

Preparation of Oxide, Dielectric, and Laser Crystals at the Leibniz-Institute for Crystal Growth (IKZ) Berlin

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Since the institute was formed in 1992, it hosts a group of experts engaged in the growth of oxide and fluoride bulk single crystals, with a clear focus on oxides. Typically, such crystals are prepared by the Czochralski method, as it is the most developed technique for growing crystals of high structural quality. Our group focuses on the high-temperature crystal growth from the melt (between 1500°C and 2200°C in Ir crucibles). The crystals grown have diameters up to 50 mm and lengths of up to 150 mm. But also other melt growth techniques such as EFG (edge-defined film-fed growth), Bridgman and Kyropoulos are pursued. Crystal fibers and rods are prepared in the group using the Laser heated pedestal growth (LHPG, capable of growth at temperatures up to 2700°C in various atmospheres) and micro-pulling down (MPD) methods. Incongruently melting compounds are grown from flux or by top seeded solution growth (TSSG); if the volatility is high, growth from the gas phase (physical vapor transport, PVT) is employed. More and more, though, novel materials require adapted or specially tailored growth conditions. One good example is the „Levitation-Assisted Self-Seeding Crystal Growth Method” (LASSGCM), which was designed in particular for preparation of In_2O_3 bulk single crystals in our group [1].

The group's main research topics as have evolved partly over more than a decade. Crystals with perovskite structure are used as substrates for the preparation of strain-induced ferroelectric and/or ferromagnetic layers which open up new fields of applications, e.g. in the oxide electronics domain. One prominent example is strontium titanate (SrTiO_3) [2], which is the only oxide material known as of today which can host a two-dimensional electron gas at the interface to another oxide crystal layer. Also, up to now the IKZ is the only institution worldwide to prepare bulk rare-earth scandate crystals which provide perovskite substrates with tailored lattice constants in the 3.95–4.02 Å range [3], and new materials with even higher lattice constant (e.g. LaLuO_3) are currently researched.

Apart from perovskites, transparent semiconducting oxides (TSOs), in particular as epitaxial, single-crystalline layers, recently got into focus in materials physics research because of their outstanding properties and possible applications. Accordingly, preparation of bulk crystals which can be used as substrates present another main topic of research at the IKZ. Interesting materials such as ZnO [4], $\beta\text{-Ga}_2\text{O}_3$ [5], In_2O_3 [6], and SnO_2 [7], as well as a new TSO material MgGa_2O_4 [8] that can be used for ferromagnetic as well as semiconducting purposes, have been successfully grown as bulk crystals using adapted growth conditions and in part also novel growth approaches.

Also, the IKZ has prepared single crystals of 15 compounds out of the Langanite-type crystal family (represented by the general type $\text{La}_3\text{Ga}_5\text{SiO}_{14}$) [9]. Such material is very important for high-temperature piezoelectric applications, such as pressure sensors and actors, that can be used up to 1470°C. Currently, the use of aluminum nitride (AlN) as a high-temperature piezoelectric single crystal for resonant applications is also investigated at the IKZ.

At all times, preparation of non-linear optical as well as laser crystals has also been researched at the IKZ. Apart from well-known rare earth (RE) doped YAG and GGG crystals, we have grown Yb:YVO_4 , RE:GdVO_4 , and $\text{RE:NaGd(WO}_4)_2$ and investigated the segregation and controlled growth of homogeneously Ti- and Cr-doped Al_2O_3 [10]. Visible, Ce^{3+} based laser material candidates $\text{Ce:CaSc}_2\text{O}_4$, $\text{Ce:SrY}_2\text{O}_4$ [11] have recently been prepared from the melt for the first time at the IKZ. Fluoride laser materials for Terawatt Lasers such as RE:YLiF_4 [12], Yb:CaF_2 , $(\text{Ca,Sr})\text{F}_2$ [13], and Cr:LiCaAlF_6 [14] can be grown in a dedicated furnace under CF_4 gas using an own fluorination line to deploy raw materials of highest purity. We have also grown garnets such as TAG, TSAG, for Faraday-Rotators [15], and BaMgF_4 single crystals for UV non-linear optics.

The IKZ is well aware that the preparation on novel and/or application-tailored laser materials is of great importance for many field of applied optics. The crystal growth expertise at the IKZ should be increasingly used by the users of such materials, especially from the R&D domain, to jointly develop and employ the materials needed for novel and improved applications with societal impact.

- [1] Z. Galazka, R. Uecker, R. Fornari, J. Cryst. Growth 388 (2014) 61-69.
- [2] C. Gugushev, D.J. Kok, Z. Galazka, D. Klimm, R. Uecker, R. Bertram, M. Naumann, U. Juda, A. Kwasniewski, M. Bickermann, CrystEngComm 17 (2015) 3224-3234.
- [3] R. Uecker, D. Klimm, R. Bertram, M. Bernhagen, I. Schulze-Jonack, M. Brützm, A. Kwasniewski, Th. M. Gesing, D.G. Schlom, Acta Physica Polonica A 124 (2013) 295-300.
- [4] D. Klimm, D. Schulz, S. Ganschow, Growth of Bulk ZnO, in: Comprehensive Semiconductor Science and Technology, P. Bhattacharya, R. Fornari, H. Kamimura (eds.), Elsevier Science, Amsterdam (2011) 302-338.
- [5] Z. Galazka, K. Irscher, R. Uecker, R. Bertram, M. Pietsch, A. Kwasniewski, M. Naumann, T. Schulz, R. Schewski, D. Klimm, M. Bickermann, Journal of Crystal Growth 404 (2014) 184-191.
- [6] Z. Galazka, R. Uecker, K. Irscher, D. Schulz, D. Klimm, M. Albrecht, M. Pietsch, S. Ganschow, A. Kwasniewski, R. Fornari, J. Cryst. Growth 362 (2013) 349-352.
- [7] Z. Galazka, R. Uecker, D. Klimm, K. Irscher, M. Pietsch, R. Schewski, M. Albrecht, A. Kwasniewski, S. Ganschow, D. Schulz, C. Gugushev, R. Bertram, M. Bickermann, R. Fornari, Phys. Status Solidi A 211 (2014) 66-73.
- [8] Z. Galazka, D. Klimm, K. Irscher, R. Uecker, M. Pietsch, R. Bertram, M. Naumann, A. Kwasniewski, R. Schewski, M. Bickermann, Phys. Status Solidi A (2015) in print, DOI: 10.1002/pssa.201431835
- [9] S. Ganschow, C. Cavalloni, P. Reiche, R. Uecker, Proc. SPIE 2373 (1995), DOI: 10.1117/12.224988
- [10] S. Ganschow, D. Klimm, R. Bertram, J. Crystal Growth 325 (2011) 81-84.
- [11] J. Philippen, Dissertation TU Berlin, Germany (2013), online at <https://opus4.kobv.de/opus4-tuberlin/frontdoor/index/index/docId/4267>
- [12] D. Klimm, I.A. Dos Santos, I.M. Ranieri, S.L. Baldochi, MRS Proceedings 1111 (2009) D01-07.
- [13] D. Klimm, M. Rabe, R. Bertram, R. Uecker, L. Parthier, J. Crystal Growth 310 (2008) 152-155.
- [14] D. Klimm, R. Uecker, P. Reiche, Cryst. Res. Technol. 40 (2005) 352-358.
- [15] S. Ganschow, D. Klimm, B.M. Epelbaum, A. Yoshikawa, J. Doerschel, T. Fukuda, J. Crystal Growth 225 (2001) 454-457.



Fig. 1: Oxide and fluoride crystals prepared at the IKZ (selection).