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Low temperature detection of phase transitions and relaxation processes in strontium titanate by means of cathodoluminescence

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Abstract

Cathodoluminescence is an effective tool for investigating phase changes and relaxation processes in insulators and data are presented for strontium titanate. The results demonstrate considerable sensitivity to the origin of the samples as the detailed spectra and intensity changes with temperature are strongly dependent on the growth conditions, trace impurities and radiation induced defects. It is of particular note that in the defective surface layer the normal second-order phase transition cited near 105 K transforms into a sharply defined first-order transition because of the relaxation of the near surface layer in doped crystals. Detection of the other main relaxation stages is also straightforward via intensity and spectral changes. Secondary effects of phase changes incorporated within the surface layers are clearly evident, particularly for the 197 K sublimation of CO₂ nanoparticle inclusions.

1. Introduction

Detection of phase transitions by monitoring the associated changes in luminescence signals is potentially a very sensitive probing of the structural relaxations in insulating materials. The technique has already been successfully applied to a variety of insulating materials such as NH₄Br [1], KNbO₃ [2], KTP and RTP [3]. Additionally, luminescence modifications from the phase changes associated with the presence of nanoparticles have been recorded, with evidence of effects from various phases of water ice [4, 5] and CO₂ [6]. Other examples are cited within a review [7]. One material of particular interest for the luminescence method is strontium titanate (STO). The literature on low temperature changes in the structure and/or relaxations of STO has reported a variety of techniques and a considerable diversity of data [8–16]. There

Table 1. Phase changes and relaxation processes cited, in strontium titanate.

Temperature of anomalies (K)	Technique	Comments and possible mechanisms	References
~105	ESR, x-ray, dielectric constants, loss, specific heat, entropy, CL ^a	Cubic to tetragonal phase change, displacement phase transition. Temperature is a function of impurities	[8–14]
~65	Dielectric, ultrasonic,	Conflict on models but well documented	[10, 12–15]
~35	RL, CL ^a		
~25	ESR, dielectric, ultrasonic, CL ^a		
~16	Dielectric and ultrasonic	Examples are sample dependent	[14]

^a Current data.

are both apparent discrepancies between the various results and also some conflict of opinion as to the processes which are involved. However, in retrospect, and indeed from the current data, it is apparent that a major source of the divergence of the interpretations can be ascribed as the material being highly sensitive to the presence of imperfections and internal strains. It appears that the various alternative phases, or relaxed structures, of STO could be sensitized or suppressed by relatively small quantities of trace impurities, non-stoichiometry or stresses associated with the growth processes or subsequent thermal treatments. Where the processes do not reflect simple first-order phase transitions, the impurities may be influencing not only the stability of the lattice against change, but also introducing long term effects of supercooling and/or hysteresis.

Since luminescence techniques can readily respond to the presence of each of these factors, including defect concentrations as low as parts per million, it seems particularly relevant to carry out investigations of STO. Trace impurities may be equally effective as stabilizers or destabilizers, and phase stability can be sensitive to the presence of impurities at the ppm level. One stabilization example is with the mixed oxide of bismuth and germanium oxides where some seven different phases have been recorded [17] but for successful crystal growth of the scintillator $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ a proprietary route to large crystal growth is by addition of a few ppm of impurities. For instability, a less familiar example is with barium azide, BaN_6 , in which standard growth produces a stable compound, but removal of ppm levels of water can generate a highly unstable material comparable with the primary explosive of lead azide, PbN_6 .

For STO, table 1 summarizes examples from the literature regarding techniques for assessing low temperature phase changes or relaxations, and lists some of the possible mechanisms. In our earlier attempts to use luminescence techniques to address this problem a number of sample sensitive features emerged. In part these relate to differences in relative signal responses with material from different sources. However, a far more intriguing feature emerged as a result of ion beam implantation into the surface of the crystals as a route to changing both the defect structures and generating stresses from the implant zone into the interior of the crystal. In unimplanted material the radioluminescence [18] of the entire sample was dominated by long wavelength emission near 800 nm, but after implantation the surface implants caused a discontinuity in the red signals and the appearance of blue/UV emission bands at the lower temperatures. Each of these features underwent intensity changes over very limited temperature ranges which match the previously documented phase and relaxation stages seen via other techniques. Thermoluminescence of STO [20] has produced strong red emission with some minor variations in the emission spectra following ion beam implantation. There was no evidence of the blue/UV bands, but major shifts in the temperatures of the glow

peaks. Once again the evidence indicated that the surface defect layer, from the implantation, caused a restructuring of the entire sample.

The present data focus on measurement of cathodoluminescence which is inevitably highly sensitive to the conditions for the near surface layer of the material, and modifications caused by either intrinsic defects or impurities.

Low temperature phase transitions in STO have been studied for a considerable length of time and a cubic to tetragonal phase transition in STO was first reported in 1964 [8]. The event is normally cited near 105 K but the precise value has small temperature variations in doped material, or when cited by different authors using a variety of techniques. Whilst there is no doubt about the existence of this structural transition, the literature also includes reference to a number of signal anomalies which may be ascribed to phase changes [9–14] but are normally discussed in terms of lattice relaxations. The events are not always clearly defined but nevertheless two such events have frequently been discussed for relaxations into modified structures near ~ 65 and ~ 35 K [10, 13–15]. References to these structural changes are mentioned in review articles [13, 14] that report that they can be detected via a wide range of techniques, including measurements of dielectric and ultrasonic properties, thermal conductivity, electron magnetic resonance and other critical phenomena. Despite the fact that these low temperature events were first noted as early as 1967, their precise details and mechanisms are subject to alternative views. Problems in detection, and hence analysis, occur partly because the changes are sensitive to the dopant levels and, further, they may only relax over an extended period of time. Hence, depending on the experimental procedures they may be overlooked in transient experiments which do not allow sufficient time for relaxation of the lattice. Equally, there may be supercooling and/or hysteresis which introduce difficulties in detection or apparent displacement in temperature. At even lower temperatures two further changes have been cited at 25 K [16] and 16 K [14]. These various transitions are summarized in table 1.

2. Experimental details

The strontium titanate crystals were nominally pure and obtained from three sources, Karlsruhe in Germany, Excitech Ltd in the UK and the Jeonju National University of Education in Korea. They are referred to as STO(G), STO(E) and STO(K) respectively. A variety of room temperature implantations were carried out using either 240 keV gold ions to doses from 5×10^{13} to 1×10^{17} ions cm^{-2} or Sb at 260 keV. The projected ion ranges are ~ 40 nm for Au and 62 nm for Sb. Low temperature cathodoluminescence data were collected on the Sussex high sensitivity wavelength multiplexed system [1–7]. The two detectors in this system cover the wavelength ranges 200–410 nm and 410–830 nm with a resolution of ~ 3 nm.

The cathodoluminescence electron beam energy was between 10 and 30 keV with beam currents of nA cm^{-2} . The corresponding maximum electron ranges for these energies are from ~ 200 nm to ~ 600 nm and the maxima in the rates of energy deposition occur between 50 and 150 nm. The CL data were recorded during cooling or heating between 25 and 300 K at a rate of 6 K min^{-1} with separate spectra collected every 0.3° , but for presentation they have been averaged over one or two degrees, particularly for data sets where the signals were weak. The recorded data were corrected for the wavelength response of the detector system.

3. Results

The cathodoluminescence spectra differ both as a function of the source of the material and the electron energy. The long wavelength red component bands, seen in both radioluminescence and thermoluminescence, are apparent for all samples, but in intensity terms are quite variable.

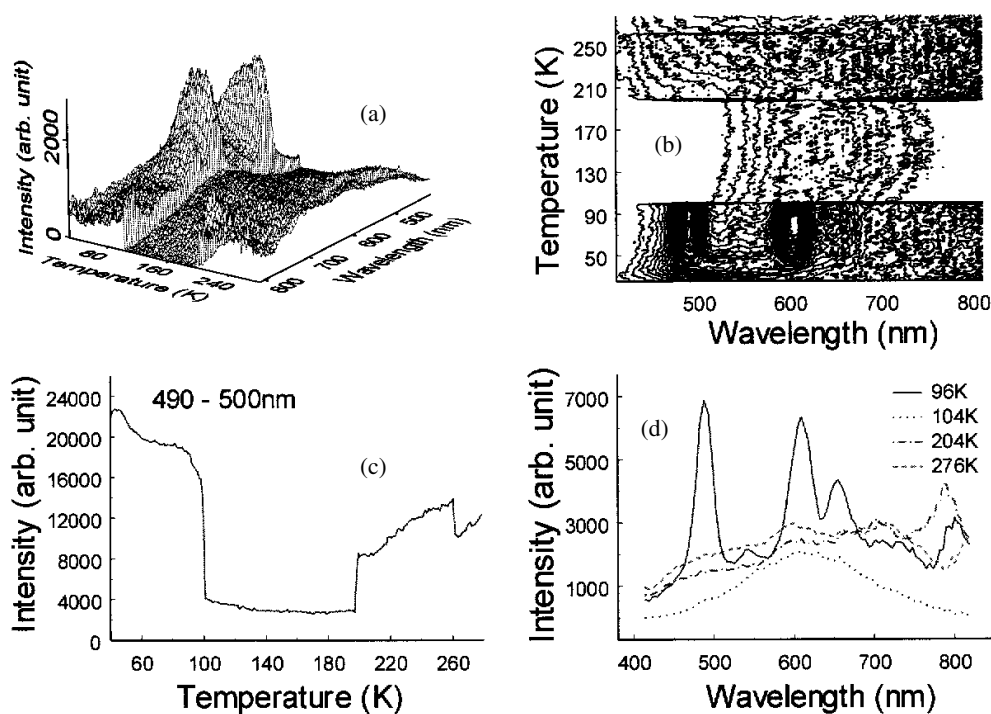


Figure 1. (a) An isometric plot of the cathodoluminescence from a Korean sample of SrTiO_3 . (b) A contour map of the data. (c) An intensity versus temperature plot for signals between 490 and 500 nm. (d) Comparisons of spectra at different temperatures. The intensity scales differ since (a) is for the original data but (b) and (c) are integrals of signals over small spectral or temperature ranges—in order to offer improved signal to noise ratios.

By contrast the low temperature blue/UV features, seen in RL, are clearly evident for many samples. In materials which display first-order phase transitions [1–7] the characteristic features are sharp intensity discontinuities and changes in spectra at the transition temperature. Despite the fact that the reported features for STO are normally assumed to be either second-order phase transitions or temperature varying relaxations, many of the CL signals display changes which are consistent with sharply defined first-order phase changes. This is particularly evident in the Korean material. Data from such a sample are shown in figure 1 which variously displays an isometric plot of the spectra as a function of temperature, a contour map of the data, an intensity plot as a function of temperature for a 500 nm slice and spectral slices contrasted for the different temperature regimes. These data were obtained with an electron energy of 12 keV. There are clearly three intensity discontinuities consistent with phase changes near 100, 200 and 260 K. The relevant events will be considered in the discussion section.

The different isometric plots have been selected to offer the clearest views of the major features and thus the perspectives differ between figures 1, 2 and 3.

In the other original samples the emission spectra differ in that they show stronger red emission bands near 800 nm, which increase with electron energy as the electrons probe deeper into the sample and offer responses more typical of the bulk signals generated by radioluminescence. Nevertheless, there are some steps in the intensity data which are apparent on closer inspection, including weak events near 100 K, as seen in figure 2(a) for the STO(G)

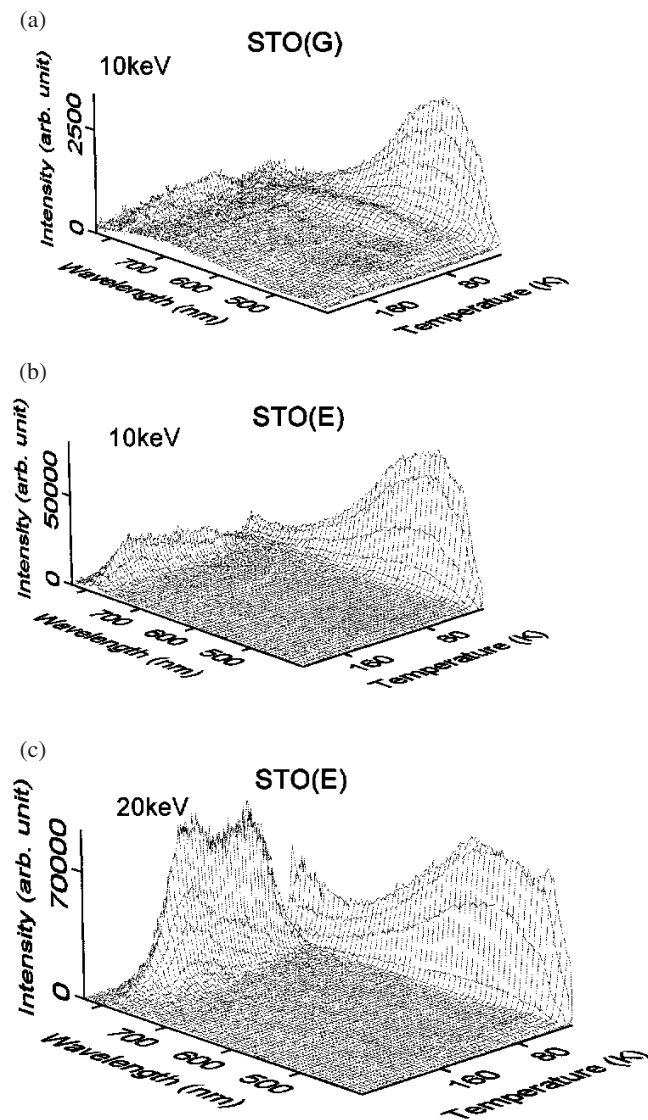


Figure 2. Examples of CL isometric data for STO of German and English origin and an effect of electron energy on the emission spectra for the English material.

material. The STO(E) crystals give similar spectra but low intensity in the visible region above ~ 80 K. Increasing the beam energy raises the intensity of the 800 nm bands and enhances some trace signals near 420 nm.

As already mentioned, there is strong evidence that the presence of defects and stress influence the ability of the STO lattice to undergo relaxations. Therefore to strongly modify the surface layer a variety of samples were implanted with either Au or Sb with different ion doses. The ion beam implant depths, ~ 40 nm for Au and ~ 62 nm for Sb, are comparable with the maximum of electronic excitation depth for 10 keV electrons, but less than their maximum penetration range (~ 200 nm). For the 30 keV electrons these values are some three times greater. Initially one might assume that the CL signals are generated by interactions

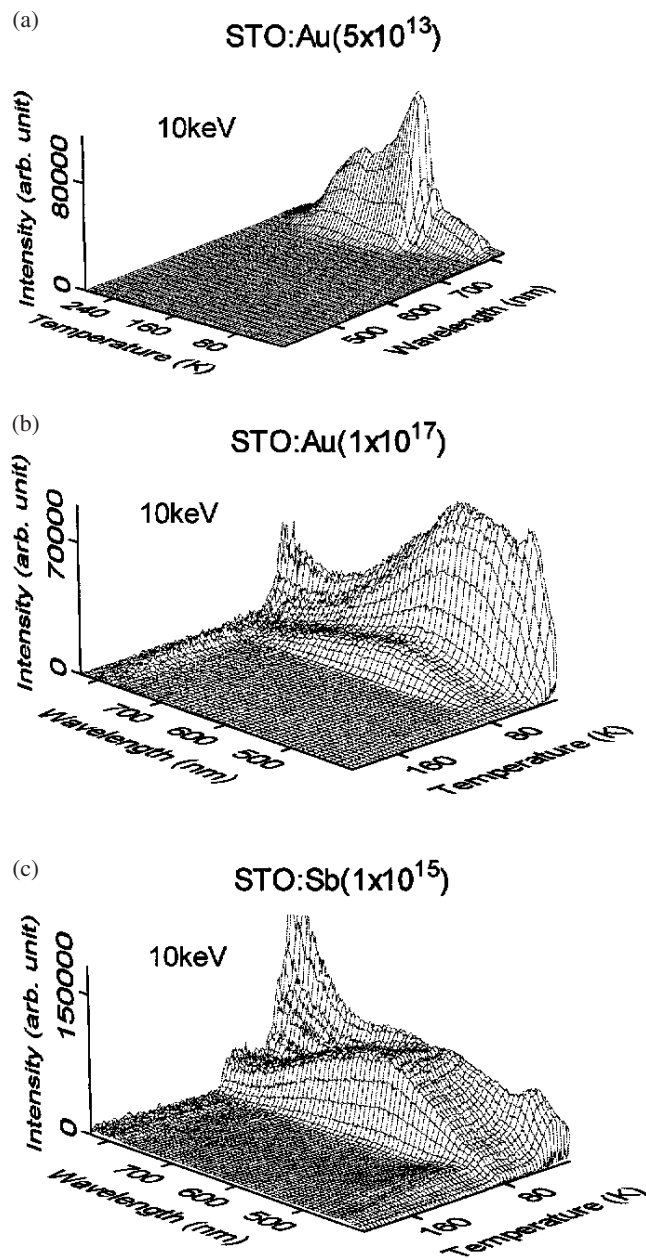


Figure 3. Comparisons of CL signals after various ion beam implantations.

throughout the range, with intensity proportional to the rate of energy transfer. This is somewhat simplistic as the energy transfer only defines the primary excitations of the electrons. The CL intensity is modified by the luminescence efficiency which is influenced by surfaces, ion implantation damage and stress. Luminescence may even occur at deeper regions of the lattice beyond the range of the electrons if there is long range energy transport via exciton migration. Consideration of these factors indicates that there is not a close correlation between

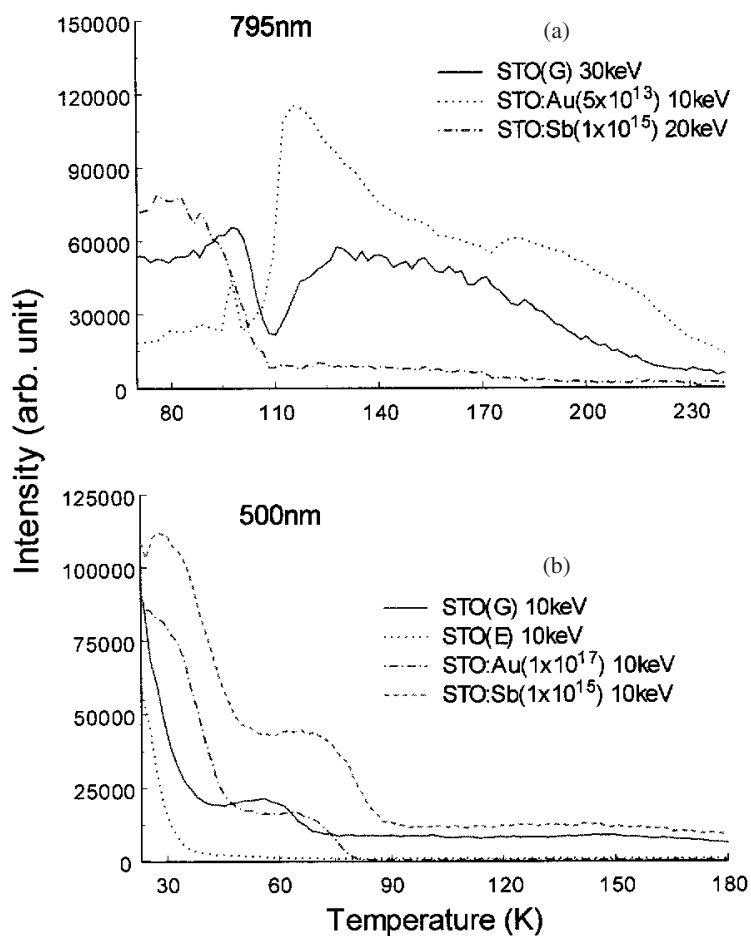


Figure 4. The temperature dependence of luminescence signals measured at either 795 or 500 nm for different samples.

the depth at which the electron beam is scattered and energy deposited, and the intensity of the generated signal. Spectral changes must therefore be viewed as global effects which subsume all these factors. Nevertheless, despite the differences in electron probe depths the implants totally change the emission characteristics in all cases. Figure 3 offers just three examples of isometric plots which typify the diversity of the changes seen for low and high dose Au implants and for Sb implants in the German STO material. In all cases the spectra include some evidence for the red bands. There is a strong contrast between the intensities seen figures 3(a) and (b) or (c). For figure 3(a) the three component bands near 800 nm differ in their temperature response, although all three decrease strongly near 105 K. By contrast, figures 3(b) and (c) have very weak red emission but at least two major intensity zones below ~ 100 K.

These various differences are emphasized in the intensity versus temperature plots shown in figure 4, which includes data from both pure and implanted material. Figure 4(a) demonstrates that near 105 K there are large changes in the intensity of the red component band near 795 nm. In some cases the data include a signal decrease during cooling, whilst for other samples the intensity rises. The behaviour for the other red bands is slightly different but not shown here.

There is a different pattern of behaviour in the visible spectrum and figure 4(b) indicates that there are several broad intensity steps which differ between the samples both as a function of the origin of the material and as the result of ion beam implantation. In this example all data were obtained at 10 keV. Altering the beam energy introduces other differences between samples, but still broadly in line with the intensity plateau zones seen here. Under constant beam conditions there were no obvious changes in the spectra as a result of prolonged electron irradiation and hence any new defects induced by the electron beam play a minor role in the present experiment.

4. Discussion

The current cathodoluminescence data underline the key reason that the literature on STO phase transitions and relaxation processes contains a diversity of claims as to the strength, or absence, of particular features when sensed by differing techniques. The CL data unequivocally indicate that there is very strong sample dependence for materials from different suppliers. For nominally pure crystals from the three suppliers the Korean material differs from the others both in the fact that the intrinsic red emission bands are very weak and also that the visible part of the spectrum has some line-like features superposed on the broadband background. The origin of the lines is unclear but rare earth transitions, particularly from Pr, occur at the relevant wavelength regions in other host lattices (i.e. near 492, 548, 590 and 651 nm for Pr). Samples from the European suppliers also show evidence of weak rare earth impurity signals. The most obvious and exciting feature of the Korean material is that there are extremely clearly defined intensity steps near at 100, 200 and 260 K. Indeed, experimentally the steps are broadened by the data processing which averages values over $\sim 2^\circ$ in these samples.

Since the second-order phase transition cited near 105 K is sensitive to defects and impurities, and from the spectra one can both sense impurity ions (e.g. rare earth) and surface defects (which quench the red emission), the intensity step seen here at 100 K is assumed to be the result of the normal 105 K transition within STO. The sharpness of the intensity discontinuity is surprising in that this is normally assumed to be second order but the intensity pattern is characteristic of a first-order event. This is certainly feasible in a CL measurement since the signals originate very close to the surface (on the micron scale) and the near surface layer provides the opportunity for the lattice to relax, and so the bulk second-order effect transforms into a first-order phase transition. Such a possibility of a change of order because of surface relaxation has been discussed elsewhere, for example by Qu *et al* [17].

Associated with phase induced intensity steps are spectral changes resulting from excitations of luminescence sites in different structural phases. Clear examples were reported in the transitions of ammonium bromide [1] and figures 1(a), (b) and (d) show similar spectral shifts in the various states of the STO.

Note that differences in precise spectral line positions caused by stress induced lattice parameter changes have been noted in the comparisons of CL (surface) and RL (bulk) of MgO:Cr [5]. The luminescence emission line spectra of the chromium doped MgO move in opposite directions along the wavelength axis in RL and CL as a result of pressure changes caused by phase changes of trapped impurities such as oxygen and nitrogen nanobubbles. The MgO data are consistent with phase transitions of the impurity inclusions producing surface lattice expansion, whereas in the bulk there is compression. The MgO data therefore support the view of an STO surface expansion to allow for a first-order transition at ~ 100 K.

Overall the new data of figure 1 demonstrate that the 100 K phase transition of STO can be clearly identified from changes in the cathodoluminescence emission spectra.

Further comment is relevant on the other sharp intensity discontinuities for the Korean STO. The distinct changes in intensity and spectra at ~ 200 K may be associated with the presence of trapped CO_2 in the lattice. Earlier data obtained with Nd:YAG showed equivalent intensity changes and perturbations of the lattice parameter of the cubic YAG host, as well as spectral shifts of Nd line emission at ~ 200 K [6]. There can be a phase transition of trapped CO_2 nanoparticles at the sublimation temperature of 197 K. This causes a particularly dramatic pressure change as the CO_2 material undergoes a thousandfold increase in volume.

Less obvious in figure 1(b), but apparent in figure 1(d), is the feature that in the green spectral region there is a further intensity discontinuity near 260 K. This could be driven equally either by an intrinsic event or by an impurity activated phase. If the latter were the case, then a prime candidate cause would be surface water because, during cooling, as shown here, there can be supercooling and/or a lowering of the water freezing point because of dissolved impurities. Further, the surface is in a vacuum system which shifts the melting point of water. Hence effects of water/ice phase changes might be sufficient to account for the green signal intensity step noted from CL for the Korean STO. This is a speculative model as the event was only clearly seen for the Korean sample, which might therefore imply the presence of small quantities of trapped nanoparticles of water in this sample. The feature was not seen for all samples so it seems unlikely to arise from water contamination within the vacuum chamber.

Figure 2 has demonstrated examples of reduction in the red emission bands for low energy electrons compared with the higher energy CL and also RL, which imply that surface defects suppress the efficiency of the red luminescence. The figure also shows that CL provides higher energy photon emission in temperature ranges linked to the lower temperature relaxations/phases of STO. Changes in the defect densities caused by ion beam implantation considerably alter the relative intensities of these different stages. Similarly figure 4 has shown that for the red emission there can variously be quenching or growth of the bands near 105 K during heating or cooling which supports the view that the STO phase transition at this temperature influences the intrinsic red luminescence efficiency. Similar quenching of the red bands had been noted in bulk studies using radioluminescence [19]. The more gradual intensity transition steps seen in figure 4 (i.e. occurring over 10° – 20°) further confirm that the relaxations are not first-order transitions. They data do however confirm that the various steps broadly match earlier documented transition regions near 65 and 35 K.

5. Conclusion

The data indicate that cathodoluminescence is an effective tool for investigating phase changes and relaxation processes in strontium titanate but the details of the various changes are strongly dependent on the growth conditions, trace impurities and radiation induced defects. It is of particular note that in the defective surface layer the normal second-order phase transition can be accommodated as a sharply defined first-order transition because of the relaxation of the near surface layer.

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