

Electro-Optical, Optical and Structural Properties of Mn Doped Potassium Chloride Crystals Prepared by a Mini Melt Growth Setup

J. Joseph¹, V. Mathew¹, K.E. Abraham²

¹St. Aloysius' College, Edathua, Alappuzha, Kerala, India

¹St. Aloysius' College, Edathua, Alappuzha, Kerala, India

Received 10 November 2008

Abstract. Mn doped potassium chloride (KCl) crystals are prepared by melt growth using a cost effective mini crystal growth setup. The material is characterized by X-ray diffraction. The optical band gap of KCl crystal is calculated as 4.94 eV from the Diffused Reflectance Spectroscopy (DRS). Photoconductivity (PC) and photovoltaic (PV) studies of the material as a function of time, intensity of irradiation light and annealing temperature are studied. Photoluminescence (PL) spectra of KCl crystals are recorded at different annealing temperature and concentration of Mn. The spectral peak of KCl photoluminor lies around $\lambda_{em} = 340$ nm with excitation wavelength $\lambda_{exc} = 274$ nm. The broad peak observed around 340 nm corresponds to the ${}^5D_0^0 \rightarrow {}^1S_0^0$ transition of Cl. Electro luminescence (EL) is measured with the help of a photomultiplier tube (PMT) and its EL brightness is measured as a function of the voltage of excitation at different annealing temperature and concentration of Mn.

PACS number: 61.10.Nz; 78.20.Jq

1 Introduction

The most common methods of crystal growth are solution growth [1] and melt growth [2]. Among the normal freezing methods, Bridgeman technique is one of the oldest methods for growing crystals and produces nucleation on a single solid-liquid interface by carrying out the crystallization in a temperature gradient. The principle is that a melt of the correct composition of the substance is slowly cooled from above the equilibrium melting point to produce the crystal desired. Melt crystallization is often considered to be commercially attractive since it offers the potential for low energy separation compared with distillation, because latent heats of fusion are generally much lower than latent heats of vaporization [3]. Because of their simple cubic structure the alkali halides have

played a very important role in the development of solid state physics and it appears that there is still much to be learned from experiments done on them. Europium doped alkali halide single crystal has been the subject of very intensive investigation due to its applications in digital medical radiography, optical memories and environmental dosimetry [4]. Solid state physics is devoted mostly to the study of crystals and electrons in the crystals [5].

The present paper reports the studies of the electro-optical properties of melt grown KCl crystals. KCl lattice is fcc; the basis consists of one K atom and one Cl atom separated by one half the body diagonal of a unit cube. There are four units of KCl in each unit cube. The structure of KCl crystal is cubic with lattice parameters of $a = b = c = 6.29170 \text{ \AA}$. The inter ionic separation of pure KCl crystal is 3.147 \AA [6].

2 Experimental

Growth from the melt is by far the fastest of the growth methods, as its rate does not depend on mass transport processes [7]. KCl crystals are prepared by melt growth using a cost effective mini crystal growth setup. They were grown by a variant of the Bridgeman method (Gradient Freeze Method) from the melt of A.R. Grade KCl powder from CDH using a mini furnace (Toshniwal, India) with heating capacity up to 1000°C . The temperature of the furnace is measured with a thermocouple and a pyrometer. The selection of particular method depends on the volatility, dissociability, chemical reactivity and melting point of the material [8]. The KCl powder to be crystallized is taken in a small crucible. The temperature of the furnace is raised till the substance melts (melting point of KCl $\sim 776^\circ\text{C}$) and the furnace is left to itself for an hour. Then the molten material is allowed to cool very slowly to room temperature. At the end of the cooling several crystals are cleaved out. This method has the merits of simplicity and low cost and requires a reasonably short time for growing crystals.

Transparent conducting oxide (TCO) thin films are essential for the conduct of PC, PV and EL experiments. We have prepared transparent conducting SnO_2 thin films in the laboratory by a cost effective vapour deposition technique. Mn doped KCl crystals were prepared by changing the concentration (from 1 wt.% to 4 wt.%) of AR grade $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (from CDH) in KCl. PC/PV/EL cells are prepared by pressing KCl crystal between SnO_2 thin films of resistance $\sim 150 \Omega/\text{cm}^{-2}$ and a copper plate at a gap of $100 \mu\text{m}$ for a given area.

3 Results and Discussion

The structure of the KCl crystals was studied by taking XRD using $\text{Cu K}\alpha$ ($\lambda = 0.154056 \text{ nm}$) radiation from Bruker, D8 Advance, Germany and was compared with JCPDS data card. The XRD pattern of precursor, undoped and

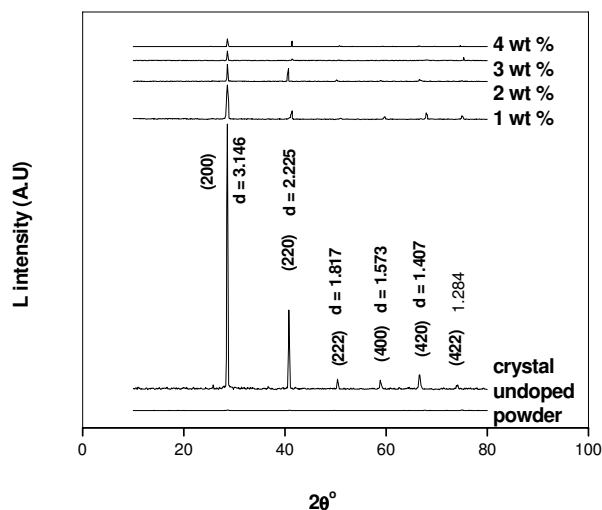


Figure 1. XRD pattern of Mn doped KCl crystal.

Mn doped KCl crystal with d and (hkl) values is shown in Figure 1, which reveals a crystalline nature oriented along the (200) and (220) planes at $2\theta = 28.612^\circ$ and 40.82° , respectively. The presence of other orientations such as (222), (400), (420) and (422) was also detected at $2\theta = 50.45^\circ$, 59° , 66.81° and 74.15° , respectively with lower intensities.

On Mn doping no extra peaks corresponding to them or their compounds were detected but the intensity of the prominent peaks was decreased. On increasing the concentration of the dopant, the intensities of the peaks were further decreased due to the decrease in the atomic density in these planes. Increase in dopant concentration leads to the movement of Mn^{2+} ions to the interstitial sites and also increases the amorphous phase and disorders.

Band gap (E_g) is measured by Diffused Reflectance Spectroscopy (DRS) taken from Jasco – V570 Indonesia. E_g is found by extrapolating the straight line in the following graph (Figure 2) at $k = 0$, where k is the absorption coefficient and s is the scattering coefficient. E_g is found to be 4.94 eV. Diffused reflectance spectrogram with % of R versus wavelength λ is given in Figure 2 (inside).

The basic process of photoconductivity (PC) is the production of ‘free’ charge carriers in the material by optical excitation and photovoltaic (PV) effect is involved when absorption of radiation by the material causes the appearance of a p.d. between the two portions of the material. The study of PC of semi conducting materials has gained industrial importance owing to its use in photovoltaic (PV) devices [9]. Like many forms of PC, the PV effect is essentially a minority carrier phenomenon [10]. PC and PV studies of KCl crystals were performed by

Properties of Mn Doped KCl Crystals Prepared by a Mini Melt Growth Setup

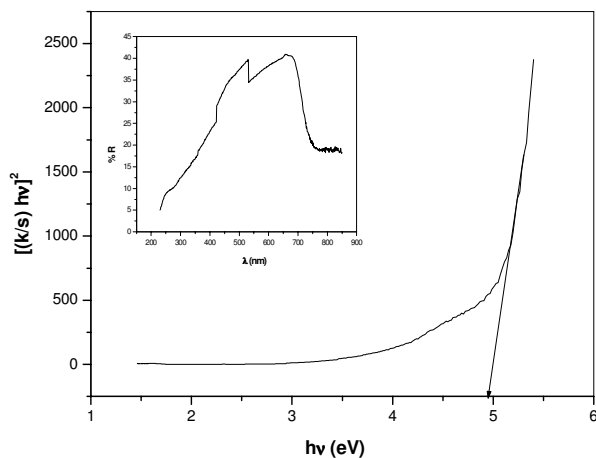


Figure 2. DRS spectrum of KCl crystals.

using a 100 W milky lamp as excitation source. The photocurrent was recorded by a digital nano ammeter, model DNM-121 (Scientific equipment, Roorkee, India) and the photo voltage was recorded by a digital micro voltmeter, model DNM-001 (Scientific equipment, Roorkee, India).

Time dependence of photocurrent of the sample at 100°C is shown in Figure 3 and that of PV is shown in Figure 4. PC and PV increase as annealing temperature increases and reaches maximum at 50°C and then decreases on increasing

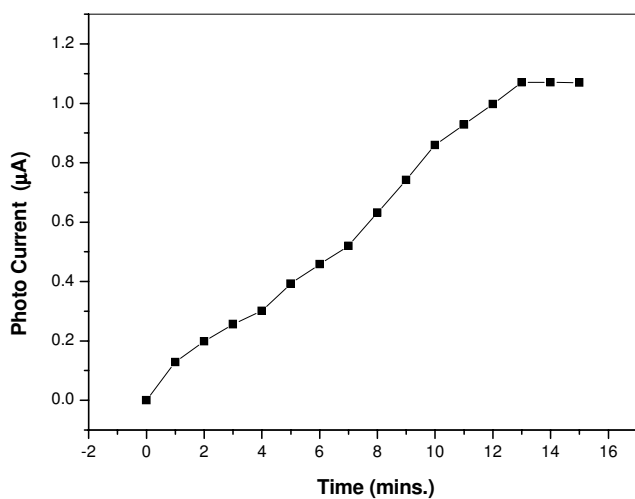


Figure 3. PC of KCl crystals with respect to time.

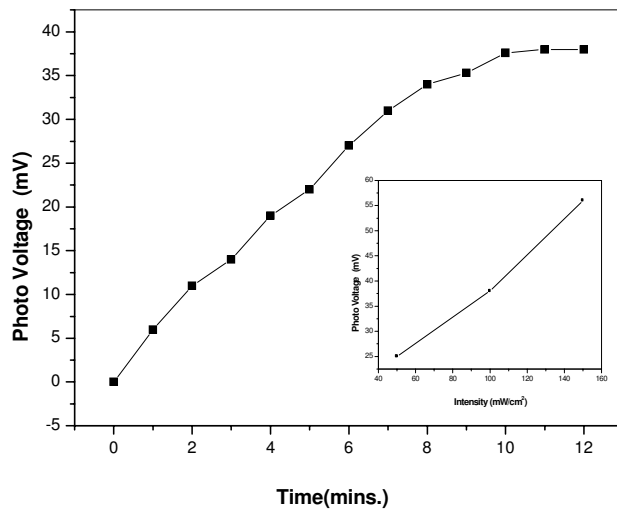


Figure 4. PV of KCl crystals with time and at different intensities of light (inside).

temperature (Figures 5 and 6). The imperfection in the crystal lattice some times results in as traps or as recombination centers. The main purpose of annealing is to increase the crystallinity of the KCl crystals, which produces an increment in photosensitivity. Increase in PC and PV at temperature 50°C can be explained

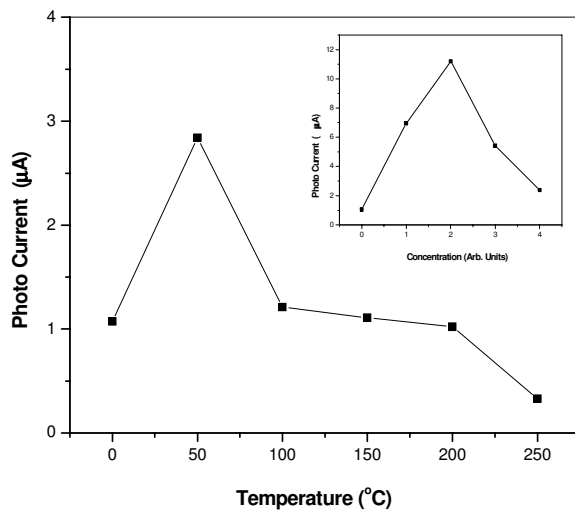


Figure 5. PC of KCl crystals with temperature and at different concentrations of the dopant (inside).

Properties of Mn Doped KCl Crystals Prepared by a Mini Melt Growth Setup

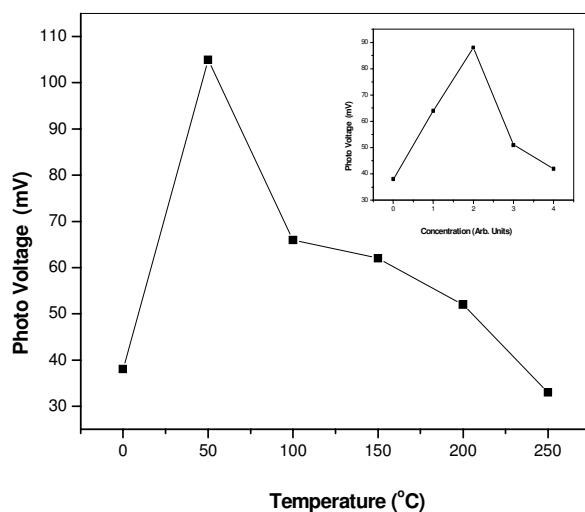


Figure 6. PV of KCl crystals with temperature and at different concentrations of the dopant (inside).

also on the basis of impurity effect in the material. Imperfections acting as efficient recombination centers decrease the photosensitivity. Also imperfections having high probability for capturing the minority carriers with subsequent small probability for capturing a majority carrier increase the photosensitivity. The decrease in PC and PV beyond 50°C is due to the increase in the amorphous phase and disorders and is also due to the recombination of electrons which are thermally freed from traps with photo excited holes held at centers as in quenching effects reported [11].

It is found that photocurrent increases with increasing intensity of excitation (Figure 7) and also with increase in applied voltage (Figure 7 (inside)). More and more charge carriers reach at the respective electrodes and the photocurrent increases with the increase in intensity and applied voltage. The non-linearity in these figures represents the dependence of maximum value of photocurrent (secondary photocurrent) on the intensity of excitation and applied voltage. Photosensitivity increases with the electron lifetime increases giving rise to super linear PC. The Photo voltage also increases with increasing intensity of excitation (Figure 4 (inside)). With the increase in intensity more and more charge carriers are separated at the respective electrodes and hence the photo voltage increases.

Figure 5 (inside) shows the variation of the maximum value of photocurrent with concentration of the dopant Mn. As the concentration increases the charge carriers also increase and it is observed that PC increases and reaches maximum at 2 wt.% concentration of Mn. At this concentration the charge concentration seems to be optimum for better PC. PC is found to be decreased on further

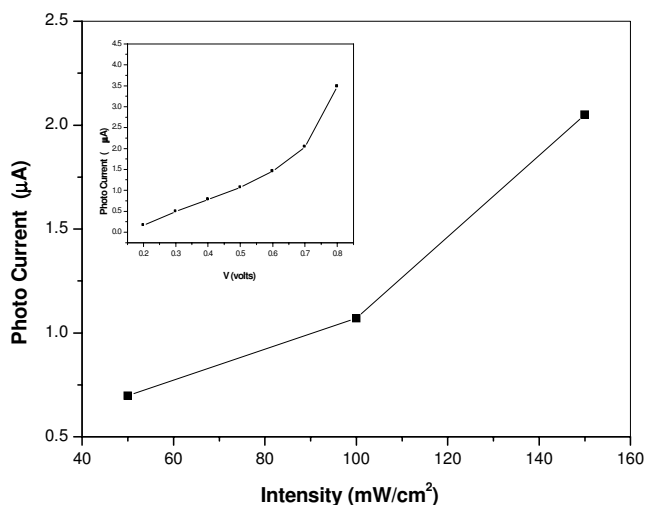


Figure 7. PC of KCl crystals at different intensities of light and applied voltage (inside).

increase in the concentration of Mn. It is because of the chance of more carrier collision probability during charge transport due to concentration quenching.

Figure 6 (inside) depicts the variation of the maximum photo voltage with concentration of the dopant Mn and it is observed that PV is maximum at 2 wt.% concentration of Mn. At this concentration the number density of charge carriers may be the maximum and hence the charge separation may be more in number compared to other cases, giving rise to higher PV. Photoelectronic properties of prepared crystals are very much influenced by the presence of defects in the original crystal lattice. PV increases on increasing the concentration of Mn and reaches maximum at 2 wt.% concentration and decreases on further increasing the dopant concentration. Decrease of PV on increasing dopant concentration may be attributed to increase in amorphous phase and concentration quenching consequent to doping.

Photoluminescence (PL) is the spontaneous emission of light from a material under optical excitation. PL investigations can be used to characterize a variety of material parameter. PL Spectroscopy provides electrical characterization and it is a selective and extremely sensitive probe of discrete electronic state [12]. PL spectrum is recorded with a Fluorimeter (Jobin Yvon Fluoromax – 3 USA). Excitation and emission spectra were obtained by changing the excitation wavelength under a fixed emission wavelength and *vice versa*. The highest resolution used was of 0.1 nm for excitation and 0.3 nm for the emission. When excited with $\lambda_{ex} = 274$ nm the KCl crystal phosphors show a broad emission band which is observed at $\lambda_{em} = 340$ nm. The broad peak observed around 340 nm corresponds to the ${}^5D_0^0 \rightarrow {}^1S_0^0$ transition of Cl.

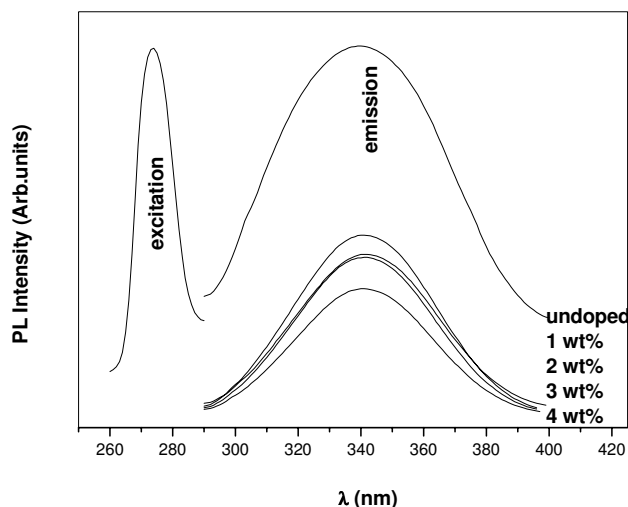


Figure 8. PL emission ($\lambda_{em} = 340$ nm with $\lambda_{exc} = 274$ nm) spectra of KCl crystals at different concentrations of the dopant (Mn).

The luminescent emission is usually originated because of presence of some foreign elements or defects in the host lattice, which produces certain impurity site or centers during the preparation. The normal luminescent bands are attributed to interaction between emission centers and the host crystal lattice [13]. Thus the luminescent emission depends upon the nature of the activator and its concentration in the host lattice. Luminescent centers formed at the cracks, voids, dislocations and stacking faults within the crystal. These defects provide sites for the precipitation of the excess carriers if it is produced. At higher concentration the activator atoms destroy the matrix, which results in quenching of emission [14]. The presence of traps also influences the PL emission. The emissions may be delayed due to their presence [15]. PL emission spectrum of KBr photoluminor doped with Mn is given in Figure 8. The peak positions are not much affected which may be due to the fact that the energy levels of these additives lie at the same level. The emission band corresponds to Mn^{2+} ion found in [16] and [17] is merged in the broad peak of KBr and KCl. The merged transitions of Mn^{2+} ion are 339 nm, correspond to the band assignment ${}^6A_1(S) \rightarrow {}^4T_1(P)$, 363 nm correspond to the band assignment $({}^6A_1(S) \rightarrow {}^4E(D))$ and 376 nm correspond to the band assignment ${}^6A_1(S) \rightarrow {}^4T_2(D)$. PL intensity decreases with increasing of Mn concentration due to concentration quenching.

PL intensity increases with increasing annealing temperature and reaches maximum at $50^\circ C$, then decreases on increasing annealing temperature Figure 9. The main purpose of annealing is to increase the crystallinity of the KCl photoluminor. Increase in PL intensity with temperature up to $50^\circ C$ can be explained

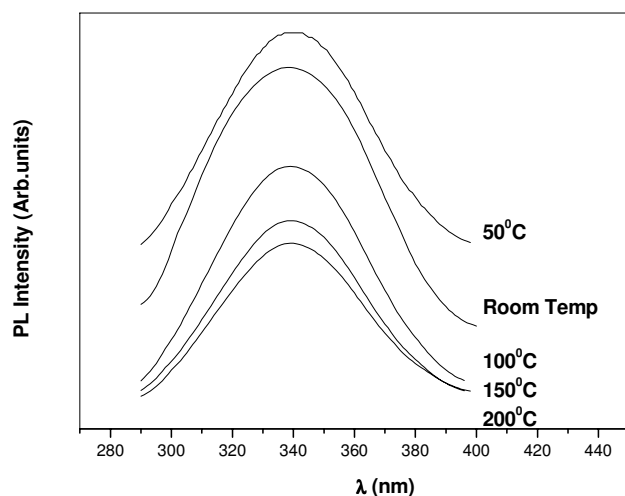


Figure 9. PL emission spectra of KCl crystals at different annealing temperatures.

on the basis of impurity effect in the material. Imperfections acting as efficient recombination centers decrease the photosensitivity. Also imperfections having high probability for capturing the minority carriers with subsequently small probability for capturing a majority carrier increase the photosensitivity. The decrease in PL intensity beyond 50°C is due to the increase in the amorphous phase and disorders and also it is due to the recombination of electrons which are thermally freed from traps with photo excited holes held at centers as in quenching effects reported [15].

Electro luminescence (EL) is the phenomenon of the emission of e-m radiation from condensed matter subjected to an external electric field. The experimental AC/DC powder EL cells used for the present investigation are essentially a parallel plate condenser with the KCl powder between the transparent conducting SnO₂ films and copper plate with no binder for enhancing the dielectric strength. The EL Brightness as a function of applied voltage was measured with a photomultiplier tube (PMT, RCA 931A). The current in this photomultiplier is proportional to the total number of photons emitted by KCl crystals on application of high voltage and is measured with the help of a digital nanoammeter. The EL emission from the KCl phosphors can be obtained by subjecting it to a fairly high electric field.

Luminescent centers formed at the cracks, voids, dislocations and stacking faults provide sites for the precipitation of the excess carriers if it is produced. Electrons and holes are injected into the host material from both electrodes and defects on the application of the field. The electrons from the donor centers or from the intrinsic electron traps are freed by the electric field and they enter the

conduction band, where they are accelerated by the positive half cycle of the field until they gain sufficient kinetic energy to ionize or excite activator centers by the elastic impact. In the reverse half cycle of the field these electrons recombine with the luminescence centers with emission of characteristic radiation. This mechanism corresponds to the impact ionization of the activator centers [18-21]. If the next pulse is of the same polarity as the preceding one, the system is already partially polarized, so that the light output is necessarily reduced, since not only the internal electric field is lower, but there are now fewer electrons trapped at the defects. The justification for this argument is that light was observed to be emitted locally in the form of comet. The light from a single appears in double comet lines, each half of which lights up alternately, as the field is reversed and the nearer electrode turns positive. The integrated light intensity of large number of comets of different length is accurately given by the expression [19,22-24]

$$B = A \exp(-C/V^{1/2}) \quad (1)$$

over many orders of magnitude of luminance, where A and C are constants independent of the voltage. The constant A more or less describes the source of charge carriers responsible for the excitation process while C is a complex quantity which relates to the local field intensity. This relationship follows the normal law over many decades of EL brightness. This expresses that the mechanism of excitation is acceleration-collision one. $\log(B)$ [Brightness] versus $V^{-1/2}$ (applied AC voltage), of KCl electroluminor is given in Figure 10. Linearity of the plots holds the above relation.

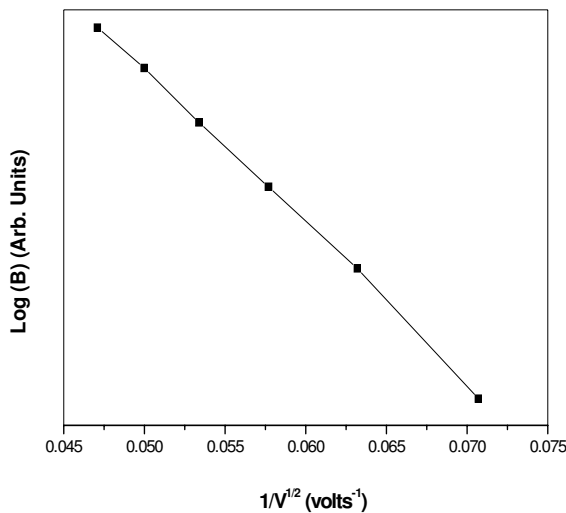


Figure 10. Plot of $\log(B)$ vs. $V^{-1/2}$ of KCl crystals.

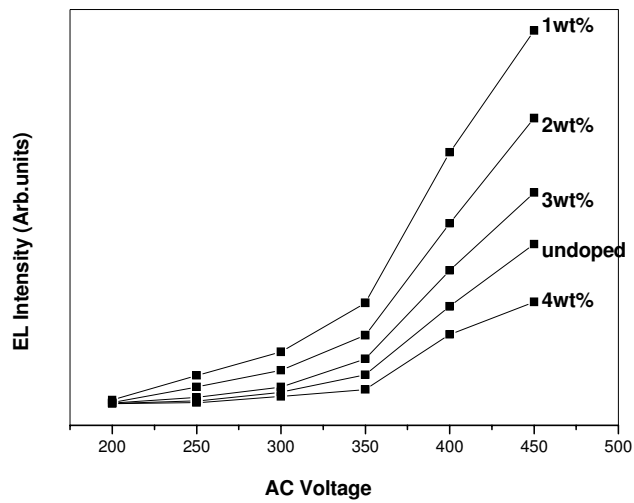


Figure 11. AC EL of KCl crystals at different concentrations of the dopant (Mn).

DCEL powder panels have become reasonably successful as displays. An efficient DC powder EL device was first reported by A. Vecht [25]. Two essential features of any DC EL panel are that the phosphor particles are in contact with each other and with the electrodes. On the initial application of a DC voltage, a high current flows and no light is observed. This is because the high conductiv-

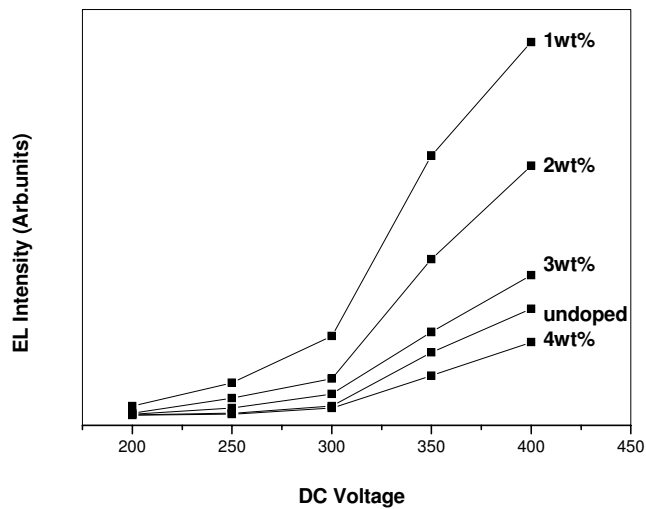


Figure 12. DC EL of KCl crystals at different concentrations of the dopant (Mn).

Properties of Mn Doped KCl Crystals Prepared by a Mini Melt Growth Setup

ity of the phosphor surface and the inter particle contacts preclude any current flow through the particles themselves. At a critical power density the current falls and light emission appear at the positive electrode. An increase in applied voltage produces a temporary rise in current density but this falls rapidly and the panel brightness increases. This is termed as forming process. To form the device a ramped DC voltage is applied with the copper electrode negative. At first the current increases with increasing voltage and no light is emitted, until the current begins to decrease at a particular voltage when the emission of visible light begins. This initial phase of forming is accompanied by a reduction in current by 3 to 100 times depending on the pre-treatment of the powder. Continued increase of the voltage leads to a further increase in resistance of the panel. Practically all the applied voltage is then dropped across the formed region and EL emission is obtained from the formed layer.

EL brightness as a function of applied AC and DC voltage of KCl electroluminor at different concentrations (1 wt.% to 4 wt.%) of the dopant (Mn) is given in Figures 11 and 12. EL intensity increases with increasing Mn concentration and reaches maximum at 1wt %, then decreases on increasing concentration due to concentration quenching. AC and DC EL intensity of KCl electroluminor at different annealing temperatures is given in Figures 13 and 14. EL intensity increases with increasing annealing temperature (crystallinity increases) and reaches maximum at 50°C, then decreases on increasing annealing temperature due to the increase in the amorphous phase and disorders. The overall AC and DC EL emission of KBr electroluminor is bluish one because the intensities of longer wavelengths are poor if they are present.

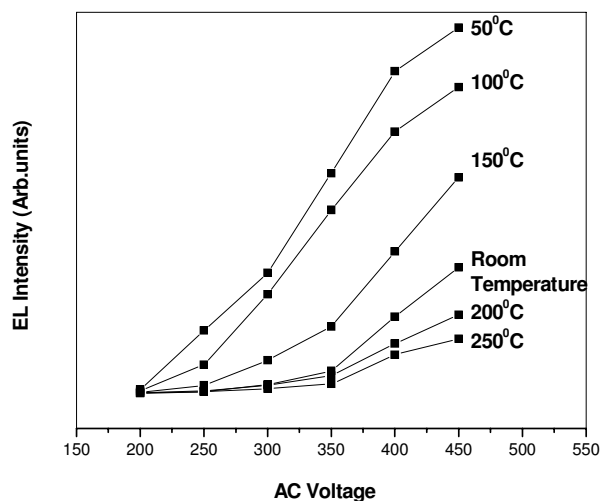


Figure 13. AC EL of KCl crystals at different annealing temperature.

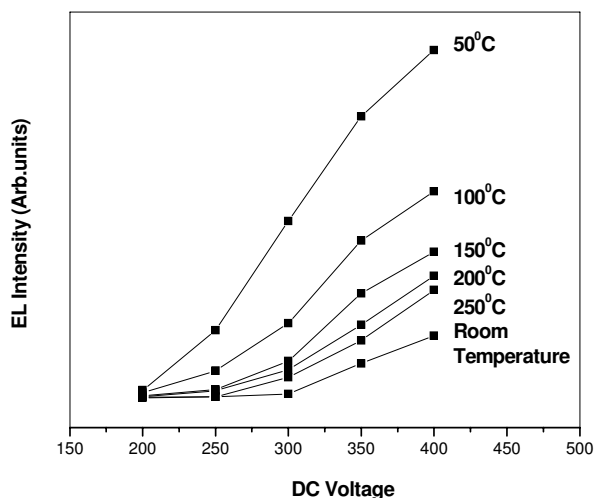


Figure 14. DC EL of KCl crystals at different annealing temperature.

4 Conclusion

The structural, optical and electro-optical properties of the undoped and Mn doped KCl crystals prepared by melt growth are presented. The XRD analysis shows crystalline nature of the crystal. On Mn doping no extra peaks corresponding to them or their compounds were detected but the intensity of the prominent peaks were decreased. On increasing the concentration of the dopant, the intensities of the peaks were further decreased due to the decrease in the atomic density in these planes. Increase in dopant concentration leads to the movement of Mn^{2+} ions to the interstitial sites and also increases the amorphous phase and disorders. The band gap is found to be 4.94 eV from DRS.

Photoconductivity and photovoltaic effects show the photoconducting behaviour of the crystal. It is found that the material is more photosensitive at 50°C and it is observed that PC and PV are in maximum at 1 wt.% concentration of Mn. The photoluminescence emission is observed at $\lambda_{em} = 340$ nm with $\lambda_{exc} = 274$ nm. The broad peak observed around 340 nm corresponds to the ${}^5D_0^0 \rightarrow {}^1S_0^0$ transition of Cl. The emission peak intensity reveals that this material could be used as a good scintillator phosphor. On doping the peak positions are not much affected which may be due to the fact that the energy levels of these additives lie at the same level of KCl photoluminor. The emission band corresponding to Mn^{2+} ion is merged in the broad peak of KBr. The merged transitions of Mn^{2+} ion are 339 nm, correspond to the band assignment ${}^6A_1(S) \rightarrow {}^4T_1(P)$, 363 nm correspond to the band assignment $({}^6A_1(S) \rightarrow {}^4E(D))$ and 376 nm correspond to the band assignment ${}^6A_1(S) \rightarrow {}^4T_2(D)$. PL intensity decreases with increasing

Properties of Mn Doped KCl Crystals Prepared by a Mini Melt Growth Setup

Mn concentration due to concentration quenching. PL intensity increases with increasing annealing temperature and reaches maximum at 50°C, then decreases on increasing annealing temperature.

Electroluminescence brightness increases with the applied electric field. Linearity of the graph $\log(B)$ [Brightness] versus $V^{-1/2}$ (applied AC voltage), of KCl electroluminor reveals that the mechanism of excitation is acceleration-collision. AC and DC EL intensity of KCl electroluminor increases with increasing Mn concentration and reaches maximum at 1 wt.%, then decreases on increasing concentration due to concentration quenching. AC and DC EL intensity increases with increasing annealing temperature (crystallinity increases) and reaches maximum at 50°C, then decreases on increasing annealing temperature due to the increase in the amorphous phase and disorders. The overall AC and DC EL emission of KCl electroluminor is bluish one because the intensities of longer wavelengths are poor if they are present.

Acknowledgements

One of the authors, Mr. Jochan Joseph, acknowledges the University Grants Commission, India for providing the financial support.

References

- [1] A. Holden, P. Singer (1968) *Crystals and Crystal Growing* (Vakils, Feffer & Simons, Bombay).
- [2] J.J. Gilman (1963) *The Art & Science of Growing Crystal* (John Wiley & Sons, New York).
- [3] J.W. Mullin (2001) *Crystallization*, IV Ed. (Butterworth-Heinemann, A division of Reed Educational & Professional Publications Ltd.)
- [4] M. Pedroza-Montero, B. Castaneda, R. Melendrez, T.M. Piters, M. Barboza-Flores (2000) *Phys. Stat. Sol.* **(b)220** 671.
- [5] R.A. Laudise (1970) *The Growth of Single Crystals* (Pentice-Hall Inc., New Jersey).
- [6] K.K. Upadhyay, K.K. Sarkar (1999) *Indian J. Phys.* **73A** 793-799.
- [7] G.J. Solan, A.R. McGhie (1988) *Techniques of Melt Crystallization* (Wiley Inter Science, NY Toronto).
- [8] W. Bradsley, D.T.J. Hurle, J.B. Mullin (1979) *Crystal Growth – A Tutorial Approach* (North Holland Publishing Company, Amsterdam).
- [9] M. Kryreski (1975) *J. Polym. Sci. Polym. Symp.* **50** 359.
- [10] R.H. Bube (1960) *Photo Conductivity of Solids* (John Wiley & Sons Inc. New York – London).
- [11] A.T. Halperin, G.F. Garlick (1955) *Proc. Phys. Soc.* **B68** 758.
- [12] T.H. Gfroerer (2000) In: *Encyclopedia of Analytical Chemistry* (ed. R.A. Meyers, John Wiley & Sons Ltd, Chichester) 9209-9231.
- [13] C.C Vlam (1954) *Brit. J. Appl. Phys.* **5** 443.

- [14] F.A. Krojer (1948) *Physica* **14** 425.
- [15] H.W. Leverenz (1950) *An Introduction to Luminescence of Solids* (John Willey & Sons, New York).
- [16] M. Moreno, F. Rodriguez, J.A. Aramburu (1983) *Phys. Rev. B* **28** 6100.
- [17] C. Marco de Lucas, F. Rodriguez, M. Moreno (1992) *Phys. Stat. Sol. (b)* **172** 719.
- [18] G. Destriau, H.F. Ivey (1955) *Proc. IRE* **43** 1911-40.
- [19] P. Zalm (1956) *Philips Res. Rep.* **11** 353, 417.
- [20] J.B. Taylor, G.F. Alfrey (1955) *Br. J. Appl. Phys. Suppl.* **4** 44.
- [21] W.W. Piper, F.E. Williams (1955) *Br. J. Appl. Phys. Suppl.* **6** S39.
- [22] P. Zalm, G. Diemer, H.A. Klasens (1955) *Philips Res. Rep.* **10** 205.
- [23] A.G. Fischer (1962) *J. Electrochem. Soc.* **109** 1043.
- [24] A.G. Fischer (1963) *J. Electrochem. Soc.* **110** 733.
- [25] A. Vecht, N.J. Werring, P.J.F. Smith (1968) *Br. J. Appl. Phys.* **21** 134.