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Influence of phase transitions of ice on near-surface cathodoluminescence

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Abstract

Luminescence signals respond to phase transitions both of the host material and of impurities on the nanoparticle-size scale. During cathodoluminescence spectral measurements of many insulators, strong intensity changes (up to 100 times) have been recorded at ~ 170 K, which are here ascribed to the phase transitions of water that has diffused into the near-surface regions, or is trapped within the bulk material in nanoparticle quantities. The intensity step correlates with the ice transition between the cubic and hexagonal phases. In many materials there are also weaker features near 230 K which match the low-pressure ice-to-vapour transition. Some signals are apparent in radioluminescence data when the water is within the bulk material. The impurity phase changes can modify the emission spectra of the host. Examples are given for several insulators (Nd:YAG, zircon, MgO:Cr, PbWO₄, strontium barium niobate) and a superconductor. The data have implications for quantitative luminescence analyses and underline the significant and influential presence of water contaminants. In many surface layers, such as surface optical waveguides or those of superconductors, the ice may significantly influence the behaviour of the host material.

1. Introduction

During an extensive ongoing search for examples of phase transitions of insulators manifested in luminescence properties, there have been a number of clear examples in which the lattice transitions have a dramatic effect on the luminescence intensity and spectra [1–3]. In many cases the luminescence features directly link to known structural transitions, and additionally

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some new transitions have been detected [4] as well as undocumented examples of hysteresis. For the intrinsic phase transitions, luminescence responses have been sought during x-ray excitation (RL, radioluminescence) and thermoluminescence (TL). Near-surface excitation with electrons (CL, cathodoluminescence) also provides characteristic signatures of phase changes with discontinuities in intensity and spectral changes [5–7]. In addition to phase changes of the host material, there are detectable secondary effects caused by the presence of inclusions of impurities. A particularly clear example was noted in a Nd:YAG crystal near 200 K where the cubic lattice changed parameter, there was a step in the intensity and the Nd emission lines were displaced in wavelength [8]. This example was attributed to the presence of nanoparticles of CO₂, which sublime near 197 K, and the consequent pressure change distorted the lattice and modified the crystal field at the Nd lattice sites, as well as influencing the overall transition probability. Less spectacular effects have been noted in many samples and these can generally be ascribed to the presence of trapped gases such as nitrogen or argon which were incorporated during crystal or thin-film growth. In other cases there is correlation with luminescence detection of phase transitions of impurities and data from other techniques, as for electrical resistivity discontinuities of gold nanoparticles [9].

The origins of the preceding examples have normally been recognized since the melting and/or boiling temperatures of the probable trapped impurities match those quoted in the literature for bulk material. Examples have included CO₂ and N₂ from the air or Ar as a background gas in pulsed laser deposition of thin films. Nevertheless, other features have the same behaviour pattern but are only sensed during CL. These examples are therefore assumed to be associated with surface impurities which have entered, or attached to, the surface. Of particular note is a major feature which occurs near 170 K. This temperature defines a boundary between strong luminescence (>170 K) and weakened, or suppressed signals for the lower-temperature CL. The emission spectra are always of that from the host lattice. The general pattern of behaviour is that this anomaly fades with repeated measurements (i.e. consistent with loss of the surface impurity by electronically activated desorption). Associated, but weaker, intensity anomalies are often noted near 230 K and sometimes near 70–100 K. The 230 feature differs from that at 170 K since it has been apparent in RL data, even when the 170 K event has faded or not been noted.

This present study offers an explanation of the origin of the 170 K intensity and spectral discontinuity.

2. Experimental system

All measurements were taken using a wavelength-multiplexed spectrometer which offers very high sensitivity as a result of photon imaging detectors to record the spectra [10]. Spectra are recorded every second at a selected temperature or during heating or cooling. The temperature range used was from 25 to 300 K and a typical heating rate was 0.1 K s⁻¹ (6 K min⁻¹). Data are corrected for the wavelength dependence of the spectrometer. Excitation can be by x-rays or electrons. Further details of the system have been reported in earlier publications [1–10]. For this CL study the electron energy is usually from 4 to 20 keV and the current density is <5 μA cm⁻². This implies near-surface excitation since at 10 keV the electron penetration is ~0.5 μm. The deposited energy can lead to a much larger depth, or volume, of excited material, so the CL is sensitive to material directly on the surface to at least a micron depth within the solid.

Unfortunately such a high-sensitivity low-temperature RL, CL and TL system with continuous wavelength-multiplexed spectral analysis appears to be unique. Many of the phenomena reported here will be obscured or undetected by scanning monochromator systems,

and those which use high CL beam current densities. This situation is reflected by the paucity of publications relevant to this study, except from those using the Sussex system, even though the signals are often very strong.

3. Results

The general pattern of behaviour is that, linked to phase transitions, there are luminescence features from the host material with discontinuities in intensity, and sometimes changes in the wavelength of the emission. These can be either from the host or from trapped impurities. The latter effects are obvious in a few cases, for example from rare-earth or chromium emission sites, but the spectrometer does not have high resolution since it was originally designed for sensitivity and rapid recording of spectra during TL. Therefore small wavelength movements may be more prevalent than noted so far. The intensity anomalies are seen from a variety of natural and synthetic insulators and figures 1 and 2 show a selection of examples. Figure 1 presents data for a zircon crystal, which is doped with samarium. Figure 1(a) is for the first CL measurement in which the sample is heated from low temperature (~ 25 K) to 300 K during electron excitation.

In this sample, re-cooling and a second measurement yielded figure 1(b). In other samples there was often a much greater persistence of the 170 K intensity step. More careful inspection of the original data reveals a small 230 K feature. In this case the signals are ascribed to Sm transitions.

Figure 2 summarizes some other examples. Figure 2(a) has an isometric plot of CL data for Nd:YAG which closely resembles the zircon data. The narrow emission bands are from Nd transitions but the intensity pattern near 170 K is identical to that from the zircon. The 230 K feature is also very clearly apparent for this sample, as are wavelength shifts near 800 nm between the different temperature regimes. Alternative views of the phenomenon are emphasized by the contour plots. Figure 2(b) is a contour map for green spodumene which emphasizes the 170 K discontinuity as the high contour line packing density causes a dense band of contour lines across the spectrum at a fixed temperature. Similar lines indicate anomalies near 197 and 230 K.

An example of data, figure 2(c), for an MgO crystal doped with 1300 ppm of Cr delineates clearly the 170 K intensity step and, less clearly, a higher-temperature one near 230 K. There are other features at lower temperatures with both intensity and wavelength steps which were attributed to solid/liquid and liquid/gas phase changes of trapped impurities such as N_2 and O_2 . The temperatures match the standard phase changes of the gases which were present during crystal growth. In MgO the same features are seen in RL as well as CL but the direction of wavelength displacements of the chromium emission bands differs from that for the RL and CL. This was interpreted [6] as evidence for phase changes causing pressure within the lattice. Within the bulk crystal the pressure compressed the lattice. By contrast, the near-surface material is unconfined and so the same transition leads to a pressure-driven expansion of the lattice. The changes in crystal fields at the Cr sites consequently cause a difference in sign of the wavelength discontinuity from the Cr luminescence sites.

Figure 4(d) presents an intensity plot for a selected wavelength range for a sample of lead tungstate. Here the 170 K step is less dramatic than for the other examples. There is also a 'spiky intensity event' near 115 K which was reproducible for this sample, but not seen in all the tungstate material investigated. Further quite similar examples have been noted from the CL of synthetic crystals of MgO:Cr and Er-YAG. For minerals such as topaz, calcite and cerusite, signals, particularly at 230 K, have also been recorded in RL.

In the case of barium strontium niobate (SBN) the CL spectra have a number of features in

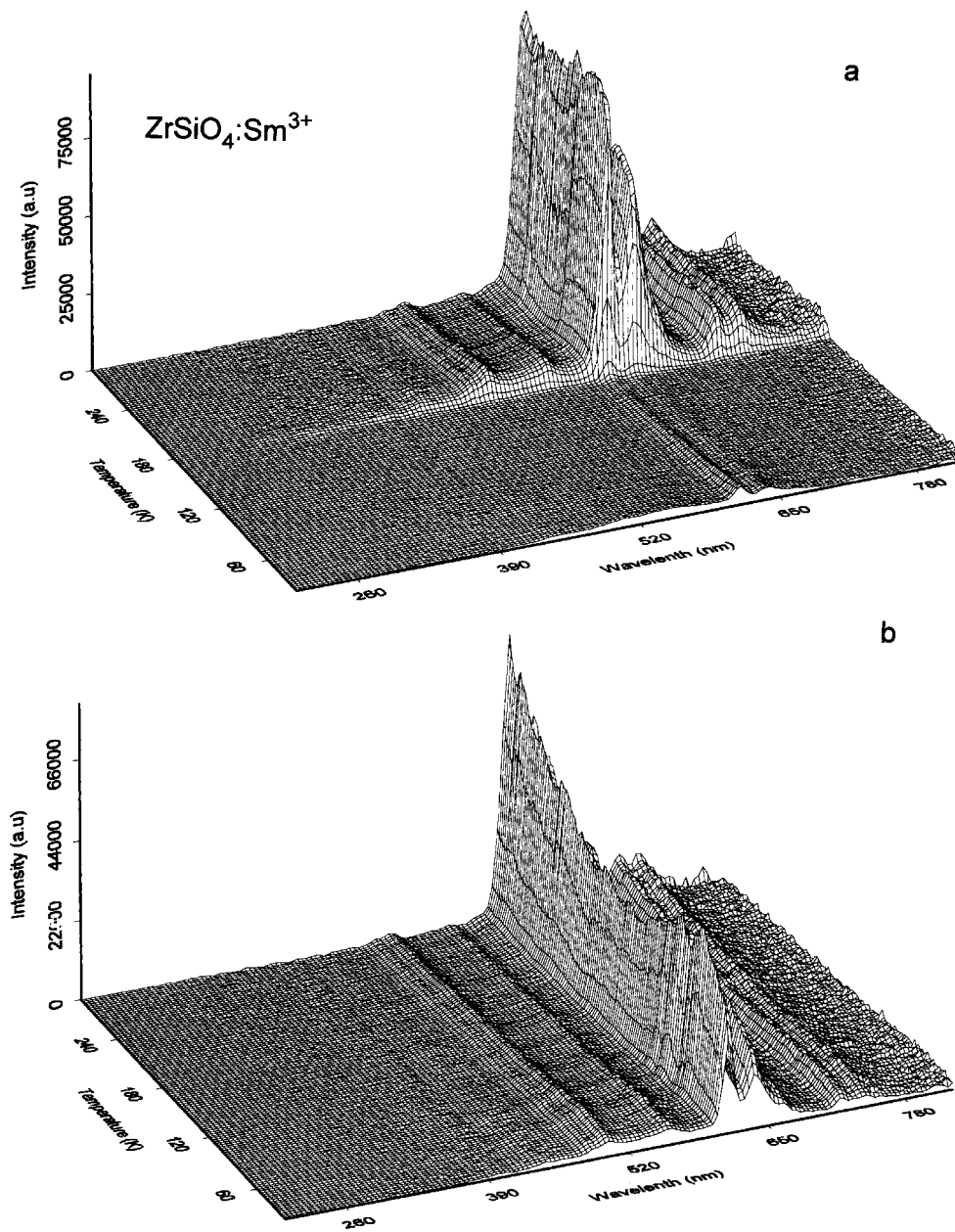


Figure 1. (a) The emission from Sm impurities in a zircon sample during the initial CL heating and (b) a subsequent re-measurement.

terms of emission bands at different temperature, but across the entire spectral range there are again indications of very sudden changes in intensity. These are apparent from the isometric plot of figure 3(a) at both 170 and 230 K. However, in the SBN case it is necessary to view both the isometric and contour plots of the data, since the 170 K discontinuity in intensity is characterized by a notch in the signal, rather than just a step. The notch behaviour of the CL intensity has been noted previously for the case of a 155 K phase transition of fullerenes [3].

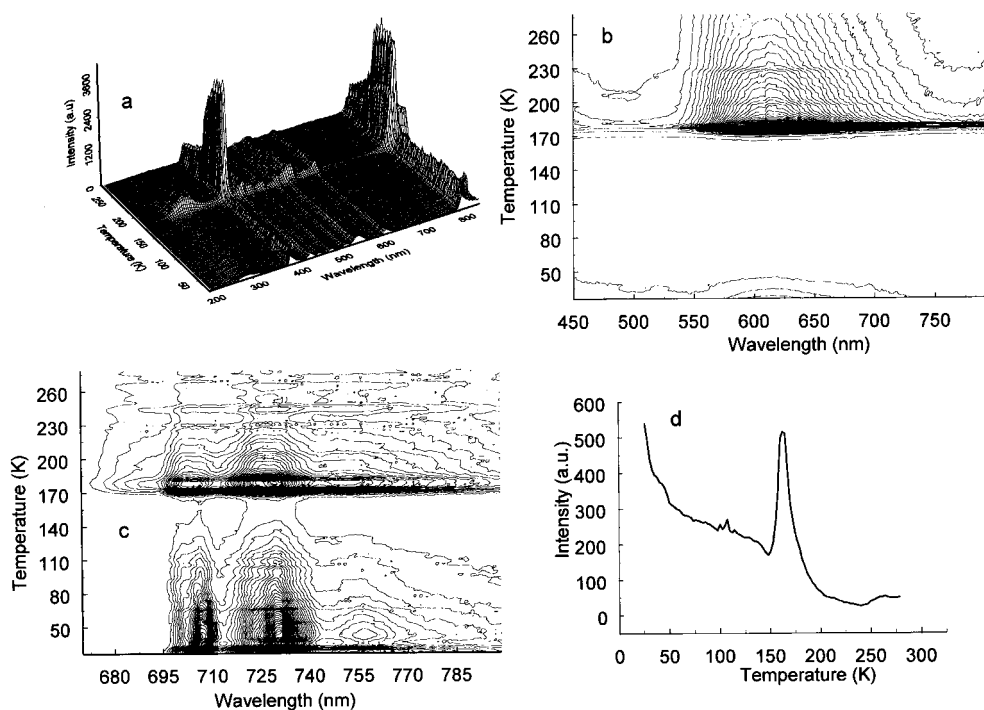


Figure 2. (a) CL spectra obtained from a crystal of Nd:YAG during heating at 6 K min^{-1} . Note the intensity steps at 170 and 230 K. Detailed examination reveals that wavelength steps occur for the lines near 400 and 800 nm. (b) The contour map from a sample of green spodumene. High densities of contour lines indicate intensity discontinuities near 170, 200 and 230 K. (c) Similar data for an MgO crystal doped with 1300 ppm of Cr. (d) An intensity versus temperature plot for an initial CL heating run for a lead tungstate crystal.

Finally, figure 3(c) demonstrates that the SBN anomalies in intensity are seen at all wavelengths, even though the temperature patterns of the intensity are different for different spectral regions. As in other materials, the 170 K feature faded with repeated measurement, but that at 230 K persisted for longer.

CL can be used to record near-surface signals from numerous materials, including those which appear visually very black. Examples include not only those for fullerenes [3] but also very early data for high-temperature superconductors [11]. A current study of a superconducting tape of $(\text{Bi}(\text{Pb}))_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x/\text{Ag}$ gives CL intensity features as in figure 4. Whilst the signals are relatively weak, they nevertheless show distinct (and reproducible) intensity steps in the isometric plot. In this case the feature near 115 K is thought to originate from the superconductivity transition [12], but those near 170 and 200 K probably originate from surface absorbed or trapped impurities. Based on the Nd:YAG example, a possible explanation for the feature near 200 K is the sublimation of nanoparticles of CO_2 . The 170 K feature and the weaker feature near 230 K were more pronounced with lower electron energies. This might imply that the ice phase is close to, or on, the surface, but equally it might indicate that the ice deeper into the surface is inhibited from changing phase.

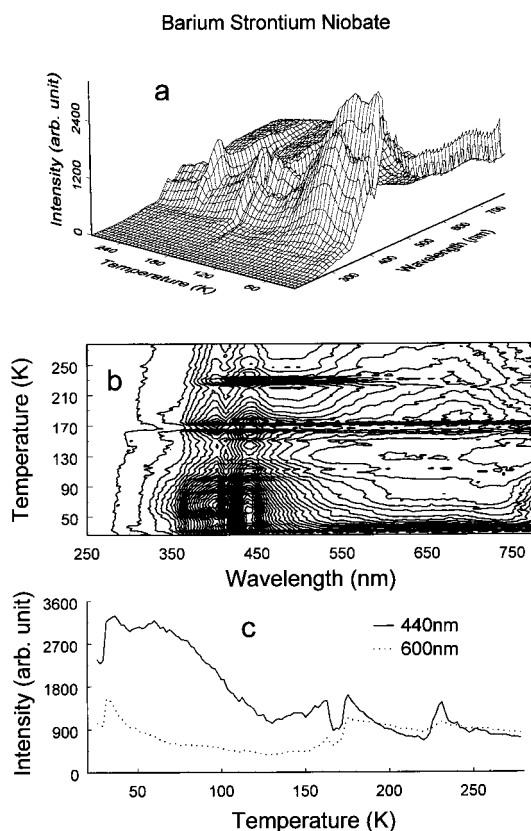


Figure 3. (a) CL from barium strontium niobate; (b) a contour plot; and (c) intensity versus temperature in two wavelength regions.

4. Discussion

The widespread appearance of an anomaly at 170 K suggests that it is related to an impurity and the obvious question to ask is what is the impurity which is so common and effective in quenching luminescence, and which has a phase transition at this temperature? Reference to the literature does not show any suitable cutting, polishing or cleaning materials with phase transitions at this temperature. However, a highly probable candidate to consider, which pervades all experimental environments, is water vapour.

Water vapour in the atmosphere has a partial pressure which will cause deposition of monolayers per second from the ambient air. Some of this water may be retained on the surface, some re-evaporated and some will penetrate into the surface via polishing cracks or dislocation lines. The dislocation density associated with polishing is high, often 10^4 cm^{-2} , and the features can extend one or more microns into the surface. This is precisely over the depth range which is probed by a low-energy CL beam. Further, excitation of the host lattice by the electron beam need not generate the luminescence at the initial lattice location where there was ionization. Indeed the electron-hole pairs are assumed to migrate to recombine at favourable lattice sites. In general these are likely to be impurity sites, rather than host lattice sites. Hence luminescence signals are dominated by the emission at impurity sites such as Sm, Dy, Nd or Cr, rather than from intrinsic emission bands that are normally observed at shorter

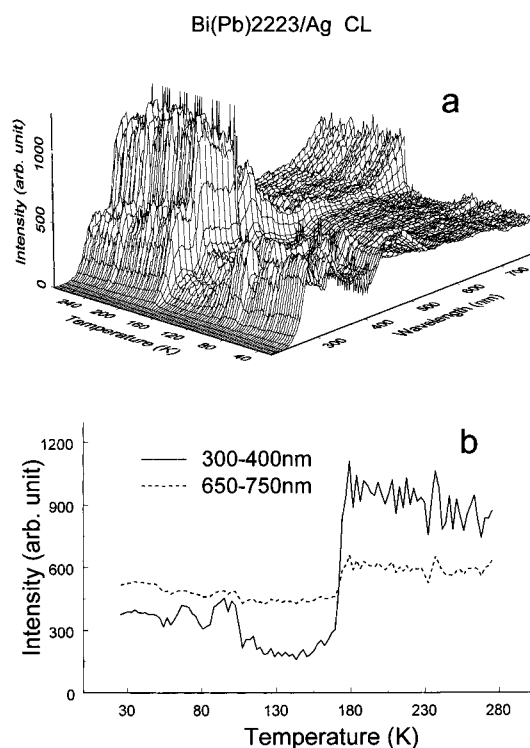


Figure 4. CL data for a Bi(Pb)2223/Ag superconductor.

wavelengths. The presence of water, either liquid or frozen into ice, will offer alternative sites for charge recombination. In some phases and/or bonding states this may be highly effective at providing non-radiative energy dissipation, and so will almost totally quench the luminescence.

In earlier studies with Nd:YAG the CL intensity as a function of electron energy showed movements in the emission spectra from the Nd lines which were sensitive to the dislocation density in the surface of the material. Whilst the bulk signals, as sensed by means of RL, were stable, the line positions induced by CL changed over the course of a few days and the assumption was that this was linked to uptake of water into the surface [13].

One of the present experiments which confirms this view contrasts controlled quantities of water which have penetrated into the surface. Figure 5 shows the intensity versus temperature plots from one zircon crystal doped with Dy. The initial normal CL measurement has inhibited the luminescence intensity below 170 K, together with the strong intensity peak near that temperature. Figure 5(b) shows that after subsequent runs the overall intensity has increased at 170 K and the intensity at lower temperatures is also steadily increasing. The same sample was then heated on a hot plate at 100 °C to drive off absorbed water and, whilst warm, re-introduced into the vacuum system. The subsequent CL, figure 5(c), shows almost no evidence of the 170 K event. Finally, the sample was heated in a jet of steam to actively introduce water vapour. The CL data of figure 5(d) show dramatically that the 170 K feature now dominates the heating curve. Further, the low-temperature signals are reduced even at 25 K.

Water is clearly the controlling impurity, but the experiments do not reveal whether the water is present as nanoparticle droplets embedded in the host, as water within dislocation

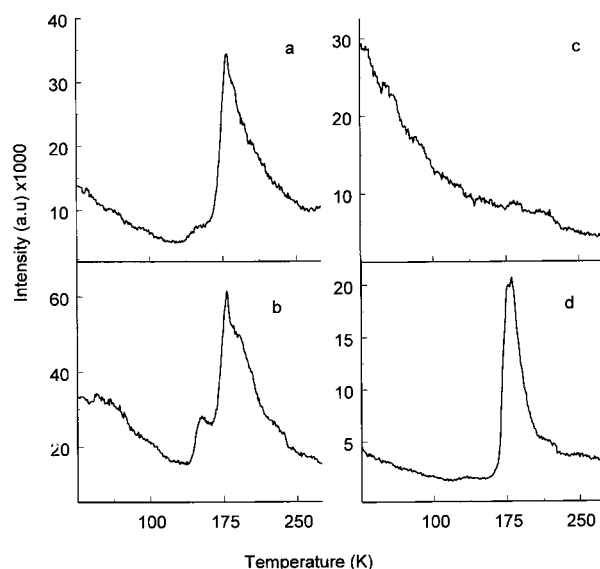


Figure 5. The data are for the same zircon crystal, which has line emission from the Dy dopants. (a) The initial heating run; (b) the second heating measurement; (c) for the sample after heating to 100 °C and returning to the CL system whilst still hot; and (d) after heating in steam. Although the intensity scale is in arbitrary units, they are approximately consistent throughout.

lines, or in some other form. If there is a restriction on the modes of movement, for example because the water has entered as a linear chain of molecules in a dislocation line, then there may be differences in behaviour from that for conventional bulk ice. Some of these options may be apparent from reference to the phase transition for ice. There is a considerable literature on the phase diagram of water ice [14–17] and a summary sketch is given in figure 6. At pressures near normal atmospheric pressure it is apparent there is a well documented transition from cubic to hexagonal ice near 170 K. It therefore appears that the lower-temperature cubic phase inhibits luminescence from the materials discussed here.

For nanoparticle or dislocation-trapped ice it is unclear how many associated molecules are required to respond with the 170 K characteristics of ‘bulk’ ice. The difficulty in assessing this results from inadequate data on the surface energies of the ice particle and the scale of interactions with the host lattices. Nevertheless a true volume response implies a minimum particle size containing some tens of molecules. Comments on the other ice/water-related luminescence intensity data are more speculative. The 230 K events are likely to be from phase changes which modify the volume of material since the line emission features are displaced from say Nd in YAG (e.g. figure 2) or from Dy in CaSO₄ [18]. Further, the clear presence of RL data for the 230 K intensity steps suggests that not only are the inclusions in the volume of the host, as well as in the near-surface layers, but also the processes responsible for the 170 K and 230 K steps are not the same. This introduces difficulties in assignment from the ice phase diagram since the only 230 K region temperature features noted in figure 6 occur either for high-pressure conditions (for the confusing phase changes near 10⁸ Pa), or for the vapour-to-solid-Ih transitions at low pressures near 200 Pa. For nanoparticles of bulk ice, the high pressures are unrealistic, but for molecules confined within a linear chain, as in a dislocation, the inhibition of bond-angle flexibility might resemble that which occurs at high pressure. However, the lower-pressure situation is much more probable since the experiments in this temperature range are always conducted within a vacuum chamber and a standard vapour-to-

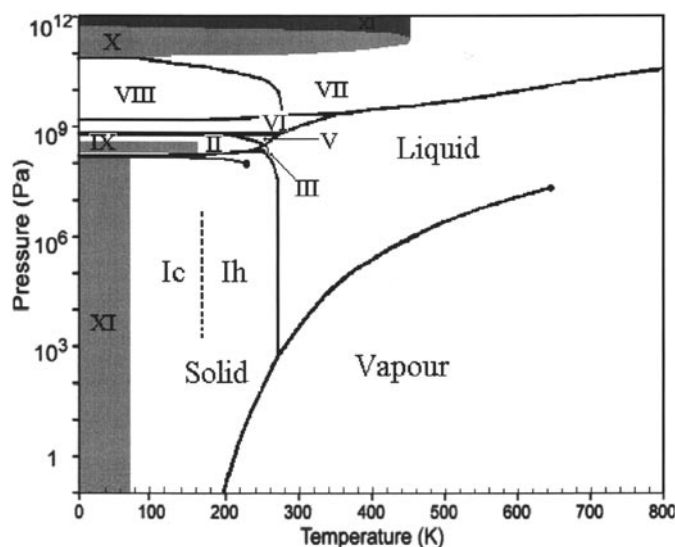


Figure 6. A sketch of the phase diagram for ice. Note that not all aspects of the sketch are fully documented and some aspects of the phase conditions are sensitive to the presence of impurities or the previous thermal history of the ice. A key feature is the conversion between hexagonal- and cubic-structured ice at 170 K.

ice transition of material within (or in the near-surface region of) a solid could be a universal effect, in line with the wide range of examples.

The origins of low-temperature ice effects near 70 K are speculative since, although there are transitions between ice phase XI and the cubic Ic, experimentally in the luminescence data these are weak features. Also the phase diagram details are not fully verified. Finally, a viscous liquid water film has been discussed as existing over the range 140–210 K and energy changes detected by differential thermal analysis (DTA), and also with anomalies near 110 K [19]. For heating rates of 10 K min⁻¹ a DTA exothermic change occurs near 200 K, but at lower rates it is near 230 K. The DTA data and ice phases can be perturbed by dissolved impurities, so some caution is needed in directly comparing temperatures of bulk and confined nanoparticle-size material.

There has long been evidence that water can penetrate into the surface of many materials, but the current data suggest that the water is not merely bonded within the lattice but can show properties consistent with bulk ice. This implies that the water is present on the nanoparticle-size scale, in order to have the associated properties of phase transitions characteristic of bulk ice. In CL terms this has a dramatic effect on the luminescence intensity, and a minor effect on the emission spectra. The strongest feature is suppression of CL by the cubic ice phase that exists below 170 K, but not by the hexagonal (or liquid [19]) phase at higher temperatures.

The frequent occurrence of a 230 K anomaly in luminescence, both in bulk and near-surface data, is best assumed to relate to ice/vapour transitions in a reduced-pressure environment.

Considerations of nanoparticle inclusions is relatively recent and so some earlier data may need reappraisal. Indeed, even in the very early high-temperature-superconductor work [11] reference is made to the resistivity and specific heat anomalies which were then of current interest and included events near temperatures of 170, 200 and 230 K. At that time they were assumed to be arising from the host superconductor, rather than any phase effects from trapped impurities. From the present perspective these features might be attributed to phase transitions of CO₂ or water.

5. Conclusions

The implications of the data are that water has penetrated the surfaces of many materials, including synthetic insulating crystals, natural minerals and superconductors, and the water/ice exists in nanoparticle scale units. Penetration is probably aided, or stabilized, by dislocations introduced by surface treatments, including polishing. As seen here, the ice influences the luminescence, but by implication it will have significant effects on many other near-surface properties. In hindsight, numerous examples can be recognized, not only for luminescence. The ubiquitous problem of water is equally relevant to the performance of superconductors, optical waveguide losses, non-linear optic guides as well as CL analyses for academic or mineralogical usage. Although measurements of low-temperature luminescence spectra are not normally considered by researchers in these fields, the data suggest that they might contribute to quality assessments of the materials.

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