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Self-Organization in the World of Crystals

State-of-the-art techniques for growing crystals are yielding materials with unique properties – such as metamaterial behavior or plasmon-enhanced optical performance.

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Order – the opposite of disorder, of chaos. Something so desirable yet so demanding, requiring considerable effort to achieve. In the world of materials engineering, order manifests itself in crystalline structures. In such structures, ions, atoms, or molecules are arranged in a characteristic pattern unique to the given material, regularly repeating across space to form a periodic network: volumetric order on the micro- and nanoscale.

Crystals are the mainstay of many industries, especially electronics. A particularly significant role is played by semiconductor materials, whose properties can be relatively easily controlled by introducing specific dopants to the crystal structure. Hence, great emphasis is placed on the development of progressively more advanced techniques for growing crystals. Polish scholars have made significant contributions to this field, a legacy initiated by Jan Czochralski. This often-cited yet still underappreciated Polish scientist developed the Czochralski method in 1915, a process for growing silicon monocrystals.

One day, as he was writing distractedly, Czochralski accidentally dipped the nib of his pen into a vessel of molten tin instead of an inkwell. As a result, he pulled out a thin fiber, which turned out to be a monocrystal of metal. This method of obtaining monocrystals, which is today crucial for the production of silicon, is named the Czochralski method in his honor. Today, materials produced using this method are obtained in large crucibles containing molten material, towards which a seed crystal with the appropriate structure is made to approach. As it is lifted up from the surface of the metal, the solidifying material is gradually pulled out, replicating the seed crystal structure throughout its entire volume. Rods obtained this way are approximately cylindrical in shape, several meters high, and weigh several hundred kilograms. They are cut into slices to obtain highly ordered semiconductor wafers. The Czochralski method laid the foundations for the

Post-process batch material, from which silicon carbide crystals are next obtained

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Crystals grown by members of the E3 staff:
(A) yttrium-aluminum garnet doped with praseodymium YAG:Pr (used in scintillation techniques),
(B) yttrium orthovanadate doped with neodymium YVO_4:Nd (used in the construction of lasers),
(C) magnesium spinel doped with cobalt $MgAl_2O_4$:Co (used in the construction of lasers),
(D) optical work underway in the E3 optics laboratory

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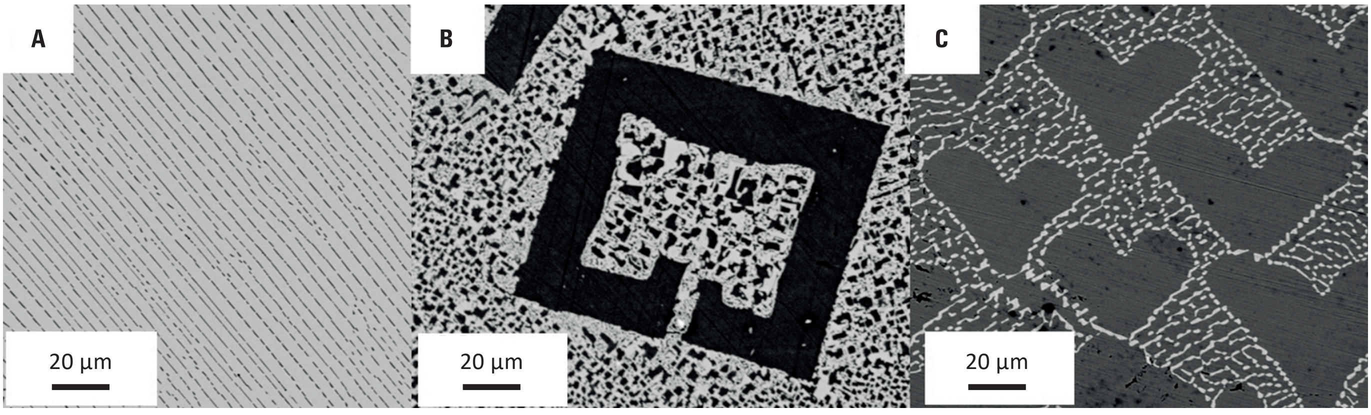
development of the modern electronics industry and is widely used in manufacturing semiconductors. One telling sign of the importance of these crystals is the fact that the Silicon Valley, the technological hub of the United States, is named after them. Similarly, the Taiwanese electronics industry, well-known for manufacturing top-notch microprocessors, owes its very existence to semiconductor technologies.

Centre of Excellence

Jan Czochralski's lasting legacy is invoked today by the entire Polish crystallographic community, including the ENSEMBLE[3] (E3) Centre of Excellence, which was established in 2019. It was established on the initiative of Dorota A. Pawlak, PhD, DSc, a Professor at the Institute of Electronic Materials Technology (now Łukasiewicz – Institute of Microelectronics and Photonics – Ł-IMiF), and grew out of the research group she leads. E3's main areas of interest is the growth of crystals and related materials, including metamaterials, for photonics, plasmonics, and optoelectronics, among other fields. Thus, the dominant theme of work within the centre is the development of new material technologies based on crystal growth and advanced materials with unique electromagnetic properties, which in the future will find applications in various industrial fields, such as photonics, optoelectronics, telecommunications, solar energy conversion, medicine or aviation. It also cannot be overemphasized that the scientists operating within the centre have many years of experience in the field of monocrystal growth with a special focus on oxide semiconductors and III-V semiconductors (i.e. compounds of a boron group element with a nitride group element, such as GaN).



RESULTS OBTAINED BY E3 STAFF

Examples of micro and nanostructures of eutectic materials:
(A) a lamellar structure of ZnO-$ZnWO_4$,
(B) a split-ring resonator structure in $SrTiO_3$-TiO_2,
(C) a structure arranged in heart shapes in $SrTiO_3$-TiO_2

Materials of this type are used in the construction of optical, laser and scintillation components, and have historically been used in the manufacture of radios. The E3 Centre is designed to foster collaboration between research units, including international cooperation. Its list of foreign partners includes Ł-IMiF and the University of Warsaw in Poland, as well as Karlsruhe Institute of Technology (Germany), University of Rome La Sapienza (Italy) and CIC nanoGUNE (Spain).

The research carried out at E3 under the International Research Agendas Programme (IRAP) focuses on the application of crystal growth methods to produce new photonic materials (metamaterials, plasmonic materials, and other materials with unique optical properties). This is achieved by using the mechanism of self-organization to obtain semiconductor structures, including eutectic crystals, and by developing new methods for producing nanoplasmonic materials, including glass nanocomposites.

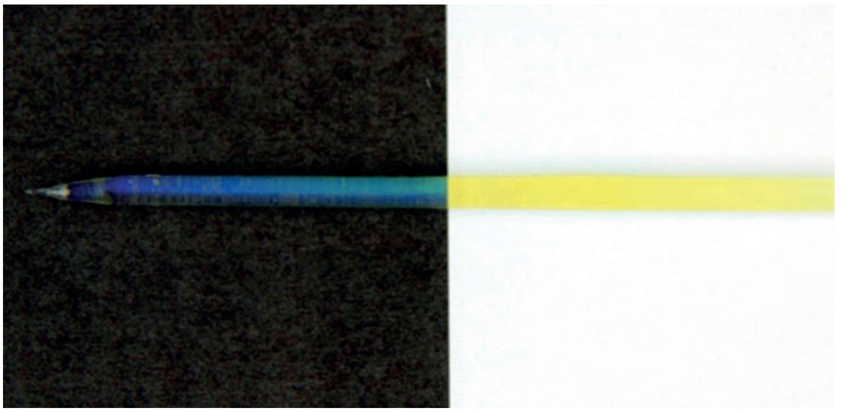
> Particularly promising is the prospect of being able to manipulate electromagnetic waves in ways that are not found in nature.

Crystal hearts

Eutectic crystals are ones that form from the crystallization of a *eutectic mixture*. A eutectic mixture, in turn, is one that has a melting point lower than that of any of its constituents. When transitioning from a liquid to a solid, the phases self-organize, creating various geometric patterns. These include lamellar (plate-like), rod-like, and globular eutectics. By adjusting the growth conditions, one can obtain materials with exceptional properties due to the diversity of the resulting structures. Particularly promising is the prospect of being able to manipulate electromagnetic waves in ways that are not found in nature. Optical metamaterials, first described theoretically by the Russian physicist Viktor Veselago in the 1960s, exhibit such behavior. Their properties would stem not from the constituent materials themselves, but from their specific structuring. These materials are supposed to have negative values for electric permittivity and magnetic permeability. This results, for instance, in a negative refractive index, causing a photon beam to bend at the interface of two media at an angle different from what occurs in nature. Achieving this necessitates using a multiphase material with a well-defined microstructure, determining the metamaterial's parameters.

A negative refractive index was demonstrated in the microwave range in the early twenty-first century, using a structure that included copper split-ring resonators (SRRs). Currently, metamaterials are being developed for sub-diffraction optical applications, allowing the diffraction limit to be surpassed using *superlenses* (microstructures produced on surfaces that exhibit different properties than conventional lenses – such as an absence of aberration). Another example is military applications, aimed at developing coatings effectively camouflaging objects across various electromagnetic frequency ranges – something along the lines of Harry Potter's cloak of invisibility.

One of the eutectic materials developed at the E3 labs is ZnO-$ZnWO_4$. It features plate-like ordering, where ZnO and $ZnWO_4$ phases form adjacent parallel lamellae. This structuring enables control of light polarization at various wavelengths, generating second harmonic emission (light emission at double the frequency of the incident light), as well as making this eutectic behave like a metamaterial in the infrared radiation range. Another eutectic material produced



RESULTS OBTAINED BY E3 STAFF

A glass fiber made of sodium borophosphate glass, doped with silver nanoparticles, exhibiting different colors depending on the light: against a bright background it is seen in transmitted light, whereas against a dark background it is seen in reflected light

at E3 is $SrTiO_3$-TiO_2, where self-organization leads to the formation of SRR-like structures, a source of metamaterial properties. When appropriate growth parameters are applied, phases in the material organize in heart-shaped structures – which have become the unofficial logo of our Centre of Excellence.

New properties of glass

Plasmonic glasses represent another very important strand of research at E3. Centuries ago, mankind developed the technology of staining glass using metal ions. Colored glass is used in a wide range of practical applications, such as in the production of decorative vessels and stained-glass windows. Among the more interesting examples of objects made of colored glass is the Lycurgus Cup, a decorated glass goblet that probably dates back to the ancient Roman Empire in the 4th century CE. Unusually, its color changes depending on the type of light: when the object is looked at in reflected light, it looks green, but when it is held up to a light source and viewed in transmitted light, it appears red. This effect was achieved by ancient craftsmen by doping glass with silver and gold nanoparticles. Such noble metal nanoparticles exhibit plasmonic properties: when illuminated with light of the appropriate wavelength, localized surface plasmon resonance (LSPR) is induced in them, which arises from vibrations of the electron cloud localized in the nanoparticle. LSPR manifests as the subtle coloring of colloids of these nanoparticles: silver appears green, while gold appears red (in the most typical cases of spherical nanoparticles of standard sizes, as the color also depends on factors like shape and size).

At the E3 labs, we are developing the technology of doping glasses with plasmonic nanoparticles using our method of Nanoparticle Direct Doping (NPDD). By introducing nanoparticles directly into the glass matrix before the material manufacturing process, we are not reliant on commonly used nanoparticle precursors, giving us greater control over the doping parameters. Furthermore, this method allows several dopants to be added to the glass material simultaneously. Glass doped with silver nanoparticles, as developed by Professor Pawlak's group, changes color similar to the Lycurgus Cup based on the lighting conditions. Apart from its aesthetic appeal, plasmonic properties enable the enhancement of optical effects. The excitation of LSPR leads to a tremendous increase in the intensity of the electromagnetic field, which amplifies various optical phenomena. In this way, a significant enhancement of the luminescence intensity of Er^{3+} ions was observed in plasmonic glass. Research efforts to improve glass parameters using plasmonic effects aims to develop materials for applications such as displays, optical components, and telecommunications.

Crucially, most materials, not just eutectic but also glass materials, are obtained using well-known crystal growth methods, with the micro-pulling method leading the way. This technique is analogous to the above-described Czochralski method; however, in this case, the melted material flows through a capillary at the bottom of the crucible, solidifying on a seed crystal pulled downward. This yields bulk materials with desired properties. This technology also allows for easy introduction of dopants, significantly expanding the range of attainable properties. Flexibility in the approach to the growth of diverse materials allows the E3 Centre of Excellence to continuously expand its areas of interest and set ever bolder goals in the field of materials engineering, responding to the growing challenges of today's world, both scientific and technological. ■

ACKNOWLEDGMENTS

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