Institution: University of Kent

Unit of Assessment: 8, Chemistry

Title of case study: Crystals for National Security and Biomedical Diagnostics

1. Summary of the impact

X-ray scanners are a staple of the security industry: their use at ports and airports is a key component of national security. In order to function effectively, these scanners require state-of-the-art scintillator materials and, given the size of the global market and importance of the industry, there is a drive to make these materials work more effectively to achieve better clarity in object identification and faster scanning times.

This case study describes the development of a new scintillator product for Hilger Crystals Ltd which was based on a long-term collaboration with materials researchers at the University of Kent. This represents a substantial contribution to: improving security at country entry/exit points; the commercial success of Hilger and the company's ability to enter new markets (for example medical diagnostic uses). In addition to the downstream security and diagnostic impact arising from this work there have been a number of concomitant benefits to the country, the company and the University.

2. Underpinning research

An on-going collaboration between Hilger Crystals and physicists/chemists in the School of Physical Sciences at the University of Kent (principally A.V. Chadwick [Kent 1970-present] and G. Mountjoy [Kent 1996-present] and later Alfredsson [Kent 2007-present] and Ph.D/KTP Associate A Blacklocks [Kent 2004-2011]) has been in existence for more than a decade. This case study describes one successful project that has arisen from this collaboration. Not all of the research described here was published in the academic literature for reasons of confidentiality. Publication [1] is directly relevant to this proposal, Publications [2,3] describe underpinning technique development pioneered by Kent staff, that was later employed in this case. Theoretical work performed by Kent staff (M. Alfredsson [Kent lecturer 2007-present]) was also key to the success of this project. The SPS contribution can be verified by Hilger Crystals [5.1].

There is a large worldwide market in scintillator materials for X-ray scanners. However, images produced during scanning are blurred due to an electronic process known as 'afterglow'. Understanding the origin of the afterglow in scintillators allows for the production of novel materials with improved properties, resulting in sharper images.

The objectives of the collaboration between Hilger Crystals Ltd (Hilger) and the School of Physical Sciences (SPS) were to:

(i) establish the origin of the afterglow process in Thallium-doped Caesium Iodide (Tl,Cs)I scintillator single crystals;

(ii) develop an industrial process in which high-quality crystals could be grown reliably, with significantly reduced afterglow, using standard commercial materials;

(iii) investigate co-doping with rare-earth elements[1] to establish whether these elements are critical for the afterglow reduction in (Tl,Cs)I.

(i) Origin of the afterglow process.

It is generally accepted that the afterglow is caused by trapping of the carriers that re-combine with the excited defect centres. The theoretical work led by Alfredsson proposed unusual behaviour of the Cs-I interactions in the system. Contrary to the general observation that band gaps decrease with increasing pressure it was found that the band gap in CsI *increases* if pressure or stress is applied. This was originally explained as a relativistic effect in the material, but our simulations showed this be a hybridisation effect. The observation is important in the understanding of the origin to the afterglow, as the relaxation time of the material is crucial for low afterglow. Thallium doping reduces the band gap significantly, but the band gap behaviour remains. Understanding and controlling this behaviour decreases the afterglow in the material

(ii) Reliable growth of high quality crystals.

New scaled-up crystal growth techniques were investigated at Hilger. These were performed in collaboration with, and guided by Density Functional Theory simulations and a number of material characterisation experiments (*e.g.* IR, TGA, XRD and SEM-EDX) undertaken at SPS. The quality of the crystal was found to be critically dependent on crystal growth parameters, particularly temperature gradient and soaking times: these were optimised. Processing of the final material, including heat treatment and storage time, were found to reduce the afterglow, as the material is allowed to relax after processing. Allowing the material to relax means storage costs for the company. The result was a new crystal growth method that yields new types of (TlCs)I crystals with substantially fewer defects. These crystals are much clearer and more reproducible than previously, and have dramatically reduced afterglow.

(iii) Co-doping with rare-earth elements.

Rare-earth doped CsI single crystals were initially grown at the SPS and Hilger. In 2006 Blacklocks (Ph.D) and Chadwick[1] measured the afterglow using X-ray excitation using combined techniques developed by Chadwick, Mountjoy and others [2,3]. Short- and long-life relaxations times were monitored for crystals with and without the presence of Eu and Sm. It was found that there are two distinct afterglows, long-term and short-term and that doping by rare-earths is only effective for short-term afterglow reduction. Further, different growth conditions were explored. It had been proposed that Tl is a determining factor controlling the afterglow in CsI as this element may form Tl-dimers or defects in the structure. For this purpose the local structure of CsI(Tl) structure was determined using X-ray absorption spectroscopy (XAFS) [1-3] in combination with atomistic simulations [unpublished, performed by M. Alfredsson and A. Blacklocks]. The introduction of rare-earth dopants decreases afterglow substantially, but other properties such as hydroscopicity increase, limiting the range of applications.

3. References to the research

Underpinning and background research was undertaken by staff at Kent as evidenced below (references [1], [2] and [3] best indicate the quality of the underpinning research). All references are to work led by staff from the School of Physical Sciences at the University of Kent, and all have an author from the University of Kent as first and/or corresponding author. Bold indicates a Kent author.

1. “Investigation into thallium sites and defects in doped scintillation crystals”, **Blacklocks, A. N.; Chadwick, A. V**.; Jackson, R. A.; Hutton, K. B., Physica Status Solidi C - Current Topics in Solid State Physics, 4, 1008-1011 (2007)
   DOI: http://dx.doi.org/10.1002/pssc.200673704
2. “Solid state NMR and X-ray studies of the structural evolution of nanocrystalline zirconia”, **Chadwick, AV; Mountjoy, G; Nield, VM**; Poplett, IJF; Smith, ME (Kent 1992-1998)**; Strange, JH; Tucker, MG**, Chemistry of Materials, 13, 1219-1229 (2001)
   DOI: http://dx.doi.org/10.1021/cm001152w
3. “A combined EXAFS and diffraction study of pure and doped nanocrystalline tin oxide”, **Davis, SR; Chadwick, AV; Wright, JP**, Journal of Physical Chemistry B, 101, 9901-9908 (1997)
   DOI: http://dx.doi.org/10.1021/jp971756w

4. Grants: KTP project (PI, **Dr. M. Alfredsson**; co-investigators **Prof. AV Chadwick and Dr G. Mountjoy**); EPSRC-CASE award (PI, **Prof AV Chadwick**; co-investigator **Dr G. Mountjoy**); INTERREG II, III (PI;**AV Chadwick**, co-investigators, **Drs G. Mountjoy and P. Lindan**) and INTERREG IV (PI, **M. Alfredsson**; co-investigators**; Prof. AV Chadwick and Dr. G. Mountjoy**

4. Details of the impact

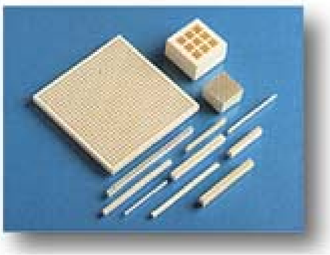
Hilger Crystals Ltd (Hilger) manufactures a range of synthetic crystals for X-ray and Infra-red applications. The collaboration between Hilger and the School of Physical Sciences (SPS) dates back more than 10 years and builds on the expertise of Prof. Chadwick and Dr Mountjoy in defect chemistry and analysis of their local structure using XAFS measurements [2,3]. The latest KTP project [4] (co-ordinated by Dr. Alfredsson) followed a CASE-studentship between Prof. Chadwick and Hilger (Drs. Telfer, Hutton and Blacklocks). This is an on-going collaboration and further results are to be expected.

The new growth method stemming from SPS's collaboration with Hilger is robust for producing moderate volumes of low afterglow (Tl,Cs)I in relatively low capital cost plant, permitting Hilger to be competitive with low cost manufacturers in China etc. Only a few crystal growers worldwide have been able to achieve this and it has given the company a competitive advantage. This has allowed Hilger to expand its market and seek customers in high-end applications of X-ray imaging such as air transport and sea cargo screening and medical diagnostic devices.

Despite the disadvantages detailed above the rare-earth doped crystals are also of interest for some specialist applications.

As a result of the new product, derived from the collaboration with the University, the company has recruited new staff, including one new research scientist as well as other high-quality technical staff - a key requirement for future growth.

The new material enables great market penetration for high-performance end sales to X-ray imaging companies throughout the world. All of the company's current customers are located outside the UK. Hence, all sales are export sales, mostly to the USA. The new material increased the annual sales turnover by c.£45k the first year it was launched in 2012 and is projected (based on past experience, by the company) to improve the annual sales turnover in the next three years' time to £250k, which corresponds to about 35% of the company's annual export volume.



Detectors and Imaging Arrays Cs(Tl)I from the Hilger Crystals Website.
http://www.hilger-crystals.co.uk/prior/detectors.htm

A positive effect on the reputation and advertisement of Hilger Crystals Ltd, resulted in the company being acquired by one of their largest competitors in 2010, becoming a partner of the Dynasil group, which specialises in advanced materials for a broad range of applications, with markets in the medical, industrial, defence, as well as the homeland security, sectors. This occurred while the product described in this case study was under development and hence the potential future profits from this product will have contributed to Hilger's attractiveness to Dynasil.

Hilger Crystals grow crystals for other companies to use in x-ray scanners and other devices. These are sold into, and employed in, the security and medical industries. Hence societal impact is "downstream" and we can only describe this aspect of the impact in general terms.

Principal Impact

- A new product has successfully been developed with a low afterglow that exceeded original expectations.
- While the new crystals only became available for sale in 2012, Hilger already has four client companies which have purchased the crystals and, thereby, have been able to manufacture and sell cheaper scanners that yield higher quality images.
- Hilger's managing director informed the University that currently (June 2013) there are about 50 detectors using these crystals in use in security and medical diagnostic roles.

Subsidiary Impact

- Indirectly this work contributes to improved security at national entry points.
- This work contributes to improved medical diagnostics (particularly mammography).
- The product is currently around 7%, and projected to reach 35%, of the company's sales.
- As all of the company's current customers are located outside the UK, all sales are export sales and hence it produces income and tax revenue to the UK.
- Current customers have been retained, and new customers secured, by the company.
- New staff has been hired, including a research scientist and high quality technical staff to expand the company's research base.
- Exclusion of rare-earth dopants makes the material less expensive than the originally proposed product.
- In 2010 Hilger was incorporated into the Dynasil group, based in the USA, improving the company's research profile with the aim to develop new X-ray imaging materials.
- A number of academic-related benefits including: (i) Hilger acting as industrial partners in the EU-funded Interreg projects and (ii) SPS is organising the international meeting EURODIM2014. The collaboration with Hilger is assisting the University in attracting world-leading speakers from industrial and academic backgrounds.
- Generated research income to the University of Kent: (directly) £150,000 and (indirectly) £300,000-£350,000.

5. Sources to corroborate the impact

1. Jim Telfer, Hilger Crystals, Managing Director. [Contact 1]
2. Keith Hutton, Hilger Crystals, Materials Development Scientist. [Contact 2]
3. Aaron Blacklocks, Hilger Crystals, KTP Fellow. [Contact 3]
4. Knowledge Transfer Partnerships Final Report Form, 08/11/2011. Partnership: KTP007000, Partners: University of Kent, Hilger Crystals Limited.
5. KTP Local Management Committee meetings, minutes and reports, 29/8/2008, 7/1/2009, 27/4/2009, 21/9/2009, 14/1/2010, 17/5/2010, 1/9/2010, 9/2/2011, 18/5/2011 (HIGHLY CONFIDENTIAL)