

## Opals

- A self assembly approach to photonic crystals -

### What are opals?

In the opposite to atomic crystals opals have no regular geometrical shape and are not as hard. Their coloration is not fixed, but changes when the stone is moved. This leads to the concept of *opalescence* - the phenomenon of angular dependent coloration in special solids. Opals have a periodic nanostructure; they consist of an arrangement of silica spheres which is densely packed and also highly ordered. The periodicity is on a scale comparable with the wavelength of visible light. Thus, opals exhibit many properties concerning photon propagation that are usually known for electrons in solids - especially the occurrence of bands and band gaps. The color of opals arises from the diffraction and interference of light by the regular arrays of spheres which each have different refractive indices. The nanostructure lattice of opals mainly shows a face centered cubic close packing which is thermodynamically preferred in comparison to the also possible hexagonal close packing.

### Opal shapes

Natural opals have each an individual appearance, they consist of silica  $\text{SiO}_2 \cdot n \text{H}_2\text{O}$ , sometimes with impurities of  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  or  $\text{Ti}^{3+}$  which affects their coloration. They can be found as thin films, as inclusions in matrix stones or as macroscopic pieces. They also contain varying amounts of water, mostly around 4 - 9 % but also a water content up to 20 % is possible, which has also an influence on their coloration.

Artificial opals were first synthesized in the 70'es for jewelry purposes. They differ from natural occurring opals by their typical growth structure.

Today, opals have gained in interest for usage as photonic crystals, for which they are a prototype.

### Opal deposition methods and formation mechanisms

Photonic crystals can in principle be performed by *top-down* and *bottom-up* techniques. Opals in special represent a basic fabrication approach of employing the bottom-up techniques, which contain self-assembly mechanism of the molecules forming the completed product. There are several methods for the deposition of artificial opals, all starting from a monodisperse solution of particles. They can be classified into Field induced-, Flow induced and Volume restriction methods, according to their driving force [1].

The field induced- and volume restriction methods represent a more classical approach for structure formation: During the increase of particle concentration in solution a critical concentration is exceeded, leading to thermodynamically favored crystal formation. Flow induced deposition methods are based on a stochastic clustering of spheres, driven by the flow of the suspension towards a growth front. In this method, the films grow from the outside, where the opal is formed first, towards the inner part of the film, which dries at last. Modifications of this method are possible, for example by varying the solvent or by applying a temperature gradient. Regardless which method is used, the synthesized opal will contain defects, but the amount and kind of those defects is related to each method. For example in flow induced deposition methods, the concentration of defects is rather low compared with the field induced- and volume restriction methods.

Regardless to the applied deposition method, the mechanism of opal formation can be split into five partial processes, which may occur parallel or sequentially at different points of the sample.

In the initial suspension a rearrangement of the particles may occur, for example driven by Brownian movement. The second step consists of a phase transition from the disordered to the ordered state, leading to the wet opal as an intermediate in which reconstructions can occur. The next step is the drying of the intermediate by the removal of water accompanied with a shrinkage and correlated formation of cracks in the nanostructure of the opal. Finally the dry opal is formed in which reconstructions are still possible.

### Defects and superstructures

Due to the absence of charge and a short range of sphere interaction, defects in opals differ in many aspects from those in atomic crystals but nonetheless they can be classified in a similar way [1]:

#### Point defects

**Schottky defect:** Due to absence of charge, lattice vacancies don't have to occur in pairs

**Frenkel defect:** Spheres can be displaced to interstitial positions in the lattice if they are notably smaller than the others

**Larger sphere:** A defect that can only occur in photonic crystals; it alters the lattice ordering and leads to long range distortions of the lattice

**Dislocations** Extended displacement of crystallographic planes due to **growth effects, slips, twinnings, step- and screw dislocations**

**Stacking faults** Partial displacements of close packed spheres lead to a **mixture of fcc and hcp stackings**

**Volume defects** **Domains** (segregated volumes in the packing) and **cracks** (formed upon shrinking) can occur which can be ranked as disturbed parts of the lattice with special optical features

Like in atomic crystals, defects in opals modify the physical features of the material, but therefore they can not only be seen as an undesirable and unavoidable characteristic, but also as an interesting phenomenon giving rise to several functional features. Concerning for example the band gap of opals, defects can introduce additional photonic states which in consequence leads to an incoherent scattering of light and a hopping-like photon transport. Thus there is research on the formation of spontaneous defects as well as on the mechanisms of intentionally fabricated and designed defects to achieve defined structures and properties.

### Opal modifications

In principle opal formation is possible for every chemical compound but in practice opal formation is limited to small spheres that can be produced in a monodisperse solution. Thus up to date opal formation established for some polymers like PMMA (Polymethylmethacrylate) or PS (Polystyrene) [2] and some other acrylate monomers [3], but of course also for inorganic building blocks like silica [1], [4].

### Photonic crystals - a short compendium

Photonic crystals can simply be defined as an arrangement of ordered optical nanostructures built of an arrangement of dielectric media. They affect the propagation of photons in a similar way as semiconductor crystals affect the motion of electrons. In analogy to semiconductors, photonic crystals also have a band gap which hinders photons with a frequency within this band gap to propagate and thus photons with such a frequency are reflected. With regard to opals it has to be mentioned that a full band gap can only be obtained in *inverse opals*, consisting of a regular arrangement of spherical void spaces which are surrounded by solid walls [5]. In conclusion photonic crystals, especially the regarded opals, are of great scientific interest as they may allow us to exercise control on the propagation of light and thus lead to new developments in the field of optical devices, sensors, photonic inks, displays and photonic crystal LEDs [6].

### References

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