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Detection of phase transitions in RbTiOPO₄ and KTiOPO₄ by luminescence

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Abstract

Luminescence signals have been recorded at low temperature during thermal cycling of crystals of RbTiOPO₄ (RTP) and KTiOPO₄ (KTP) excited by x-rays. In both crystals there are well resolved intense intensity spikes and changes in emission spectra consistent with first-order phase transitions. The transitions are not reversible, except by high temperature annealing. The observations imply that new phases of RTP and KTP can be formed, and in some cases these may relate to nanoparticle-size inclusions. Crystal quality assessment from the luminescence behaviour may have value for non-linear optics. Cathodoluminescence of the RTP surface reveals different emission spectra from the bulk material with consequent implications for usage in surface waveguide devices.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The growth and characterization of new materials for non-linear optics is inevitably a labour intensive process and for many structures there can be subtle variations in stoichiometry which result in alternative phases. Such phases may only be metastable or localized within the bulk material as inclusions and the conversion between alternative phase changes can be enhanced, or suppressed, by relatively few defects in the structures which allow nucleation and growth of the various structures. For the less developed materials even the existence of phase variations may be poorly recognized and, where they exist, may be related to the starting materials and method of growth if the relevant lattice imperfections exist as a result of impurity inclusions during growth or thermal processing. Particularly near the surface there may be further changes from subsequent in-diffusion of contaminants from the atmosphere.

Additionally, many materials undergo surface changes as a result of surface polishing and heat treatments [1]. Whilst these can induce near-surface effects such as surface phase variations can be of consequence for optical performance, particularly in waveguide applications. There is also evidence that development of metastable phases is energetically more favourable at the surface [2], and in some cases the surface structures can initiate propagation of unexpected bulk phase changes. Further, if stoichiometric variations can enhance differences in phase stability, as for example in bismuth germanate or lithium niobate, then these may also be non-uniformly incorporated in the growth boule. There is thus a need to devise a rapid route to seek evidence for phase transitions in the materials and investigate if they are stable or reversible, and if their presence is beneficial for the non-linear objectives of the material. Having once detected their presence, in this case via luminescence signals, one can proceed to more detailed lattice structure and optoelectronic property studies.

Two materials which have been produced in the present growth studies are RTP (RbTiOPO_4) and KTP (KTiOPO_4) [3]. These crystals have been developed over the last two decades since they are well suited for non-linear optics. Their optical performance is relatively robust with respect to variations in sample quality but nevertheless the influence of growth conditions is documented and affects numerous properties, not least of those being the Curie temperature. In an extensive review of crystal growth [3] evidence was summarized and considered for the very rich range of phases which result from the composition, growth fluxes, impurities, cooling rate, twinning, inclusions and strains in the sample. More recent data on the growth-dependent property changes (including the Curie temperature) are discussed by Roth *et al* [4] and structure-sensitive optical properties are also evident [5]. All of these possibilities have some influence on the non-linear optical properties and, for the current experiments, are potentially factors which could introduce phase changes between metastable zones in the material. There can be a considerable spread in performance between material from different growth centres, and indeed between samples from the same supplier. Hence there is a need to assess if the performance changes are related to intrinsic properties, such as phase transitions, or extrinsic features, such as impurities. The present study has concentrated on the search for evidence of phase transitions, although some indications of purity are mentioned, not least because the presence of impurities can induce transitions.

2. Background to luminescence detection of phase transitions

A Sussex programme has recently been initiated to make a survey of phase changes in optical materials by recording luminescence properties as a function of temperature. This possibility exists since the luminescence intensity from both intrinsic and extrinsic sites will depend on both the local symmetry of the core of the luminescence site and the longer range interactions which can enhance or suppress the transition probability. Consequently measurements of luminescence intensity can undergo a discontinuity both in intensity and emission spectra at a first-order phase transition. A 'classic' example of the changes in intensity and spectra at each phase change of the host lattice during heating, or cooling, whilst exciting with x-rays (radioluminescence, RL), was published for ammonium bromide [6]. In that case the phase transitions were reversible and cleanly identified. By contrast, the signals from potassium niobate [7] were relatively weak but during the transitions the large changes in polarization fields allowed a burst of charge release which generated a luminescence intensity spike at precisely the phase transition temperature. The signal extended over a wide spectral range and the spike temperature differed by $\sim 20^\circ$ between heating and cooling, indicating a strong structural hysteresis which had not previously been discussed for this material. Indeed it resolved the apparent anomaly in cited values of the transition temperatures used by different

manufacturers who had characterized their material during heating in one case and cooling in another.

Since detection of luminescence is a sensitive process such phase transition signal changes can be readily recorded, even if they only originate at phase inclusions within a bulk lattice or from a modified surface layer. In order to focus on near-surface material (as is relevant for optical waveguides) cathodoluminescence (CL) has been used to probe surface phases and it has often revealed numerous differences between the surface and the bulk material [8]. CL data have recorded phase changes which are suppressed in the bulk material and have also revealed the presence of impurity nanoparticles. For example, for many insulators the presence of water vapour at the surface, and/or in the subsurface by penetration via dislocations, has a dramatic effect on luminescence intensity [9]. Most obviously the many examples show that water, and also impurities such as CO₂ [10], O₂, N₂, etc [11], are not atomically dispersed in the material but exist as small impurity nanoparticles which can exhibit bulk-type phase transitions. When the inclusions undergo characteristic phase transitions they reveal themselves by their modifications of the luminescence signals of the host. The effects are considerably larger than expected on the basis of the impurity concentration, for example the phase change of CO₂ from solid to gas at 197 K introduces a significant pressure rise which alters the luminescence intensity and altered the transition energy between Nd states in Nd:YAG. For flux grown materials, as for KTP and RTP, there is the possibility that contaminants from the precursors, flux and growth process might also exist in the form of nanoparticle inclusions. Note in particular that water is a reaction product of many of the routes to KTP and RTP growth, and the crystals normally show strong infrared absorption signals from OH vibrations linked with a wide range of sites, as well as signals typical of pure water [3]. The changes in signal intensity linked to the 170 K ice transition can be very dramatic and, for example, are a factor of 10–100 times in Nd:YAG [10].

The topic of luminescence detection of phase transitions in inorganic insulating materials has recently been briefly reviewed, with examples from more than 20 materials [12].

3. Experimental details

3.1. Crystal growth

Considerable effort was invested in crystal growth in order to avoid problems of strain, impurity and contaminants such as products of reaction foaming (e.g. CO₂), not least because each of these problems may initiate a range of metastable structures and/or complicate the phase diagram of the material. The crystal growth equipment used in the present study comprises a crystal puller with the necessary rotation and translation assembly and a resistively heated three-zone furnace [13]. For the top seeded growth of MTiOPO₄ (M = K, Rb) crystals, the temperature gradients are critical factors and the current three-zone furnace design provides the requisite uniformity and control of axial and radial temperature gradients, for example over 70–80 mm there is a maximum gradient of ± 0.5 °C. The system is computer controlled within ± 2 °C and visual information is achieved via a CCD camera [14].

Good quality KTP and RTP single crystals of up to 35 × 15 × 20 mm³ were produced using K₆P₄O₁₃(K₆) or Rb₆P₄O₁₃(Rb₆) fluxes and high purity (>99.9%) precursors of KH₂PO₄, K₂HPO₄, TiO₂ and Rb₂CO₃. The chosen charge/flux ratios (gMTP/gM₆) were 0.55 and 0.6 for KTP and RTP, respectively. The problem of multi-nucleation due to the highly viscous nature of the solvents was considerably reduced by the addition of MoO₃ (0.02 g) as a flux modifier [15] and homogenization was made at 950 °C (i.e. 50 °C above the saturation temperature) for 36 h for KTP and 900 °C for RTP. Note that temperatures and heating rates were selected which avoided decomposition and frothing problems of the Rb₂CO₃ and NH₄H₂PO₄.

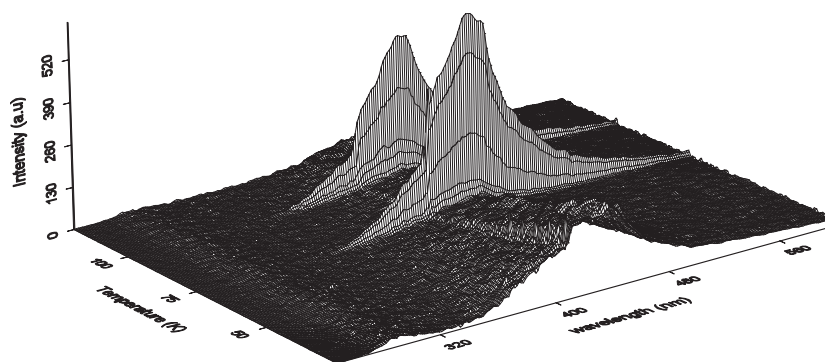


Figure 1. The RL emission spectra from KTP during the first cooling measurement.

Growth was commenced with good quality KTP and RTP seed crystals and the nucleation and/or dissolution of the seed was monitored via the CCD system. Unidirectional seed rotation rates varying from 60 to 30 rpm, depending on the growth, aided the homogenization of the solution. The initial cooling rates were found to be crucial and these started from 970 to 940 °C for KTP and 870 to 840 °C for RTP at the extremely low rates of 1 °C/day. Subsequently the furnace was cooled to room temperature at 10–15 °C h⁻¹. The colourless crystals had no visible inclusions. The morphology of the crystals is predominantly of {100}, {201}, {011} and {110} faces. Crystals were cut into rectangular plates of thickness 1 mm perpendicular to the crystallographic *a*, *b* and *c* axis having (100), (010) and (001) faces, respectively.

3.2. Luminescence

Luminescence data were recorded in an apparatus at Sussex which allowed wavelength multiplexed spectral recording with a high sensitivity, as described in numerous earlier publications [6–12]. The optics are *f*/2.2 and there are two diffraction gratings (blazed for peak performance in the blue/UV or in the red spectral regions) which address a pair of photon imaging tube detectors. The system can be excited by either x-rays (RL) or an electron beam (CL) whilst held at a fixed temperature, or during heating or cooling at a constant rate. For the low temperature range used here, from 20 to 300 K, the rate was 6 K min⁻¹. Complete spectra were thus recorded in parallel every second and then averaged to offer a temperature resolution of about one degree, which is a compromise between detail and a good signal-to-noise ratio. Absolute temperatures of the emitting samples are probably within ~2° as at the low heating rates the temperature gradients between the cryostat and the samples are relatively small, even though the insulators are poor thermal conductors. Spectral resolution is sacrificed to about 5 nm as a compromise for strong signal-to-noise ratio for transient events such as light emission at phase transitions, and originally the equipment was designed for the transient signals emitted during thermoluminescence. It should be noted that signal intensity matching between the two detectors is normally near 420 nm and, in some cases, was not optimized due to a problem with the blue/UV detector electronics.

4. Luminescence from KTP

4.1. Luminescence data for KTP

Figure 1 shows the luminescence intensity during the *first* RL cooling run of a KTP sample. The intensity pattern displays two remarkable high intensity features which spread across the

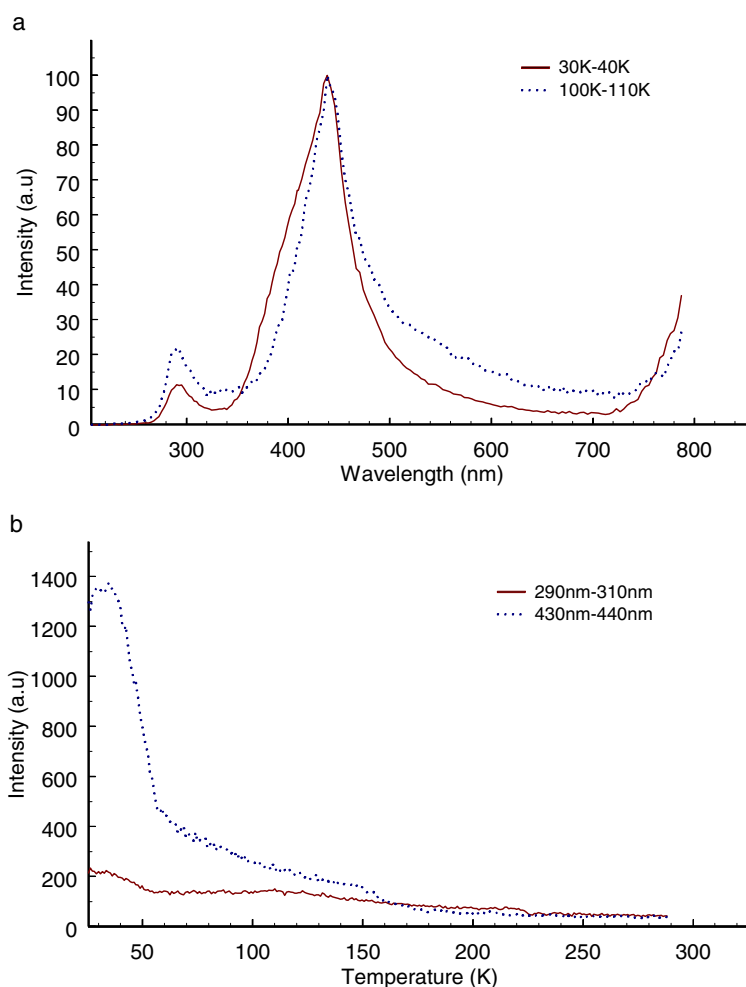


Figure 2. (a) RL emission spectra at 30–40 and 100–110 K taken during the second KTP cooling measurement. (b) RL temperature dependence of emission near 300 and 440 nm during heating.

spectral range from about 350 to 600 nm, but do not appear as any enhancement of the small emission band near 300 nm. There is an underlying broad emission pattern which is increasing as the temperature is lowered towards 20 K. The data clearly display emission spikes peaking at ~ 75 and 100 K. The spectra are quite similar both during the intensity spikes and at nearby temperatures.

The cooling cycle apparently modifies the material considerably since for subsequent heating and cooling RL experiments the two main spikes are suppressed. Nevertheless some spectral changes can be resolved and figure 2(a) presents normalized spectra integrated from 100 to 110 K and from 30 to 40 K during the second cooling. The spectra recorded over the 30–40 K temperature range are identical during heating and cooling, but there are some differences evident between heating and cooling for the signals near 100 K. Initially there are steps in the rate of change of intensity for light emitted from 290 to 310 nm near 160 and ~ 70 K, figure 2(b), but these are not apparent in later measurements.

For the same sample the emission spectra can be modified in terms of the relative intensity of the component bands by heat treatments, for example, in a sample annealed in air at 850 °C the green emission became of comparable intensity to the blue signals. However, the heat treatment did not reintroduce the intensity discontinuities shown in figure 1.

4.2. Discussion of the KTP data

The preceding data strongly indicate that during the first cooling cycle the KTP crystals undergo irreversible phase transitions near 75 and 100 K. In general the detection of signal discontinuities (including luminescence) could result from (a) phase transitions of the host KTP crystal, (b) changes resulting from impurities within the KTP lattice or (c) signals generated by phase transitions of trapped impurities in, say, the form of nanoparticles. The comment applies equally to the current crystals and to others reported in the literature. The expectation is that the purer materials will therefore show the fewest anomalies. The present samples were grown with considerable care in terms of purity, homogenization, inhibition of foaming and extremely low initial cooling rates. They are therefore expected to be crystals of high quality. Indeed, they indicate phase transition type events only during the first cooling cycle, which is consistent with a pure single-phase material. Nevertheless the initial very obvious events near 75 and 100 K still require an explanation.

Assuming that the current crystals are relatively pure then a rather speculative origin could be the presence of trapped nanoparticles of water since the ice literature includes reference to a phase transition of ice with dissolved KOH at 75 K with an ill-defined second event near 100 K.

By contrast, many of the earlier studies of KTP discuss a variety of phase transitions or critical temperatures, some of which may be related to impurity effects. Literature values for phase transitions of KTP include, of course, the Curie temperature feature near 945 °C, but super-ionic and pyroelectric changes were noted near 200 K [3, 16–18] and nmr charge effects, possibly linked to potassium ion migration, near 200 and 300 K [3, 18]. A range of property changes have been reported at low temperatures by Jiang *et al* [19] in terms of ferroelectric, conductive and dielectric data which include a change in the activation energy for K⁺ motion at 295 K, a superionic phase transition at 170 K together with an anomaly in the thermal expansion, a phase change at 140 K linked to spontaneous polarization and, finally, a frequency-dependent conversion between ionic and electronic conduction. In studies with dopants [20] anomalies and hysteresis in electrical conductivity were noted near 160 °C. Note the latter temperature matches the region where there was a very weak event recorded in the UV luminescence intensity.

In hindsight one could reconsider if such events, considered as KTP phase transitions, might be explicable by changes in trapped nanoparticles of impurities. For example, the recent data reported by Jiang *et al* [19] report phase transitions near 295 and 170 K. It should also be noted that they suggest that their 295 K signal may be the same as that reported elsewhere at 268 K [21]. This temperature range is thus potentially where one might expect phase changes from water to ice. An unconstrained liquid water to ice transition would be at 273 K, but impure water trapped within the KTP might be supercooled or superheated (i.e. to span the range 268–295 K).

There is a much cleaner option for the 170 K event where there is a cubic to hexagonal ice transition at 170 K. (Additionally, water sublimates from a surface in a vacuum system at ~235 K.) Water is often a detected contaminant in KTP and is an inherent product of the growth chemistry and the 170 K ice phase transition has been linked to several luminescence intensity anomalies [9–12]. Similarly the KTP anomalies reported near 200 K [3, 16–18] would match

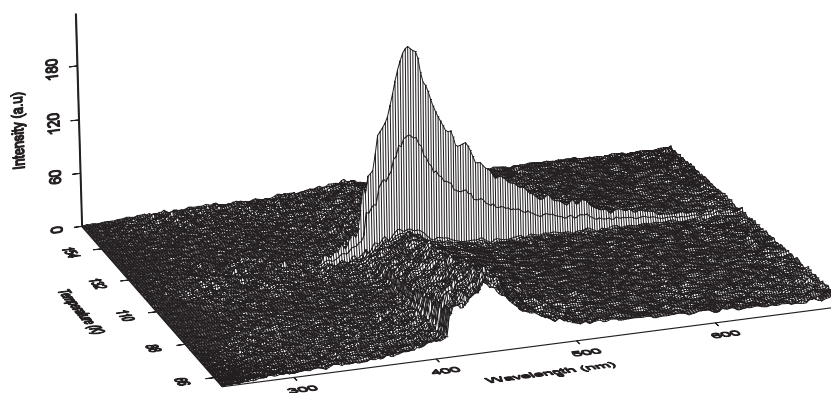


Figure 3. The RL spectral map of a RTP sample taken during cooling.

well with pressure changes induced by sublimation of CO_2 . The absence of events at 200 K with the present material may be significant and a result of the inhibition of bubble and foam formation during homogenization of the growth material.

The overall conclusion is that well prepared KTP has no intrinsic low temperature phase transitions.

5. Luminescence from RTP

5.1. Luminescence data for RTP

During the first RL cooling measurement there is an intensity spike (as for the KTP figure 1) but in RTP this occurs at 42 K. The emission bands peak between 430 and 440 nm with tails spreading across the entire recorded spectrum. There are some small differences between the emission spectra in the spike region (42–44 K) and the lower temperature signals at, say, 30–35 K. On reheating the sample there is a minor discontinuity in the luminescence intensity near 135 K. RTP differs from the behaviour of KTP in that there are major emission spikes recorded during the second cooling cycle. In this case the event occurs at a higher temperature of 122 K, as seen in figure 3.

Since the material had been modified as the result of cooling it was decided to use higher temperature anneals to try to regenerate the original signal. Heating to 600 °C for 40 min in air regenerated the feature near 37 K and introduced several weaker intensity spikes. More obviously the heating makes significant differences to the RL emission spectra and examples are shown in figure 4. Spectra were integrated over the temperature bands 30–40, 100–110 and 200–210 K. The spectra differed yet again after a further heating cycle, although there are a common set of emission bands in each example, but with changes in their relative intensities. Higher temperature annealing, at 750 °C, generated a single sharp intensity spike at 85 K, again with modified different spectral characteristics. Examples of spike temperatures are summarized in table 1.

5.2. CL of RTP

CL probes the near-surface layer and is thus sensitive to surface imperfections and relaxation events which may be inhibited in the bulk material. It is also responsive to changes in surface stoichiometry caused by annealing and/or ingress of contaminants such as water vapour.

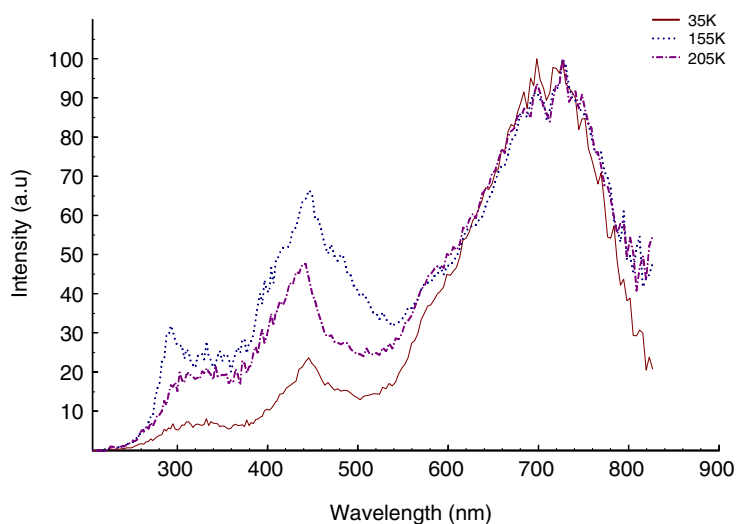


Figure 4. RTP RL spectra centred on 35, 155 and 205 K taken after the 600 °C anneal.

Table 1. Summary of phase transition type luminescence signals from KTP and RTP.

Material	Treatment	Luminescence spike temperatures (K)	Comments
KTP	Cooling during RL	100, 75	Both major features
	Subsequent heating or cooling	100, 75	Very weak features but some permanent spectral changes
RTP	First cooling during RL	42,	Spike spectrum differs from lower temperature signals
	Heating during RL	135	Stronger blue RL up to room temperature with a 20% step increase at ~135 K
	Second cooling during RL	122	Clean spike for both blue and green signals
	Second heating during RL	135	Small, 20%, intensity spike
	600 °C anneal and then cooling during RL	37, 100–110, 200–210	37 K feature is very clear Very weak features
	750 °C anneal and then cooling during RL	85	Spikes are very distinct and spectra differ as a function of anneal temperature
	850 °C anneal and then cooling during RL	66, 63 122 (broad)	
	CL after the 650 °C anneal	235, 170	Clear enhancements for blue and green and the dominant peak is at ~720 nm
			Many small peaks

Therefore examples of the CL intensity discontinuities are presented in figure 5 for the RTP material which had been annealed to 600 °C. The luminescence intensity shows two narrow regions of enhanced signal near 235 and 170 K.

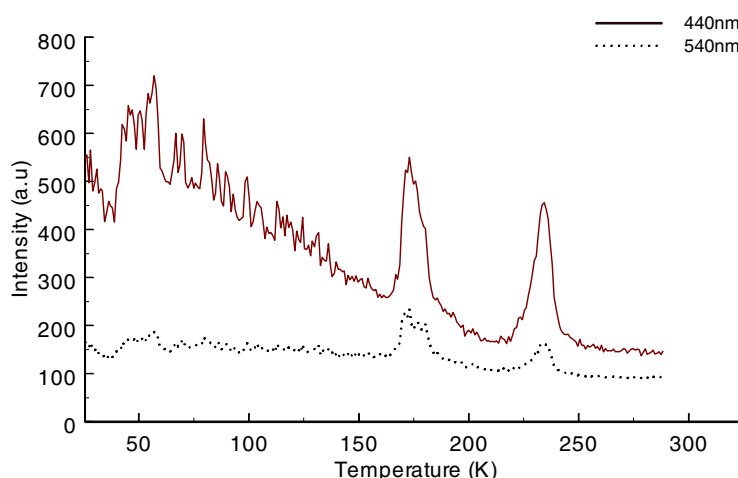


Figure 5. CL emission spectra centred on 35, 155 and 205 K after the 600 °C anneal.

The emission spectra differ between cooling and heating and include longer wavelength emission bands than were noted in the RL excitation. The immediately obvious difference between CL and RL spectra is that the dominant emission peak is now beyond 700 nm for CL, rather than at 440 nm for RL.

5.3. Discussion of the RTP data

Unfortunately there is very little literature relating to measurements of low temperature phase changes for RTP. Thus these optical signals offer the first examples for RTP. The first RL cooling cycle has an unequivocal intensity spike which spreads over a broad spectral range and this is certainly so narrow that it is almost certainly a result of a first-order phase transition. However, as with KTP, the subsequent heating and/or further cooling cycles have a very different behaviour, which suggests the titanyl phosphate lattice has permanently entered a modified lattice structure or there were impurity phase transitions which have been altered. There are small changes between the emission spectra at different temperatures during cooling but these are not as dramatic as, for example, were seen with ammonium bromide [6] or strontium titanate [22]. Thus the assumption is that the RTP structures, both above and below the phase transition event, are closely related. Hence the intensity spikes may be from impurity phases rather than the host. Further, there is some latent instability since, in different cooling cycles, there are again excellent luminescence signatures from first-order phase transitions, but they occur at different temperatures. Models may thus include considerations of supercooling or progressively modified nucleation sites (e.g. changing impurity nanoparticle size).

In order to re-establish conditions which would more closely resemble the initial growth material, attempts were made to anneal the sample. The annealing conditions were in air and the cooling was much faster than for the crystal growth, but nevertheless the 600 °C anneal immediately re-established a signal near 37 K, which, allowing for temperature inaccuracies in remounting and sample handling, may well be basically the same feature as initially seen at 42 K. The data from the annealed sample were not totally identical to the original as there were changes in the spectra and the temperature dependence of the emission. In particular the width of the blue emission band was narrower at 25 K but there was a fairly constant intensity up to at least 100 K.

Higher temperature anneals introduced very clean spike signals. After the 750 °C anneal the signal spike at ~85 K was three times the height of the constant background (and >50 times the noise level) with a temperature width of ~2 K. There were also clear differences in the spectra for signals above and below this transition temperature in which the green signals fell from equalling those in the blue to being only ~30% of the blue intensity (i.e. consistent either with a structural phase change or a different concentration of emission sites). Similarly the 850 °C anneal generated very clean spike signals, with the main event at 66 K and a smaller (~10%) spike at 63 K. There was also a small broad feature at ~122 K (i.e. precisely in the temperature range seen in the second cycle of the original crystal). Further, the green signals were more obvious at higher temperatures.

In conclusion the RL data indicate that there is at least one low temperature phase transition from the RTP crystals measured here. The clarity of the spike signals is consistent with a first-order structural phase transition. It is less obvious if this is from the host RTP or impurity inclusions.

The CL data are responsive to surface properties and the two features near 235 and 170 K match transitions of the ice to vacuum sublimation and the hexagonal to cubic phase changes of ice. They both extend over about 10 K, which is much broader than is seen for the RL spike signals. The events are thus consistent with other surface ice associated luminescence signals. Whilst most examples had shown luminescence quenching from the ice this is not ubiquitous since, for SrTiO₃, the 170 K phase change enhanced the lower temperature signal [22].

6. Conclusion

Both KTP and RTP display low temperature luminescence signals which are characteristic of phase changes within the materials. The relaxation into new phases is not readily reversed, except by high temperature annealing. The signals may reflect the presence of trapped nanoparticles, rather than the host material, but the data offer a sensitive monitor of sample quality.

Acknowledgment

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