Structural and impurity phase transitions of LiNaSO$_4$:RE probed using cathodo-thermoluminescence

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Abstract
Spectrally resolved cathodo-thermoluminescence spectra of rare earth (RE) doped LiNaSO$_4$ measured from 20 to 673 K reveal several anomalies in the RE emission lines and intensities. The low (20–300 K) temperature data show a discontinuous change in intensity at ∼170 K that is either a marked intensity enhancement or a drop truncating the entire spectrum. Such an effect on the host luminescence has previously been assigned to a transition between cubic and hexagonal polymorphs of ice nanoparticle inclusions. Similar, but less profound anomalies are seen above room temperature (300–673 K) where the changes take the form of either a discontinuity in intensity at ∼480 K or reduced intensity in the range 430–530 K. There are changes in the relative intensities of different emission lines of the same dopant in this temperature range. Such high temperature variations are ascribed to structural phase changes within the LiNaSO$_4$ crystals. The behaviours may result from Li-poor surfaces or twin boundaries behaving like Na$_2$SO$_4$. This phase change is suggested in the open literature for LiNaSO$_4$ but not yet fully documented, perhaps because the effects span a wide range of temperatures or due to experimental features inherent in most luminescence facilities.

1. Introduction

Sulfate-based radiation dosimeter materials doped with RE ions have been extensively investigated due to their high luminescence sensitivity. Several sulfate-based phosphors have been prepared (either single or double doped) and their TL characteristics are well quantified. Calcium sulfate, CaSO$_4$:Dy or Tm [1–4] are perhaps the most studied TL phosphors after LiF:Mg, Ti. The sulfate family includes MgSO$_4$ [5], BaSO$_4$ [6], K$_2$Ca$_2$(SO$_4$)$_3$ [7] and LiNaSO$_4$ [8–10] etc. For the current material, LiNaSO$_4$:RE, the TL sensitivity is higher than that of CaSO$_4$:Dy when doped with Eu [9]. In addition the material has a linear luminescence response over a wider range of radiation doses, stored charge has only a moderate rate of fading, and both reusability and reproducibility (recyclability) are close to one.

Despite these advantages, the wavelength-resolved luminescence spectra available for this system are restricted to photoluminescence data [9, 10]. Spectrally resolved data collected via wavelength-multiplexed spectrometers should provide crucial information for TL modelling, or for assessing the quality of the material under study. Such information is irresolvable in automated TL readers or systems using scanning monochromators, but is essential for a full interpretation of the luminescence properties of the solid. For example, differences in T_{max} between different emission sites, intensity changes, or wavelength shifts associated with phase transitions, are poorly detected with scanning monochromators or not resolved in TL readers. In each example this may result in misleading data.

The present study, therefore, provides spectral data for the LiNaSO$_4$:RE system, with particular interest in whether the material undergoes a phase transition near ∼500 K as suspected by Mata *et al* [11]. They conducted x-ray diffraction measurements and showed that the lattice parameter increases linearly with temperature up to ∼500 K at which temperature there is a change in the slope. This inflexion led the authors to suspect a phase transition at that temperature. Previous TL data on this material show that, for all dopants used in study,

the material has two groups of peaks [8]. The first group occurs <430 K and appears at relatively the same temperature irrespective of the RE dopant. Meanwhile, the second group occurs >550 K and moves with the RE ion size. In addition, kinetic analysis show that the <430 K peaks are first order and have frequency factors comparable with the lattice vibrations whereas the high temperature ones are of mixed order and with frequency factors lower by three orders of magnitude. These observations are consistent with the hypothesis that this material has a phase transition as proposed by [11]. Unfortunately, the absence of any TL peaks in the suspected region preclude the confirmation of such structural changes and it is inferred that luminescence spectra with continuous excitation and heating would provide the necessary signals to observe changes related to phase transitions. Indeed, the intensity steps and the subtle changes in the emission lines seen in this study over the suspected temperature range confirm the existence of a new phase for this material.

2. Experimental details

Stoichiometric ratios of Analar grade Li_2SO_4 and Na_2SO_4 were dissolved in double deionized water. 0.01 mol% RE was added as RE-nitrate. The solution was then evaporated at 100 °C, the resulting powder annealed at 400 °C under atmospheric conditions for one hour in a quartz crucible, and then quenched by rapidly taking the crucible out of the furnace and putting it on a metal block. Samples for RE ions of Dy, Tm, Tb and Yb were prepared. The composition of the product as $LiNaSO_4$:RE was confirmed by x-ray diffraction in the School of Geography and Geosciences, University of St Andrews, UK using a Philips 1050 x-ray diffractometer with monochromatic Co Kα-radiation. The products were also examined using a polarizing light microscope. The product is a white or transparent coarse crystalline powder with crystal sizes typically ∼1 mm.

For each luminescence measurement, 2–3 mg of the powder was retained on a thin aluminium disc by silicon spray. In turn the aluminium disc is attached to the heater strip or to the cryostat by high vacuum grease. Luminescence measurements were carried out on a high sensitivity wavelength-multiplexed spectrometer built by the University of Sussex, UK but now housed at the University of St Andrews, UK. Its high sensitivity stems from the fact that the equipment uses two diffraction gratings, one of which is blazed in the UV/blue region while the other is in the green-red region. Each spectrum is imaged by photon imaging plates. The equipment has *in situ* facilities for both electron and x-ray radiation which allows the user to perform cathodo-thermoluminescence (CLTL) or RLTL measurements (i.e. continuous electron or x-ray irradiation as a function of temperature). All spectra were corrected to the spectral response of the system. Measurements were carried out using a beam of 12 keV electrons at a current of 0.2 mA. The spot size was ∼5 mm diameter giving an incident power density of ∼30 kW m^{-2}. Low heating rates of only 0.1 or 1 K s^{-1} for the low or the high temperature measurements were used in order to minimize temperature gradients and measurement errors at the sample.
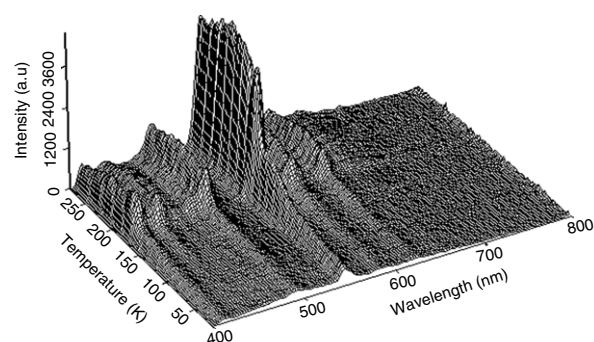

Figure 1. Isometric plot of the low temperature CLTL data of $LiNaSO_4$:Tb.

3. Results

The general trend of all data presented in this study is that sudden intensity changes occur within a restricted temperature range for all samples. The intensity changes may vary in magnitude between samples, but the effect can easily be recognized in each case. In order to emphasis such changes the data are presented as either three dimensional isometric or contour plots of intensity data versus wavelength and temperature. Alternatively, data are displayed as wavelength slices integrated along the main emission line of the RE dopant.

Figure 1 shows the low temperature CLTL data of Tb doped samples. The emission is from the Tb dopant with its main emission line appearing at 545 nm. The Tb lines emit at low intensity from 20 to 170 K at which temperature a sudden intensity enhancement occurs. Thereafter the Tb lines preserve this high and fairly constant intensity level, as might be expected from CLTL or RLTL measurements. The behaviour observed here for Tb samples closely reflects the behaviour of Nd-YAG during CLTL measurements [12], MgO:Cr [13] and other materials including zircon [14]. The sudden intensity change at 170 K also appeared in other RE doped samples, but this time as an intensity cut across the entire spectrum. Figure 2 presents the CLTL of $LiNaSO_4$:Yb which increases gradually over the temperature range 20–170 K, falls rapidly over 10 K, after which the signal recover its normal level. Figure 3 indicates the temperature dependence at two Tm lines. The Tm lines at 170 K respond in different ways. The 455 nm line shows intensity enhancement whereas the Tm lines at longer wavelengths show intensity drops. The behaviour of the Tm lines summarizes the two effects seen in Tb and Yb samples.

The high (300–673 K) temperature data reflect the effects seen at low temperature where there is intensity increase or decrease at 480 K or reduced intensity extending over some 100 K around 480 K. The CLTL yield above room temperature is relatively low compared with the low temperature data. Nevertheless, the intensity jumps can clearly be identified. Figure 4 shows an intensity drop from the Tb ion at 480 K. Apart from this temperature, the CLTL yield is fairly constant with temperature. For Dy doped samples, figure 5, the Dy lines emit at constant level up to 430 K where a sudden intensity decrease occurs. The Dy lines continue to emit at this reduced
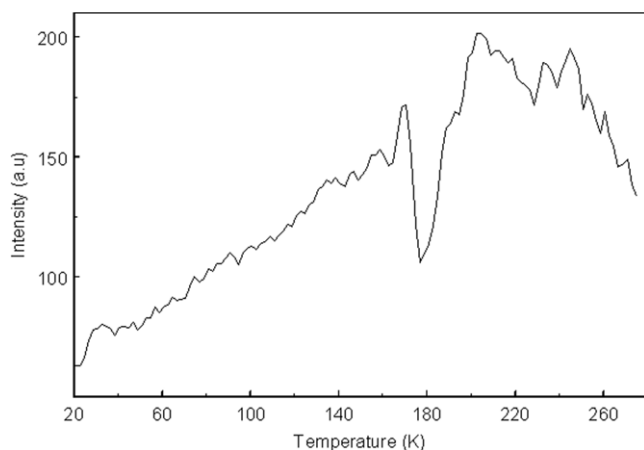
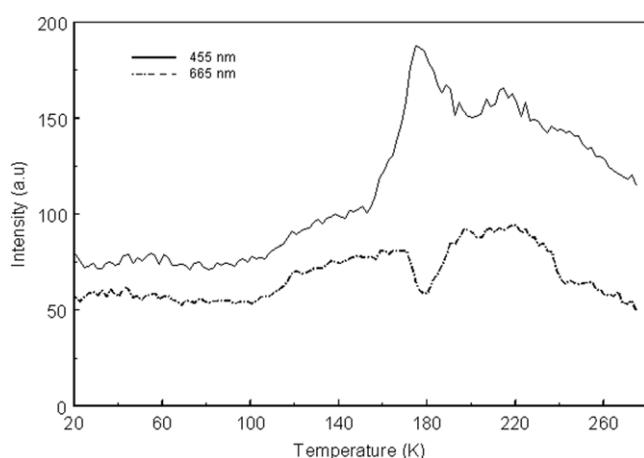**Figure 2.** Wavelength slice taken from the low temperature CLTL data of LiNaSO$_4$:Yb.

Figure 3. Wavelength slices taken from the low temperature CLTL data of LiNaSO$_4$:Tm.

Figure 4. Isometric plot of the high temperature CLTL data of LiNaSO$_4$:Tb.
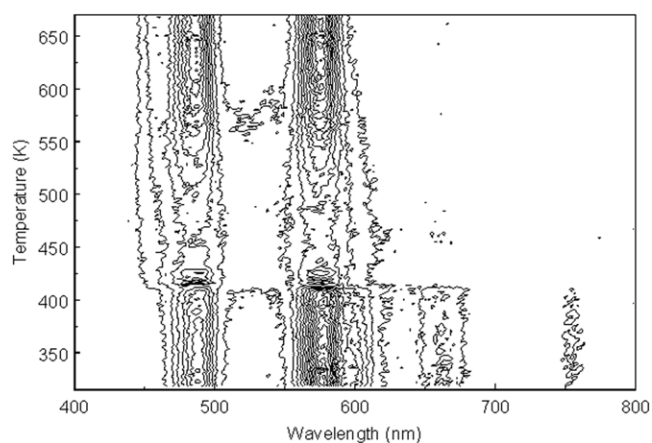
Figure 5. Contour plot of the high temperature CLTL data of LiNaSO$_4$:Dy.

level up to 550 K where there is a gradual intensity increase reverting the signal to the constant level seen below 430 K. Again the Tm dopant shows a combination of the previous two effects similar to the Tm low temperature data. In figure 6(a) the Tm line at 455 nm shows a major intensity increase around 480 K. Figure 6(b) presents wavelength slices from another Tm doped sample. In intensity terms this figure is identical to figure 3 of Tm doped samples below room temperature. In temperature terms it reflects the observation seen in Dy doped sample (figure 5) where the intensity variations occur over some 100 K. Moreover, the differences between the various Tm emission lines clearly appear in figure 6(b) where the intensity jump for the 455 nm line at 430 K is much more defined than for the 665 nm line. The situation is reversed at 530 K where the intensity jump becomes more obvious at longer wavelength.

4. Discussion

Luminescence techniques have been successfully applied to detect phase transitions from a variety of materials [15],
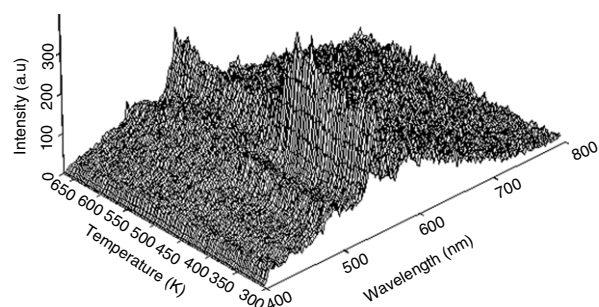
and the topic has recently been extensively reviewed [16]. Since luminescence is an exceptionally sensitive probe of the local structural state in solids. Examples of structural phase transitions are clearly expressed in luminescence and data include NH$_4$Br [17], KNbO$_3$ [18], SrTiO$_3$ [19] RbTiOPO$_4$ and KTiOPO$_4$ [20]. Equally, detection of phase transitions from impurity inclusions (e.g. CO$_2$, solvents, ice etc) in the form of nanoparticles is possible. Indeed impurity-related phase transitions have been recorded from a variety of materials such as Nd-YAG [12], MgO:Cr [13], zircon and other minerals [14]. In the case of fullerenes C$_{60}$ [21], the structural phase transition from the bulk material was sensed by changes in the luminescence of solvents. In either case, whether the transition is from the bulk or from impurity inclusions, the effects on the luminescence intensity and the emission lines of the RE dopant appear to be the same. A common feature that frequently appears (as in the above cited references) is that the luminescence efficiency during the phase transition changes abruptly has a sudden intensity change at the transition temperature. Shifts in the emission wavelength are also sensed in some cases, but the present system can only resolve substantial wavelength shifts. One suspects higher spectral resolution would more clearly identify many more.

The intensity changes shown in figures 1–6 are consistent with those expected during phase transitions. The low temperature data of all dopants show a clear sudden increase
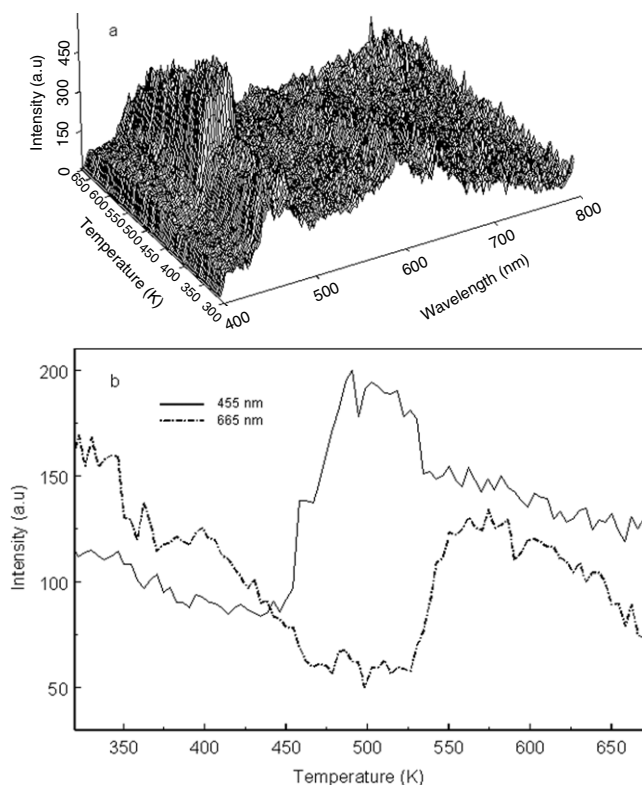
Figure 6. Isometric plot of the high temperature CLTL data of LiNaSO$_4$:Tm (a) and (b) wavelength slices of LiNaSO$_4$:Tm taken from different sample.

or decrease in intensity at 170 K. This effect is not restricted to this system, but has been recorded from several materials [14] and ascribed to long range effects on the host luminescence intensity induced by transitions between cubic and hexagonal polymorphs of ice. Water can diffuse to the near surface region from the atmosphere with a possibility of being trapped either within the bulk, or at dislocations and grain boundaries, as nanoparticles of water. A particularly clear confirmation of the cause of the 170 K event which assigned it to ice was previously done for zircon doped with Dy. Heating the sample in air or heating it in a jet of steam to drive off or introduce the water resulted in quenching or enhancing the anomaly at 170 K [14]. Note the use of CL is particularly sensitive to such near surface changes and the electron beam may actually assist in the impurity phase transition.

The intensity steps for the high temperature measurements are similarly consistent with those associated with phase transitions. The intensity steps reflect either increases or decreases in intensity and both may occur from the same sample for different emission bands (see figure 6(b)). Rare earth transitions are sensitive to the local crystal field and the luminescence undoubtedly encodes information about the local coordination of the RE site. Therefore, any change in the lattice is reflected by variations in the precise position of the emission lines and their relative intensities. Different emission lines of Tm respond to the variations in the LiNaSO$_4$ structure in different ways. One possible explanation of this is that the Tm ions occupy two or more nonequivalent lattice

sites. At the transition temperature variations in the ratio of radiative to non-radiative transitions occur and emission from one site becomes more favourable leading to intensity enhancement from particular transitions and quenching from others. Alternatively, a polymorphic phase transition may result in modification of the point symmetry of a single Tm site, since the favourability of particular radiative decay pathways is sometimes dependent on the presence or absence of centres of inversion. We infer that the room temperature LiNaSO$_4$ polymorph is unstable in this temperature range and the major event occurs at 480 K. The instability of the host lattice or reduced intensity in this temperature range may assist in explaining earlier TL data [8, 9]. The TL data for the RE dopants (RE = Eu, Ho, Tb, Gd, Sm, Ce or La) have no TL peaks in this temperature region. Also two groups of peaks of different kinetics are observed either side of this region [8]. This is consistent with the observation that TL peaks in the new phase might have different TL kinetics compared to those preceding the phase transition. Further, the observation that the Dy ion is an inefficient activator in this matrix [9], despite its high efficiency in other sulfates like CaSO$_4$, is also in line with the reduced intensity in the range 430–530 K. Dy has two relatively small TL peaks at 398 and 469 K [9]. The second one (the dosimetric peak) falls within this temperature range, so emits at low intensity. Apparently, the instability of the lattice in this temperature range prevents formation of stable charge traps and when they exist as in the Dy case, the recombination energy in inefficiently coupled with the RE and most of the energy is dissipated through successive emissions of phonons.

The alternative routes of excitation with electrons (CL) or x-ray (RL) generate signals from the near surface region and the bulk material respectively. For coarse powder samples, grain size the ratio of surface to volume is high and the two routes are expected to yield, to some extent, similar results. Although some systems show a particle size effect even when the particles are microns in size, the present study uses relatively large crystals, typically 1 mm in size and hence we expect such effects to be minimal. Unfortunately, the intensity steps above room temperature which are believed to arise from the host bulk are not seen with continuous x-ray irradiation and heating. This may be because the intensity changes are rather small and to observe such changes a high incident power density is needed, which is not available in the case of x-rays. Therefore, it should be of no surprise that such restructuring in the host material is not seen in other techniques and hence not reported. The only documented observation is a small change in the lattice parameter of the material around 490 K [11]. Differences between RL and CL are also seen in fullerene C$_{60}$ where the CL data reveal a major intensity step across the spectrum and absence of such event in the RL data [21].

It is interesting to note that evidence for phase transitions in the temperature range 430–530 K is strongly reminiscent of the behaviour of Na$_2$SO$_4$, which has a series of transformations precisely at that temperature range. The room temperature polymorph V–Na$_2$SO$_4$ transforms via a series of intermediate steps to I–Na$_2$SO$_4$ [22]. However XRD shows that our samples are not contaminated with Na$_2$SO$_4$, hence the behaviour we observe is a property of LiNaSO$_4$. Two interpretations

can be placed on the similarities in behaviour between the present system and Na_2SO_4. First, the electron beam may cause Li^+ ions in $LiNaSO_4$ to migrate at the surfaces of the crystals, leaving a defect structure which behaves akin to Na_2SO_4. Such an explanation is supported by the exceptional Li ion conductivities in Li_2SO_4 and would explain why the transformations are more obvious in CL than RL (since electrons penetrate shallowly into the sample). Variability in the degree of Li loss may explain the wide range of temperatures at which the transformation is observed.

A second explanation arises from the fact that $LiNaSO_4$ is invariably twinned [11]. The twinning results from the fact that the $LiNaSO_4$ structure is enantiomorphic and left- and right-handed forms of the structure are possible. What is of interest here is the twin plane itself at which the left- and right-handed forms join. At these interfaces, strain gives rise to a local configuration that has higher symmetry than the host phase. Depending on twin densities and the width of the strain field, the twins can constitute a significant volume of the bulk. The contribution of twin planes to luminescence may be further enhanced if dopants such as lanthanides preferentially reside there. Luminescence from the twin planes would make the properties very sensitive to cooling rate during preparation (dictating twin density) and the nature of the lanthanide. Hence the data may also be interpreted to suggest that the twin planes within $LiNaSO_4$ are effectively domains with Na_2SO_4 structure which may also be preferentially lanthanide-rich. This observation is consistent with the published TL data [8, 9] which suggests a contribution to luminescence from the interior of the grains.

To summarize, the CL during heating is very sensitive to changes in site symmetry and lattice spacing, hence is a very powerful tool to probe phase transitions from either the host material or from impurities trapped in the near surface region. The CL data clearly demonstrate a host signal intensity step at 170 K resulting from long range effects of phase transitions within ice nanoparticle inclusions. By contrast the high temperature intensity jump around 480 K is believed to result from the restructuring of the host material. This may encode transitions in Li-poor regions at the surface, or it may be as a result of atypical luminescence from twin interfaces. The restructuring process may be a second order phase transition so will occur very slowly within a temperature heating cycle. The strongest event appears near 480 K.

5. Conclusions

CLTL data of $LiNaSO_4$:RE (RE = Dy, Tm, Tb and Yb) reveal two anomalies in the CL intensity attributed to phase transitions, one from ice impurity and one from the host material. The similarities between the temperatures of changes in luminescence intensity above room temperature and the reported temperatures of transformations in Na_2SO_4 may represent domains where Li loss or twinning has given rise to domains with Na_2SO_4-type structure. The phase diagram of this material may need to take into account the observations seen here in the temperature range 430–530 K. More investigations are needed to confirm the exact transition temperature, and indeed if it is sensitive to impurities and other distortions. Such data will however require high quality crystals in order to see the effects at a well defined temperature.

Acknowledgments

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