

ULTRAVIOLET ABSORPTION SPECTRA OF Eu^{2+} IONS IN RbCl , RbBr AND RbI SINGLE CRYSTALS

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ABSTRACT

Single crystals of rubidium chloride, bromide and iodide were doped with divalent europium (Eu^{2+}) ions by heating them in europium atmosphere. The absorption spectra of the doped crystals were measured at room and liquid nitrogen temperatures. Each absorption spectrum was found to consist of two strong broad structured bands located mainly in the ultraviolet spectral region. The absorption bands were ascribed to the Laporte-allowed $4f^7(^8S_{7/2}) \rightarrow 4f^6(^7F_J)5d$, $J = 0, 1, \dots, 6$ transitions of the Eu^{2+} ions in the crystals. Values of the crystal field parameter, Dq , determined for the $\text{RbX}:\text{Eu}^{2+}$, ($X = \text{Cl}, \text{Br}, \text{I}$) crystals were found to vary according to a spectrochemical series in which the coordinating ligand ions were arranged in increasing order of magnitude of Dq , namely: $\text{I}^- < \text{Br}^- < \text{Cl}^-$. It was established that $Dq \propto d^n$, where d is lattice parameter, and $n = -2.23$ for the $\text{RbX}:\text{Eu}^{2+}$, ($X = \text{Cl}, \text{Br}, \text{I}$) crystals at room temperature while $n = -2.16$ for the same crystals at liquid nitrogen temperature.

KEYWORDS: Absorption spectra, divalent europium, crystal field parameter, metal vapour diffusion, octahedral approximation.

INTRODUCTION

Divalent ions europium (Eu^{2+}) ions occupying substitutional cation sites in transparent insulators such as alkaline earth fluoride, chloride and chalcogenide crystals as well as in alkali halide crystals have been widely studied both in optical absorption and fluorescence for several decades [Kapyanskii and Feofilov (1962), Reisfeld and Glasner (1964), Freiser, *et al.* (1968), Kisiuk, *et al.* (1968), Mehra (1968), Loh (1968), (1969) Asano and Nakao (1979), Hernandez, *et al.* (1980), (1981) and Bland (1985)]. The considerable interest in the study of Eu^{2+} ions in these crystals derives from the potentials for use of the Eu^{2+} - doped crystals as phosphors, high energy tunable lasers and several types of solid state devices [Waite (1974), Hernandez, *et al.* (1979)]. It is worthy of note that $\text{CaF}_2:\text{Eu}^{2+}$ and $\text{LiI}:\text{Eu}^{2+}$ crystals are widely used as scintillation phosphors for nuclear radiation detection. Moreover, the results of studies of Eu^{2+} ion impurities in crystals have improved scientists' understanding of the properties of europium compounds of great technological interest. [Hufner (1978)].

The optical absorption spectrum of Eu^{2+} ions at substitutional cation sites in any fluorite - type or NaCl-type crystal consists of two broad structured bands located mainly in the ultraviolet spectral region [Kapyanskii and Feofilov (1962), Reisfeld and Glasner (1964), Loh (1968), (1969), Hernandez, *et al.* (1980), (1981), Bland (1985)]. The authors attribute the two absorption bands to the allowed electric dipole $4f^7(^8S_{7/2}) \rightarrow 4f^6(^7F_J)5d$, $J = 0, 1, \dots, 6$, transitions of the Eu^{2+} ions in the crystals. It is believed that the cubic crystal field strongly splits the 5d electron states into two components $|\Gamma_{3e_g}\rangle$ and $|\Gamma_{5t_{2g}}\rangle$ which are coupled to the multiplet states, $4f^6(^7F_J)$, $J = 0, 1, \dots, 6$, of the core configuration of the Eu^{2+} ions in the crystals. As a result, the $4f^6(^7F_J)5d$ sub-configuration splits into two components, namely $4f^6(^7F_J)\Gamma_{3e_g}$ and $4f^6(^7F_J)\Gamma_{5(t_{2g})}$ components.

When a divalent impurity ion takes up a cation site in an alkali halide crystal, a cation vacancy is formed in the vicinity of the impurity ion. The divalent impurity and the nearby vacancy therefore constitute an impurity - vacancy complex. Electron spin resonance (ESR), studies of Eu^{2+} ions in alkali halide crystals show that the formation of Eu^{2+} ion - cation vacancy complex lowers the point symmetry of the site of the Eu^{2+} ion from octahedral, O_h , to orthorhombic, C_{2v} , point symmetry [Nair, *et al.* (1968), Rubio, *et al.* (1974), (1975), Aguilar, *et al.* (1974), Munoz, *et al.* (1975)].

However, several studies involving the $4f^N \rightarrow 4f^{N-1}5d$ electronic transitions of divalent rare-earth ions in alkali halide crystals have demonstrated, that it is a good first approximation to regard the site symmetry of the divalent rare earth ions as octahedral [Hernandez, *et al.* (1980), (1981), Tsuboi (1981), Bland and Smith (1985), Mejeha and Smith (1998a), (1998b)].

This study is concerned with an investigation of the optical absorption spectra of Eu^{2+} ions in single crystals of rubidium chloride, bromide and iodide. As has been noted earlier, the absorption spectra of Eu^{2+} ions in these crystals have been reported previously [Hernandez, *et al.* (1980), (1981)]. But the $\text{RbX}:\text{Eu}^{2+}$ ($X = \text{Cl}, \text{Br}, \text{I}$) crystals used in those studies were grown from melt. However, in this study, the metal vapour phase diffusion (MVPD), technique will be used in doping the crystals. This will enable to compare the absorption spectra of Eu^{2+} ions in the crystals produced using the two fundamentally different techniques. This represents the first time the absorption spectra of rubidium halide crystals doped with Eu^{2+} ions by this method has been reported.

EXPERIMENTAL METHOD

The single crystals of RbCl , RbBr and RbI used in this study were obtained from BDH Chemicals Ltd, Poole, England. The europium metal used was supplied by the Rare-Earth Products Ltd., Cheshire, England, in the form of ingots of certified purity of 99.99%. A small disc of the crystal to be doped and about 25 mg of europium metal were put in a special device called the primary diffusion ampoule, PDA. The latter was then evacuated by means of a diffusion pump to an ultra-high vacuum and lowered into another special device called the secondary diffusion ampoule, SDA which was being pre-heated in an upright furnace. The detailed features of the PDA and SDA as well as the special procedures adopted in the doping process can be found elsewhere [Bland and Smith (1985), Mejeha and Smith (1995)].

The duration of doping ranged from 6 to 8 hours. After doping, the PDA was lowered into a dewar of liquid nitrogen so as to quench the doped crystal. The doped crystals were usually coloured as a result of the presence of colour defect centers. If considered necessary, the doped crystal was thermally bleached to eliminate or reduce the concentration of the defect centers as explained by Mejeha and Smith (1995). The optical absorption spectra of the doped crystals were then measured using a Varian DMS-90 UV-VIS-NIR

spectrophotometer at room temperature (RT) as well as at liquid nitrogen temperature (LNT).

RESULTS

The absorption spectra of the RbCl:Eu^{2+} , RbBr:Eu^{2+} and RbI:Eu^{2+} crystals obtained in this study at RT and LNT consist of two broad strong structured bands located in the ultraviolet spectral region. Even at RT, the "stair-case" structure of the low energy bands in the spectra is quite evident. This feature of the low energy bands was observed in previous studies of the optical absorption spectra of Eu^{2+} ions

in CaF_2 -type crystals. The structure of high energy bands found in the RT spectra of RbCl:Eu^{2+} crystals is not pronounced. However, the high energy band in the RT spectrum of RbI:Eu^{2+} has some pronounced peaks. Nevertheless, in the LNT spectra of the doped crystals, the structure in the low and high energy bands become better resolved. Figures 1 and 2 which show the absorption spectra of RbCl:Eu^{2+} and RbI:Eu^{2+} crystals at RT and LNT clearly illustrate the features of the spectra outlined above. The RT and LNT spectra of RbBr:Eu^{2+} crystals have almost identical features as the respective RT and LNT spectra of RbCl:Eu^{2+} crystals and need not be displayed for want of space.

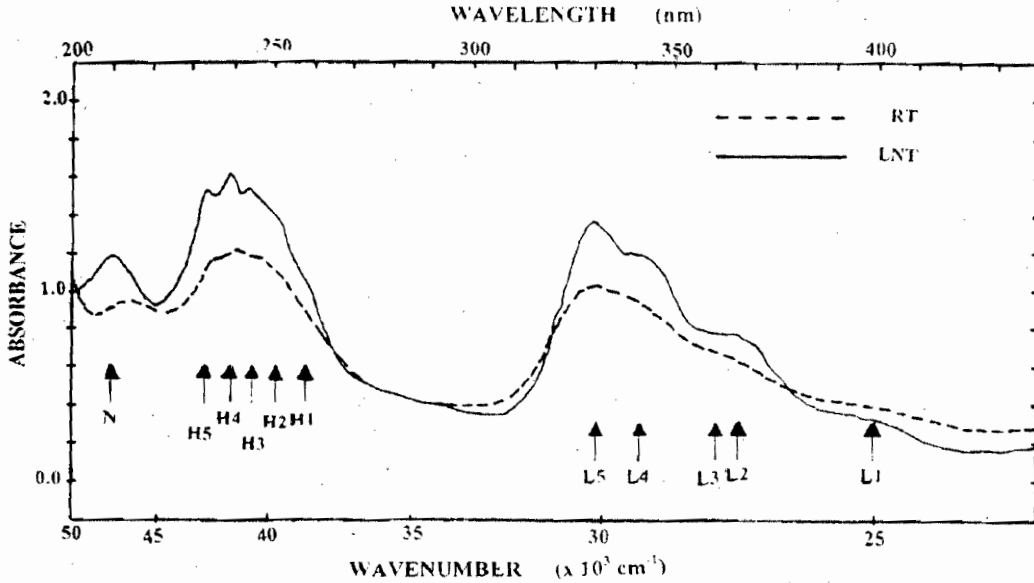


Fig.1 Ultraviolet absorption spectra of Eu^{2+} ions in RbCl crystal, at room and liquid nitrogen temperatures.

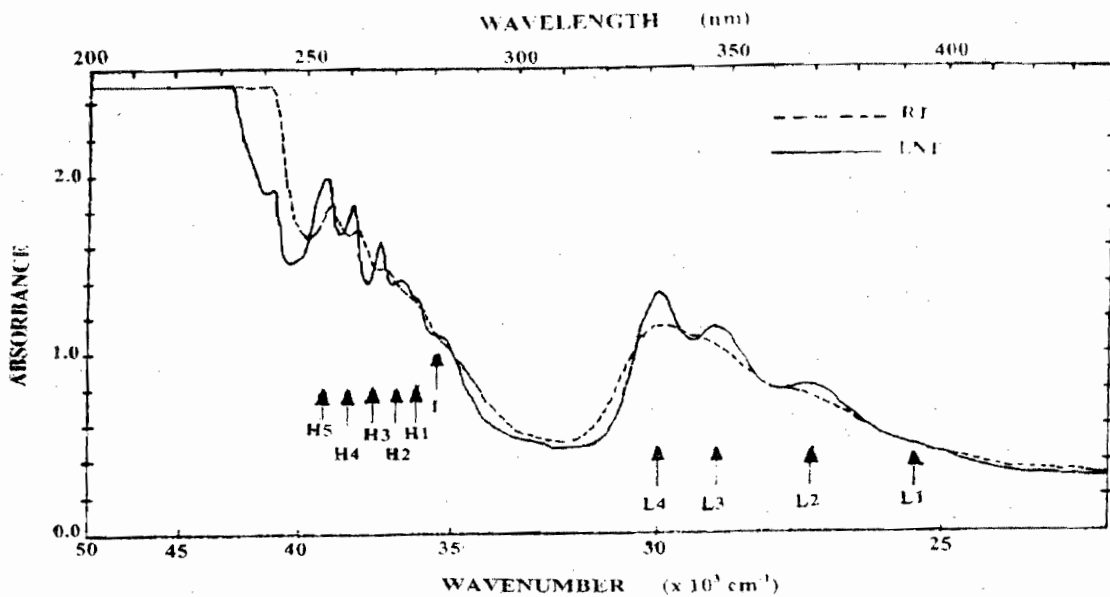


Fig.2 Ultraviolet absorption spectra of Eu^{2+} ions in RbI crystals at room and liquid nitrogen temperatures.

The features of the absorption spectra of the Eu^{2+} - doped rubidium halide crystals presented above are similar to those of the absorption spectra of Eu^{2+} -doped sodium and potassium halide crystals produced using the MVPD technique [Bland (1985)]. They are also similar to those obtained by previous investigators [Reisfeld and Glasner (1964), Hernandez, *et al.*, (1980), (1981)] who used Eu^{2+} - doped alkali halide crystals produced from melt, as well to those of Eu^{2+} - doped alkaline earth fluoride, and chloride crystals. [Kapiyanskii and Feofilov (1962), Loh (1968), (1969), Kisliuk, *et al.* (1968)]

It was possible to decompose each of the two broad absorption bands in each spectrum into a number of Gaussian shaped bands. The peak positions of the component bands were located and have been recorded in Table 1. In each absorption spectrum, the component bands were grouped into L-bands and H-bands, representing the low energy and high energy bands respectively. The numeral attached to the letters L and H in the spectrum of one doped crystal does not necessarily correspond to an L- or H-band with the same numeral label in the spectrum of another doped crystal.

Table 1: Peak positions of the component bands of the low and high energy bands in the absorption spectra of RbCl:Eu^{2+} , RbBr:Eu^{2+} and RbI:Eu^{2+} crystals at room and liquid nitrogen temperatures.

(a) RbCl			(b) RbBr			(c) RbI		
Band	Peak Position (cm^{-1})		Band	Peak Position (cm^{-1})		Band	Peak Position (cm^{-1})	
	RT	LNT		RT	LNT		RT	LNT
L1	24 938	25 094	L1	25 907	25 773	L1	-	25 478
L2	27 248	27 360	L2	27 510	27 472	L2	27 322	27 027
L3	-	27 701	L3	29 240	29 320	L3	28 902	28 815
L4	29 197	29 240	L4	30 558	30 570	L4	29 985	30 008
L5	30 211	30 234						
H1	-	38 760	H1	-	37 037	H1	35 907	36 166
H2	-	39 841	H2	-	38 095	H2	-	38 095
H3	40 323	40 733	H3	-	39 120	H3	37 209	37 383
H4	41 322	41 754	H4	40 900	41 005	H4	38 057	38 314
H5	42 373	42 735				H5	39 024	39 370

The absorption band labeled N and located at 210 nm ($47\ 619\ \text{cm}^{-1}$) in the LNT spectrum of RbCl:Eu^{2+} crystal is not due to electronic transitions of Eu^{2+} ions in the crystal. The transition intensity of that band relative to that of any other component band, say the L5 band, varied from sample to sample. An absorption band located at the same spectral position in the LNT spectrum of rubidium chloride doped with divalent ytterbium (Yb^{2+}) ions using the MVPD technique was earlier identified by Mejha (2007). The latter author also noted that the transition intensity of that band relative to a well-

defined Yb^{2+} - band varied from sample to sample. Moreover, the intensity of the band relative to the other bands in the spectrum was reduced when the RbCl:Yb^{2+} was thermally bleached. He concluded that the band must be due to an unidentified colour center present in the doped crystal. The absorption band labeled I and located at 282 nm ($35\ 461\ \text{cm}^{-1}$) in the LNT spectrum of RbI:Eu^{2+} crystal is due to an unidentified impurity present in the nominally pure crystal obtained from the supplier.

Table 2: Values of the centres of gravity of the low and high energy bands in the absorption spectra of RbCl:Eu²⁺, RbBr:Eu²⁺ and RbI:Eu²⁺ crystals at room and liquid nitrogen temperatures. Values of the separation of the broad band centres, $\Delta = 10Dq$ and lattice parameter d are included.

Crystal	Lattice parameter d	Centre of gravity of low energy band (cm ⁻¹)		Centre of gravity of high energy band (cm ⁻¹)		10Dq (cm ⁻¹)	
		RT	LNT	RT	LNT	RT	LNT
RbCl	3.291	28 986	28 860	40 650	40 816	11 664	11 956
RbBr	3.427	29 412	29 412	40 078	40 322	10 666	10 910
RbI	3.671	28 653	28 531	37 807	38 023	9 154	9 492

In Table 2, the spectral positions of the centers of gravity of the broad absorption bands identified in the RT and LNT spectra of Eu²⁺-doped rubidium chloride bromide and iodide crystals were compared. In each absorption spectrum, the separation in energy of the centers of the low and high energy bands is a measure of the strength of the crystal field splitting of the 5d electron orbitals into the two components $\Gamma_5(t_{2g})$ and $\Gamma_3(e_g)$ in an octahedral crystal field. It is designated as $\Delta = 10Dq$ where Dq is called the crystal field parameter in an octahedral (or cubic) environment. Values of the lattice parameter, d , of the host crystals were included in the table. An interesting observation is that in general, the center of gravity of a low energy band shifts to lower energies while that of the high energy band shifts to higher energies as a given doped crystal is cooled from RT to LNT.

DISCUSSION

A comparison of the absorption spectra of the RbX:Eu²⁺, (X = Cl, Br, I) crystals reported in this study with those of Eu²⁺-doped alkali halide crystals produced from melt [Hernandez, *et al.* (1980), (1981)] shows that the similarity between the two sets of spectra is very striking in spite of the difference in the methods of producing the crystals. Following Hernandez, *et al.* (1980), (1981), the low energy band in any of the absorption spectra obtained in this study is ascribed to transition of the Eu²⁺ ions from the 4f⁷(⁸S_{7/2}) ground state to the lower component 4f⁶(⁷F_J) $\Gamma_5(t_{2g})$ of the 4f⁶(⁷F_J)5d sub-configuration of the ions while the high energy band is ascribed to 4f⁷(⁸S_{7/2}) \rightarrow 4f⁶(⁷F_J) $\Gamma_3(e_g)$ transitions of the same ions in the crystals. In making the band assignments, it was assumed that the effective site symmetry of the substitutional Eu²⁺ ions is octahedral, O_h.

Group theoretical considerations show that in a cubic crystal field, the 4f⁶(⁷F_J) $\Gamma_5(t_{2g})$ and 4f⁶(⁷F_J) $\Gamma_3(e_g)$ components of the 4f⁶(⁷F_J)5d sub-configuration of Eu²⁺ ions decompose into 163 crystal field levels. Incidentally, electric dipole transitions of the Eu²⁺ ions from the 4f⁷(⁸S_{7/2}) ground state are allowed to each of these levels. Clearly, the number of the component bands identified in each spectrum is by far smaller than the predicted number of crystal field levels. Each of the two broad absorption bands in a given spectrum of the Eu²⁺-doped crystals can be thought of as a superposition of spectral bands arising from transitions of the Eu²⁺ ions from the ground state to the numerous crystal field levels.

It has earlier been pointed out that the full symmetry of the site of the Eu²⁺ ions in alkali halide crystals is orthorhombic, C_{2v} instead of octahedral, O_h. As a result of the

lowering of the point symmetry of the site of the Eu²⁺ ions from octahedral to orthorhombic, further crystal field splitting of the low and high energy bands would be expected. Group theory predicts that the 163 crystal field levels derived from the 4f⁶(⁷F_J) 5d sub-configuration of the Eu²⁺ ions in a cubic crystal would decompose into 490 crystal field levels. However, this study and other studies of Eu²⁺-doped alkali halide crystals show that the absorption spectra of Eu²⁺ ions in these crystals are not different in any fundamental way to those of the same ions in alkaline earth chalcogenide crystals in which the ions experience six-fold coordination as they do in alkali halide crystals but with full octahedral symmetry. Moreover, the absorption spectra of Eu²⁺ ions in alkali halide crystals are similar to those of the same ions in alkaline earth fluoride and chloride crystals in which they experience eight-fold coordination.

The above result suggests that the presence of a cation vacancy in the vicinity of an Eu²⁺ ion may have only small effect on the eigenstates of the 4f⁶5d configuration of the Eu²⁺ ions in alkali halide crystals. The result is consistent with the result of studies of Eu²⁺ ions in alkali halide crystals by Newman (1976) who showed that the Eu²⁺ ions indeed occupy a slightly distorted octahedral sites in alkali halide crystals, a conclusion re-echoed by Abragam and Bleaney (1986). It is therefore a good first approximation to ignore the orthorhombic distortion and regard the point symmetry of the site of the Eu²⁺ ions in alkali halide crystals as octahedral in any study involving the states of the first excited 4f⁶5d configurations of the ions. Some research workers [Tsuboi, *et al.* (1981) Bland and Smith (1985), Mejeha and Smith (1988a), (1988b)] have adopted the octahedral approximation successfully in the theoretical analyses of the electric dipole 4f^N \rightarrow 4f^{N-1}5d transitions of divalent samarium and ytterbium ions in alkali halide crystals.

The values obtained for Δ (=10Dq) from the RT spectra of RbCl:Eu²⁺, RbBr:Eu²⁺ and RbI:Eu²⁺ crystals are 11 664 cm⁻¹, 10 666 cm⁻¹ and 9154 cm⁻¹ respectively. These agree remarkably well with the values of 11 658 cm⁻¹, 10 271 cm⁻¹ and 9081 cm⁻¹ obtained for Δ from RT spectra of the same respective crystals by Hernandez and co-workers (1981). The largest observed difference between the two sets of values occurred for RbBr:Eu²⁺ crystal. The value of Δ obtained in this study for that crystal is within 3.8% of that obtained by those authors. It is also remarkable that the values of Δ obtained for RbX:Eu²⁺ (X=Cl, Br, I) crystals at either RT and LNT vary according to a spectrochemical series in which the coordinating ligands are arranged in increasing order of the magnitude of Dq, namely [Newman, (1977)].

Free ion ($Dq \approx 0$) $< \text{I}^- < \text{Br}^- < \text{Cl}^-$.
This result is in agreement with a similar trend observed for values of Δ in alkali halide crystals doped with divalent

samarium, europium or ytterbium ions [Hernandez, *et al.* (1981), Bland and Smith (1985) and Mejeha and Smith (1998a), 1998b)].

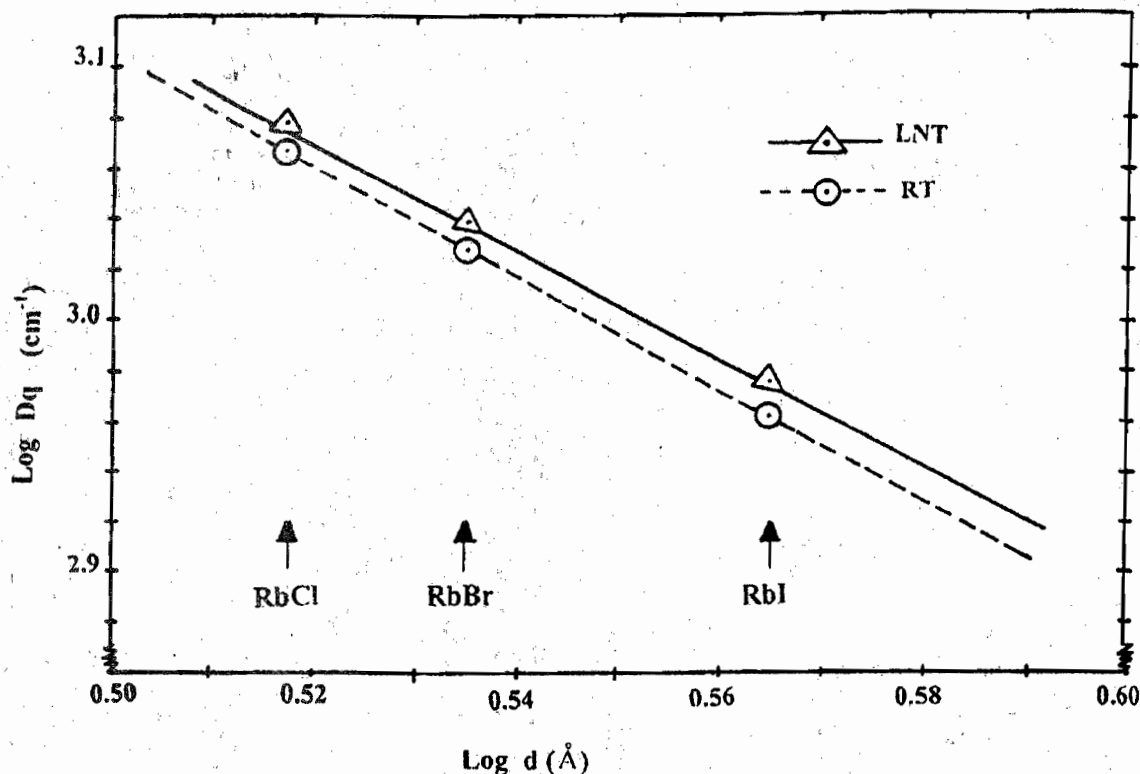


Fig. 3 Plots of $\text{Log } Dq$ versus $\text{Log } d$ for RbX: Eu^{2+} ($X=\text{Cl, Br, I}$) crystals at room and liquid nitrogen temperatures.

Plots of $\text{Log } Dq$ versus $\text{Log } d$ for the crystals at RT and LNT are shown in Fig. 3. It can be deduced from the plots that $Dq \propto d^n$ with $n = -2.23$ for the crystals at RT while it is -2.16 for the crystals at LNT. These values of n represent some deviation of the empirical results from the predictions of the point-ion model of crystal field theory which gives a value of -5 for n [Hutchings (1964)]. These results and similar ones earlier observed for divalent rare-earth ion in octahedral crystals [Hernandez, *et al.* (1981), Bland and Smith (1985), Mejeha and Smith (1998a)] further illustrates the inadequacies of the theory which had previously been pointed out. [Shulman and Sugano (1963a), (1963b) Ferguson (1970), Gerlock (1983)].

It can also be deduced from Fig. 3 that Dq decreases with increase in d . This conclusion is consistent with the observed increase in the value of Dq for a given Eu^{2+} -doped rubidium halide crystal as the crystal is cooled from RT to LNT, since cooling leads to a decrease in the lattice parameter d of the crystal.

CONCLUSIONS

In this study, single crystals of RbCl:Eu^{2+} , RbBr:Eu^{2+} and RbI:Eu^{2+} have been produced by using the MVPD technique. This represents the first time single crystals of RbX , ($X=\text{Cl, Br, I}$) doped with divalent Eu^{2+} ions with the technique has been reported. Each of the absorption spectra of the Eu^{2+} -doped crystals obtained at both RT and LNT consists of two broad intense structured bands located mainly in the ultraviolet spectral region. The low energy band in any of the absorption

spectra is ascribed to transitions of the Eu^{2+} ions from the $4f^7(^8S_{7/2})$ ground state to the lower component $4f^6(^7F_3)\Gamma_5(t_{2g})$ of the crystal-field split $4f^6(^7F_3)5d$ sub-configuration of the ions in the crystals while the high energy band is ascribed to the $4f^7(^8S_{7/2}) \rightarrow 4f^6(^7F_3)\Gamma_3(e_g)$ transitions of the ions.

Values of $10Dq$ obtained in this study vary according to the spectrochemical series of coordinating ligand ions, namely: $\text{I}^- < \text{Br}^- < \text{Cl}^-$. It was also established that for RbX:Eu^{2+} , ($X=\text{Cl, Br, I}$) crystals Dq and d are connected by an n^{th} power law, namely: $Dq \propto d^n$ with $n = -2.23$ for the crystals at RT and -2.16 for the crystals at LNT.

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