# BIRD - Development of an order of magnitude better mercurous bromide broadband IR polarizer and acousto-optic tuneable filter

## Executive summary

**Early technology development**

*IDEA: I-2022-04392*

*Affiliation(s): BBT – Materials Processing, Ltd.*


**Activity summary:**

A significant number of remote sensing applications require imaging of a scene in the thermal infrared (TIR) region. Therefore, the project has successfully implemented a technology for the growth of mercurous bromide ($Hg_2Br_2$) crystals. The crystal exhibits unique optical properties over the entire spectral range from VIS (0,42 um) up to TIR (24 um): high birefringence, extremely low acoustic wave propagation speed and high acousto-optic interaction coefficient. Thanks to these parameters, it finds application in many areas of Earth observation.



Publishing Date: 01.08.2024
Contract Number: *4000140465/23/NL/GLC/ov*
Implemented as ESA Initial Support for Innovation

# 1. Introduction

The main objective of this activity is to develop the technology of crystal growth and testing of mercurous bromide ($Hg_2Br_2$) single crystals potentially suitable for broadband infrared (SWIR, LWIR) polarization optic and acousto-optics, incl. the acousto-optic tuneable filter (AOTF).

The objectives of this activities were:

1. Implementation of mercurous bromide crystal growth technology into the standard production process.
2. Tests & Analysis of the crystals.
3. Optimization of manufacture process based on obtained results.

# 2. Project Background

Mercurous halides are the only group of crystals, which was originally developed by BBT and it is still the only company worldwide to be able to produce and supply other world-unique crystal (mercurous chloride) in a sufficient quality and therefore has all the prerequisites to successfully address the development of technologies related to the growth and testing of mercurous bromide single crystals

The main innovative contribution lies in the fact that the newly developed polarization and acousto-optic elements will allow a significant broadening of the spectral range of applications into the far-infrared region, including, among others, the characteristic absorption spectra of many organic molecules (fingerprints). In addition, one can expect up to an order of magnitude higher ER (extinction ratio, polarisation contrast) values and high resistance to high-energy laser beams.

# 3. Methodology

The methodology and approaches used come from BBT's long history dedicated to materials engineering. The project therefore adopted an experimental approach to validate new concepts and Lean methodology (i.e. modification of value stream mapping) to improve every single production step in order to achieve the result.

# 4. Key Findings

The fundamental finding was the spectral transmittance of the crystal ranging from 0.42 to 24 microns. According to the available literature, a transmittance of up to 30 microns was expected, however, an anti-reflective coating would need to be applied to achieve this value.

# 5. Conclusion

Within the framework of the project, mercurous bromide single crystals have been successfully grown and processed, thus fulfilling the main objectives and demonstrating the feasibility of the chosen technology. This result will have a significant impact on IR spectrum and acousto-optics technologies for both space and terrestrial applications.

# 6. Future Work

All objectives of this project were fully achieved; therefore the company is seeking opportunities to continue its development and would like to follow up with a project with ESA to develop polarisation and acousto-optic components.  In the upcoming GSTP activity BBT would like to further optimize the crystal quality and increase the size. At the same time develop the basic components (polarizers, Savart plates, etc.), design AOTF (/ AOM) and introduce other MVP (minimal viable product) implementing these world - unique crystals.

# BIRD

## Development of an order of magnitude better mercurous bromide broadband IR polarizer and acousto-optic tuneable filter

**Executive Summary Report**

ESA Contract No. 000140465/23/NL/GLC/ov

# Introduction and scope of the project BIRD

A considerable number of applications in remote sensing necessitate the measurement of the light spectrum within the so-called **thermal infrared (TIR) range**, spanning from 3 to 20 µm. This range is particularly useful for the unique identification of molecules. Potential applications include the monitoring of plastic waste in the ocean, the tracking of oil spills, the identification of fire hazards, and the detection of atmospheric gases.

The main objective of this activity is to develop the technology of crystal growth and testing of mercurous bromide ($Hg_2Br_2$) single crystals potentially suitable for broadband infrared polarization optic and acousto-optics. The crystal exhibits unique optical characteristics in the full **0.5 - 30 µm** spectral range: broad optical transmission, high birefringence, extremely low velocity of acoustic wave propagation and high coefficient of acousto-optical interaction.

**Mercurous halides** are the only group of crystals, which was originally developed in the Czech Republic by the Czech company BBT-Materials Processing, Ltd. (hereinafter "BBT"). BBT is still the only one worldwide to be able to produce and supply other world-unique crystal (mercurous chloride) in a sufficient quality and therefore has all the prerequisites to successfully address the development of technologies related to the growth and testing of mercurous bromide single crystals.

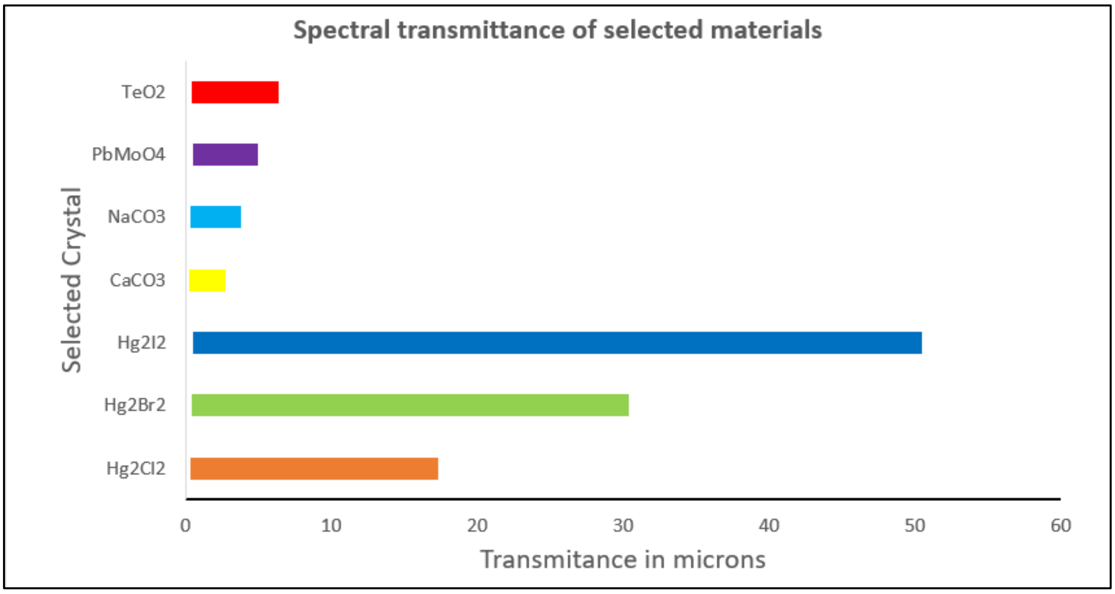


*Figure 1 - Spectral transmittance of selected materials*

# Crystal growth

The theoretical aspects of crystal growth were studied, and parameters were tuned to optimize the growth process. Extensive research was carried out, crystal structure, growth kinetics and other important factors were investigated. Theoretical models and simulations were used to predict growth behaviour and optimize growth conditions. Parameters such as temperature (and temperature change over time, rate of change), **temperature gradients**, (axial and radial gradients), **pressure, growth rate** and overall conditions were adjusted to achieve the desired crystal properties.

According to above suitable furnace design was selected, tested and optimized, heating elements, shutters, temperature control systems and all necessary resources were set up. The first furnaces and components were carefully calibrated to ensure accurate control of the growth conditions. The proposed system is based on a successfully proven technology for growing another mercurous halide - calomel (mercurous chloride $Hg2Cl2$). In doing so, it had to be modified especially with regard to decomposition temperature and different heat capacity, etc.

The chosen method for cultivation is the **PVT (Physical Vapour Transport) technique**. The PVT process is a technique used to grow high-quality single crystals, particularly for materials that have high melting points or are otherwise difficult to process. The PVT process involves the sublimation of a source material, the transport of the vapor, and the deposition of the vapor to form a crystal.
The process takes place in a sealed furnace, under vacuum. The source material, which will be sublimed, is placed in a high-temperature zone within the chamber. A lower temperature zone is set up in another part of the chamber, where the crystal will grow. The source material is heated to a temperature where it **sublimates**, meaning it transitions from a solid phase directly to a gas phase without passing through a liquid phase. The vaporized material is **transported** through the chamber by a temperature gradient. The movement of the vapor is driven by the difference in temperature between the high-temperature zone (where sublimation occurs) and the lower-temperature zone (where deposition and crystal growth occur). When the vapor reaches the cooler zone, it undergoes **desublimation** (condensation), transitioning from the gas phase back to the solid phase.

This results in the formation of a crystal, which grows layer by layer on a substrate or on the walls of the cooler zone. The growth process in case of mercurous bromide was closely monitored, and adjustments were made to optimize the growing conditions. This phase initially served as a preliminary assessment of the growth technology and helped to identify any problems or areas for improvement.

*Figure 2 - First unsuccessful attempt to grow a crystal (left). A successfully grown crystal (right).*

## Crystal Processing

For crystal processing, BBT used its existing facilities, in particular the grinding, polishing and cutting units with modification for its own purposes. **New abrasives, different cutting (but also grinding and polishing) speeds, pressures and machining system settings were tested**. It was decided to make plates with different crystallographic orientations (001) and (110). However, according to the photographs in the SEM (see Fig. 4), it turned out that it was necessary to implement an even finer abrasive to achieve a surface quality (20-10 according to the Scratch-Dig parameter).

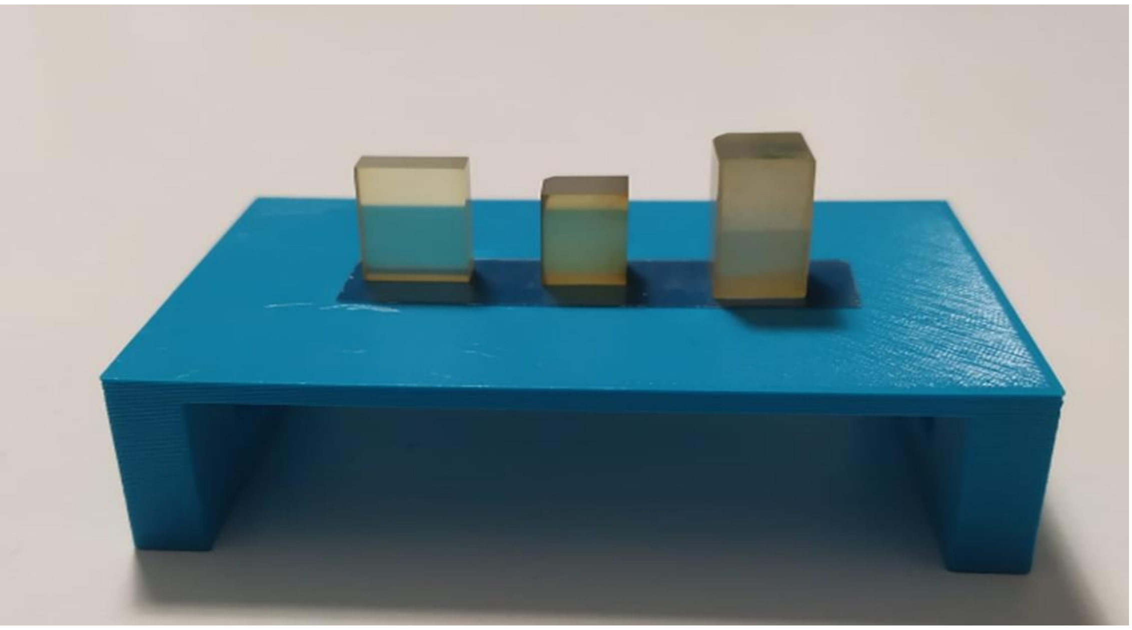

*Figure 3 - Processed plates*

# Crystal Tests & Analysis

The aim was **to collect as much relevant information as possible** about the mercurous bromide crystal for necessary further development and research. The quality of the raw material (stoichiometry, XRD, XRF) and the characteristics of the processed crystal (e.g. transmittance, S-D parameter, flatness, SEM – scanning eletron microscopy, ellipsometry etc.) were measured and evaluated.

In cooperation with the Institute of Physics of the CAS (https://www.fzu.cz/en/home), results for optical constants ( ndex of refraction, Extinction coefficient and absorption coefficient) were obtained in the range of 0.413 - 5 microns. The actual measurement will be the subject of **scientific paper**, given the non-trivial and unique nature of the new material.

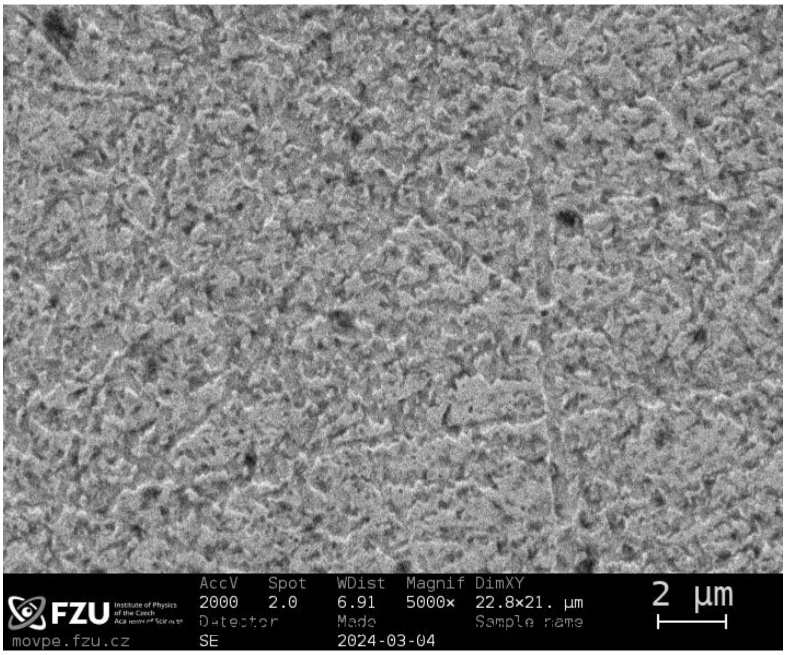


*Figure 4 - SEM output*

# Optimization phase of the whole process

Due to the time and technological demands of the entire growing and processing technological chain any feedback from the processed crystal to optimize the growing process is **a long-term, constantly iterating circle.**

Given by a low quality of the feedstock BBT developed a technological procedure for chemical and physical purification of the feedstock, which it is currently gradually implementing in its corporate processes. The analysis for comparison of purified feedstock material was carried out in the VSCHT laboratories (University of Chemistry and Technology, Prague). It was shown that the purification process eliminated a large part of the impurities, which was confirmed not only by analyses, but by a successfully grown crystal.

In addition to the preparation of the feedstock itself, BBT also focuses on the preparation, design and cleaning of the growth ampoules, which also influence the entire growth process. New ampoule designs have been proposed and are being tested.
Last but not least, BBT engineered and upgraded the vacuum system to additionally remove the remaining moisture, which is also undesirable.


*Figure 5 - Crystal from the original raw material (top) and the partially purified one (bottom)*

During the optimization phase, BBT has introduced an experimental horizontal refining furnace layout. This approach will ensure heavier molecules can more easily overcome gravitational forces, but more precise and time-consuming adjustment is required. For the vertical arrangement, active adjustment of the aperture or temperature profile for a particular growth phase had a positive effect. This highlighted the need for a multi-zone active furnace with a separate winding, which BBT intends to gradually integrate into the production process.

# Conclusions

Within the framework of the project, mercurous bromide single crystals have been grown and processed, thus fulfilling the main objectives and demonstrating the feasibility of the chosen technology. The theoretical parameters have been successfully set and fine-tuned, allowing the growth conditions to be optimized. The assembly and installation of the refining furnaces and components went smoothly and ensured precise control of the conditions in the growth environment. A number of tests have been performed on the manufactured crystals, in particular the spectral transmittance from visible to about 24 micrometres is impressive and offers many potential applications.

**All objectives of this project were fully achieved**; therefore the company is seeking opportunities to continue its development and would like to follow up with a project with ESA to develop polarisation and acousto-optic components. In the upcoming GSTP activity BBT would like to further optimize the crystal quality and increase the size. At the same time develop the basic components (polarizers, Savart plates, etc.), design AOTF (/ AOM) and introduce other MVP (minimal viable product) implementing these world - unique crystals.

In the final phase, the results of this ESA-supported research activity will be transformed into commercial solutions in both the space and ground domains. Depending on the platform deployed, areas of interest include remote sensing, smart agriculture, as well as civil security.

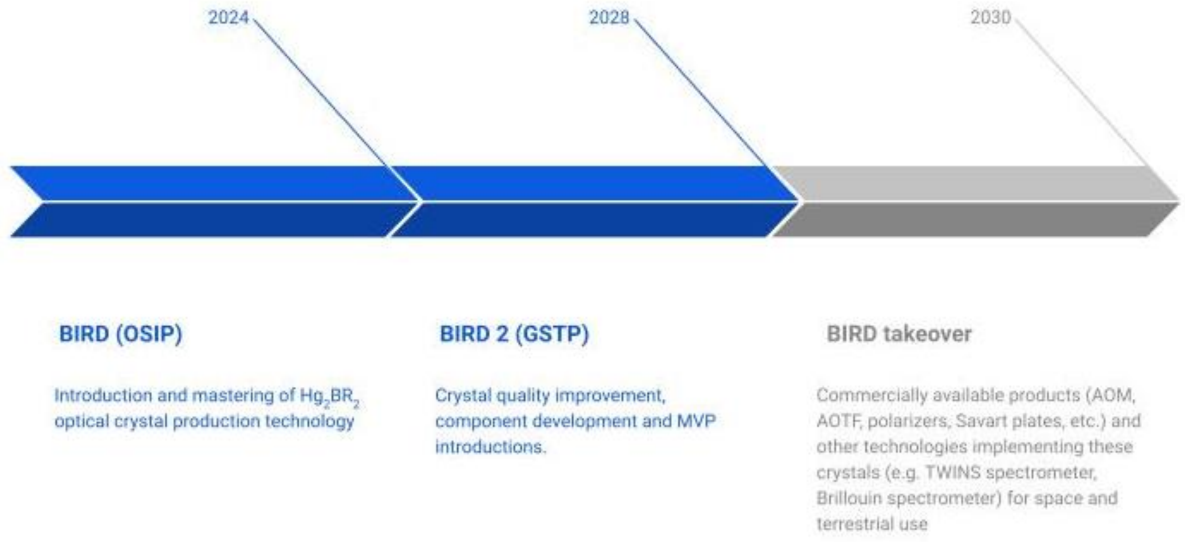


*Figure 6 - BIRD Roadmap*

# Scope



# List of Figures: