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Change of Symmetries in Nanocrystals

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Abstract: Change of crystallographic symmetries introduced and studied in nanocrystals. Crystallographic point-group symmetries analyses qualitatively and explains mathematically the main properties of nanoporous silicon, provides the understanding of phase-matching abilities of nanocrystal materials in nonlinear optics and allows tensor properties of linear and nonlinear-optical parameters of nanocrystals to be analyzed.

INTRODUCTION

Modern nanotechnologies open the ways to radically modify the properties of materials and to tune their parameters within a remarkably broad range. Nanostructured materials become more and more common in various areas of fundamental and applied research, solving many problems in physics, chemistry and biology. Modification of physical and chemical parameters and even symmetry properties of optical materials in a desirable way in order to enhance or suppress various different optical processes is probably one of the most exciting opportunities offered by modern nanotechnologies. Although the fact that the nanoscale structure of matter may have a considerable influence on optical processes was understood more than a century ago [1], it was only recently that experiments allowing the vast advantages of this approach to be fully appreciated became possible. More generally, phase matching due to an artificial birefringence demonstrated in [2], in fact, implies that a method for engineering new materials for nonlinear optics has been developed. Tiginyanu et al. [5] and Golovan et al. [6] have recently shown that the efficiency of second-harmonic generation can be considerably improved in porous materials. Since the structure of porous materials is generally very complicated and materials of this class exhibit nontrivial effects of different origin [8], displaying, depending on the regime of light-matter interaction, the properties of nanocrystals and disordered structures, as well as quantum-size phenomena and very intriguing luminescence and nonlinear properties, it is sometimes not very easy to interpret the results of optical experiments in such materials. It seems useful, in this context, to think of porous materials in terms of structures with changed crystallographic symmetries. This approach is based on the fact that the pores usually grow along crystallographically well-defined directions [7]. Thus, if the typical size of the pores is much less than the wavelength of incident light, some effective symmetry of such a medium can be considered, to provide a qualitative understanding of artificial anisotropy, birefringence, and phase matching abilities of such materials. Such an analysis is the main goal of this paper.

CHANGE OF SYMMETRY BY NANOSTRUCTURING:

We start our consideration with symmetry properties of porous silicon, which seems to provide an especially instructive example of symmetry changes in nanocrystal materials. Crystal silicon has an $m\,3\,m$ point-group crystal lattice of cubic symmetry (Fig. 1). This means that

crystalline silicon is an optically isotropic material. It displays no birefringence, as its refractive index tensor is represented by a sphere, which implies that the refractive index is independent of propagation direction. A system of pores changes the symmetry of the material, breaking some symmetry characteristics of the cubic lattice of crystalline silicon. We will model a system of pores as a set of cylindrical holes oriented along certain crystallographic directions. Adopting this attitude, we should keep in mind that the pore growth in silicon is, of course, by no means restricted to the crystallographic axes, but intrinsically involves also a substantially random component. The ratio of these two components in the pore-formation process depends on many experimental parameters. With an appropriate orientation of a substrate [e.g., using (110) Si wafers], one can predominantly propagate these pores along two equivalent (010) and (100) crystallographic directions simultaneously [6,7].These directions define a crystallographic plane (see Fig. 1), and the resulting porous material can be then modeled as a laminar structure. Since we consider the case of silicon, we have a lattice of cubic symmetry (Fig. 1) before the etching process, resulting in pore formation. Although the symmetry of the real configuration of Si atoms in a Si crystal unit cell slightly differs from the symmetry of a cube, macroscopic properties of Si crystals can be adequately described in terms of a cubic lattice and the m3m (O_h) point group. The symmetry of a cubic lattice is fully characterized by three fourth-order, four third-order, and six second-order symmetry axes, nine planes of symmetry, and a center of inversion symmetry [9]. All these symmetry elements are shown in Fig. 1.

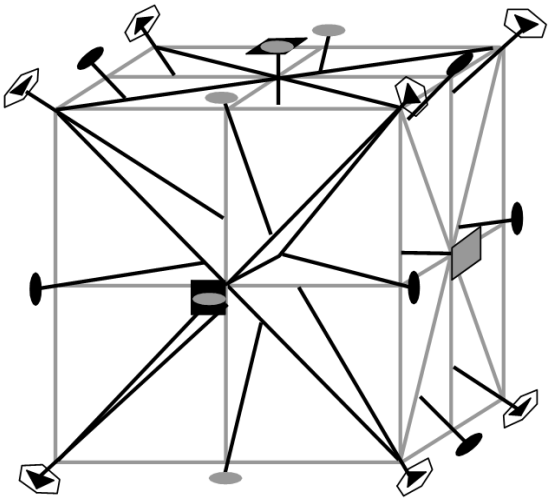

Fig. 1. Symmetry elements corresponding to a cubic lattice of the *m*3*m* point group.

In the case when typical sizes of pores in silicon are much less than the optical wavelength, it is useful to analyze morphology modifications related to pore formation in terms of crystal-symmetry categories. Although such an analysis is, of course, not exact, because pore sizes are at the same time typically much larger than the characteristic unit-cell sizes (which means, in particular, that it would be difficult to expect that the changes in the point-group symmetry considered in this paper can ever be detected, for example, with the use of conventional x-ray diffraction analysis), it allows many important properties of porous materials to be explained in a unified way, as will be shown below, due to the fact that the pores predominantly grow in some easily identifiable crystallographic directions. Suppose that a crystal-silicon sample is oriented in such a way that the etching process results in a predominant pore propagation along the (010) and (100) directions. This silicon-etching arrangement was recently studied in several papers [10, 12]. Such pores modify the symmetry of our crystal unit

cell, leaving us with one fourth-order, no third-order, and four second-order symmetry axes, five planes of symmetry, and a center of inversion symmetry (Fig. 2). This means that we end up with the 4/mmm (D_{4h}) symmetry group, which is characteristic of many materials, such as rutiles (TiO_2), stishovites (SiO_2), pyrolusites (MnO_2), cassiterite (SnO_2), etc. Once the symmetry group is known, we can fully characterize linear and nonlinear-optical properties of porous material. This will be done in the following sections.

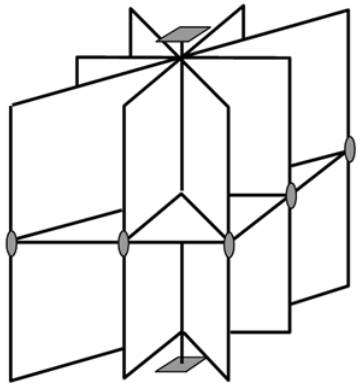

Fig. 2. Symmetry elements corresponding to a tetragonal lattice of the 4/*mmm* point group

DIELECTRIC TENSOR AND PHASE-MATCHING ABILITIES OF NANOCRYSTALS WITH CHANGE OF SYMMETRIES

We start with linear optical properties of nanocrystal materials. Crystals with a lattice of the 4/mmm point group are uniaxial crystals, with their optical axis oriented along the principal symmetry axis. In our case, this axis coincides with the only fourth-order symmetry axis we have in our lattice, which means that the optical axis of the resulting uniaxial material is perpendicular to the planes defined by the (100) and (010) crystallographic directions. Moreover, this result is completely consistent with the predictions of classical works [3, 4], in fact, modifies an optically isotropic material exactly in the same way as the pores growing along the above-specified crystallographic directions change the symmetry of an isotropic cubic lattice of silicon.

The refractive index of the 4/mmm point-group material is represented by an ellipsoid of revolution, which allows birefringent properties of the material to be understood in a very clear way. Ordinary and extraordinary waves propagating in such a material are characterized by different phase and group velocities. In the case of porous silicon with pores grown along the (100) and (010) directions, as described above, we deal with a negative uniaxial crystal, which is also consistent with Wiener predictions [4] (see also Born [4]). The phase matching ability of nanostructured materials allows the ideas of artificial birefringence of the ways, in particular, to the phase matching of nonlinear-optical interactions in recently developed highly nonlinear materials (e.g., see [10]). An artificial birefringence of nanocrystals also suggests the way to solve the problem of group-velocity matching in nonlinear optical interactions of ultra short laser pulses.

Recently, much attention has been focused on using photonic crystals to achieve phase and group-velocity matching in nonlinear optical interactions [11-12]. Nanocrystals considered in this paper differ from photonic crystals by much smaller scales of spatial in homogeneities and by the absence of periodicity in the spatial modulation of the refractive index, which is

inherent in photonic crystals. On the other hand, a combination of the possibilities offered by nanocrystals and photonic band-gap structures seems to be highly promising, as shown by recent experiments with porous silicon multilayers [13], for phase- and group-velocity-matched wave-mixing processes.

MODIFICATION OF NONLINEAR-OPTICAL PROPERTIES

The concept of symmetry change by nano-structuring offers new solutions to the problems of non-linear optics not only through phase and group-velocity matching, but also through the change of the symmetries of nonlinear-optical susceptibility tensors. These tensors are responsible for nonlinear wave mixing and harmonic generation processes. We shall illustrate this possibility by resorting again to an example of porous silicon, although many other examples can be found among nanostructured materials engineered by means of modern nanotechnologies. Etching of silicon, as shown above, switches the symmetry of the material from cubic (m3m point group) to tetragonal (4/mmm point group). This means that neither crystal silicon nor its porous modification allows $\chi^{(2)}$second-harmonic generation in the dipole approximation, as the quadratic susceptibility tensor is identically zero due to the inversion symmetry of crystal and porous silicon. Cubic nonlinear-optical susceptibilities, on the other hand, are much more sensitive to the change in the symmetry accompanying the etching process. In particular, the form of the $\psi(2\omega; 0, \omega, \omega)$,$\varphi(3\omega; \omega, \omega, \omega)$, and $\chi(\omega 4; \omega 1, \omega 2, \omega 3)$ cubic susceptibility tensors, responsible for dc-field-induced second harmonic generation, third-harmonic generation, and general four-wave mixing processes, respectively, noticeably changes due to change of symmetris. In the case of materials with a cubic lattice of the m3m point group, these tensors are written as [9]

$$\psi(2\omega; 0, \omega, \omega) = \begin{pmatrix} a1 & a2 & a2 & 0 & 0 & 0 & 0 & 0 & 0 \\ a2 & a1 & a2 & 0 & 0 & 0 & 0 & 0 & 0 \\ a2 & a2 & a1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & a3 & 0 & 0 & a3 & 0 & 0 \\ 0 & 0 & 0 & 0 & a3 & 0 & 0 & a3 & 0 \\ 0 & 0 & 0 & 0 & 0 & a3 & 0 & 0 & a3 \end{pmatrix} \quad \text{.....(1)}$$

$$\varphi(3\omega; \omega, \omega, \omega) = \begin{pmatrix} b1 & 0 & 0 & b2 & 0 & 0 & b2 & 0 & 0 \\ 0 & b1 & 0 & 0 & b2 & 0 & 0 & b2 & 0 \\ 0 & 0 & b1 & 0 & 0 & b2 & 0 & 0 & b2 \end{pmatrix} \quad \text{.....(2)}$$

$$\chi(\omega 4; \omega 1, \omega 2, \omega 3) = \begin{pmatrix} c1 & c2 & c2 & 0 & 0 & 0 & 0 & 0 & 0 \\ c2 & c1 & c2 & 0 & 0 & 0 & 0 & 0 & 0 \\ c2 & c2 & c1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & c3 & 0 & 0 & c4 & 0 & 0 \\ 0 & 0 & 0 & 0 & c3 & 0 & 0 & c4 & 0 \\ 0 & 0 & 0 & c4 & 0 & c3 & 0 & 0 & c4 \\ 0 & 0 & 0 & c4 & 0 & 0 & c3 & 0 & 0 \\ 0 & 0 & 0 & 0 & c4 & 0 & 0 & c3 & 0 \\ 0 & 0 & 0 & 0 & 0 & c4 & 0 & 0 & c3 \end{pmatrix} \quad \text{.....(3)}$$

Thus, we have 3, 2, and 4 different tensor components for the ψ (2 ω; 0, ω , ω), φ(3 ω; ω , ω , ω), and $\chi(\omega_4;\omega_1, \omega_2, \omega_3)$ tensors in this case. The number of different tensor components in these tensors increases in the case of the 4/mmm point group, when the $\chi^{(3)}$

tensors can be represented as [9]

$$\psi(2\omega;0,\omega,\omega)=\begin{pmatrix} a1' & a2' & a3' & 0 & 0 & 0 & 0 & 0 & 0\\ a2' & a1' & a3' & 0 & 0 & 0 & 0 & 0 & 0\\ a4' & a4' & a5' & 0 & 0 & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & a6' & 0 & 0 & a7' & 0 & 0\\ 0 & 0 & 0 & 0 & a7' & 0 & 0 & a6' & 0\\ 0 & 0 & 0 & 0 & 0 & a8' & 0 & 0 & a8' \end{pmatrix} \quad \ldots\ldots(4)$$

$$\varphi(3\omega;\ \omega,\omega,\omega)=\begin{pmatrix} b1' & 0 & 0 & b3' & 0 & 0 & b4' & 0 & 0\\ 0 & b1' & 0 & 0 & b4' & 0 & 0 & b3' & 0\\ 0 & 0 & b2' & 0 & 0 & b5' & 0 & 0 & b5' \end{pmatrix} \quad \ldots\ldots(5)$$

$$\chi(\omega 4;\ \omega 1,\omega 2,\omega 3)=\begin{pmatrix} c1' & c2' & c3' & 0 & 0 & 0 & 0 & 0 & 0\\ c2' & c1' & c3' & 0 & 0 & 0 & 0 & 0 & 0\\ c4' & c4' & c5' & 0 & 0 & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & c6' & 0 & 0 & c10' & 0 & 0\\ 0 & 0 & 0 & 0 & c8' & 0 & 0 & c7' & 0\\ 0 & 0 & 0 & 0 & 0 & c9' & 0 & 0 & c11'\\ 0 & 0 & 0 & c7' & 0 & 0 & c8' & 0 & 0\\ 0 & 0 & 0 & 0 & c10' & 0 & 0 & c6' & 0\\ 0 & 0 & 0 & 0 & 0 & c11' & 0 & 0 & c9' \end{pmatrix} \quad \ldots\ldots..(6)$$

giving 8, 5, and 11 components for ψ (2ω; 0, ω, ω), φ (3ω; ω, ω, ω), and χ (ω_4; ω_1, ω_2, ω_3), respectively.

This sensitivity of $\chi^{(3)}$ processes to the morphology symmetry can be employed for both the enhancement of nonlinear-optical processes and for nonlinear-optical visualization of the pore-growing process in real time. Crystals with no inversion symmetry allow nano-morphology changes to be detected with $\chi^{(2)}$ processes. Formation of pores parallel to the (111) direction in this case switches the cubic symmetry of GaP (the T_d point group) to a uniaxial trigonal symmetry (the C_{3v} point group), changing the form of the quadratic susceptibility tensor. Obviously, the sensitivity of nonlinear-optical methods of morphology diagnostics becomes especially high whenever a polarization configuration or a nonlinear optical process can be found with a nonlinear optical signal completely vanishing in one of the symmetry changes. At the same time, there is a class of optical effects that can be observed in materials with the 4/mmm point group lattice and that are forbidden for the m3m point group crystal lattice. These effects are related to electric field induced optical activity i.e., electro gyration effect. Electro gyration effect [14] is understood as an artificial optical activity induced by an electric field. In the presence of an electric field E, the gyration pseudo tensor is written as

$$G_{ij}(E) = G_{ij}^{(0)} + A_{ijk}E_k, \quad \ldots\ldots\ldots (7)$$

Where is the pseudo tensor of gyration due to the natural optical activity and A_{ijk} is the pseudo tensor responsible for the electro gyration effect. The A_{ijk} tensor is identically equal to zero for systems of the m3m point group. In the case of the 4/mmm point group, the tensor $A_{i\mu}$,

whose components are related to the components of the symmetric third-rank tensor A_{ijk} in according
to the formula $A_{i\mu} = A_{ijk}$ (kl→ μ = 1, …, 6),
has the following form [9]:

$$Ai\mu = \begin{pmatrix} 0 & 0 & 0 & A & 0 & 0 \\ 0 & 0 & 0 & 0 & -A & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \qquad \text{.....(8)}$$

Thus, in contrast to the Faraday effect, which can be observed in isotropic materials, no electro gyration effect is possible for the m3m point group. Therefore, since the A_{ijk} tensor remains substantially non vanishing for the 4/mmm point group.

CONCLUSION

Thus, the analysis of changes in the crystallographic symmetry accompanying the pore formation in various materials allows several important properties of nonporous materials to be qualitatively explained. In particular, this approach is very instructive in explaining the nature and the properties of the artificial birefringence arising in porous silicon samples. Based on this analysis, we were able to correctly predict the direction of the optical axis in nanoporous silicon, to understand phase and group velocity matching abilities of nanocrystals, and to realize the potential of nanotechnologies for modifying linear and nonlinear-optical properties of a broad class of natural and synthetic materials. Nonlinear optical susceptibility tensors are shown to be sensitive to symmetry changes in nanostructured materials. In particular, the electro gyration effect, giving no signal in the case of materials with the m3m point-group crystal lattice, which is characteristic of crystal silicon, and leading to a substantially non vanishing signal in porous-silicon-like materials with the 4/mmm point group lattice.

REFERENCES

1. 4-Born, E. and Wolf, E., 1980, Principles of Optics, 6th ed.(Oxford: Pergamon).
2. 2-Fiore, A., Berger, V., Rosencher, E., et al., 1998, Nature,391, 463.
3. 10-Giorgetti, E., 2000, Proceedings of the Second Italian-Russian Symposium on Ultrafast Optical Physics (ITARUS'99): Tribute to N.I. Koroteev, Ferrante, G., Vaselli, M., and Zheltikov, A.M., Eds. (Moscow: Intel-lect Center), p. 317.
4. 6-Golovan, L.A., Timoshenko, V.Yu., Fedotov, A.B., et al.,Appl. Phys. B (in press).
5. 7- Kovalev, D., Polisski, G., Diener, J., et al., 2001, Appl.Phys. Lett., 78, 916.
6. 1- Lord Rayleigh, 1892, Philos. Mag., 34, 481.
7. 11-Scalora, M., Bloemer, M.J., Manka, A.S., et al., 1997,Phys. Rev. A, 56, 3166; Centini, M., Sibilia, C., Scalora, M., et al., 1999, Phys. Rev. E, 60, 4891.
8. 9- Sirotkin, Yu.I. and Shaskol'skaya, M.P., 1979, Basics of Crystal Physics (Moscow: Nauka) (in Russian).
9. 8- Theiss, W., 1997, Surf. Sci. Rep., 29, 91.
10. 5- Tiginyanu, I.M., Kravetsky, I.V., Monecke, J., et al.,2000, Appl. Phys. Lett., 77, 2415.
11. 3- Wiener, O., 1912, Abh. Sachs. Ges. Akad. Wiss. Math.-Phys. Kl., 32, 575.