PHASE PRECIPITATION OF Yb^{2+} IONS IN RbCl MONOCRYSTALS MONITORED BY OPTICAL ABSORPTION MEASUREMENTS AT ELEVATED TEMPERATURES

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(Submitted: 12 October, 2007; Accepted: 20 November, 2007)

Abstract

Optical absorption spectra of RbCl:Yb^{2+} crystals have been measured at several elevated temperatures up to 300°C. Results showed that in hot RbCl:Yb^{2+} crystals, the Yb^{2+} ions occupied lattice sites with effective octahedral, O_h, point symmetry. Values of an energy parameter ∇, which is an approximate measure of the strength of the crystal field splitting of the 5d electron states of the $4f^{13}5d$ configuration of the Yb^{2+} ions in an octahedral crystal field, were obtained for the crystals at different temperatures. The variation in the value of ∇ with increase in temperature was used to identify three precipitate phases of the Yb^{2+} ions in the crystal. Type 1 precipitates were identified as I-V dipoles in freshly quenched RbCl:Yb^{2+} ion - Rb^{+} ion vacancy complex. Type II precipitates were tentatively identified as metastable $YbCl_2$ type precipitates in the RbCl lattice which occur when the RbCl:Yb^{2+} crystals were heated to temperatures in the range 200- 270°C. The third precipitate phase was tentatively identified as the stable $YbCl_2$ precipitates in the RbCl lattice, which were formed in the temperature range 320 - 360°C.

Keywords: *Phase precipitates, optical absorption spectra, divalent ytterbium, rubidium chloride and variable temperature optical cell*

Introduction

It has been shown in several studies that precipitates phases of divalent metal ions can be formed in single crystals of alkali halides (Miyake and Suzuki, 1954; Lilly and Newkirk 1967; Lopez *et al.*, 1980; Garcia *et al.*, 1980; Garcia Sole *et al.*, 1980, 1981 and Medrano *et al.*, 1984). The precipitation of the divalent ions occur because they are capable of migrating through the lattice of the host crystal through a diffusive process. When the local concentration of the impurity ions exceeds the solubility limit, the ions can aggregate forming micro precipitates in the host crystal lattice (Garcia *et al.*, 1980). These form nucleation centres from which larger precipitates grow. The precipitates take different structural forms depending on the concentration of the impurity ions, the thermal history of the doped crystal as well as duration of storage of the crystal at room temperature, or other chosen temperature. The crystal structure of the precipitates is usually studied using X-ray diffraction techniques while their morphology can be studied by using optical or electron microscopes (Miyake and Suzuki, 1954, Suzuki, 1961, Lilley and Newkirk, 1967).

Optical absorption and luminescence studies of alkali halide crystals doped with divalent europium, Eu^{2+}, ions have shown that the formation of precipitate phases of the Eu^{2+} ions in the crystals modifies the optical absorption spectra of the ions in the lattice of the host crystals. This is attributed to changes in the coordination environment of the Eu^{2+} ions resulting from the precipitation. A change in the local environment of a Eu^{2+} ion at a substitutional cation site results in a change in the strength of the crystal field splitting, Δ (=10Dq), of the 5d electron orbitals of the $4f^6 5d$ configuration of the Eu^{2+} ions in octahedral crystal field. Since the energy parameter Δ is determined from the absorption/emission spectra of the Eu^{2+} ions in alkali halide crystals, Δ has proved to be a very important parameter for monitoring the precipitate phases.

Recently, Mejeha (2007), reported on an investigation of the high temperature (HT) optical absorption spectra of Yb^{2+} ions in single crystals of rubidium bromide. It turned out that the study mirrored the existence of the precipitate phases of the Yb^{2+} ions in the $RbBr:Yb^{2+}$ crystals at elevated temperatures. It can therefore be said that the measurement of HT absorption spectra of the Yb^{2+} - doped crystals served as an optical probe of the precipitate phases of the Yb^{2+} ions in the crystals.

It must be remarked that when a divalent rare earth impurity ion takes up a substitutional cation site in an alkali halide crystal, the full point symmetry of the site of the impurity ion is orthorhombic C_{2V} point symmetry instead of octahedral. (Bron and Heller, 1964; Nair *et al.*, 1968; Bradbury and Wong, 1971; Rubio *et al.*, 1974; Sundberg *et al.*, 1974; Guzzi and Baldini, 1974 and Ramponi and Wright, 1984). However, as has been pointed out (Newman, 1976 and Abragam and Bleaney, 1986), that the crystal field potential at the site of the impurity ion is predominantly octahedral, with a small orthorhombic component. To a first approximation the orthorhombic distortion of the crystal field can be ignored when analyzing the absorption and emission spectra of divalent impurity rare earth ions involving $4f^N \leftrightarrow 4f^{N-1}5d$ electronic transitions of the ions in alkali halide crystals. Consequently, the effective site symmetry of Yb^{2+} ions in a freshly doped $RbCl:Yb^{2+}$ crystal shall be taken to be octahedral. This type of approximation, known as the octahedral approximation has been used successfully by several authors in the study of $4f^N \leftrightarrow 4f^{N-1}5d$ electronic transitions of Eu^{2+}, Sm^{2+} and Yb^{2+} ions in alkali halide crystals (Hernandez *et al.*, 1981; Tsuboi *et al.*, 1981; Bland and Smith, 1985, and Mejeha and Smith, 1998). It shall be adopted in this study.

In this study, we shall be concerned with the measurement of HT absorption spectra of Yb^{2+} ions in Yb^{2+} - doped RbCl crystals. In doing so, we shall monitor and identify the possible precipitate phases of Yb^{2+} ions in the RbCl crystal lattice. The investigation of the precipitation kinetics in $RbCl:Yb^{2+}$ crystals shall be reported a future paper.

Theory

Phase precipitation in the solid state is analogous to solidification of a pure substance from melt as well as to crystallization in metallic glasses. Each of these phenomena involves two diffusion controlled processes, namely, nucleation and growth, the theories of which have been well documented (Scott, 1983; Raghavan, 1989; Ragone, 1995 and Gupta and Kumar, 2004). In the case of precipitation, the microprecipitates which form as a result of supersaturation of the solid solution (in this case an alkali halide crystal doped with divalent metal ions) constitute the nuclei or embryos which eventually become supercritical (nucleated) particles by more ions being added onto them. These grow into a new (product) phase.

The classical theories of nucleation and growth (Scott, 1983; Raghavan, 1989 and Gupta and Kumar, 2004) show clearly that the rates of nucleation and growth depend on temperature and time. One therefore expects the rate of nucleation and growth of a new (or product) phase in a solid solution (parent phase) will have both time and temperature dependences. Accordingly, the overall precipitation rate will reflect these dependences. If one therefore denotes by x, the fraction of the divalent impurity metal ions in the parent phase which have been transformed into the product phase, the precipitation rate can be written as a function of the nucleation rate, N, and growth rate, g, as follows (Raghavan, 1989 and Gupta and Kumar, 2004)

$$dx/dt = f(N,g) \qquad (1)$$

However, for solid state transformation, x can be described by the Johnson Mehl Avrami equation (Scott, 1983) viz:

$$x(t) = 1 - \exp[-\eta(t-t_o)^n] \qquad (2)$$

where t_0 is the incubation time (formation time for a new nucleus), n is the Avrami exponent and η is a rate constant.

The Avrami exponent, n, can be partitioned as follows: $n = n_N + ng$; where n_N describes the time dependence of the nucleation rate, N, while n_g embodies the time dependence of the growth rate, g. The rate constant, η can be expressed as (Scott, 1983)

$$\eta = \eta_0 \exp(-Q/RT) \qquad (3)$$

where η_o is a constant, Q is the activation energy for the overall precipitation process, R is the molar gas constant and T is the absolute temperature at which nucleation takes place. Ranganathan and Von Heimendahl (1981) have shown that

$$Q = (n_N/n)Q_N + (ng/n)Q_g \qquad (4)$$

where Q_N and Q_g are the activation energies for nucleation and growth respectively.

Experimental Methods

Materials and handling

The single crystals of rubidium chloride used in this study were supplied by BDH Chemicals Ltd, Poole, England. The ytterbium metal was obtained from Rare-Earth Products Ltd, Cheshire, England, in form of metal ingots of certified purity level of 99.99%. These materials were stored in a glove box. In order to prevent the deterioration of the materials, a slow and continuous stream of dry nitrogen was run through the glove box all year round. All Yb^{2+} - doped RbCl crystals were also stored in the glove box before and after use.

Doping of the rubidium chloride crystals

Small discs of RbCl single crystals were doped with divalent ytterbium ions by adopting the metal vapour phase diffusion, MVPD technique which consists of heating the crystals in ytterbium atmospheres. Details of the procedure adopted and the special devices used have been described elsewhere (Bland and Smith, 1985, and Mejeha and Smith, 1995). The doped crystals were usually heavily coloured as a result of the presence of colour defect centres such as F-centres, F-aggregate centres and U-centres. The concentration of these colour centres were drastically reduced by bleaching them thermally as described by Mejeha and Smith (1995).

Measurement of Absorption Spectra of RbCl: Yb^{2+} Crystals

The Varian DMS-90 UV-VIS-NIR spectrophotometer was equipped with a variable temperature optical cell, VTOC, which was housed in the sample compartment. The VTOC contained the doped crystal whose absorption spectra were to be measured. It was designed for use in the measurement of the absorption spectra of the doped crystals at temperatures ranging from LNT to 800^0 C. Details of the features of the VTOC and the procedure for using it for HT and LNT measurements have been given elsewhere (Mejeha, 2007a).

The HT absorption spectra of the RbCl:Yb^{2+} crystals were measured at several elevated temperatures up to 360° C. At a temperature greater than 360°C, the response of the spectrophotometer became unreliable. The HT measurements were, therefore, restricted to a maximum temperature of 360°C. Before each HT measurement, the RT absorption spectrum of the sample of the RbCl:Yb^{2+} crystal to be used was measured. After the HT measurement, the sample was allowed to cool to RT and the RT spectrum recorded again. When deemed necessary, the LNT absorption spectrum of the sample was also measured. Whenever the RT and LNT absorption spectra of a sample were measured, the second derivative absorption spectra of the sample were also recorded so as to locate the peak positions of the absorption bands more precisely

Results and Discussion

The absorption spectra of a sample of RbCl:Yb^{2+} crystal were measured at nine elevated temperatures. The absorption bands lie mostly in the ultraviolet spectral region. Shown in Fig. 1 are the absorption spectra obtained at RT and three other temperatures. Each spectrum shown is representative of a group of spectra measured within a certain temperature range and carriers some information different from those in other temperature ranges. The labeling of the RT spectrum follows a scheme used in characterizing the absorption spectra of RbCl:Yb^{2+} crystals at RT and LNT (Mejeha, 2007b).

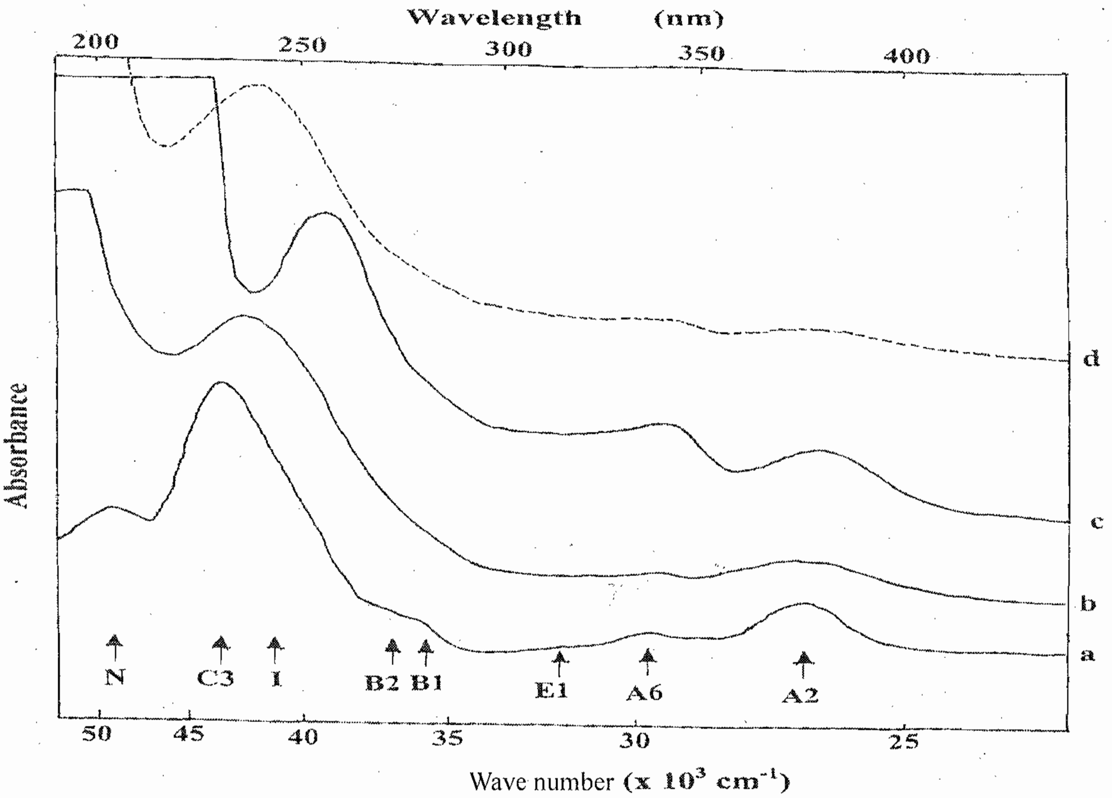

Fig. 1: Optical absorption spectra of RbCl:Yb^{2+} crystals measured at (a) room temperature; (b) 160° C; (c) 230° C; (d) 345° C.

It was found that at sample temperatures below 200°C, the A2-band was practically insensitive to temperature increase. However, the C3-band shifted significantly to longer wavelengths. At 200° C, both the A2- and C3-bands shifted to the red, with the shift in the C3-band being more considerable. In the temperature range 200° - 270° C, the two bands were found to be insensitive to temperature increase. As can be seen from Fig 1, the bands labeled E1, B1 and B2 could not be unambiguously identified in the high temperature spectra. The B1 and B2 bands were enveloped in the long wavelength tail of the stronger C3 band. The N-band, a colour centre band was completely bleached out thermally. More information about the variation of the peak positions of the A2- and C3-bands with temperature are shown in Table 1. Also given in Table 1 are the values of an energy parameter, ∇, which is the energy separation of the C3 and A2 bands in the spectra. It represents an approximate measure of the strength of the crystal field splitting ($\Delta = 10Dq$) of the 5d electron orbitals of the $4f^{13}5d$ configuration of the Yb^{2+} ions in an octahedral crystal field, (Mejeha and Smith, 2002, Mejeha, 2007a).

It was found that when a sample of $RbCl:Yb^{2+}$ crystal previously used for HT measurement at a temperature above 200°C was slowly cooled to RT, subsequent measurement of its RT spectrum could not reproduce the RT spectrum of a freshly quenched $RbCl:Yb^{2+}$ crystal sample. However, when the sample of $RbCl:Yb^{2+}$ crystal with any form of thermal history was heated at 600°C for two hours, and quenched to LNT, both the RT and LNT spectra of a freshly quenched sample of $RbCl:Yb^{2+}$ crystal were reproduced. Similar behaviour had been reported for $RbBr:Yb^{2+}$ crystals (Mejeha, (2007a). In Fig. 2 are compared the RT spectrum of a sample of $RbCl:Yb^{2+}$ crystal used for HT measurement at 345°C and

Table 1: Peak positions of the A2 - and C3 - bands in the optical absorption spectra of Yb^{2+} ions in rubidium chloride crystals measured at several elevated temperatures. The last column gives values of the energy parameter, ∇.

Temperature (°C)	Peak positions (cm⁻¹) A2 - band	C3 - band	Energy Parameter ∇ (cm⁻¹)
RT	26 649	43 526	16 877
50	26 667	43 290	16 623
160	26 667	43 194	15 527
200	26 455	39 216	12 761
230	26 455	39 216	12 761
250	26 455	39 216	12 761
270	26 455	39 216	12 761
320	26 490	42 017	15 527
345	26 490	42 017	15 527
360	26 490	42 017	15 527

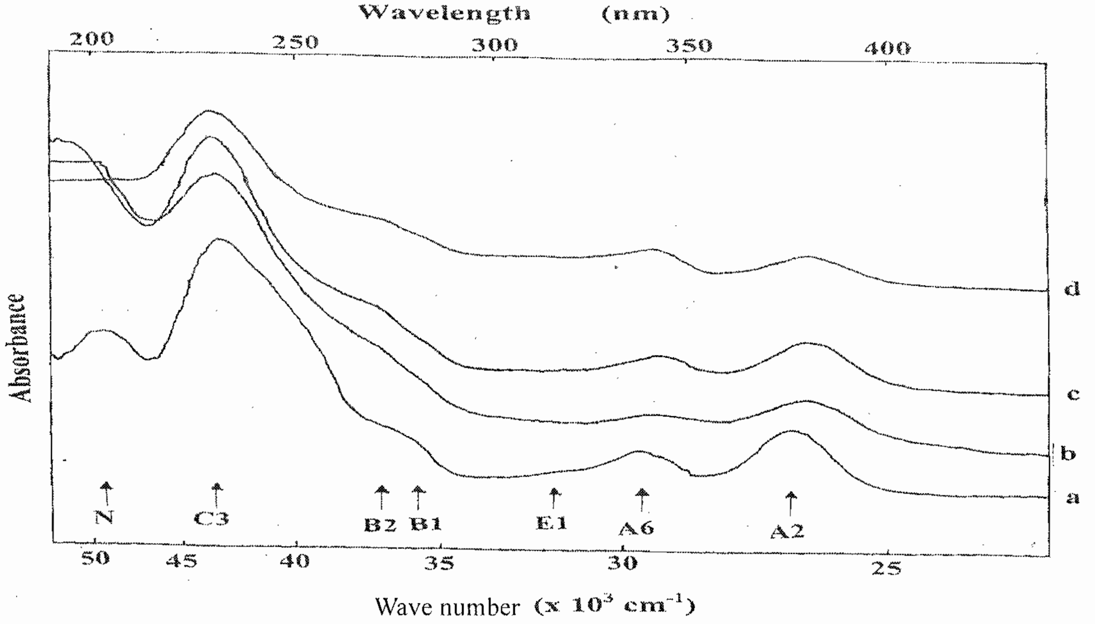

Fig. 2: Optical absorption spectra of RbCl:Yb^{2+} crystals measured at; (a) room temperature spectrum of a freshly quenched sample, (b) Spectrum of sample slow-cooled from 345°C to 50°C (c) room temperature spectrum of sample slow cooled from 345°C to room temperature (d) room temperature spectrum of a 195 day old sample.

slow-cooled to RT with the RT spectrum of a freshly quenched sample of RbCl:Yb^{2+} crystal. Included in the figure are the RT spectrum of a 195 day old sample of RbCl:Yb^{2+} crystal stored at RT and with no previous thermal history and the spectrum of a sample slow-cooled from 345°C to 50°C and measured at 50O C. The RT spectrum of the RbCl:Yb^{2+} crystal sample slow-cooled from 345°C was found to be practically identical with the RT spectrum

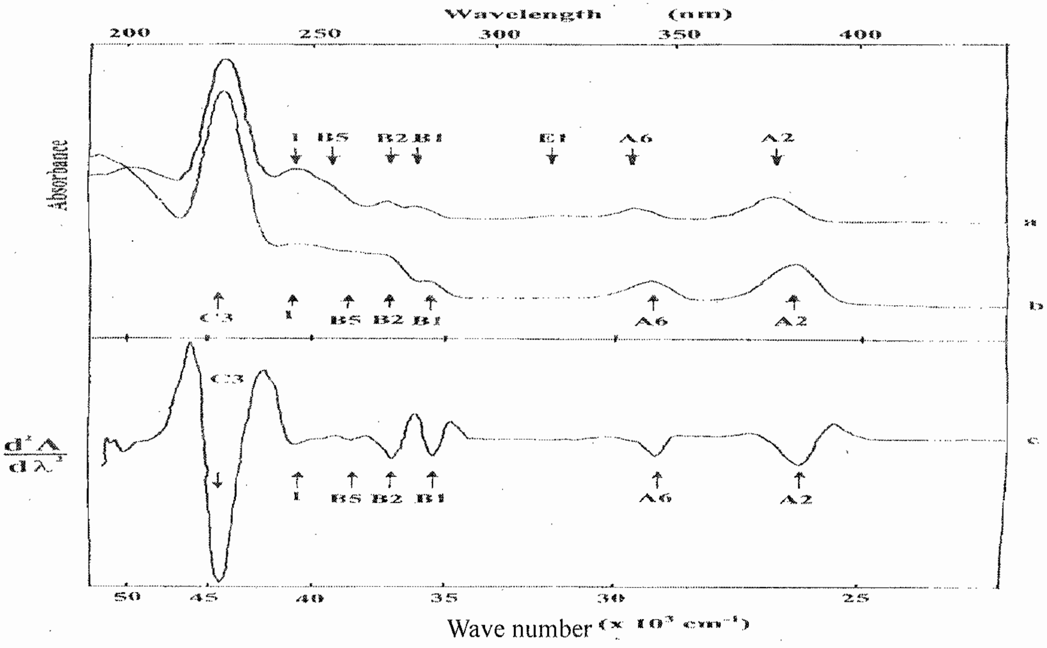

Fig. 3: Optical absorption spectra of RbCl:Yb^{2+} crystals measured at liquid nitrogen temperature: (a) Spectrum of freshly quenched sample, (b) spectrum of sample slow-cooled from 345°C to room temperature, (c) second derivative spectrum of a sample slow-cooled from 345°C to room temperature.

of the 195 day old sample of the same material.

It was more revealing, however, to compare the LNT spectrum of a freshly quenched sample of RbCl:Yb^{2+} crystal with that of a sample of Yb^{2+}-doped RbCl slowed-cooled to RT after HT measurement at 345^{0}C. This was done in Fig.3. The LNT second derivative spectrum of the slow-cooled sample was included to indicate the precise location of the peak positions of the bands. It is remarkable to note that when the 195 day old sample of RbCl:Yb^{2+} crystal was heated at 600^{0}C for two hours, and quenched to LNT, the RT and LNT absorption spectra of the freshly quenched crystal were recovered on subsequent measurements. The peak positions of the major bands in the RT and LNT absorption spectra of a freshly quenched sample of RbCl:Yb^{2+} and those of the sample slow-cooled from 345^{0}C to RT after HT measurement was summarized in Table 2. The peak positions of the absorption bands in the RT spectrum of the 195 days old sample were included for comparison. It is interesting to note that the value of 17 257 cm^{-1} obtained for the energy parameter, ∇, from the RT spectrum of the slow-cooled sample is comparable with the value of 17 318 cm^{-1} obtained for the same parameter from the RT spectrum of the 195 day old sample. The difference of 61 cm^{-1} between the two values is smaller than the maximum experimental error of 104 cm^{-1} characterizing the spectral region involved.

An examination of Fig.3 reveals that the HT absorption spectra of the RbCl:Yb^{2+} crystals have the same basic structure as that of the RT absorption spectrum of a freshly quenched RbCl:Y^{2+} crystal. It has

Table 2: The Peak positions of the major bands in the room and liquid nitrogen temperature optical absorption spectra of a freshly quenched sample of RbCl:Yb^{2+} crystal and of a sample slow-cooled from 345^{0}C at high temperature measurement. Included for comparisons are the peak positions of the bands in the room temperature spectrum of a 195

Bands	Peak positions at RT (cm^{-1})			Peak positions at LNT (cm^{-1})	
	FQS	SSC 345	SS195	FQS	SSC345
A2	26 649	26 316	26 316	26 543	26 144
A6	29 652	29 240	29 240	29 532	29 070
E1	31 949	-	-	31 646	-
B1	35 746	35 714	35 714	35 810	35 336
B2	36 866	36 900	36 900	36 900	36 832
B5	39 216	38 610	38 610	39 139	38 388
C3	43 526	43 573	43 688	44 101	44 248
∇=(A2,C3)	16 877	17 257	17 318	17 558	18 104

Legend: FQS ≡ Freshly quenched sample doping temperature
SSC345 ≡ Sample slow-cooled from 345^{0}C
SS195 ≡ Sample stored for 195 days

earlier been demonstrated (Mejeha, 2007b) that the RT and LNT absorption spectra of freshly quenched $RbX:Yb^{2+}$, (X=Cl, Br, I) crystals can be ascribed to the Laporte allowed $4f^{14} \rightarrow 4f^{13}5d$ transitions of theYb^{2+} ions in the crystals. It is therefore reasonable to attribute the HT spectra of the $RbCl:Yb^{2+}$ crystals obtained in this study as due to similar transitions of the Yb^{2+} ions in the RbCl crystals at the temperatures studied. This result suggests that at these elevated temperatures, the Yb^{2+} ions occupy lattice sites whose effective point symmetry is octahedral, O_h.

As expected, in the temperature range, RT-160° C,∇ decreases as sample temperature increases. But the large decrease in ∇ from its value of 15 527 cm^{-1} at 200°C to a value of 12 761 cm^{-1} at 230° C and the similarly large increase in its value from 12 761 cm^{-1} at 265°C to 15 527 cm^{-1} at 320°C cannot be accounted for by the expected decrease in its value with temperature increase. Explanation is therefore sought for this result. It appears that in the temperature ranges RT-50°C, 200° - 270°C and 320 - 360°C, the Yb^{2+} ions exist in different precipitate phases in the $RbCl:Yb^{2+}$ crystals. This is suggested by the fact that values of ∇ for a freshly quenched sample at RT and 50°C are comparable. But within each of the temperature ranges 200 - 270° C and 320° - 360° C, the values of ∇remain (practically) constant although the values defer for each temperature range. As mentioned earlier, when the RT spectrum of a sample of $RbCl:Yb^{2+}$ crystal slow-cooled to RT after a HT measurement at a temperature higher than 200°C was measured, the RT spectrum of a freshly quenched sample could not be reproduced. This suggests that the some precipitate phases of Yb^{2+} ions in the crystals could have been formed at temperatures higher than 200° C.

One precipitate phase of Yb^{2+} ions is found in a freshly quenched sample of $RbCl:Yb^{2+}$ crystal. It is made up of isolated impurity vacancy -(I-V) dipoles; each dipole consisting of a substitutional Yb^{2+} ion and a Rb^+ ion vacancy. This precipitate phase shall be designated here as Type I precipitate. The precipitate phase of the Yb^{2+} ions in $RbCl:Yb^{2+}$ crystals which exists in the temperature range 320° - 360° C is quite stable at temperatures below 320°C. It is identified as the $YbCl_2$ precipitates in the lattice of RbCl crystals. It very much like the $YbBr_2$ precipitates identified in Yb^{2+} - doped RbBr crystals (Mejeha and Smith, 2002)..

In general, dihalides of divalent metals are known to be stable substances (Lilley and Newkirk, 1967; Lopez *et al.*, 1980; Aguilar *et al.*, 1982 and Medrano *et al.*, 1984). Although the crystallographic data on $YbCl^2$ is not available to the author, some useful information which support the identification of the precipitate structures as $YbCl_2$ precipitates exists as given below. The Wychoff ratio, R_{cation}/R_{anion}, for $YbCl_2$ crystal is 0.55. This is greater than the minimum value of 0.41 for the ratio of oppositely charged ions to be six-fold coordinated in a crystal (Chanda, 1981; Goodman, 1983 and Raghavan, 1989). Of course, $YbCl_2$ cannot have the NaCl type structure. However, it has been established that dihalides of divalent metals have the CaF_2 type structure if the cations are large and the rutile structure if the cations are small (Wychoff, 1963, 1964, Lilley and Newkirk, 1967, and Goodman, 1983). In the case at hand the radius of Yb^{2+} ions is small compared with that of Cl- ions. Based on this, it is expected that $YbCl_2$ will crystallize in the rutile structure. In this crystal structure, each divalent metal ion has six halide ions as nearest neighbours while each halide ion has three divalent ions as nearest neighbours. (Goodman, 1983 and Gupta and Kumar, 2004). If therefore $YbCl_2$ has the rutile crystal structure, the site symmetry of Yb^{2+} ions in the structure would be octahedral. This conclusion is consistent with the experimental observation that the absorption spectrum of the Yb^{2+} ions in RbCl:Yb^{2+} crystals at temperatures in the range 320°-360°C are similar to the spectrum of the Yb^{2+} ions at octahedral sites. Clearly the Yb^{2+} - Cl- separation in $YbCl_2$ precipitate will be different from that in a freshly quenched sample of RbCl:Yb^{2+} crystal. This explains the difference in the value of ∇ for freshly quenched RbCl:Yb^{2+} crystal and for the crystal at temperatures in the range 320° - 360° C (See Table 1).

The finding that the RT spectrum of the sample of a RbCl:Yb^{2+} crystal slow-cooled from 345°C to RT and that of a sample of the same material stored away at RT for 195 days are practically identical is very insightful. It suggests that the Yb^{2+} ions in the sample temporally aged at RT and those in the sample show-cooled to RT after thermal aging at 345°C are basically in identical coordination environments. The time scale of 195 days is large enough for the Yb^{2+} ions in a freshly doped RbCl:Yb^{2+} crystal to migrate within the crystal to form stable precipitates. The precipitates can however be formed in much shorter time by annealing the crystals at 345° C. The formation of precipitate phases of Eu^{2+}, ions in some alkali halides crystals as a result of temporal aging at RT have also been observed in Eu^{2+} - doped alkali halide crystals (Lopez *et al.*, 1980, Aguilar, *et al.*, 1982 and Garcia *et al.*, 1980).

The precipitate phase in which the Yb^{2+} ions exist in the temperature range 200° - 270°C shall be designed here as Type II precipitate. This precipitate phase does not exist in RbCl crystal lattice at temperatures below 200°C. It does not seem to exist at temperatures higher than 270°C. This precipitate phase is therefore unstable. The value of obtained for the RbCl:Yb^{2+} crystal in the temperature range 200°-270° C is significantly smaller than for the freshly quenched crystals at RT. This means that the Yb^{2+} ions in Type II precipitates occupy lattice sites in which they experience smaller crystal field than the Yb^{2+} ions in Type I precipitates. But the Yb^{2+}, ions in Type II precipitates experience coordination environments that are effectively octahedral just like the Yb^{2+} ions in $YbCl_2$ precipitates do. These results suggest that the Type II precipitate is very likely to be a metastable $YbCl_2$ type precipitate from which the stable $YbCl_2$ precipitate grow at temperatures higher than 270° C. In some studies of Eu^{2+} - doped alkali halide crystals, including RbCl and RbBr crystals, metastable precipitates which have structure similar to that of the stable EuX_2 (X=Cl, Br, I) precipitates were identified. (Lopez *et al.*, 1980, 1981; Rubio *et al.*, 1981; Aguilar *et al.*, 1982 and Medrano *et al.*, 1984). These metastable EuX_2 precipitates have characteristics similar to those Type II precipitates reported here.

The identification of the phase precipitates made in this study are tentative since it is based solely on optical absorption data only. Additional data will be needed for more definitive identification of the precipitate structures. Specifically, X-ray diffraction experiments performed at elevated temperatures can be used to obtain some crystallographic information about the precipitate structures. In addition, optical and electron microscope techniques could reveal the morphology of the precipitates. One of the drawbacks in using these techniques in studying phase precipitates formed in alkali halide crystals doped with divalent metal ion impurities using the MVPD technique is that the impurity concentration achievable is rather low (Mejeha and Smith, 2002). This makes the use of techniques rather difficult.

Summary and Conclusions

The optical absorption spectra of Yb^{2+} ions RbCl single crystals have been measured at several elevated temperatures up to 360°C in this study. Each of the spectra obtained has the same basic structure as the RT spectrum of a freshly quenched RbCl:Yb^{2+} crystal. The Yb^{2+} ions in the hot RbCl:Yb^{2+} crystals are believed to occupy lattice sites which have effective octahedral point symmetry.

It was found that the Yb^{2+} ions could exist in different precipitate phases. One of the precipitate phases, designated as type I precipitates consist of Yb^{2+} ion Rb^{2+} ion vacancy complexes dispersed within the RbCl lattice. They constitute isolated I-V dipoles and are formed in freshly quenched RbCl:Yb^{2+} crystals.

Another precipitates phase, the type II precipitates are formed in the RbCl lattice when the RbCl:Yb^{2+} crystals are at temperatures in the range 200° - 270° C. They are tentatively identified as metastable $YbCl_2$ type precipitates. The third precipitate phase identified consists of $YbCl_2$ precipitates which are stable and are formed when RbCl:Yb^{2+} crystals are heated to temperatures in the range 320°C-360° C.

Acknowledgments

The author is grateful to Dr. M. J. A. Smith of the Department of Physics, University of Warwick, Coventry, U.K. for designing the variable temperatures optical cell and for some useful discussions and to Mr. Cliff Randle for his technical support.

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