# Effect of yttrium doping on ionic conductivity of NaCl crystals

**Ch. Gopal Reddy\*, Y.Vijaya Kumar, M.V.Ramana Reddy, A.Laxma Reddy, K.Narasimha Reddy**
Department of Physics, Osmania University, Hyderabad - 500 007, (INDIA)
E-mail: ch_gopalreddy@yahoo.com

## ABSTRACT

An investigation of the ionic conductivity in sodium chloride (NaCl) crystals doped with different concentrations of yttrium (Y) is undertaken in the temperature range $180^0$C to $525^0$C to understand the nature of impurity vacancy (I-V) complexes, their formation and how these I-V complexes affect the conduction process. The conductivity temperature plots of NaCl: Y showed two distinct regions. These regions are explained on the basis of Dreyfus and Nowick notation. It is found that ionic conductivity in Y doped NaCl crystals decreases with increasing Y concentration. Quenching and annealing studies indicate that the ionic conductivity increases due to the former and decreases due to the later. Possible mechanisms for the above results are explained in terms of formation of various defects such as IV complexes, vacancies, etc.　　　© 2011 Trade Science Inc. - INDIA

## INTRODUCTION

One of the most convenient methods of studying the nature of defects and their mobility in ionic crystals is the ionic conductivity and measurements of its temperature dependence. The studies of ionic conductivity in doped alkali halide crystals have provided a great deal of information about the state of lattice defects and their interactions in ionic crystals. The ionic conductivity in doped alkali halide crystals depends on the thermal history of the sample and on the nature of the concentration of impurity ions and their aggregation process[1-3]. If the crystal (doped or undoped) is quenched from high temperatures, the cation vacancies introduced by impurities will be predominant. Excess free cation vacancies and isolated impurity ions are retained in the quenched crystal and they are responsible for the increase in the conduc-

tivity in the impurity region during the subsequent heating. In some cases a decrease in conductivity in the impurity region was also reported[4-7]. This has been attributed to the precipitation of inherent divalent cation impurities of the cystal. Although a large amount of work on ionic conductivity studies in various impurity doped alkali halide crystals has been reported, data on ionic conductivity studies of yttrium-doped alkali halide crystals is scarce. The way the yttrium impurity in an alkali halide matrix influences the defect controlled properties depends on many factors such as the amount of impurity added, its solubility and the history of crystal growth and subsequent heat treatments. The choice of yttrium (Y) as a dopant in sodium chloride (NaCl) matrix was made because the electronic structure of the yttrium is the same as that of $Sr^{2+}$, and the role of strontium as a dopant in an alkali halide matrix is well understood[8].

*Full Paper*

## EXPERIMENTAL

Single crystals of NaCl containing 0.1, 0.3 and 0.5 mole % of yttrium used in the present investigation were grown by slow cooling technique, the details of which were reported earlier[9]. The actual concentration of yttrium doped NaCl crystals was estimated by using inductively coupled plasma (ICP) emission spectroscopy method. All crystalline samples used in the present investigation were grown under identical conditions. The d.c. ionic conductivity of freshly cleaved samples was measured by increasing the temperature at a rate of $60^0$C/h. The currents were measured by using a high sensitive electrometer. The sample temperature was determined to a precision better than $\pm 0.5^0$C by means of calibrated chromel-alumel thermocouple that was placed very close to the sample in the conductivity mount. For good electrical contacts, the samples were coated with aquadag paint. The polarization currents in the measurements were avoided in the usual way by applying an electric field for a short duration of time (less than 30 sec) across the crystal and noting the temporary pause of the meter display. For quenching studies, the samples were annealed at $550^0$C for 4h and rapidly placed on a metallic sheet at room temperature.

## RESULTS

The conductivity of NaCl crystals containing 0.1, 0.3 and 0.5 mole % of yttrium has been measured in different samples at considerable number of temperatures. The graph of log $\sigma$T plotted against 1/T for all the three samples is shown in Figure 1. Such a conductivity plot can be divided into regions I, II, III, III′, and IV according to Dreyfus and Nowick[10]. Region I (above $550^0$C) is the high temperature region which is called intrinsic region. Slope $E_I$ of the conductivity curve in this region is given by, $E_I = E_m + E_s/2$. Here $E_m$ is the activation energy for the motion of free charge carrier. $E_s$ is the formation energy of schottky defect. Region II (550 to $300^0$ C) is the extrinsic unassociated region, where the impurities have a dominant role. The activation energy in this region is same as $E_m$, i.e. $E_{II} = E_m$. Region III (300 to $200^0$C) is extrinsic associated region, where the complexes

formed due to the impurity and cation vacancies affect the conductivity. The effective activation energy in region-III is given as $E_{III} = E_m + E_a/2$, where $E_a$ is the association energy. With further decrease of temperature (region III′ and IV), the impurity either segregates or precipitates from the solid solution. Interpretation of results below region III is difficult.
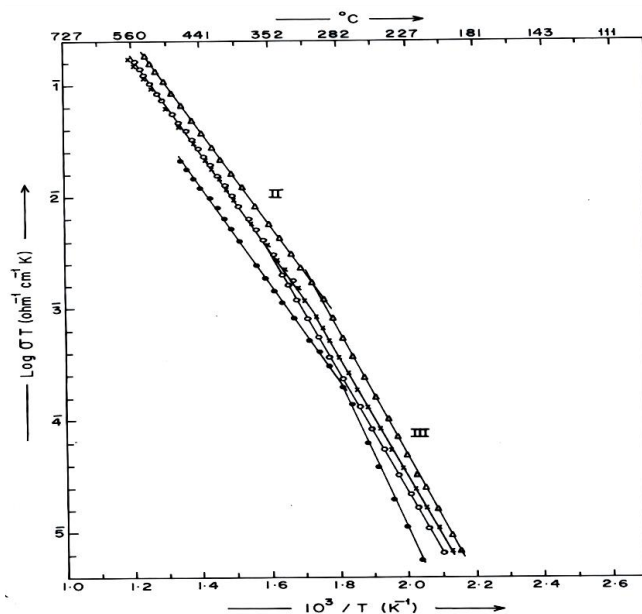


(●) Undoped, (Δ) NaCl+0.1 mole% Y, (x) NaCl+0.3 mole% Y, (o) NaCl+0.5 mole% Y.

**Figure 1 : Plot of ionic conductivity versus $(10^3/T)(K^{-1})$ for NaCl and Y doped NaCl crystals.**

The plot presented in Figure 1 represents the data obtained in measurements with increasing temperature. The slopes $E_{II}$, $E_{III}$ of the corresponding parts of the ionic conductivity curves are shown in TABLE 1. The third column in TABLE 1 contains the concentration of impurity gone into the crystal matrix estimated by inductively coupled plasma (ICP) emission spectroscopy. Figure 2 shows the conductivity isotherms of yttrium doped NaCl crystals as a function of yttrium concentration. Figure 3 shows the conductivity plot of as grown, annealed and quenched NaCl : Y (0.5 mole %).

**TABLE 1 : Activation energies in regions II and III.**

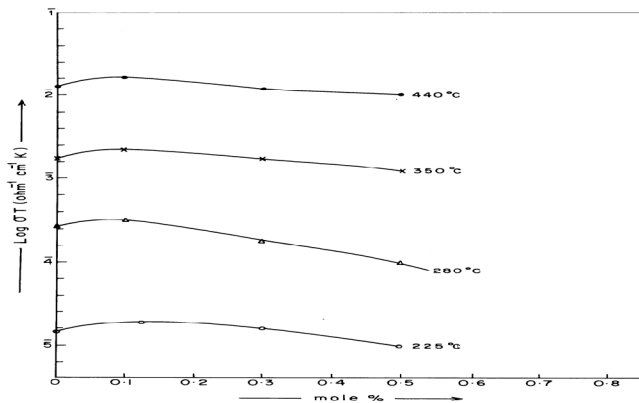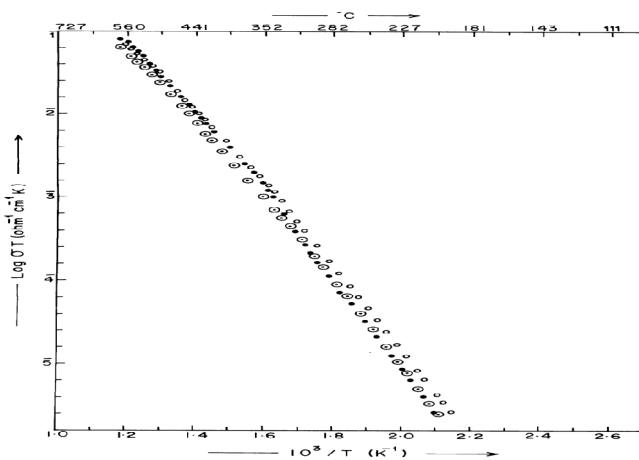| Crystal | Concentration of impurity | | $E_{II} = E_m$ (eV) | $E_{III}$ (eV) |
|---------|---------|---------|---------|---------|
| | mole % (in the melt) | ppm (in the crystal) | | |
| NaCl : Y | 0.1 | 610 | 0.86 | 1.14 |
| NaCl : Y | 0.3 | 800 | 0.87 | 1.03 |
| NaCl : Y | 0.5 | 1050 | 0.90 | 1.00 |

*Full Paper*



**Figure 2 : Conductivity isotherms of Y doped NaCl crystals as a function of Y concentration.**



(•) as grown, (o) quenched from 550⁰C and (⊙) annealed.

**Figure 3 : Plots of log ($\sigma$ T) vs. ($10^3$/T) (K$^{-1}$) for NaCl:Y (0.5 mole%) crystals**

## DISCUSSION

It is well established that rare-earth impurities doped in alkali halide crystals exists in the divalent state rather than trivalent state[11-14]. From the Figure 1 it is clear that conductivity of yttrium doped crystals is greater than pure NaCl crystals. But with increasing yttrium concentration there is a decrease in conductivity. It is difficult to understand why there is decrease in conductivity and activation energy in region-III (with increasing yttrium concentration), while the activation energy for region-II is not much altered. The decrease in activation energy of region-III cannot be assigned to the modification of cation vacancy mobility with the concentration of impurity precipitates, as the activation energy for region-II is found to be almost independent of yttrium concentration. At the same time the change in

the activation energy cannot be explained by different rates of cation vacancy delivery subsequent to dissolution of precipitates by heating in the region-III. Therefore, more possible explanation is the fraction of precipitated impurities rises with increasing yttrium concentration. Around those precipitates there arises a region of strain within the lattice, regions in which the concentration of cation vacancies occurs. The occurrence of this possibility of binding cation vacancies could be detrimental to dipole formation in the heavily doped (0.5 mole% Y) crystals. This leads to lower effective association energy of the dipole partners and consequently decrease in activation energy of region-III with increasing yttrium concentration.

The plot of Figure 3 indicates that the conductivity of quenched crystal was slightly more as compared to as grown and annealed crystals. It is normally to be expected that quenching of crystals from elevated temperatures results in the dissolution of the precipitated impurity, dissociation of higher order impurity vacancy complexes and creation of large number of cation vacancies in the crystal[15]. Owing to higher mobility of these thermally produced vacancies, the probability of $Y^{2+}$ ions in the neighborhood of positive ion vacancies will be enhanced at such temperatures. This will give rise to I-V dipoles. These I-V dipoles might have been responsible for slightly increased conductivity in quenched samples. On the other hand, during annealing, precipitation may take place. The impurity ions whether free or in the form of dipoles coagulate to form clusters during annealing. The decrease in conductivity may be due to the decrease in effective concentration of free cation vacancies as a result of formation of pairs, clusters, impurity precipitation, etc.

## CONCLUSIONS

Sodium Chloride crystals doped with different concentrations of yttrium are grown using slow cooling method. The conductivity plots indicate two distinct regions. It is found that the conductivity in doped crystals is decreasing with increasing concentration of yttrium dopant. Quenching and annealing studies show that the conductivity increases in former case and decreases in later case. Possible mechanisms for the above results are explained.

*Full Paper*

## REFERENCES

**[1]** D.L.Kirk, A.R.Kahan, P.L.Pratt; J.Phys.D, **8**, 2013 **(1975)**.

**[2]** D.M.G.Pinatti, S.C.Zillo, M.Desouza; Phys.Stat. Solidi.B, **94**, 749 **(1979)**.

**[3]** S.C.Jain, D.C.Parashar; J.Phys.C, **2**, 167 **(1969)**.

**[4]** R.C.Bhuniya; Czech.J.Phys., **27**, 1164 **(1977)**.

**[5]** K.Narasimha Reddy, R.Sayanna; Cryst.Res.Technol, **21**, 269 **(1986)**.

**[6]** S.Kar, A.K.Maiti, M.Sengupta, K.Goswami; Fizika A, **9**, 159 **(2000)**.

**[7]** B.Kantha Reddy, K.Narasimha Reddy; J.Mater. Sci., **23**, 2693 **(1988)**.

**[8]** E.Laredo, E.Dartyge; J.Chem.Phys., **53**, 2214 **(1970)**.

**[9]** Ch. Gopal Reddy, K.Narasimha Reddy; Mater. Chem.& Phys., **27**, 325 **(1991)**.

**[10]** R.W.Dreyfus, A.S.Nowick; Phys.Rev., **126**, 367 **(1962)**.

**[11]** S.Chandra, J.Rolfe; Canadian J.Phys., **49**, 2098 **(1971)**.

**[12]** J.N.Maycock; J.Appl.Phys., **35**, 1512 **(1964)**.

**[13]** J.Rolfe; Canadian J.Phys., **42**, 2195 **(1964)**.

**[14]** H.Grundig; Z.Phys., **182**, 477 **(1965)**.

**[15]** Ch. Gopal Reddy, S.Narender Reddy, K.Narasimha Reddy; Mater.Letts., **58**, 1127 **(2004)**.