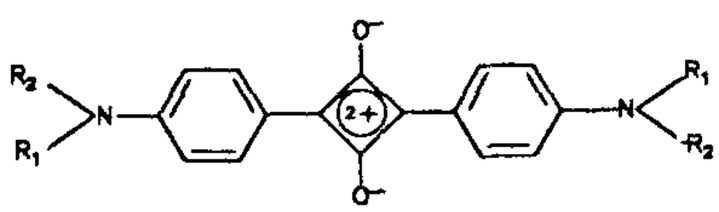
$$P = \chi^{(1)}E + \chi^{(2)}E \cdot E + \chi^{(3)}E \cdot E \cdot E \cdot + \ldots$$

and the other $\chi^{(n)}$ produce the different NLO effects; for example, $\chi^{(2)}$ leads to phenomena such as frequency doubling, also called second-harmonic generation (SHG). In a centrosymmertric medium, reversal of $E$ should cause exact reversal of $P$, and, as seen from the above expression, this is possible only if all $\chi^{(n)}$ with even $n$ are zero In other words, nonzero even-order $\chi$ can be realized only in noncentrosymmetric systems. Frequency doublers in use today employ inorganic crystals like potassium dihydrogen phosphate, lithium niobate and β-barium borate which have noncentric arrangement of the atomic lattice. Recent efforts have been directed at exploiting the large hyperpolarizabilities of selected organic molecules (like donor–acceptor-substituted benzenes, quinones, stilbenes, etc.) gathered in a suitable noncentrosymmetric array in a crystal, polymer matrix or thin film. Large molecular hyperpolarizabilities which lead to high bulk $\chi^{(2)}$ values are usually associated with strong intramolecular charge transfer in the molecular dipoles.

Obtaining a noncentrosymmetric array of molecules is a challenging problem. A noncentrosymmetric molecule with a permanent ground state dipole moment does not guarantee a noncentrosymmetric crystal lattice. On the contrary, they often form centrosymmetric crystals. However, it is the common experience so far that if one is to fabricate noncentrosymmetric lattice, one should build it with a noncentrosymmetric molecule, not a centrosymmetric one, though there are rare exceptions where centrosymmetric molecules with octupolar moments have formed noncentric lattices which showed moderate SHG. Crystal engineering utilizing H-bond interactions, chirality, etc., to build noncentric lattices, growth of Langmuir–Blodgett (LB) films of the X or Z type, where molecules are deposited in a head-to-tail fashion and electric field poling of molecular dipoles embedded in a matrix or attached to polymer chains are some of the common approaches to obtain noncentric arrangement necessary for SHG materials.

With this background the recent report by Ashwell and coworkers[1] on the detection of very strong SHG from centrosymmetric squarine dye molecules (Figure 1) deposited as LB films comes as an interesting surprise. Crystal structure of **1** is found to be centrosymmetric, belonging to the $P2_1/c$ space group and the diphenyl-substituted squarine moiety is flat and centrosymmetric. As expected, the crystals showed no SHG but the LB films (though of poor quality) were found to be SHG-active. Ashwell and coworkers report that **2** and similar systems (with R = other alkyl groups) provide better films and reproducible SHG which is among the highest seen so far in LB films. Reflectivity studies indicated that the LB films consisted of monolayers with the chromophores lying nearly parallel to the substrate surface. Absorption spectra of the films showed characteristic bands due to intermolecular charge transfer in the 660–690 nm range depending on the film deposition pressure.

The crystals of **1** consist of noncentric chromophore dimers which arrange themselves in a centrosymmetric lattice. The authors, therefore, suggest that in the LB films of **2** and similar molecules, noncentric dimers may be present which, however, form a noncentrosymmetric array, thus enabling $X^{(2)}$ to be nonzero. Since the chromophores themselves are centrosymmetric, intramolecular charge transfers do not contribute to SHG. Interfacial effects cannot give rise to such strong SHG as seen in these LB films. Therefore, the authors attribute the strong SHG to intermolecular charge transfer interactions in the dimer units. These charge transfers occur between the dialkylaminophenyl group of one molecule and the squarine moiety of the other in the dimer unit. It is also notable that a good correlation exists between the absorption wavelength variation from 656




**1** $R_1 = R_2$ = butyl

**2** $R_1$ = methyl, $R_2$ = hexyl

**Figure 1.** Squarine dye molecules deposited in LB films by Ashwell *et al.*[1].

to 694 nm and the increase of SHG efficiency as a function of film deposition pressure The compression process appears to influence strongly the orientation of the chromophores (or chromophore dimers) in the noncentrosymmetric array.

The LB film structure is not fully understood and, therefore, the mechanism by which the strong SHG arises has to be treated as tentative. Film characterizations were carried out on samples deposited on silver-coated slides, but different film characteristics for samples deposited on plane glass slides used in the SHG studies cannot be ruled out. Though some of these questions remain, the discovery of Ashwell and coworkers is notable for the following important insights gained. There is no reason to believe any more that centrosymmetric molecules cannot be coaxed into noncentric arrays useful for SHG. Intermolecular charge transfers can be an efficient mechanism to obtain large bulk optical nonlinearities. This work is likely to initiate a fresh approach to the fabrication of quadratic nonlinear optical materials. The technological promise of these materials is enticing enough to justify detailed investigation and appraisal of such novel ideas.

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