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Monte Carlo simulation of vacancies produced in lead-free piezo-ceramics by X-ray radiation damage

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This work presents the results of a simulation by the Monte Carlo method, performed through the GEANT4 code, of the irradiation and energy deposition by high flux X-rays on the piezoelectric ceramic Bismuth-Sodium Titanate doped with Barium. X-rays energies were around the Ti-K absorption edge emulating a transmission experiment, and the irradiation with 5300 eV X-rays for a fluorescence experiment. The method consists of introducing the data that describe a characteristic R3c structure of the polarized ceramic, reported in the literature. The absorption coefficients for the energies of interest, as well as the energy deposited in the form of radiation doses, are calculated. Intensity changes for specific energy lines in the micro-fluorescence spectra, which suggest the presence of vacancies in the crystal structure, are verified via simulation. The vacancy density produced by a typical photon flux of a fourth-generation synchrotron beam is calculated through the threshold displacement energy for vacancy production. Consequently, the simulation is carried out for a structure with appropriate Bi and O vacancies, and the ability to detect the radiation damage is verified by comparison with μ-XRF and XAFS experimental results. Simulation predicts a maximum dose of 1.21-1.27$\times 10^5$ Gy irradiating 10^7 photons for the given energy and a maximum vacancy density of 1.10$\times 10^8$ μm^{-3} for oxygen atoms, and 6.90$\times 10^7$ μm^{-3} for bismuth atoms.

Keywords: Synchrotron radiation; ferroelectrics; radiation damage; vacancies; Monte Carlo simulation

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1. Introduction

Fourth-generation synchrotrons, such as ESRF - EBS (European Synchrotron Radiation Facility - Extremely Brilliant Source), produce X-rays beams with huge intensities. This light is produced in pulses of very short duration, which allows experiments with high spatial, energetic and temporal resolutions. These X-rays can produce damage in samples with a medium atomic number during the experiments in the fourth-generation synchrotrons. These could be the case of experiments on ferroelectric materials.

Radiation damage in ferroelectrics is reported in the literature. Among the consequences of ionizing radiation damage is the production of vacancies. Most of the studies have been carried out in lead zirconate-titanate (PZT) and using intense beams of gamma-rays, whose energy is much higher, but the probability of interaction much lower than X-rays [1]. However, due to the toxicity of lead, restrictions have been imposed on the manufacture and use of this ceramic [2].

As an alternative, another ceramics have been suggested like the perovskite type $Na_{0.5}Bi_{0.5}TiO_3$ (NBT). A strong choice is the (1-x) ($Na_{0.5}Bi_{0.5}$) TiO_3 - $x$$BaTiO_3$ (BNBT100x), with a morphotropic phase boundary (MPB) in the range $0.05 \leq x \leq 0.07$ for its piezoelectric phase [3,4].

Ionizing radiation produce defects in two steps. First, they generate fast electrons through the photoelectric or Compton effects: then, these electrons in turn transfer energy and momentum to lattice ions [5]. The ionization and induced atomic displacements raise the defect's concentration, which implies changes in their threshold energy of formation and their physical properties.

Radiation damage depends on the energy deposited. The latter is expressed by the Absorbed dose, which is the concentration of energy deposited in the material as a result of a given exposure. The unit of absorbed dose is 1 Gray = Joule/kg.

Since the transport of ionizing radiation is a stochastic process and hence can be described completely in statistical terms, it readily lends itself to computer simulation. Physical cross-sections are directly represented by probability distributions and the use of random numbers enables us to sample from these distributions in order to simulate the cross-sections. Techniques which use random numbers in this way to simulate statistical processes are commonly called Monte Carlo methods [6].

Considering the possibility of higher radiation damage caused by fourth-generation synchrotrons, we do this research in which we estimate, via Monte Carlo simulation, the dose imparted by a fourth-generation synchrotron beam that could modify the sample. In order to do this, there were simulated the X-ray irradiation in a BNBT6 perovskite, in a photon energy range in the order of the K edge in Ti atoms. The dose calculated is used to estimate a maximum for the density of atomic vacancies in the sample.

2. Materials and methods

The energy deposition in the material was calculated using the toolkit GEANT4 for the simulation of the passage of particles through matter using the Monte Carlo method [7]. The physical models used were defined by the Livermore Electromagnetic Model for Low Energies. The information used for the determination of cross sections and for the sampling of the final state is extracted from a set of publicly distributed libraries of evaluated data. Interaction mechanisms included: photoelectric effect, Compton scattering, Rayleigh scattering, as well as atomic deexcitation via fluorescence and Auger electron emission. These effect are considered for elements with atomic number between 1 and 99, and for energies down to 10 eV; upper limit depends on the process [8].

In order to calculate the energy deposited in the material there were simulated two BNBT6 ceramic compositions. The first one with an ideal stoichiometric composition and density $\rho = 5.953$ g/cm^3. The second one emulating a structure with Bi-O vacancies with the stoichiometric composition $Bi_{0.41}Na_{0.47}Ba_{0.06}TiO_{2.91}$ and density $\rho = 5.563$ g/cm^3. Density was calculated with the software PowderCell for crystal structure manipulation [9] and using the BNBT6 data reported [3].

The atomic vacancy density simulated for Bi and O atoms was approximately 3 and 14%, respectively. The vacancy density for O atoms observed experimentally in [3] was 2%.

As a result of the Monte Carlo algorithm used by GEANT4, materials are modeled as amorphous. This means that the effects produced by a given crystal structure in an absorption spectrum are not reproduced in the simulation.

In order to run a simulation some input parameters are needed. These includes:

- The physics list which includes the physical models and interaction mechanisms, i.e. photoelectric effect, Compton scattering, Rayleigh scattering and electrostatic interactions.
- The particles to simulate: photons and electrons.
- The energy, shape and intensity of the incident photon beam.
- The geometry, composition and density of the materials involved.
- The threshold cut energy for particle production.

GEANT4 tracks the primary and secondary particles produced simulating all the possible interaction processes according to the material's cross section. The threshold cut energy is especially important because this parameter is the criteria that will terminate the track of a particle and therefore end the simulation. A particle with an energy lower than the threshold cut energy will not make any interaction.

Once these parameters are input, GEANT4 will model:

- If the photon interacts with the material and in what position.
- The atom with which the interaction occurs, if it is a composite material.
- The interaction mechanism.
- The electronic orbital for the interaction.
- The secondary particles produced: photons and electrons.

The output results include the transmitted fraction of the beam and histograms of the energy deposited in the material along the profile of the simulated sample.

2.1. Fluorescence experiment

The fluorescence experiment was performed simulating the irradiation of a 5300 eV on the BNBT6 target, in both compositions ideal and with vacancies, and measuring the fluorescence X-rays in a Si detector. Figure 1 shows a snapshot of the simulation where an incident beam of X-rays impacts a BNBT6 target producing secondary photons (green) and electrons (red).

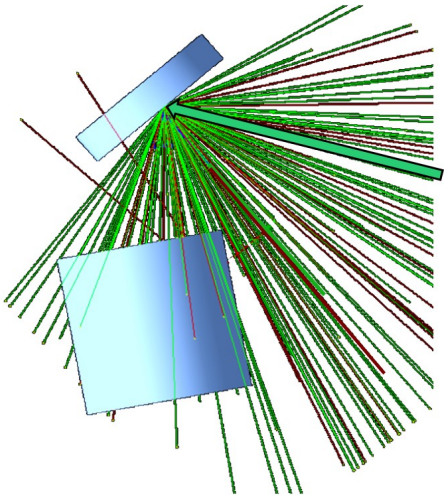

FIGURE 1. Simulation, obtained by GEANT4, of the experimental arrangement of the sample and the Si detector, of the irradiation with a X-ray beam and of the quanta resulting from the interaction. X-rays are drawn in green color and electrons in red. The green arrow indicates the incident beam.

The figure shows the incident beam of X-rays hitting the BNBT6 target and the deflected and emitted radiations in the deexcitation process.

2.2. Transmission experiment

For the transmission experiment it was modeled the BNBT6 ceramic with a 12 μm length and a $100 \times 100\,\mu$m^2 area. It was modeled the transmission for 8 different energies in the

range from 4900 to 5100 eV, corresponding to the Ti K absorption edge, 4966 eV. A scheme of the simulation is shown in figure 2.

In figure 2 it can be appreciated the path of the particles and the position where secondary particles are produced. As before, photons are drawn in green and electrons in red. If the incident photon beam energy is equal or higher than the absorption edge energy, most of the photons will be absorbed.

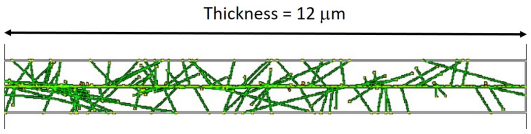

FIGURE 2. Simulated interactions of the X-ray transmission experiment in a BNBT6 target. X-rays are drawn in green color and electrons in red.

The simulation calculates the absorbed and transmitted fractions of the incident X-ray beam resulting from all interaction effects within the material. The energy deposited in the material by the interacting X-rays is accounted for further calculations.

2.3. Vacancy density calculation

The number of vacancies generated was calculated accounting the total energy deposited in the material (calculated by the simulation) and the threshold displacement energy (TDE) for vacancy formation reported by González, *et al.*, for the $BaTiO_3$ structure [10]. The TDE values reported for Ti, O and Ba atoms are 40, 97 and 64 eV, respectively. The energy value for Ba was used as approximation to model the Bi atom in BNBT6.

The maximum number of vacancies generated was calculated as follows:

$$\text{Number of vacancies} = \frac{\text{Energy deposited}}{TDE}\,, \qquad (1)$$

and the vacancy density as:

$$\text{Vacancy density} = \frac{\text{Number of vacancies}}{\text{Volume } [\mu m^3]}\,. \qquad (2)$$

The total energy deposited was estimated as an average accounting the average energy deposited per irradiation before and after the K edge energy of Ti. Average energy before the edge was multiplied by a factor of 32, average energy after the edge by a factor of 91, for a total of 123 energy steps from 4900 to 5100 eV, emulating a real life experiment of X-ray irradiation in a typical 3rd generation synchrotron facility.

The vacancy density was estimated accounting a volume of $1 \times 1 \times 12\ \mu m^3$. In the following results, this volume will be referred as a pixel.

3. Results

3.1. Fluorescence experiment results

Results for the fluorescence experiment are shown in figures 3 and 4, and in table I. Figure 3 shows the fluorescence spectra for the irradiation on the ideal composition BNBT6 while figure 4 shows the spectra for the BNBT6 composition with vacancies.

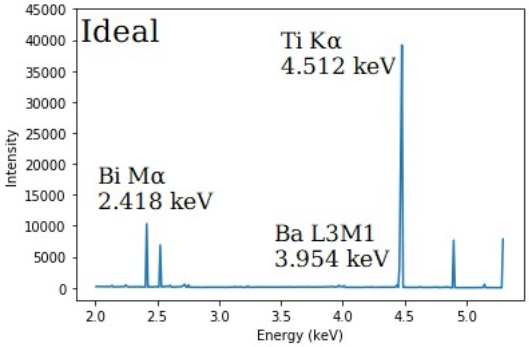

FIGURE 3. Simulated fluorescence X-ray spectra for the irradiation of 5×10^7 X-rays of 5300 eV on the ideal composition sample.

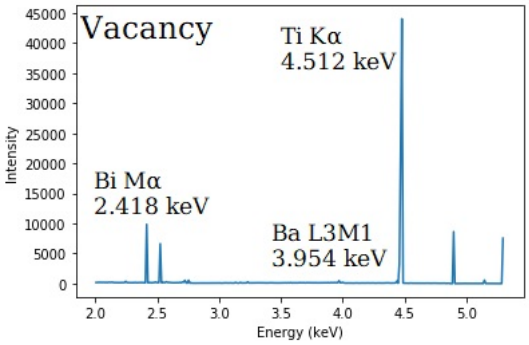

FIGURE 4. Simulated fluorescence X-ray spectra for the irradiation of 5×10^7 X-rays of 5300 eV on the sample with Bi-O vacancies.

Figures 3 and 4 reveals a higher intensity in the spectral lines of Ba and Ti, and lower intensity of Bi, in the sample with vacancies. Numerical data is shown in table I.

TABLE I. Fluorescence measurement simulation results for the irradiation of a beam of 5×10^7 X-rays of 5300 eV.

Spectral line	Energy (eV)	Counts	
		Ideal	With vacancies
Bi M_α	2414	$1.03(1)\times10^4$	$9.86(10)\times10^3$
Ba L_3M_1	3969	$4.27(21)\times10^2$	$4.89(22)\times10^2$
Ti K_α	4475	$3.92(2)\times10^4$	$4.40(2)\times10^4$

These results are in agreement with the experimental intensities detected and reported in [3] and they verify the interpretation about the Bi-O vacancies presence as the cause

of the differences in the Ti, Ba and Bi fluorescence lines intensities.

3.2. Transmission experiment results

Table II shows the beam fraction absorbed by the BNBT6 sample with ideal composition, and the number of X-rays which deposit their total energy in the absorber. It can be appreciated the intensity jump in the step from 4940 to 4960 eV, corresponding to the Ti K edge.

TABLE II. Beam fraction absorbed in a 12 μm sample of BNBT6 with ideal composition for the irradiation of 1×10^6 X-rays.

Energy (eV)	Ideal composition	
	Absorbed (%)	Counts ($\times10^5$)
4900	38.42	3.83(6)
4920	38.07	3.79(6)
4940	37.73	3.76(6)
4960	92.82	8.38(9)
4980	92.64	8.36(9)
5000	92.47	8.35(9)
5050	92.03	8.31(9)
5100	91.55	8.26(9)

The "Counts" column was used to build a graphic of the absorption coefficient as a function of the energy, as it is shown in figure 5. There were performed simulations with smaller steps of energy but the linear behaviour remains, verifying the fact that GEANT4 does not simulate the crystal structure features of a material.

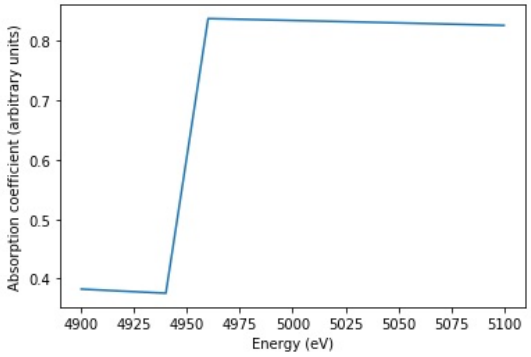

FIGURE 5. Simulated absorption coefficient for the BNBT6 sample with ideal composition.

3.3. Estimated vacancy density

The energy deposited before and after the edge, in the measured range of energies, is very similar in each segment. The average of these energies is used to calculate the total energy and dose deposited in the material, as is shown in tables III and IV for the irradiations of 10^6 and 10^7 X-rays per step, respectively.

TABLE III. Energy and dose deposited in BNBT6 samples. Irradiation of 10^6 X-rays per step, in a range of 4900 to 5100 eV in 123 steps and a volume of $1 \times 1 \times 12$ μm^2.

	10^6 X-rays	
	Ideal	With vacancies
Energy (keV) deposited in 12 μm	5.42×10^6	5.30×10^6
Dose deposited in 1 pixel (Gy)	1.21×10^4	1.27×10^4
Dose deposited in 1 pixel (Mrad)	1.21	1.27

TABLE IV. Energy and dose deposited in BNBT6 samples. Irradiation of 10^7 X-rays per step, in a range of 4900 to 5100 eV in 123 steps and a volume of $1 \times 1 \times 12$ μm^2.

	10^7 X-rays	
	Ideal	With vacancies
Energy (keV) deposited in 12 μm	5.42×10^7	5.30×10^7
Dose deposited in 1 pixel (Gy)	1.21×10^5	1.27×10^5
Dose deposited in 1 pixel (Mrad)	12.1	12.7

The simulation predicts a deposited dose in a range between 1.21 and 12.7 MRad, which is consistent with the measurements performed in piezoelectric materials irradiated with X-rays and reported in the literature [1]. According to Brewer, *et al.*, this dose might produce degradation in perovskite type piezoelectric materials. The deposited energy was used to estimate, by equations (1) and (2), the number of vacancies per mass unit and the vacancy density expressed in %, as is shown in tables V and VI.

This estimate of vacancy density assumes that all energy is expended in the single process of creating atomic vacancies, so it should be treated as an upper bound. This means these calculations does not account energy used to produce another type of vacancies or heating in the sample, as well as it does not account recrystallization.

The results of Table VI for the irradiation of the BNBT6 ceramic with 10^6 X-rays per step can be compared with the results of the vacancy calculation corresponding to the Bi-depleted zones of Canche-Tello, *et al.* [3]. The Monte Carlo results are consistent with those obtained there for the vacancy density of Bi-O.

TABLE V. Estimated maximum new oxygen vacancy density in BNBT6 samples. Irradiation of 10^6 and 10^7 X-rays per step, in a range of 4900 to 5100 eV in 123 steps and a volume of $1 \times 1 \times 12$ μm^2.

	O vacancies [μm^{-3}]	
	Ideal composition	Composition with vacancies
10^6 X-rays	1.13×10^7	1.10×10^7
	0.0050%	0.0053%
10^7 X-rays	1.13×10^8	1.10×10^8
	0.050%	0.053%

TABLE VI. Estimated maximum new bismuth vacancy density in BNBT6 samples. Irradiation of 10^6 and 10^7 X-rays per step, in a range of 4900 to 5100 eV in 123 steps and a volume of $1 \times 1 \times 12$ μm^2.

	Bi vacancies [μm^{-3}]	
	Ideal composition	Composition with vacancies
10^6 X-rays	7.06×10^6	6.90×10^6
	0.041%	0.043%
10^7 X-rays	7.06×10^7	6.90×10^7
	0.41%	0.43%

This does not mean that this beam intensity causes that vacancy density in the ceramic. The result of the beam intensity of 10^7 X-ray per step, however, is proportionally higher and it could indicate the production of radiation damage in a study sample, and the corresponding complication of the interpretation of experimental results produced with high-intensity beams like those of fourth-generation synchrotrons.

4. Conclusions

Third-generation synchrotrons can damage and "burn" low atomic number compounds, like organic samples [11]. Higher beam intensities, like the produced by a fourth-generation synchrotron, could produce significant damage in medium atomic number compounds, as are the constituents of most piezoelectric materials. This work shows that Geant4 code for Monte Carlo can be used for the study of radiation damage in perovskite type materials.

Through fluorescence modeling for stoichiometric and vacant BNBT6, it was verified that the anomalous regions reported by Canche-Tello et al. [3] indeed they correspond to vacancies of Bi-O.

The energy deposited and absorbed dose in the 12 μm thickness and 1 μm^2 cross-sectional area were calculated. A dose of 1.21-1.27 $\times10^4$ Gy was obtained for fluxes of 10^6 photons, and proportionally for 10^7. These results are consistent with those reported from the experiments.

Using the reported values for the atomic displacement energy for O and Ba, the vacancy density generated by a third-generation synchrotron beam was calculated. The results are of the same order of magnitude as those observed experimentally by Canche-Tello, *et al.* for the vacancy density of Bi-O.

Modeling predicts that more intense beams will cause a higher vacancy density and considerably more significant degradation. Therefore, the damage that a fourth-generation synchrotron could produce in medium atomic number, like perovskite type piezoelectrics materials would be significant.

5. Acknowledgments

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