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# Unexpected effects in non crystalline materials exposed to X-ray radiation

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## ABSTRACT

The interaction of high intensity synchrotron radiation X-rays in the energy range  $5 < E < 30$  keV with matter can produce a large number of expected and less expected effects. Whether these be considered radiation damage or are simply ignored, perhaps depends on the context or the eye of the beholder. In many cases however, X-ray induced effects can easily be mistaken for experimental results, and non-crystalline materials and liquids are most affected. We give a brief overview of possible X-ray induced effects, including structural changes and nanoparticle formation in glass, reaction rates in catalysis, the formation of bubbles in aqueous environments due to the presence of salts, and discuss possible mechanisms. The results shown are relevant for time-resolved processes studied by X-ray methods in catalysis, glass devitrification and for liquid samples.

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## 1. Introduction

Although X-rays are often viewed as a non-destructive and benign technique by the inorganic materials community compared to electron microscopy for example, where the materials under investigation are known to be damaged by the probe beam, some recalibration of this attitude may be required. The interaction of intense beams of synchrotron radiation based X-rays with a variety of materials has been found to alter the state of the materials. Damage is not only sustained to samples in static experiments but there is also evidence that X-ray interactions can change the dynamics [1], or even induce, structure forming processes [2–5], or influence the reaction rate of catalytic processes [6].

The fact that radiation damage can occur after exposure to X-ray photons in the 5–40 keV range is well known and probably most widely studied in the protein crystallography community [7–9]. Biological systems in buffer solutions [10–12] or even in the dry state [13] are also known to suffer. In synthetic polymers it has been observed that upon extended exposures to a monochromatic X-ray beam micro-Raman spectroscopy can be used to observe radiation damage [14]; even macroscopic parameters like the Differential Scanning Calorimetry signal reveal modification of the material as function of the X-ray exposure dose [15,16]. The occurrence of radiation damage, and the failure of experiments due to this, is likely to be much more widespread than the number of instances reported. Radiation damage due to electromagnetic waves is more obvious in some photon energy ranges than in others. In the Vacuum UltraViolet (VUV) wavelength range damage is often encountered [17–20] and even used as a fabrication method in lithography

[21,22].  $\gamma$ -rays are used as a method to induce cross linking in polymeric systems [23–25] or as a biological sterilization method which intrinsically implies radiation damage [26,27]. In this text we will limit ourselves to the photon energy range which is commonly used in techniques such as powder diffraction, X-ray absorption spectroscopy and SAXS/WAXS. Although exceptions can be found most of the experimental work using these techniques with X-rays takes place in the range  $5 < E < 40$  keV. In this energy range photons do not possess enough energy to induce atomic displacements directly in crystalline materials nor are they able to alter the position of an atom in an amorphous environment substantially. Any radiation effect observed will therefore be due to indirect effects such as electronic excitations, e.g. creation of colour centres, bond breaking, photo reduction etc.

Understandably most interest regarding the influence of X-rays on the structure of matter has historically been directed towards characterizing and mitigating the destructive aspects. Whilst theoretically it is feasible for every entity carrying energy to be involved in creating more ordered structures, i.e. reduce the enthalpy of a system, for X-rays there is little reported practical evidence. A single Nature manuscript dating to 1959 is the earliest evidence that we have been able to find [28]. These authors reported that radiation induced formation of sucrose crystals inside a raspberry flavoured Jelly-O matrix.

In recent years several cases have been found where the X-ray beams used in synchrotron radiation research have been the source of sample modifications in such a way that ordered structures have been created. It seems timely to make an inventory of these phenomena and try to ascertain if one can pin point some of the underlying mechanisms by which this structure formation is taking place. This is not a quest towards a commercial method of creating new materials via synchrotron X-ray beams. High intensity beams tend to be small and

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unsuited to treating large areas; any such process would be uneconomical. In this respect we note that for one of the few techniques with potential industrial manufacturing prospects, first described in 1991 [29] a manuscript dating from 2010 stated in the abstract 'Automation and enlargement of formats will reduce production costs for LIGA components and help LIGA technique for industrial breakthrough' [30]. Such a breakthrough period is in materials science research the equivalent of geological time scales.

However, it is important to see where one should be careful with data interpretation when unexpected structure formation or interference with chemical reactions during 'operando' style online chemical reactions takes place. X-ray induced changes are possible, not only in the case where high intensity broad wavelength spectrum (pink) beams are used, but also in the case of the highly monochromatic beams used in X-ray spectroscopy.

Our interest in structure formation due to exposure by X-rays stems from two consecutive experiments in glass ceramic formation which, in hindsight, can only be called failures with respect to the original aims of the experiments. The structure/ordering that was observed was not created by the heat treatments but by the combination of heat treatment and X-ray irradiation [31,32].

Here a brief overview of radiation effects, not focused on the damage aspect but more on the unexpected effects, is given with an emphasis on non crystalline materials exposed for an extended period to an X-ray beam. In other words, the conditions created when performing slow time-resolved X-ray spectroscopy or X-ray scattering/diffraction measurements in for instance devitrification or catalysis experiments. Literature surveys and our own experiences show that non-crystalline materials are vulnerable even when they are in the solid state.

We have deliberately avoided mentioning calculated or experimentally determined dose rates and avoided providing a full description of the effect of photon energy. The dose rates over which radiation interactions become observable is very wide ranging and the same is true for the photon energy dependence. This text should be considered as a warning that the irradiation during synchrotron X-ray experiments can induce physical and chemical changes in samples which are easy to overlook and misinterpret.

In the following text we have taken several examples and placed some emphasis on certain observable aspects of the interaction of X-rays with matter. We do not have the illusion that in these examples only the single phenomenon that we describe plays a role. All the effects like heating, electronic excitations etc. will be present at the same time but not all parameters that are influenced will be observable in that specific experiment.

There is also a philosophical aspect if some of the phenomena that are being observed should be classified as damage or not. For instance in an example that will be discussed later the formation of Pb nanoparticles due to irradiation is observed. The original Small Angle X-ray Scattering experiment was intended to follow the formation of PbS nanoparticles therefore the experiment can be called a failure. However, if no cross correlations with other techniques would have been performed the Pb particle formation could easily have been mistaken for the PbS particle formation. It is the intention of this manuscript to highlight the potential errors and misconceptions in the analysis of experimental results.

## 2. Beam interactions

### 2.1. Thermal effects

The interactions of radiation with matter have many different aspects and it is not the intention to provide a full oversight in this text. Instead we concentrate on some aspects that have been encountered in the study of non-crystalline solids and to a lesser degree liquids. The well known text book of Knoll [33] on radiation interactions and a

more recent publication by Leroy and Rancoita [34] are available for deeper surveys.

The absorption by X-rays in matter, and thus how much energy is deposited, is governed by the Beer-Lambert law:

$I_t(d) = I(0)e^{-\mu(\lambda)d}$  in which  $I(0)$  is the incoming beam intensity,  $I_t(d)$  the intensity as the X-ray beam has traversed a distance  $d$  through the sample and the factor  $\mu(\lambda)$  or  $\mu(E)$  the wave length dependent absorption coefficient with  $\lambda$  and  $E$  related via  $\lambda[nm] = \frac{12.4}{E[keV]}$ . The factor  $\mu(\lambda)$  is conventionally not provided but instead one tabulates the values for  $\frac{\mu}{\rho}$  ( $\lambda$ ) in which  $\rho$  is the material density. The inclusion of  $\rho$  reflects the fact that different morphologies of the same elemental composition can have different X-ray transmissions (e.g. diamond versus graphite). With the abundance of websites that allow one to calculate these factors rather easily it is sometimes easy to forget that the underlying basis for the absorption is determined by the number of electron-photon interactions and that therefore an on average more electron dense material will absorb more. For a composite material the total absorption factor can be determined as follows:

$$\frac{\mu}{\rho}(\lambda)|_{sample} = \sum_i \frac{w_i \mu_i}{w \rho_i}(\lambda)$$

in which  $w$  is the sample weight and  $w_i$  are the weight fractions of the different components.

In the energy range that we consider here the most relevant mechanism in which X-ray lose energy in a solid is the photo electric effect [33] (Knoll p54). This means that energetic photo electrons are created with energy  $E_{electron} = E_{photon} - E_{binding}$ , i.e. at maximum the original photon energy minus a small fraction.

Although the mean free path between collisions of electrons in the solid state is only of the order of nanometers, this energy is dissipated over a significantly larger distance as the electron loses its energy via a cascade of several inelastic collisions, in each of which new electrons are potentially liberated. Each photon absorbed by the sample creates a small transient 'cloud' of secondary electrons with a range of energies, with a diameter of approximately 4  $\mu m$ .

These photoelectrons are not energetic enough to cause direct atomic displacements but are capable of causing electronic rearrangements. X-ray absorption creates a mess of free radicals, colour centres, dangling bonds etc. What exactly is created and how long these effects persist depends on the sample and sample temperature. For instance it is well known that glass windows exposed to X-rays can turn brown nearly permanently due to the creation of colour centres but that these colour centres can be eliminated, and the glass returned to its normal transparency, by a simple heat treatment [35].

The situation with liquids is rather different compared to the solid state. The basic interactions, like the photoelectric effect, are the same but due to the nature of the liquid no lasting radiation damage is likely to occur. However, highly reactive radiolysis products can be created. These have a finite lifetime and a velocity which is determined by the diffusion processes. In the literature not much can be found on this topic. Details on the lifetime and path lengths of certain hydrolysis products can be found [36] and taking into account the diffusion speed and the finite lifetime one can expect to find these hydrolysis products in a sphere centered on the original absorption event with a radius of approximately 4  $\mu m$ .

In synchrotron radiation research it is common to boast about the power of the beams generated by third generation X-ray beams and discuss at length the effects of radiation damage. This often confuses referees.

In particular, synchrotron users tend to attribute more relevance than is realistic to thermal effects. Kazmierczak et.al. have used IR imaging to investigate synchrotron X-ray heating of millimeter sized glass beads cooled by a nitrogen gas cryostream and find both experimentally and theoretically a local rise of around 7C above room temperature [37]. Furthermore, their numerical analysis of localized synchrotron X-ray heating of spherical biocrystals shows that thermal diffusion results in efficient spreading of the energy and an almost uniform internal crystal

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