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Energy dependence of radioluminescence spectra from strontium titanate

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Abstract: X-ray excited luminescence spectra of strontium titanate are reported over the temperature range from 20-300 K. The range includes several crystalline phases, each with different emission spectra. The signals are thermally quenched above ~220 K. There are spectral shifts and intensity changes around the temperatures associated with phase changes and overall there are nominally three spectral emission bands. A remarkable observation is that at fixed lower temperatures the spectra undergo major changes with the energy of the X-rays. A possible cause of the effect is discussed in terms of inner shell excitation from the K shell of the strontium. Comparisons with thermoluminescence spectra from the strontium titanate are reported.

Keywords: radioluminescence; SrTiO₃; low temperature phase changes; X-ray energy dependence;

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1. Introduction

Strontium titanate SrTiO₃ (STO) is a perovskite structure oxide and it is an insulator with an indirect band gap [1]. The material has been widely studied with report on properties ranging from quantum paraelectricity [2, 3], photo-excitation [4] and photo-induced phenomena [5, 6]. Doped STO shows low temperature superconductivity [4] and an insulator-metal transition [7]. The crystal is used as a substrate material for epitaxial growth of high temperature superconductor film [8, 9].

The various results are complicated by the fact that the structure can undergo a number of low temperature phase transitions, some of which are very sensitive to trace impurities, stress or defect properties[10, 11]. Therefore not all transitions are apparent in every sample or detection method. Variability in STO responses is thus most obvious at low temperatures. Around 38K, the STO crystal experiences a transition from a classical to a quantum paraelectric state [2, 3]. Moreover, there is a well documented phase transition from cubic to tetragonal at 105K, as noted by optical [12], X-ray diffraction [13] and calorimetric studies [14]. In optical studies with T<Tc of this phase change there are more complex responses than in the high temperature regions.

Luminescence techniques are sensitive and responsive to phase changes, intrinsic defects structures, impurities and stress as evidenced by the literature using photoluminescence (PL), cathodoluminescence (CL), radioluminescence (RL) and thermoluminescence (TL). Nominally stoichiometric STO shows no PL emission signal at room temperature, but it both exhibits green (~540nm) and near infrared (~800 nm) signals in the low temperature range [15-17]. However, blue CL and PL appeared at room temperature when STO is irradiated by an Ar⁺ ion beam [18]. Nevertheless, after thermal annealing STO thin films have generated PL at room temperature [19]. The benefits of using luminescence techniques in the detection of phase transitions has been considered for many materials with reviews such as [20-22] and specifically addressed to STO with RL [23], CL [24] and TL [25] plus studies of other bulk changes induced by surface implants [22, 26].

The phase transition responses detected in STO differ slightly from those reported in many other materials in that for "normal" first order phase transitions they are precisely defined at a specific temperature (albeit with hysteresis). By contrast, both optical and other techniques used with STO show a signal gradation over a small temperature range, rather than a step change. For STO they are described as second order phase transitions. This may be consistent with the fact that they are sensitive to stress and impurities. Since neither type of distortion of the lattice will be uniformly spread through the crystal (i.e. there are preferential associations of imperfections [27]) the lattice will progressively change phase at the perturbed lattice zones. This is consistent with the literature that not all phase relaxations are reported in all STO experiments. The suggestion is also compatible with the observation that the PL signals change near 70 K [12], but the intensity change is much less cleanly defined when the crystal is simultaneously illuminated with red light, and hence has defects in different excited states and with electron interactions over a different local volume of ions within the crystal.

The result of such defect associations and variations means it is difficult to exactly specify the defect structures, and hence the precise sources of the luminescence emission bands. It also implies that the earlier simplistic models for the energy levels of defect sites located uniquely within the energy band diagram are too simplistic. Similarly the concept that defect sites were tightly localized is now outmoded, and there are many examples of long range interactions [27, 28]. Overall this leads to suggestions that imperfections and heterostructures all play a crucial role. Models such as the association of the broad emission bands to self-trapped - exciton transitions are controversial, although discussed by different groups [29, 30]. Note that the red emission bands, as reported here and elsewhere, may have much finer component structure [14] when resolved with better spectral resolution.

2. Experimental

Nominally pure $SrTiO_3$ samples oriented with (100) faces were used. They were produced by Hefeikejing Materials Technology Ld. Co .China. The sample size is $10 \times 10 \times 0.5$ mm. One side of the

sample has been polished. All the measurements have been carried out with the polished side facing the X-ray source, and also facing the spectrometers.

A high sensitivity luminescence system at the University of St Andrews was used to collect RL excited by X-rays at low temperature. The nominal voltage of the X-ray generator was varied between 13 to 20kV because there are unexpected changes associated with the energy of the X-rays. The optics of this spectrometer had been reported previously from its construction at Sussex [31] but significant modernization improvements in detectors and time resolution are now available after relocation to St Andrews. After data collection the signals were processed to correct for the wavelength sensitivity of the spectrometer and detector system. Only corrected spectra are presented here. Note that the wavelength multiplexing allows spectral resolution within a temperature range of about one degree even during linear temperature ramping.

Thermoluminescence (TL) measurements were also performed over the same temperature range and heating rate as for the RL. For the TL the initial radiation treatments were with an X-ray radiation dose of 150 Gy at 20 K.

The low temperature stage was operated from 20 to 300 K with a heating rate of 6 K/min. The low heating rate ensured that the monitored temperature was matched by the surface of the sample. One should note that the commonly used higher rates employed above room temperature in many dosimetry measurements are acceptable for dosimetry but result in major temperature gradients and misinterpretations of the glow peak temperatures [32]. The problem was avoided in the current work.

3. Results

RL signals were collected during X-ray irradiation whilst the sample was heated at a constant rate. The spectral data thus offer a three dimensional overview of intensity versus wavelength and temperature. The unexpected feature is that these spectra vary remarkably with the X-ray energy and data are presented in figure 1 for the energy values of the X-ray generator set at nominal values of 13

kV, 15 kV and 20 kV. For simplicity these will be discussed in terms of three broad emission bands of "infra-red" (~800 nm), "green" (~570 nm) and "blue/green" (~500 nm). The fig. 1a to 1c show that each zone has several components and they vary with temperature. As for the earlier literature the infra-red emission zone is very narrow, but the other two are broader. In this work only the red feature is seen for low energy X-ray excitation and this has almost vanished for the 20 kV X-ray setting. Whilst these are the same components reported in [23], in that example only high energies were used and then the signal for the "pure" material was totally in the red region. Nevertheless, all the other features emerged in material stressed by surface ion beam implantation.

The other clear features are that each of the component bands has totally different temperature responses. Further, when the green and blue bands are present, the red signals are almost totally suppressed at those temperatures. The same behaviour was noted earlier [23]. The current evidence for this is apparent from both the contour maps of figure 2 and the spectral slices of figure 3. At the lower temperatures there are many more differences in detail that are apparent with higher magnification of the data. Examples selected here are for temperature slices at 20, 50 and 70 K in figure 3a to 3c.

Examples of the differing temperature dependences in three spectral regions are contrasted in figure. 4. Finally, figure 5 contrasts the RL spectra at three different temperatures all taken under identical X-ray irradiation conditions with an X-ray energy of 20 keV.

The preceding data show the temperature dependence of the RL signal and for comparison the spectral dependence of the thermoluminescence of the sample irradiated with 20 kV X-rays is presented in figure 6. In this case the luminescence signals are totally confined to emission in the red region, but a number of component glow peaks are revealed, notably with a strong feature near 70 K (i.e. where a phase transition is cited in STO). There are small variations between the spectra at each peak. Very similar patterns were noted previously [25] both for unimplanted and implanted material (i.e. stressed).

4. Discussion

There are several interrelated factors to consider in the data. The first is that the material has the potential to relax into different structural phases and consequently the emission spectra will differ in each phase. Secondly the earlier literature suggests that the relaxation processes are driven not just by temperature changes, but also by stress and/or impurities. There is also luminescence evidence that the transitions are influenced by the density of excited states, or even suppressed by simultaneous illumination with red light [8].

The detailed origin of the emission is unclear and the early suggestion by Feng [8] was that it involved chromium impurities since he noted a number of closely spaced red emission lines produced from the lowest temperatures up to around 220 K. Nevertheless the red emission is characteristic of every sample, independent of origin, and is seen in each type of excitation from PL, RL, CL to TL, and is normally the dominant feature. Consequently other models for the red emission include a recombination state ~ 1.58 eV below the conduction band and/or a link to a bound exciton state [8, 12].

Phase related spectral changes were summarised in [24] to suggest transitions near 16, 25, 35, 65 and 105 K. Precise values differ between sources, method of detection and excitation. Overall this implies that assignments of the numerous emission components are highly speculative. Additional difficulties arise as the "sharpness" of the phase related changes (as seen by the emission signals) are influenced by the excitation conditions (i.e. the relative concentrations of electrons and holes or preferential depletion of traps by simultaneous optical stimulation) [16, 29]. Overall this implies that the emission is best discussed in terms of signals from each phase, rather than attempting a global overview across a wide temperature range.

Fig. 1 indicated that the relative importance of each phase, and ionisation conditions, is a strong function of the X-ray energy. There are of course many examples of colour centres which have several component emission bands and on changing the X-ray energy or intensity there are resulting shifts

between the intensities of the different emission features. However, figure 7 reveals very clear and unexpected energy dependencies for signals from different phases. At the lowest temperatures used here (20 K) there is a totally different pattern on moving from X-ray energies of 16 to 17 keV (figure 7a). Not only does the red signal reduce at the higher energy but also a totally new blue-green emission band is dominant.

The example in figure 7b for the higher phase around 50 K is less dramatic from 400 to 750 nm, but nevertheless it is extremely effective in terms of suppression of the red emission (>750 nm) on moving from 14 to 15 keV energy X–rays. It appears there is a competition between alternative decay routes and emission in these two spectral regions.

Since the X-ray set is operated at a fixed current the radiation intensity increases with the voltage setting. One therefore expects the overall intensity to increase, and in situations with competition between different emission bands, a change in relative intensities is feasible. This is a very different pattern from the observed intensity step function noted between energies of 16 and 17 keV. Our proposal is thus to suggest that this is feasible because the higher energy X-rays are able to stimulate excitation from inner shell levels of strontium. The strontium K shell sits at 16.1 keV, so not only can the higher energies offer a step function in the excited electron density, but they also generate a range of deep hole states. Overall this offers the possibility of higher energy photon transitions from the conduction band to recombination levels (e.g. as seen in the 20K RL spectra contrasting the 16 and 17 keV energy X-rays).

For the higher temperature phases there are again spectral changes with X-ray energy (and dose rate) but these are more conventional and do not require a step function model.

5. Conclusion

These new data on radioluminescence signals from strontium titanate crystals at low temperature confirm that the material is undergoing a range of phase relaxations, each of which has its own

characteristic emission signals. The totally new observation of a discontinuous intensity change with Xray energy is consistent with a model of electron excitation from the inner shell of the strontium ions in the lattice.

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Figure captions

- Figure 1 On the left side are the three dimensional views of low temperature RL of STO, and figure 2 (on the right hand column) shows the contour plots. The three X-ray energies are (a) 13 keV, (b) 15 keV and (c) 20 keV.
- Figure 3 RL spectra from STO at different temperatures (a at 20 K, b at 50 K and c at 70K) as a function of X-ray energy (13 keV, 15 keV and 20 keV).
- Figure 4 Integrated intensities of RL emission bands with temperature for two different X-ray energies (a) for 15 keV and (b) for 20 keV.
- Figure 5 RL spectra from the same sample of STO at 20 K, 50 K and 70 K with an X-ray energy of 20 keV.
- Figure 6 TL from STO with resolved red peaks near 29, 78, 120 and 170 K (a) is a 3D plot, (b) is the contour map and (c) is a glow curve for infra-red emission band.
- Figure 7 An RL spectra from STO which demonstrate how the X-ray energies define the emission components. The examples are (a) for 16 and 17 keV energies at 20 K; and (b) for 14 and 15 keV at 50 K.



Figure1. (left) and Figure2. (right)



Figure3.



Figure 5.







Highlights:

- ▶ Radioluminescence spectra of SrTiO₃ are reported from 20 to 300 K.
- > X-ray luminescence spectra depend on crystal phase.
- > Direct evidence for inner shell excitation of Sr controlling emission spectra.