Imaging Plates as Detectors for X-ray Diffraction

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Introduction

X-ray detectors based on imaging plate technology have become very popular for the home laboratory in the past decade. The imaging plate (IP) is a reusable two-dimensional X-ray recording film. It consists of a photostimulable phosphor powder in an organic binder with a thickness between 25 and 150 μm deposited on a flexible polymer support film of about 250 μm thickness. The IP is exposed to the x-ray source and stores the impinging x-rays as a latent image in the phosphor. This image is recovered by scanning a laser beam across the IP, causing photostimulated luminescence (PSL). This PSL is recorded by a photomuliplier that is scanned across the IP at the same time as the laser. The resultant signal is digitized and stored in a file for data processing.

The family of compounds comprising $BaFX:Eu^{2+}$ (X = Cl, Br) have been known to have high luminescence efficiency for X-ray excitation for over thirty years. The first studies of the lifetime of the phosphorescence of BaFCl were performed in 1964 [1]. In the early 1970s, $BaFCl:Eu^{2+}$ was used in fluorescence sensitizing screens [2,3]. This seminal research led to the development of imaging plates by the Fuji Photo Film Co. in the first half of the 1980s as a device to replace film for x-ray radiography using $BaFX:Eu^{2+}$ (X is Cl, Br, and I) [4,5].

Other luminescence materials, Zn_2SiO_4:Mn [6], SrS:Ce,Sm [7], RbBr:Tl [8], for example, were studied for use in X-ray computed automated tomography. These materials do not have the properties required for large area imaging: the ability to be formed into large films, suitable luminescence lifetimes, etc.

Imaging plates are sensitive not only to X-rays, but other types of radiation as well: gamma radiation, alpha and beta particles, neutrons and electron beams, and serve as the primary radiation detector in many fields [9,10]. Although the IP is used for many applications in fields such as radiography and non-destructive testing, this manuscript will focus on the use of IPs for X-ray diffraction.

The properties of the IP that make it so useful in the x-ray diffraction experiment are high sensitivity, low noise, wide dynamic range, good linearity, good-to-high spatial

resolution, no image distortion and large x-ray aperture. In the range of wavelengths suitable for x-ray diffraction the sensitivity is high as a result of the large absorption coefficients for barium, iodine and bromine, and the high conversion efficiency of the phosphor formulation. The dynamic range extends to nearly six orders of magnitude and is limited by the electronic circuitry used to extract the stored image, not the imaging plate itself. The linearity is better than 1% in modern instruments across the entire dynamic range. The IP is not subject to chemical fog, which is a problem for film, or dark current, which can be a problem for detectors using silicon (CCDs for example). Imaging plates provide spatial resolution in the range of 50 μm to 200 μm, which is well suited to the x-ray diffraction experiment. Imaging plates do not need corrections for spatial distortion or nonuniformity of response, which simplifies the detector system. Finally, the large apertures obtainable, 400 mm x 400 mm in an automatic system and 400 mm x 800 mm in a manual system, allow for many orders of Bragg reflections to be collected concurrently.

It was obvious the properties of imaging plates were well matched to the needs of structural biologists at synchrotron sources who needed to collect data quickly and accurately [11,12]. The first imaging plate detectors were manual devices. Shortly thereafter, automated systems were developed for use at synchrotrons [11,13,14]. These systems were capable of collecting data sets of more than 100 images unattended.

Once the imaging plate detectors were proven suitable for x-ray diffraction, several manufacturers began offering commercial versions suitable for use in the home x-ray laboratory [15,16]. This helped to fuel the explosion of structural biology in the early 1990s.

The physics of imaging plates

The process of x-ray exposure of an IP resulting in a latent image, readout, and erasure is shown in Figure 1.

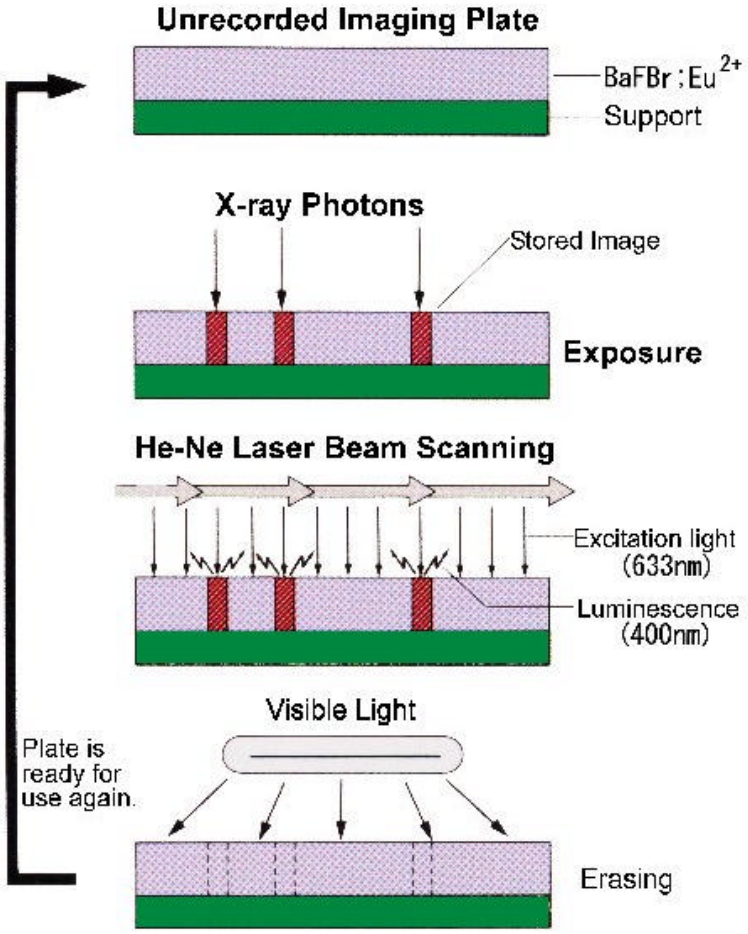

Figure 1. The process of recording an x-ray radiation image on an imaging plate, and subsequent read-out and erasure.

Step 1. Exposure to x-rays and creation of the latent image

An x-ray photon is absorbed by the phosphor matrix and the energy is transferred to a number of Eu^{2+} sites. Eu^{2+} is oxidized to Eu^{3+} and a photoelectron is ejected into the conduction band. The photoelectron becomes trapped in a lattice defect created by the absence of a halogen (F or X) counter ion. These vacancies are created during the manufacturing process and are called *F*-centers or color centers. The *F*-centers are metastable, and thermally activated spontaneous recombination of the trapped electron and the Eu^{3+} can occur [3,17,18]. This is called fading and is described by a complicated exponential function [12,17].

Step 2. Recovery of the latent image

Originally, HeNe laser light (λ = 632nm) was used to irradiate the IP to generate the photostimulated luminescence. More recently, laser diodes have become available in wavelengths (l = 658 nm) and power levels (> 20 mW) well-suited for use for reading out IPs. The visible light photons excite the trapped photoelectron in the *F*-center into the conduction band where it recombines with the Eu^{3+} in less than 0.8 μseconds, re-

leasing a visible light photon at l = 400 nm. This wavelength is sufficiently different from the excitation energy, Figure 2, that the two can be readily separated with interference filters or dichroic mirrors. The wavelength of the luminescence is well matched to the detection capabilities of bi-alkali photo-multiplier tubes (PMTs), which have a sensitivity range of about 300 nm to 600 nm.

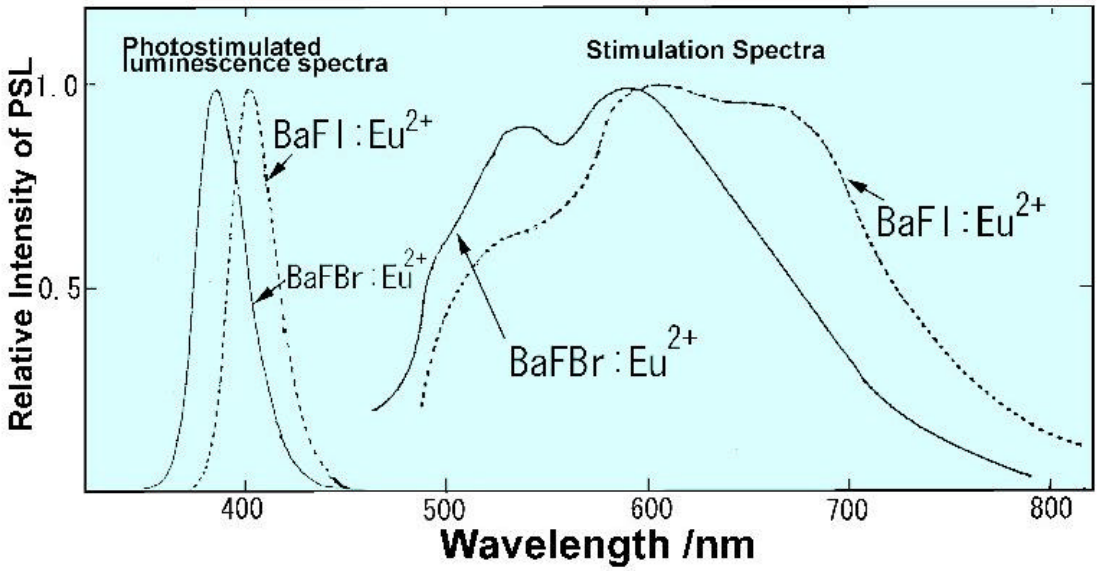

Figure 2. Photostimulated luminescence (PSL) spectra and stimulation spectra of $BaFBr:Eu^{2+}$ and $BaFI:Eu^{2+}$.

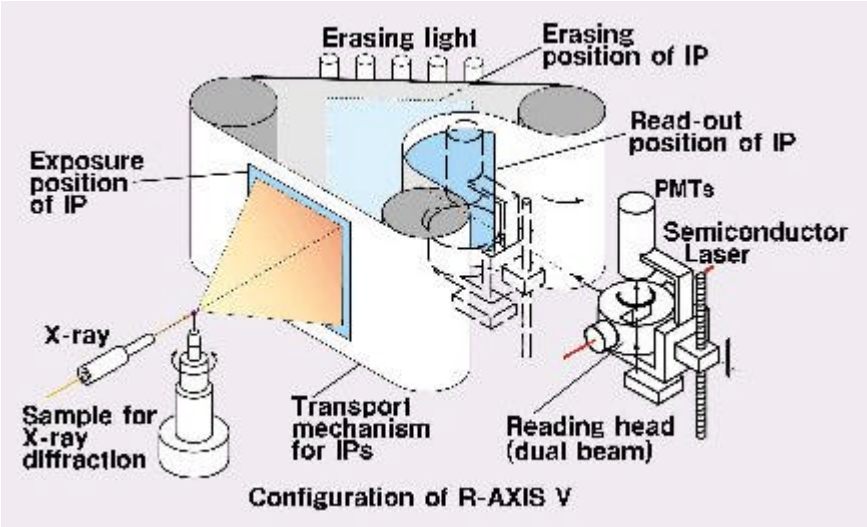

Figure 3. An example of an imaging plate system with three imaging plates. At any point during the diffraction experiment one imaging plate is in the expose position, another is in the read position and the last is in the erase position.

The readout process removes 80% to 90% of the stored image. In order to prepare the IP for reuse all the *F*-centers must be depopulated. This is accomplished by bleaching the IP with visible light whose spectrum has been adjusted to enhance this depopulation.

An example of a machine designed specifically for x-ray diffraction experiments at synchrotrons is shown in Figure 3. In this particular instrument, exposure, readout and erasure are performed on the three independent imaging plates simultaneously, maximizing data collection throughput.

In the example, shown the laser beam passes through the center of the read head and is deflected by a dichroic mirror into a condensing lens. The lens focuses the laser beam on the IP. The PSL is collected by the same lens and reflected away from the incoming laser beam by the dichroic mirror. A second mirror divides the PSL between two photo-multiplier tubes. This dual PMT system is designed to register both weak and strong signals and convert the PSL to an analog electrical signal with a dynamic range of 10^6. A high-speed analog-to-digital converter digitizes the data stream into an image. Modern detectors can extract a latent image as large as 400 mm x 400mm with 100 μm resolution in 50 seconds. After the image is read out, the IP is transferred to a position where it is erased and prepared for another exposure.

Advances in Imaging Plate Design

Diagnostic imaging dominates the use of imaging plates. Evaluation of these products in the context of performance for medical imaging is an active field [19]. The major manufacturers of imaging plates are Agfa, Fuji, Kodak, and Konica. Imaging plates produced by Fuji Photo Film IP have been found to be the most suitable for x-ray diffraction experiments.

Until 1989 the standard imaging plate was the BAS-II (HR-II) with the composition $BaFBr:Eu^{2+}$. In 1989, one of the authors received a batch of imaging plates that were found to be significantly more sensitive than previous batches. X-ray fluorescence analysis showed that approximately 15% of the bromine had been replaced by iodine [20], thus, the improved sensitivity was the result of increased absorption by the iodine. This serendipitous formulation of $BaFBr_{0.85}I_{0.15}:Eu^{2+}$ became the standard. In conjunction with reduction of the particle size to 5 μm, this new formulation allowed the thickness of the phosphor layer to be reduced to 100 μm while increasing the sensitivity by 50% for 8 KeV X-rays [21] providing the BAS-III imaging plate.

There is a second type of IP commonly referred to as the "blue IP" and is designated by Fuji as BAS-UR. This imaging plate provides much higher spatial resolution than the BAS-III. This IP gets its name from the bluish tint caused by a dye which is mixed in with the $BaFBr_{0.85}I_{0.15}:Eu^{2+}$ phosphor. The dye is used to absorb stray laser light reducing the spread of the photostimulated luminescence. In addition to the blue dye, the phosphor particle size is 5 μm further reducing the point spread function. If the BAS-UR imaging plate is used in conjunction with a 50 μm raster, a spatial resolution of 25 μm is possible with 8 KeV x-rays. The sensitivity to 8KeV X-rays for the BAS-UR IP is about 50% of that of the BAS-III IP.

The Use of Imaging Plates X-ray Diffraction

There are many examples of protein crystal structure analysis performed using data collected with imaging plates in the literature. Imaging plates have also found use in the

measurement of x-ray diffraction from fibers and polymers as well as x-ray topography of semiconductor materials.

Imaging plates can be used in-time resolved X-ray diffraction experiments. Such experiments are performed by taking an exposure, quickly displacing the IP a distance appropriate to the experiment, and repeating the exposure. In this way several data sets can be collected in rapid succession, tracking the time evolution of the changes in the sample [12,22].

An example of such an experiment is shown in Figure 4. The change in x-ray diffraction for a liquid crystal as a function of temperature is shown. As the temperature of the sample is cooled from 140° C, the structure changes from the isotropic phase to the smectic phase as evidenced by the formation of new powder rings [23].

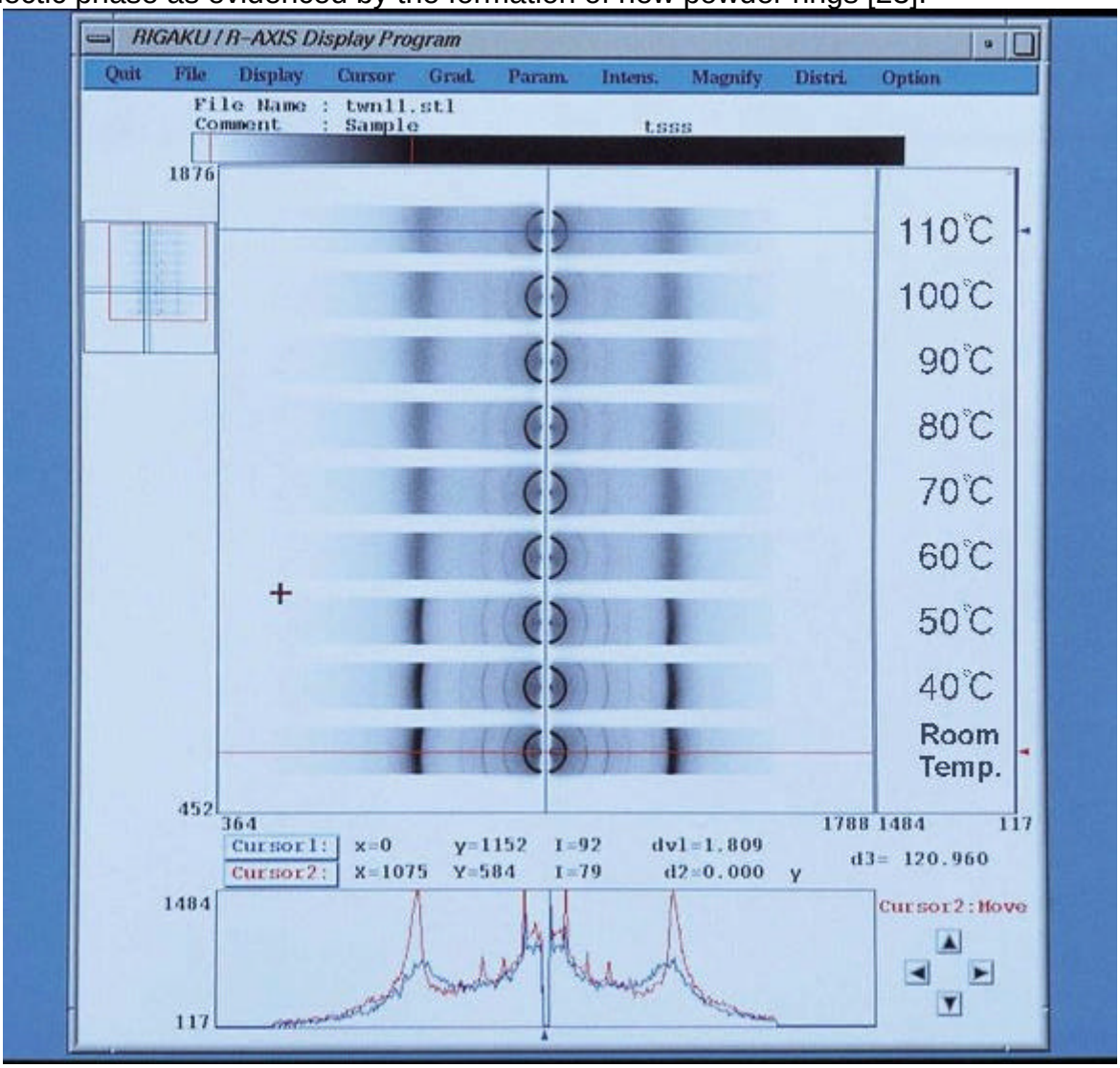

Figure 4. An example of a time resolved measurement with imaging plates. Observed is the structural change during cooling process of a high molecular weight polymer liquid-crystal sample.

Characteristics of Image Plates

Imaging plates are an integrating detector and the detector itself is the storage medium. They cannot be used for energy discrimination or in experiments requiring very fast readout.

Imaging plates can provide seamless apertures up to 400 mm x 600 mm.

Imaging plates are flexible. They can be exposed while curved in the Weissenberg geometry allowing for collection of data to very high resolution. The flexibility also allows them to be exposed in a flat position and read out in an efficient cylindrical format.

Imaging plates provide better than 2% error in spatial distortion or nonuniformity without correction. This is comparable to CCD based detectors with corrections.

Imaging plates have a dynamic range of up to six orders of magnitude giving them the capability to record very strong and very weak x-ray events concurrently and in close spatial proximity.

Imaging plates do not have significant signal accumulation (dark current) as a function of time. This means they can be used for long exposures. Imaging plates do accumulate cosmic ray events, but at a much lower rate than CCD detectors because the large mass of glass found in the taper used in CCD based detectors is absent. Multiple exposures to correct for these cosmic ray events are not necessary with imaging plates. Imaging plates have been shown to be less efficient for very short exposure times at very low exposure levels [24].

Imaging plates have a longer readout time as compared to CCD based detectors. However, imaging plate detectors are capable of concurrent expose and readout, or concurrent exposure, readout and erasure, making the duty cycle limited by the speed of the transport of the imaging plate from one position to the next. This makes imaging plate detectors very efficient in experimental regimes where the exposure time is tens-to-hundreds of seconds.

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References

[1] F. K. Fong and P. N. Yocom , J. Chem. Phys , **41** , 1383 (1964)
[2] J.L. Sommerdijk , J.M.P.J. Verstegen and A. Bril; J. Lumin., **8** , 502 (1974)
[3] A.L.N. Stevels and F. Pingault, Philips Res. Repts., **30**, 277 (1975)
[4] M. Sonoda , M. Takano, J. Miyahara and H. Kato; Radiology , **148** , 833 (1983)
[5] J. Miyahara and H. Kato; Oyo Buturi (Japan Applied Physics Society, in Japanese), **53**, 884 (1984)
[6] I.F. Chang , G.A. Sai-Halasz , J. Electrochem Soc., **127**, 2458 (1980)
[7] J. Gasiot, P. Braunlich, and J.P. Fillard, Appl. Phys. Lett. **40** , 376 (1982)
[8] K. Amitani, A. Kano, H. Tsuchino, and F. Shimada, Konica Tech. Rep., **1 ,** 120 (1988)
[9] C. Mori and A. Matsumura; Nucl. Instrum. Meth., **A312**, 39 (1992)
[10] M. Takebe; Oyo Buturi (Japan Applied Physics Society, in Japanese), **65** , 601 (1996)
[11] J. Miyahara, K. Takahashi, Y. Amemiya , N. Kamiya and Y. Satoh; Nucl. Instrum. Methods A246, 572 (1986)
[12] Y. Amemiya, N. Kamiya and J. Miyahara; Oyo Buturi (Japan Applied Physics Society, in Japanese), **55** , 957 (1986)
[13] N. Kamiya, Y. Amemiya and J. Miyahara; Journal of the Crystallographic Society of Japan (in Japanese), **28**, 350 (1986)

[14] A. Nakagawa; Journal of the Crystallographic Society of Japan (in Japanese), **32** , 274 (1990)
[15] A. Shibata; The Rigaku Journal, **7**, 28 (1990)
[16] I. Tanaka, M. Yao, M. Suzuki, K. Hikichi, T. Matsumoto, M. Kozasa, C. Katayama; J.Appl. Cryst. **23**, 334 (1990)
[17] R. H. Templer; Nucl. Instr. and Meth., **A300**, 357 (1991)
[18] M. Hoben , R. Schmechel, R. W. Henn and H. Seggern ; SPIE, **3768**, 280 (1999)
[19] C.D.Bradford, W.W.Peppler, J.T. Dobbins 3rd; J. Digit. Imaging, **12,** (Suppl.1), 54 (1999)
[20] S. Munekawa and T. Higashi; The Investigation Report about Imaging Plate (in Japanese), issued by Japan Synchrotron Radiation Research Institute(JASRI), p.235 (1992)
[21] K. Takahashi and J. Miyahara; Journal of the Crystallographic Society of Japan (in Japanese), **35**, 256 (1993)
[22] T. Fujimura, J. Shimomura, S. Gomi, M. Katayama, and Y. Kobayashi; Materia Japan (in Japanese) **43**, 783 (1995)
[23] K. Sasaki, H. Yamazaki, K. Masuda and G.-H. Hsiue; Advances in X-Ray Analysis, **37**, 385 (1994)
[24] N. Kamiya et al.; Abstract of the Annual Meeting of the Crystallographic Society of Japan (in Japanese), p.47 (1999).