It was recently demonstrated that application of a moderate electric field (E-field) at elevated temperatures modifies structural, electrical, optical, and other properties of a vast majority of crystalline and polycrystalline materials effectively turning them into new materials. For example, when a $\sim$100 V/cm E-field is applied to a single crystal of rutile TiO_2, and it is very briefly heated far above room temperature, its electrical conductivity increases dramatically and it begins to glow in an electroluminescence (EL) like phenomenon described as "flash" [1]. Materials revert to their original state when the E-field has been removed, but the new state can be effectively frozen in via a liquid nitrogen quench. EL in polycrystalline materials was originally attributed to Joule heating at grain boundaries [1], but the discovery of EL in single crystals casts doubt on this model, revealing that little is understood. This is a very active area of basic science as well as technology (e.g. ceramics sintering). The discovery paper has been cited nearly 1000 times [2], 100's of papers have already have been published, and many patents issued in the last 15 years.

There are two main challenges in this field: (i) to understand the underlying microscopic mechanism and (ii) to learn how to harness it to create new materials. Both will be addressed in the proposed project where we aim to investigate the effect of EL under the E-field as well as under a combination of the E-field and magnetic field (B-field) on materials with great scientific and technological importance: relaxor ferroelectrics ("relaxors"). Relaxors exhibit strongly frequency and temperature dependent dielectric properties; this behavior is believed to be related to "short ranged polar order" (SRPO) itself due correlated ordering of the ions in the crystal. Relaxors form polarized domains that respond non-trivially to applied fields: the field response makes them novel candidates to study under EL conditions.

To understand the local ordering and its response to applied fields, we plan to probe the crystal at the atomic scale by neutron diffuse scattering. Diffuse scattering provides a huge volume of extremely complicated data ("big-data") requiring the use of advanced analysis tools and simulations. Moreover, the only way to make sense of the physics encoded in the data is with novel computational models: the physics we aim to study involves an interacting system of electrons, photons, and phonons driven far from equilibrium. Modelling this phenomenon will require the use and development of cutting-edge tools (cf. the *Computational Materials Science* program). We propose to use a hybrid approach combing the big-data from neutron diffuse scattering (NDS) with advanced computational methods to study the EL state in the classic relaxor PMN-PT. Precisely what advanced computation tools are needed (density functional theory, molecular dynamics simulations, Monte Carlo, many body methods, etc.) will remain unknown until the local structure of the EL state is understood: this is our first goal.

With the technical help from the SNS engineering team, we have already designed and commissioned an apparatus for *in situ* NDS measurements of samples under controlled E-field and high temperatures at the CORELLI diffractometer. CORELLI combines the high efficiency of white-beam Laue diffraction with energy discrimination, which enables users to measure both elastic scattering and total scattering signals from a single experiment over large volumes of reciprocal space, with sufficient Q resolution to distinguish the diffuse signal from strong Bragg peaks.

The first set of measurements using this *in situ* apparatus on a prototypical "flash" material, rutile TiO_2, has already completed and the analysis/simulations are well under way (Fig. 1). The original hypothesis for the mechanism of EL in TiO_2 was based on a formation of Frenkel pairs where oxygen atoms jump into interstitial sites [1]. However, our simulations based on this model predict broad diffuse scattering shoulders (Fig. 1**c**), whereas the experiment shows "porcupine"-like structures with long needles in reciprocal space implying planar dislocations (Fig. 1**a**). Our

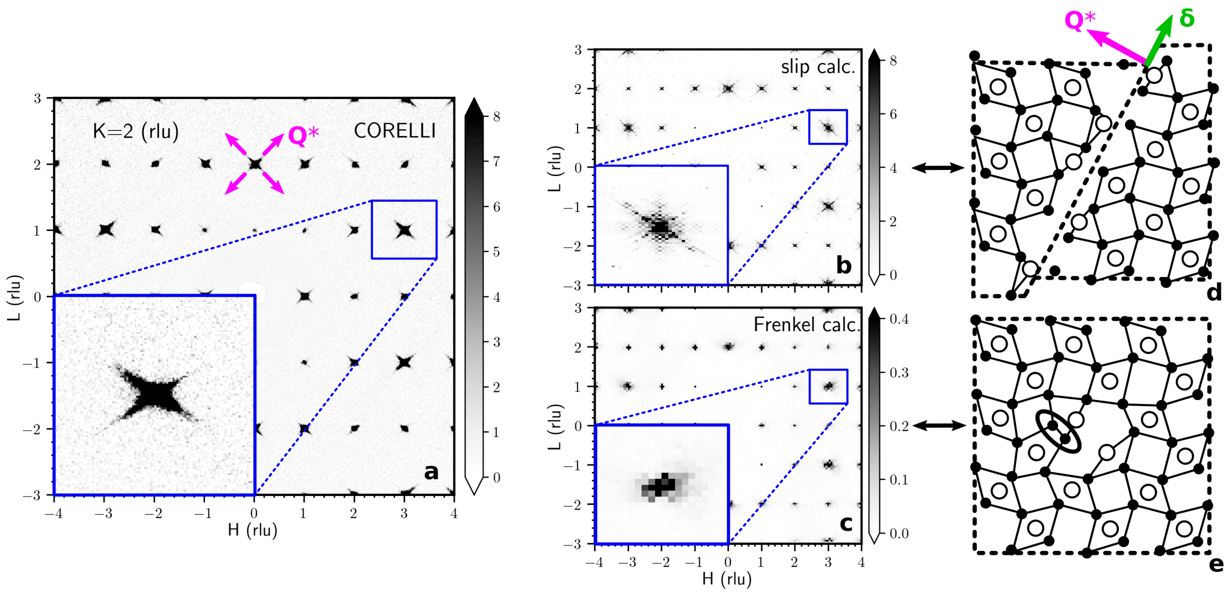

Figure 1: Quenched electroluminescing rutile TiO_2 measured on CORELLI **a** compared to calculations with planar slip defects **b** and with oxygen Frenkel defects **c**. Only the slip defects reproduce the needles seen in the NDS experiment. **d** A cartoon diagram of a slip defect in TiO_2. **e** A cartoon of an oxygen Frenkel defect. The atoms relax contributing the broad scattering in **c**.

new calculations based on planar defects describe the experimental data well (Fig. 1**b**). The next step is to understand the effect of these dislocations on bulk properties as well as the origin of their formation: we will use computational modelling where Tyler C. Sterling has expertise. The work on TiO_2 proves the feasibility of this proposal and can be considered as a “seed” of a much broader and deeper effort.

This proposal is also based on another recent development. Our collaborators at the University of Colorado (Raj group) have discovered a “proximity effect”: an electroluminescing sample under applied magnetic field ($\sim$ 0.05 Telsa) induces EL of another piece of ceramic crystal placed in close proximity (patent pending). This discovery points to a way to use EL to manipulate samples to which electrical leads cannot be attached (e.g. rapid sintering of dental crowns is under development). Development of an *in situ* apparatus that allows simultaneous application of a moderate B-field with the E-field with temperature from 100 K to 750 K is expected to be complete by the start of the fellowships. The sample environment upgrade will make it possible perform *in situ* experiments under simultaneous E and B-fields on CORELLI and other neutron scattering instruments at the SNS. Tyler will then use these new capabilities for *in situ* experiments on relaxors.

It has been definitively shown that polycrystalline $BaTiO_3$ based relaxors can enter the EL state [3]. However, no *in situ* analysis of the EL state has been carried out nor have there been any EL experiments on single crystal relaxors. Compared to the previous *in situ* experiments, the EL conditions introduce significant yet controlled structural defects, which can be quenched by immersion into LN_2. The work we propose will investigate a classic, commercially available relaxor PMN-PT. We will require $\sim$7 days of beam time at CORELLI (coordinated by the collaborating scientist Dr. Feng Ye) for the NDS experiment. The experiment (and its analysis) can be divided into 3 conceptual stages that are aimed to address the following specific scientific problems:

(i) **“Reference” material:** previous NDS experiments have revealed several different features that correspond to different types of local order. Most have only looked at one of the features, the "butterfly," in a small subset of reciprocal space ("Q-space"). Recent experiments by Dr. Feng Ye and collaborators [4] showed that the features vary in an unexplained way in other parts of Q-space and that the "butterfly" scattering is uncorrelated with relaxor behavior. Both of these discoveries exemplify the need to look at a larger volume of Q-space to understand the ground state of relaxors. Other (non-EL) experiments under applied E-field [5] have shown how the diffuse scattering responds to E-field: this puts important constraints on a valid model for SRPO. However, the studies under applied field have looked mainly at the butterfly in small regions of Q-space. By measuring and simulating a larger volume of Q-space outside of the EL state, we will gain new insights into the normal nonluminescing phase and establish a necessary "reference" with which to compare measurements in the EL state.

(ii) **EL under E-field:** the EL state represent a dramatic change from the normal state: there are drastic changes to many properties, effectively resulting in a new phase of matter that is stabilized under non-equilibrium steady state conditions. To understand the nature of this phase, we first need to understand its local structure. We will do this with *in situ* NDS and modelling: the proposed experiment on CORELLI will measure a huge amount of Q-space with excellent resolution. Modelling these data will solve the local structure as was already done in TiO_2 in Fig. 1. Then we will develop computational models for the non-equilibrium many body processes involved in EL.

(iii) **EL under simultaneous E and B-fields:** Our collaborators found that even a small B-field on a sample in the EL state has a measurable and nontrivial effect on bulk properties, but little is known about how it modifies the local structure. With the apparatus proposed above, we will be able to investigate the non-equilibrium effects on the atomic structure directly via *in situ* NDS experiments. Based on observed changes to bulk propereties we expect to see a new behavior when the B-field is applied. The response of the local order will be apparent in the *in situ* NDS experiments, providing another angle from which to study the EL state and the non-equilibrium processes involved in its formation.

We estimate that about 6-8 days of beamtime (1 day to set up + 12 hrs per run, with runs with no field, E-field alone and combination of E and B-field) will be needed. These will be scheduled near the beginning of Tyler's stay. Then Tyler will work with Dr. Feng Ye and others to develop and use computational tools necessary to solve the local structure and go beyond. We hope to make tremendous progress on understanding the non-equilibrium physics of the EL state in relaxors.

This work will be central to Tyler C. Sterling's doctoral dissertation: *Physics of Energy Materials Investigated by Neutron Scattering*. Already several related projects have been completed. Some have required inelastic neutron scattering, some neutron and xray diffuse scattering, and all of them have included computational modelling. The work outlined in this proposal will combine existing tools and skills with newly developed instrumentation and models to explore both the basic physics and properties of non-equilibrium EL in relaxors. This latter work will be the main focus of Tyler's dissertation.

[1] Bola Yoon et al. In: *Journal of the American Ceramic Society* 101.5 (2018), pp. 1811–1817.

[2] Marco Cologna, Boriana Rashkova, and Rishi Raj. In: *Journal of the American Ceramic Society* 93.11 (2010), pp. 3556–3559.

[3] Ahmed Taibi et al. In: *Ceramics International* 47.19 (2021), pp. 26947–26954.

[4] Matthew J Krogstad et al. In: *Nature materials* 17.8 (2018), pp. 718–724.

[5] Guangyong Xu et al. In: *Nature materials* 5.2 (2006), pp. 134–140.