ULTRAVIOLET ABSORPTION SPECTRA OF RbBr:Yb^{2+} CRYSTALS AT ELEVATED TEMPERATURES

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ABSTRACT

High temperature ultraviolet absorption spectra of Yb^{2+} - doped rubidium bromide crystals have been measured at elevated temperatures up to 358°C with the aid of a specially designed variable temperature optical cell and a Varian DMS–90 NIR – Visible – UV spectrophotometer. Results showed that the high temperature absorption spectra of RbBr:Yb^{2+} crystals have the same basic structure as that of a freshly -doped RbBr:Yb^{2+} crystal measured at room temperature. Results also showed that the energy parameter ∇ which is an approximate measure of the strength of crystal field splitting of the electronic states of the $4f^{13}5d$ configuration of Yb^{2+} ions in RbBr crystals heated to temperatures below 200°C decreased below its value when the crystal is at room temperature. However, ∇, increased when the RbBr:Yb^{2+} crystals were heated to temperatures above 200°C. Evidence obtained suggested that in crystals heated to temperatures of about 354°C, the Yb^{2+} ions existed in two separate precipitate phases.

KEYWORDS: Ultraviolet absorption, optical cell, high temperature spectra, divalent ytterbium ions, rubidium bromide.

INTRODUCTION

It is a well-recognized fact that when a divalent metal ion occupies a cation site in an alkali halide crystal with sodium chloride structure, the charge balance in the neighbourhood of the impurity metal ion is upset. A charge – compensating mechanism is therefore required to restore the charge neutrality in the vicinity of the substituting metal impurity ion [Bron and Heller (1964), Bradbury and Wong (1971a), (1971b), Sundberg, et . al (1974), Guzzi and Baldini (1974)]. Experimental results obtained using a variety of techniques suggest that the most prevalent charge compensating mechanism consists of the existence of a cation vacancy in one of the twelve nearest neighbour cation sites in the <110> direction [Watkin (1959), Nair, et. al. (1968), Rubio, et. al. (1974), Bradbury and Wong, (1971a), (1971b), Sundberg, et . al. (1974), Ramponi and Wright (1984). This implies that for a divalent metal ion occupying an alkali metal ion site as an impurity ion in an alkali halide crystal, the site symmetry of the substitutional divalent impurity ion is nominally orthorhombic C_{2v} symmetry.

However, it has been pointed out [Abragam and Bleaney (1986)] that the crystal field perturbing the electronic states of the substitutional impurity metal ion would be predominantly octahedral with a small orthorhombic distortion. As a result, the splitting of the electronic states of the divalent metal ion in the alkali halide crystal due to the orthorhombic component of the crystal field is expected to be very small compared with the spitting due to the octahedral component of the crystal field. To a first approximation, therefore, the effect of the orthorhombic distortion of the crystal field can be ignored in a theoretical analysis of the electronic structure of divalent metal impurity ions in alkali halide crystals. This is referred to as the octahedral approximation. It has been used successfully in many studies [Hernardez, et al. (1980), (1981), Tsuboi, et al, (1981), Bland and Smith (1985)] in analyzing the absorption and excitation spectra attributable to $4f^N \leftrightarrow 4f^{N-1}5d$ electronic transitions of some divalent rare-earth ions in alkali halide crystals. Nevertheless, the orthorhombic distortion cannot be ignored in studies involving $4f^N \leftrightarrow 4f^N$ transitions of divalent rare-earth ions in the crystals.

In spite of the above, it is quite reasonable to question the validity of the octahedral approximatation. It has been shown [Watkin, 1959] that at temperatures as high as 300°C, any charge-compensating vacancy in the KCl:Eu^{2+} crystals are no longer localized. The cation vacancies are believed to move in such a manner that they are not attached to any particular substitutional impurity Eu^{2+} ion. As a result, The effective local symmetry at the site of the Eu^{2+} ions is octahedral. [Nair, et al. (1968) .This, infact, is the basis of the practice of quenching doped crystals from doping temperatures to a lower temperature such as room temperature (RT) or liquid nitrogen temperature (LNT). It is hoped that on quenching, the impurity ions and vacancies in the doped crystals would be frozen in at their sites at doping temperature. In view of the above, it has become attractive to measure that absorption spectra of divalent rare-earth metal ions in alkali halide crystals at elevated temperatures.

In this paper are presented the results of the measurement of the spectra of rubidium bromide crystals doped with divalent ytterbium ions at high temperatures. Already, the spectra of RbBr:Yb^{2+} crystals have been measured and characterized at RT and LNT. [Mejeha and Smith (2006)]. It is hoped that comparison of the high temperature spectra of the RbBr:Yb^{2+} crystals with those obtained at RT and LNT would lead to useful insight as to the behaviour of the impurity Yb^{2+} ions at high temperatures.

EXPERIMENTAL METHODS

Doping of Rubidium Bromide Crystals

The single crystals of rubidium bromide used in this study were obtained from BDH Chemicals Ltd, Poole, England while the ytterbium ingots used were obtained from Rare – Earth Products Ltd, Cheshire, England. The certified purity level of the metal ingots is 99.99%. Doping of the RbBr crystals was done by adopting the metal vapour phase diffusion technique in which the nominally pure single crystals of RbBr were heated in ytterbium atmosphere. Details of how this is done has been described by Bland and Smith (1985). The freshly doped crystals were usually coloured because of the presence of colour defect centers such as F – centers and F – aggregate centers. These were however eliminated by thermally bleaching the crystals as described elsewhere (Mejeha and Smith, 1995).

The Variable Temperature Optical Cell

A variable temperature optical cell was designed and constructed for the measurement of the absorption spectra of the crystals at temperatures ranging from LNT to 800°C. Figure 1 shows a cross – sectional view of the optical cell. It consists of a cell tube (identified in the figure as stainless steel cylinder), a sample holder and a cell jacket.

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The cell tube is a cylindrical tube open at the top end and made of Immaculate V stainless steel which is capable of withstanding continuous exposure to temperatures as high as 1100°C for long periods of time without being degraded. It houses the heating element and serves as a heat reservoir during high temperature measurements.

The cell tube is coupled to a sample holder which is also made of Immaculate V stainless steel. It is equipped with heat shields, slots for thermocouple access, radiation beam slots as well as a gravity holder. The latter holds the sample in place without obstructing the path of the radiation beam. It only provides a minimum possible constraint for the sample so that the latter can expand or contract as the temperature is varied without being damaged.

The cell jacket consists of a cylindrical tube made of brass and joined to a rectangular box also made of brass. The cylindrical portion of the cell jacket houses the cell tube and the thermocouple wires by means of which the temperature of the sample is monitored. The rectangular portion of the cell jacket serves as the sample chamber which houses the sample holder. On opposite faces of the box are two quartz (spectrosil) windows through which the radiation beam passes. Pumping access is provided by means of a brass tube joined to another face of the box. Through it the sample chamber can be evacuated by means of a diffusion pump: Four water ducts or channels bored into the base of the cell jacket and connected to a copper tubing form an integral part of the water cooling system of the optical cell. On the upper part of the cell jacket is a brass tube with a valve which serves as an inlet for dry nitrogen. The optical cell can be screwed onto a set of two brass plates which serves as a base adapter for the spectrophotometer.
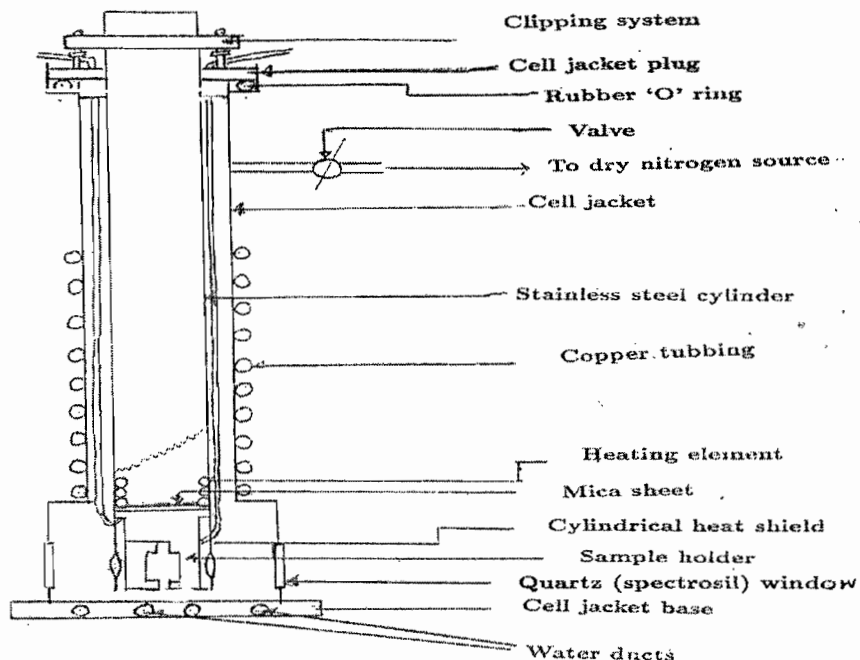

Figure 1: Optical cell set up for high temperature measurement.

Measurement of High Temperature Spectra

Heating a sample of thermally bleached RbBr:Yb2^{+} crystal was provided by means of the heating element. The heating element drew current from a mains supply through a 12 V Varian step-down transformer which also was connected to an Ether "Mini" Type 17–90B temperature controller. The temperature controller was capable of maintaining the temperature of a system constant to within ± 3 °C. A mica sheet isolated the heating element from the bottom of the cell tube.

Before the heating of a sample was commenced, the sample chamber was flushed with dry oxygen – free nitrogen and evacuated by means of a diffusion pump. As the sample was heated, water at room temperature was pumped through the water cooling system to prevent moisture from settling on the quartz window. The cell tube was filled with quantities of fine sand and ceramic balls and finally stuffed with fibre glass. This enabled it to retain the heat generated by the heating element and so served effectively as a heat reservoir. The actual temperature of the sample was measured means of two thermocouples.

The high temperature (HT) absorption spectra of RbBr:Yb^{2+} crystals were obtained at several elevated temperatures. As a matter of procedure, the RT spectrum of each crystal sample was measured before and after the HT measurement. The highest temperature at which the high temperature spectrum of a crystal sample could be measured was 358°C. Beyond this temperature the spectrophotometer became unstable. This was attributed to the unreliable response of the photodetecter of the device which had been exposed to copious infra-red radiation emitted by the framework of the sample holder and the sample itself. Because there were real prospects of damage to the spectrophotometer, a decision was taken to restrict measurements to a maximum temperature of 358 °C.

Measurement of Spectra of RbBr:Yb^{2+} Crystals at Liquid Nitrogen Temperature

To measure the spectra of samples of RbBr:Yb^{2+} crystals at LNT, the heating element and the mica sheets were removed while the fine sand, ceramic balls and fibre glass were replaced by liquid nitrogen. With these changes in the set up, measurements of spectra proceeded as in the previous section.

RESULTS

The absorption spectra of a sample of RbBr:Yb^{2+} crystal measured at RT and three other temperatures are shown in Fig.2. Only the spectra that provide new information were included in the figure. Clearly the spectral bands occur partly in the visible region but mostly in the ultraviolet. Following Mejeha and Smith (2006) the major absorption bands were labeled as A2, A6, E1, B1 and C4. Evidently, as the temperature of the sample was increased to a value below 200 °C, the A2 – and A6 – bands shifted to shorter wavelengths while the C-4 band was unshifted. The B1 – band was enveloped within the long wavelength tail of the C4 – band. At temperatures above 200°C, the A2 – and A6 – band.

shifted to longer wavelengths while the C4 – band was only slightly shifted to the red. This trend continued until a sample temperature of 358°C was reached. Further measurement of HT spectra could not be continued because of the experimental difficulties already mentioned. Table 1 shows the variation of the peak positions of the A2-, A6 – and C4 – bands at various temperatures. The parameter, ∇, is the energy separation of the A2 – and C4 bands in the spectra. It is an approximate measure of the crystal field splitting of the 5d states of the first excited 4f^{13}5d configuration of Yb^{2+} ions in an octahedral crystal field [Mejeha and Smith (2002)].
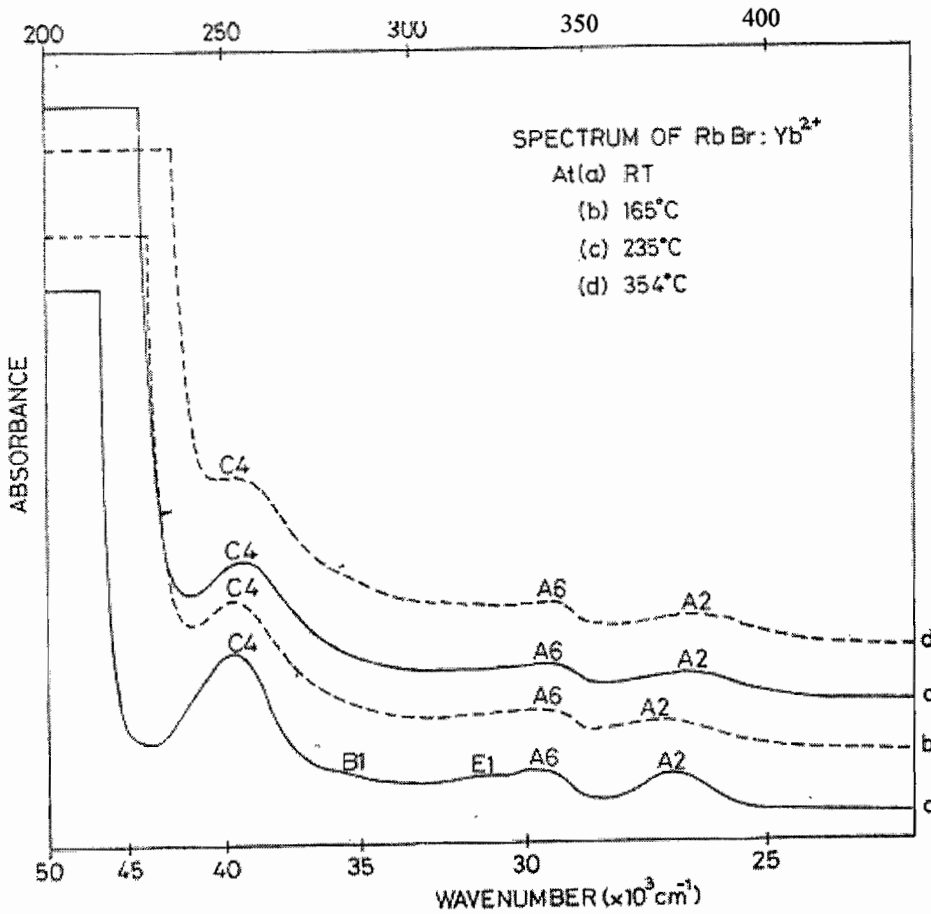

Fig 2: Absorption spectra of RbBr:Yb²⁺ crystals at different temperatures.

Table 1: Spectral positions of the A2-,A6-, and C4-bands of Yb^{2+} ions in RbBr crystals at several elevated temperatures. The last column gives the energy parameter ∇

Temperature (°C)	Spectral Positions (cm⁻¹)			
	A2-band	A6-band	C4-band	∇ (cm⁻¹)
RT	26 631	29 671	39 841	13 210
100	26 846	29 718	39 841	12 995
165	26 882	29 762	39 841	12 959
200	26 525	29 326	39 683	13 158
235	26 525	29 326	39 683	13 158
252	26 525	29 326	39 683	13 158
300	26 525	29 326	39 683	13 158
354	26 316	29 283	39 683	13 367
358	26 316	29 283	39 683	13 367

An interesting finding was that when the absorption spectrum of the RbBr:Yb^{2+} crystal was recorded at a temperature above 200°C and the crystal sample allowed to cool to RT, the subsequent measurement of the RT spectrum of the sample did not yield the same RT spectrum as for a freshly doped sample of the crystal. Figure 3. illustrates this point. The difference between the spectrum of a freshly doped RbBr:Yb^{2+} crystal sample and that of a sample of the crystal used for HT measurement above 200°C but allowed to cool slowly to RT became more striking when the LNT spectrum of the slow-cooled sample was measured. Figure 4 shows the LNT spectrum of a sample of RbBr:Yb^{2+} crystal used for HT measurement at 354 °C, and subsequently, allowed to cool slowly to RT. New absorption bands could clearly be identified.

Each of the absorption bands A2-, A6 -, E1 and E2 appeared to have a companion band labeled respectively as U2 -, U6 -, W1 – and W2 – bands. The reason for these labellings becomes clear when Fig 4. is compared with the spectra of freshly doped sample of RbBr: Yb^{2+} crystal recorded at RT and LNT as contained in Fig.5. The dotted traces in Fig. 4 show the decomposed energy bands if the background absorption is subtracted. By measuring the second derivative RT and LNT spectra of the freshly doped RBr:Yb^{2+} crystal sample and those of the samples used for HT measurements at 354°C, it was possible to determine precisely the spectral positions of the identified absorption bands. The highlights of the results of the exercise were summarized in Table 2.
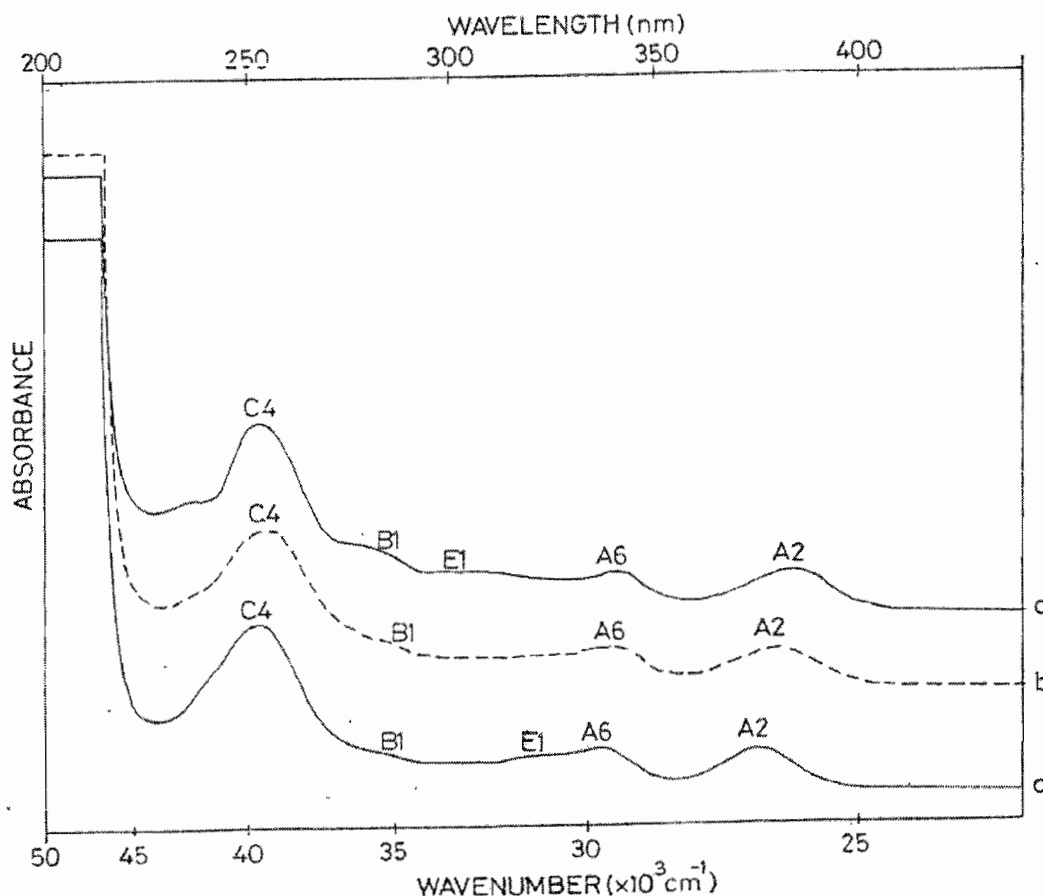

Fig. 3: Room temperature absorption spectra of RbBr: Yb $^{2+}$ crystal slowly cooled from (b) 252 ^{0}C (c) 354 ^{0}C. Trace α is room temperature spectrum of the freshly doped sample of RbBr: Yb^{2+} crystal.
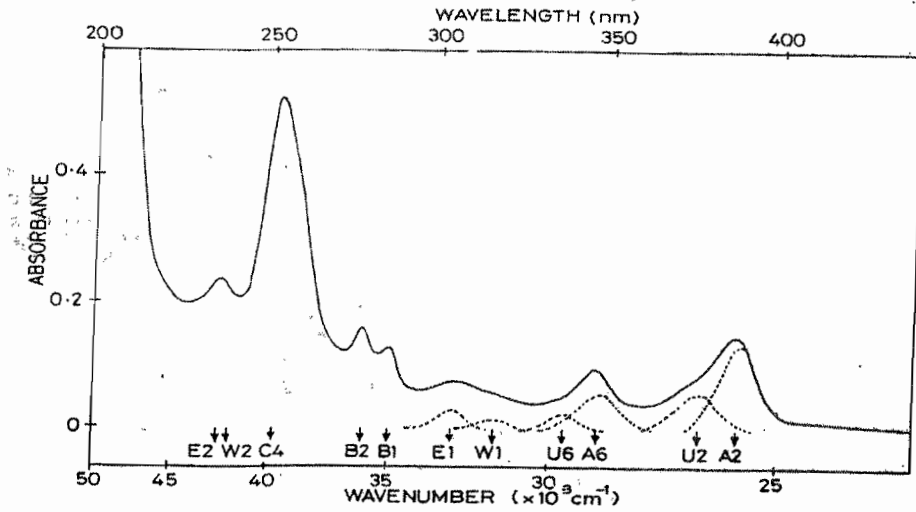
Fig. 4: Optical absorption spectrum at liquid nitrogen temperature of a *RbBr:* Yb²⁺ crystal at slow cooled from 354⁰ C to room temperature.
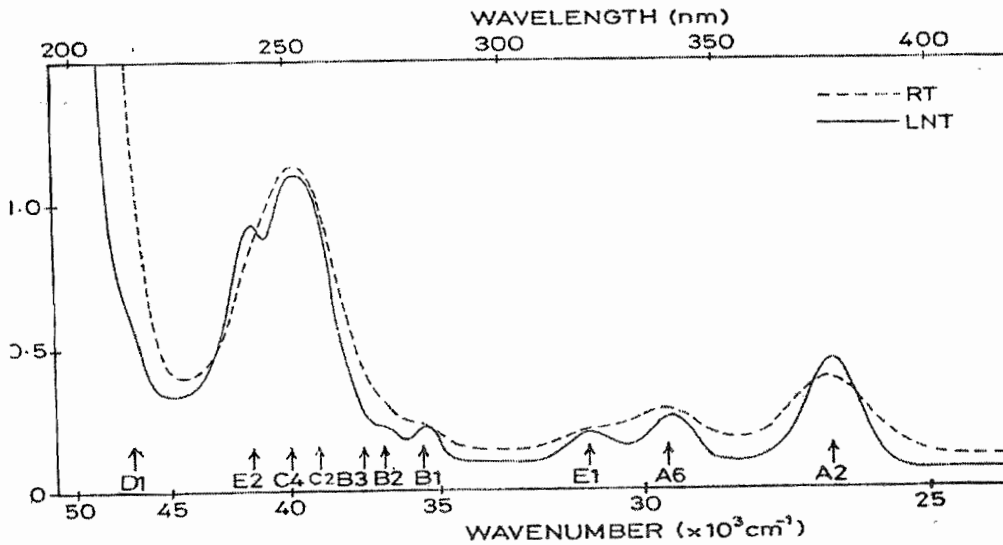
Fig. 5: Absorption spectra of freshly doped samples of RbBr: Yb²⁺ crystals measured at room and liquid nitrogen temperatures (After: Mejeha and Smith (2006)

Table 2: Peak positions of absorption bands at the room temperature and liquid nitrogen temperature spectra of freshly doped crystal of RbBr:Yb²⁺ and crystals used at high temperature measurement of 354 °C but allowed to cool to room temperature

Band	Spectral energy at RT (cm⁻¹)		Spectral energy at LNT (cm⁻¹)	
	FDS*	HTM354**	FDS	HTM354
A2	26 631	26 008	26 490	25 740
U2	-	-	-	26 525
A6	29 674	29 240	29 499	28 818
U6	-	-	-	29 586
W1	-	-	-	31 546
E1	31 153	32 468	31 299	32 573
B1	35 587	35 211	35 398	34 965
B2	-	36 232	36 563	35 971
C4	39 841	39 761	39 920	39 683
W2	-	-	-	41 754
E2	41 667	42 017	41 494	42 463
(A2, C4)	13 210	13 753	13 430	13 943

*   FDS   ≡   Freshly doped sample
** HTM354   ≡   Sample used for HT measurement at 354 °C

An estimate of the intensity of the U2-band relative to that of the A2-band in the LNT spectrum shown in Fig 4 gave a ratio of 42:100. This is the same as the intensity of U6-band relative to that of A6-band in the same spectrum.

Another interesting finding was that when a sample of RbBr:Yb^{2+} crystal had been used for a HT measurement at a temperature higher than 200 °C, a previous HT spectrum could not be reproduced if the HT measurement was repeated. Nevertheless if the sample was annealed at 600 °C for two hours and quenched to LNT, the RT and LNT spectra of a freshly doped sample of RbBr:Yb^{2+} crystal were reproduced.

DISCUSSION

It is remarkable to note that all the HT absorption spectra of RbBr:Yb^{2+} crystals obtained in this study have basically the same structure as that of a freshly doped RbBr:Yb^{2+} crystal measured at RT. This suggests that the observed absorption bands are due to $4f^{14} \rightarrow 4f^{13}5d$ electronic transitions of Yb^{2+} ions in the crystals as in the case of Yb^{2+} ions in the crystals measured at RT and LNT [Mejeha and Smith, (2006)]. It also suggests that at elevated temperatures, the effective site symmetry of the Yb^{2+} ions undergoing the transitions that yield those absorption band is the same as that Yb^{2+} ions in the crystals at RT and LNT. It is therefore reasonable to conclude that at elevated temperatures, up to 354°C, the Yb^{2+} ions experience crystal fields that are effectively octahedral in character.

The experimental evidence that at elevated temperatures below 200 °C the energy parameter, ∇, was reduced below its values as for RT was expected. Heating a sample of a crystal causes an increase in its lattice parameter, d. Increase in d would usually lead to a decrease in the crystal field strength experienced by the Yb^{2+} ions. But the increase in ∇ at sample temperatures above 200 °C to values larger than its value at RT was not expected. Instead it was expected to decrease further.

An explanation is sought for the last result. Firstly, it has to be noted that the basic structure of the absorption spectrum of the Yb^{2+} ions in an octahedral environment was still observed at temperatures above 200 °C. It is therefore reasonable to conclude that in that temperature regime, the Yb^{2+} ions experience a coordination environment similar to that which Yb^{2+} ions experience in a freshly doped RbBr:Yb^{2+} crystals at RT. However, the separation of the substitutional Yb^{2+} ions from the coordinating Br^- ions would be smaller in the hot crystal samples than in a freshly doped RbBr:Yb^{2+} crystals at RT, hence an increase in ∇.The finding that the original RT of a sample of RbBr:Yb^{2+} crystal used for HT measurement could not be recovered when the sample was allowed to cool to RT strengthens this view point. It suggests that at elevated temperatures above 200 °C, the crystal could have undergone some precipitate phase changes probably involving some form of association of Yb^{2+} , Br^- and Rb^+ ions. Such changes have been identified in some alkali halide crystals doped with Eu^{2+} ions [Lopez, et. al (1980), (1981), Aguilar, et. al, (1982), Medrano, et. al. (1984), Garcia-Sole, et. al (1982). Whatever association the Yb^{2+} ions must have entered into, it is evident that the Yb^{2+} ions occupy lattice sites whose symmetry is effectively octahedral.

The additional energy bands observed in the LNT spectrum of a sample of RbBr:Yb^{2+} crystal previously used for HT measurement at 354°C suggests that the Yb^{2+} ions could indeed exist in two separate precipitate phases. The spectral positions of the U2 -, U6 -, and W1 – bands are practically the same as those of A2 -, A6 -, and E1-bands respectively in the LNT spectrum of a freshly doped sample of a RbBr:Yb^{2+} crystal. This view point becomes more compelling if account is taken of the additional fact that in the LNT spectrum of the sample used for HT measurement at 354 °C, the intensity of the U2-band relative to that of the A2-band is the same as that of the U6-band relative to that of the A6 – band. It indicates that the relative concentration of the Yb^{2+} ions in the two

different phases is about 42:100. That the B1, and C4 – bands did not have obvious "companion" bands could be because the possible "companion" bands might have been overlapped by these bands. If the above model is correct, the U2 -, U6 -, W1 – and W2 – bands are very likely to be due to Yb^{2+} ions in a coordination environment similar to that of Yb^{2+} ions in a freshly doped sample of RbBr:Yb^{2+} crystals. The other bands labeled A2, -, A6 -, E1, C4 and E2 would then be due to Yb^{2+} ions in a different precipitate phase.

The view point expressed in the proceeding paragraph is further strengthened by the evidence that when the RbBr:Yb^{2+} crystal sample used for HT measurement at 354 °C was annealed at 600 °C and quenched to LNT, the RT and LNT spectra of a freshly doped samples of the crystal were reproduced. It can be argued that during the thermal annealing, the precipitate structures or complexes became unstable and got dissolved with Yb^{2+} ions being statistically dispersed within the crystal. The suggestion that the Yb^{2+} ions could exist in separate precipitate phases has since been taken up and investigated [Mejeha and Smith, (2002)].

SUMMARY AND CONCLUSIONS

The results obtained in this study showed that the HT absorption spectra of RbBr:Yb^{2+} crystals have the same basic structure as that of the doped crystal measured at RT. This suggests that at elevated temperatures up to 358 °C, the crystal fields perturbing the electronic states of the $4f^{13}5d$ configuration of Yb^{2+} ions in the crystals is effectively octahedral in character.

Results of HT measurements indicated that the energy parameter, ∇, decreased as expected, when the RbBr:Yb^{2+} crystals were heated to temperatures below 200 °C but increased when the sample temperature was raised above 200 °C contrary to expectation.

The study revealed evidence that the Yb^{2+} ions may exist in two separate phases in RbBr:Yb^{2+} crystals used in HT measurements a temperature of 354 °C.

Experimental difficulties made it impossible to obtain HT spectra of RbBr:Yb^{2+} crystals at temperature higher than 358 °C. As a result it was not possible to obtain the spectrum of the crystals at doping temperature.

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