Bull. Mater. Sci., Vol. 27, No. 5, October 2004, pp. 459–466. © Indian Academy of Sciences.

Study of effect of quenching and deformation on KCl: Gd^{3+} crystals by using conductivity measurements

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MS received 27 November 2003; revised 15 July 2004

Abstract. The study of ionic conductivity vs reciprocal temperature of pure KCl and KCl crystal doped with 0·1, 0·3 and 0·5 mole% gadolinium has been carried out in as grown, quenched from elevated temperatures (100, 350 and 500°C) and annealed at various timings i.e. 2–3 h and deformed by different percentages. The plots exhibit three well-known regions, II, III and IV (extrinsic regions). The intrinsic region I was not observed in the plots as the conductivity measurements were taken up to 575°C. From the analysis of these plots, activation energies for the migration of cation vacancy and the association of gadolinium ion with cation vacancy in the lattice of KCl crystals are calculated. These values are compared with previously reported values. Further, an attempt is made to explain the existence of oxidation state of gadolinium ion in + 3 state rather than in + 2 state as reported earlier. The variation in conductivity with effect of concentration of impurity ion, quenching and annealing and deformation with various percentages are explained on the basis of formation of impurity vacancy dipoles, vacancy – vacancy pairs (which appear in the form of precipitation), storage of cation vacancies in the form of defects, introduction of fresh dislocations, etc.

Keywords. Impurity; conductivity; *I–V* dipoles; vacancy – vacancy pairs; dislocations.

1. Introduction

During last few decades, considerable attention has been devoted to study the nature of lattice defects in alkali halide crystals doped with divalent cations (Alnatt *et al* 1972; Nadler and Rossel 1973; Kessler 1992; Saibabu 1995) and to a much lesser extent with divalent anions (Saibabu *et al* 1991, 2002; Saibabu 1998). On the other hand, there is very little data available on trivalent cations doped in alkali halides (Prizbram 1975; Beniere and Rokbani 1977). The nature of lattice defects can be studied by using various techniques like ionic conductivity, thermally stimulated depolarization currents, dielectric relaxation etc. Among these, ionic conductivity provides valuable information on the state of point defects, impurity precipitates, complexes etc.

Ionic conductivity as a function of temperature has been measured (Saibabu *et al* 1991, 2002; Kessler 1992; Saibabu 1995, 1998) on alkali halide crystals doped with divalent cations as well as anion impurities. The effect of quench-induced changes on conductivity of doped crystals has been investigated by a number of workers (Buniya 1977; Saibabu *et al* 1991, 2002; Saibabu 1995, 1998). The effect of deformation-induced changes in conductivity on doped crystals has been investigated by a few workers (Frohlich and Shuisky 1964; Buniya 1977; Saibabu 1995). Very less work has been reported on trivalent cation doped alkali halides and no systematic studies were made on alkali halide crystals. This may be due to the following reasons.

(I) The condition for electrical neutrality is that one divalent cation introduces one cation vacancy. Similarly in case of trivalent cations one cation introduces two cation vacancies. This has been clearly shown for divalent cations (Saibabu 1995; Saibabu *et al* 2002). But whether this condition is satisfied or not, is to be carefully studied in trivalent ion doped systems.
(II) A review of literature shows that the ion occurs as divalent or trivalent depending on conditions of crystal growth (Gruen *et al* 1956; Prizbram 1975; Beniere and Rokbani 1977).
(III) Some trivalent ions favour the formation of precipitates and some do not.

Due to this peculiar behaviour of the trivalent ion in crystal matrix, very little work is reported on KCl: Gd^{2+} on optical, ITC and luminescence properties (Narasimha Reddy *et al* 1979, 1982; Rucskanen 1981; Vijayan and Murthy 1988; Narasimha Reddy and Subba Rao 1989; Vasanth Kumar 1997).

In all the above investigations, the properties are studied in as grown state of the crystals only and no systematic studies were made on KCl: Gd^{2+} crystals either by quenching, annealing or deformation. Further the existence of impurity ion in impurity divalent state was only speculated. There was no discussion on whether Gd exists

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in divalent state or trivalent state (Narasimha Reddy *et al* 1979, 1982; Vijayan and Murthy 1988; Narasimha Reddy and Subba Rao 1989; Vasanth Kumar 1997). Further no attempts are made to study the transport properties of gadolinium doped KCl crystals. Therefore, in the present investigation, an attempt is made to study the ionic conductivity of KCl crystals doped with gadolinium ion in (a) as grown state, (b) quenched from various temperatures, (c) annealed for various timings and (d) deformated to various percentages. An attempt is also made to explain the existence of gadolinium ion only in trivalent state other than divalent state by using Hund's rule and also on nature of growth of crystals with various techniques.

Further attempts are also made to calculate the activation energies for migration of cation vacancies, dissolution of impurity ion, the formation of separated pair of schottky vacancies in host lattice, and a plausible mechanism is suggested to explain the variation of conductivity in the present studies.

2. Experimental

The single crystals of pure KCl and KCl crystals doped with 0·1, 0·3 and 0·5 mol% of gadolinium were grown by using melt technique in air. The starting material used for the growth of the crystals were Sarabhai; Merck analar grade KCl salt, gadolinium oxide and SCl_4 solution. Before growing the crystals, the $GdCl_3$ salt was prepared by using chemical reaction method as shown below.

$$2Gd_2O_3 + 3SCl_4 \longrightarrow 4GdCl_3 + 3SO_2\uparrow$$

The prepared $GdCl_3$ powder was in the form of fine precipitate. The precipitated powder was once again dissolved in SCl_4 for purification. Later the precipitate was replaced into a watch glass and allowed to dry by introducing the watch glass into air tight chamber. The prepared powder was used for dopant in the present investigation.

For growing crystals, the weighed salts were ground separately to form fine powders and then mixed, so that the two salts would mix uniformly. The fine powder was melted in a platinum crucible in a furnace. The melt was kept at a temperature of 100–120°C above the melting point of 950°C for 4–5 h to ensure a steady temperature. Further the melt was brought to room temperature at the rate of 50°C/h to 100°C/h.

The cooled sample was ground once again and made to a fine powder. Finally the sample was grown by using melt technique. In this method, the fine powder was once again melted as described above and brought to above 100°C as mentioned. The samples were cooled at the rate of 4–10°C/h down to 50°C below the melting point. The samples temperature was further decreased at a rate of 50°C/h. When the crucible was taken out at above 100°C of furnace temperature, the sample showed cracks in the cooled melt after bringing to room temperature. The sample was broken into pieces and small crystals of about 1·0 × 0·5 × 0·4 dimensions were achieved. They were annealed at 600°C for 4–5 h and cooled to room temperature at the rate of 50°C/h. After annealing of the samples, the presence of gadolinium was analysed by using optical absorption spectra, which showed a single peak around 535–550 nm similar to earlier reported values (Vijayan and Murthy 1988; Vasanth Kumar 1997).

The d.c. conductivity of KCl: Gd samples were measured from 20–575°C. For measuring the conductivity, a two-probe conductivity cell was used. The apparatus consisted of two electrodes made of copper. The samples were mounted in between the electrodes and kept in a furnace. For measuring the current a potential difference of 1·5 V (dry battery) was applied in between the electrodes. The currents were measured by using Keithley nano meter 610C model. The temperature of the sample was measured with a chromel–alumel thermocouple. For quenching, the samples of 0·5 mol% gadolinium doped KCl crystals were used: first the samples were annealed at 100°C, 350°C and 500°C for 3–4 h separately and then suddenly quenched to room temperature by pouring the sample on a metal plate. For annealing the samples, the quenched samples were heated at 350°C for 2–3 h and brought to room temperature slowly by decreasing the temperature at the rate of 30°C/h. Further for studying the deformation effect, the sample of 0·5 mole% gadolinium doped KCl crystals were inserted between the two studs of a screw gauge and plastic deformation of various percentages was applied. The sample thickness was measured. The thickness value is multiplied with 0·01 value. Here actually completion of one revolution of head scale is equal to 100%. So the value is calculated as $t \times 0{\cdot}01 \times$ percentage of deformation = percentage of deformation in the sample. The conductivity of as grown, quenched, annealed and deformed samples was measured under identical conditions.

3. Results

The results of ionic conductivity measurements of pure KCl crystals and KCl crystals doped with gadolinium ions in different percentages are shown in figure 1. The conductivity vs temperature is plotted as $\log sTV_S 10^3/T$. The domains of intrinsic and extrinsic conductivities have been marked as I, II, III and IV regions according to Dreyfus and Nowick (1962). The region I is not shown in all earlier studies neither in as grown quenched annealed nor deformed samples.

When the KCl crystals are doped with 0·1 and 0·3 mol% of gadolinium ion, the conductivity increases in low temperature and shows a peculiar anomalous increase in conductivity compared to pure KCl crystals. But as temperature increases, the conductivity of 0·1 mol% of gadolinium doped KCl crystals increases as compared to pure crystals, in extrinsic associated and unassociated regions (III and II regions). But as concentration increases to 0·3 mole% of gadolinium, the conductivity increases at low temperature. But as temperature increases, the conductivity decreases in extrinsic associated region [region III] and extrinsic unassociated region (region II). When the concentration of gadolinium increases to 0·5 mole%, the conductivity decreases in extrinsic associated and unassociated regions.

The conductivity of 0·5 mole% gadolinium doped KCl crystals quenched from 100°C, 350°C and 500°C is shown in figure 2. The conductivity studies of quenched crystals have shown that as quenching temperature increases up to 350°C, the conductivity increases in extrinsic associated region (region III) and extrinsic unassociated region (region II). As quenching temperature increases to 500°C, the conductivity decreases compared to as grown crystals in extrinsic associated region (region III) and extrinsic unassociated region (region II).

The conductivity of 0·5 mole% gadolinium doped KCl crystals of as grown state quenched from 350°C and annealed at 350°C for 2 and 3 h are shown in figure 3. From the plots, it appears that as samples are quenched from 350°C, the conductivity increases in extrinsic associated (region III) and unassociated (region II) regions compared to as grown states. As the quenched samples are annealed for 2 and 3 h, the conductivity of these crystals lies in an intermediate state relative to as grown crystals and quenched crystals and try to preserve their as-grown state.

The conductivity of 0·5 mole% gadolinium doped KCl crystals of as grown state and deformed 1%, 2% and 3% are shown in figure 4. As the samples are deformed for 1%, 2%, the conductivity increased up to 2% compared to as grown crystals of conductivity in extrinsic associated and unassociated regions (i.e. regions III and II). But increase in conductivity for 2% deformed crystals is less compared to 1% deformed crystal. When the crystal was deformed to 3%, the conductivity decreased compared to as grown crystals.

The activation energies for the corresponding regions are calculated and presented in table 1. The values are compared with previously reported values on various alkali halide crystals and are shown in table 2.

4. Discussion

In alkali halide crystals, ionic conductivity is mostly due to the migration of cation vacancies at lower temperatures. At higher temperatures the conductivity is due to migration of cations as well as anions. But the mobility

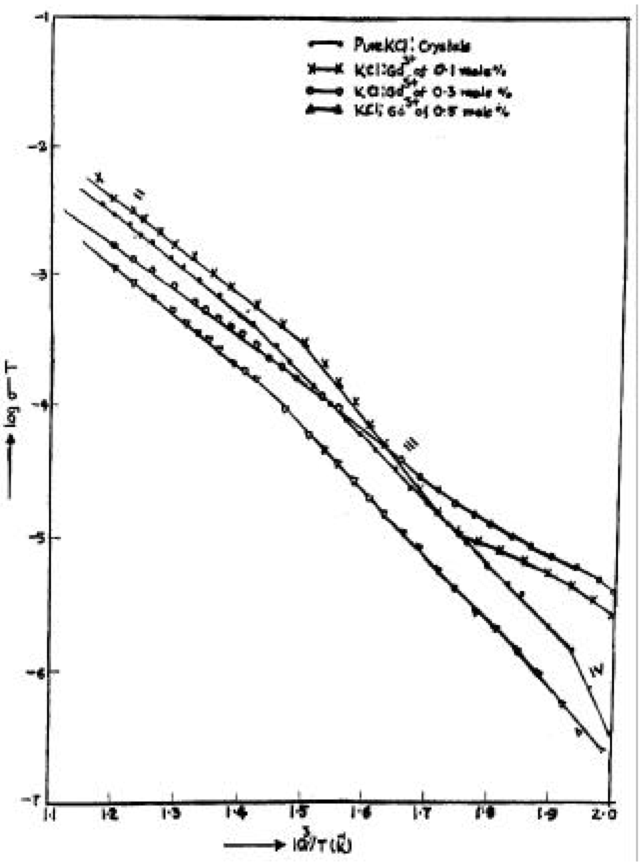


Figure 1. Conductivity vs temperature plots of pure and Gd^{3+} doped KCl crystals of different concentrations.

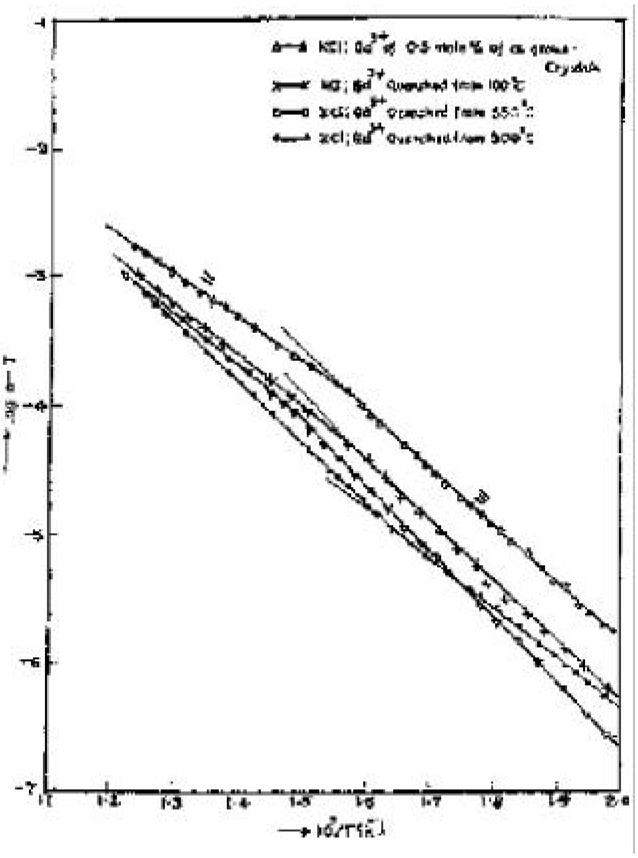


Figure 2. Conductivity vs temperature plots of KCl crystals doped with 0·5 mole% of gadolinium ion of as grown and quenched from elevated temperatures.

of anions is less than that of cations due to higher anionic radius. The mobility of anions is appreciable only near the melting point of the host material. So the migration of anion is negligible in these studies because the conductivity measurements were made up to 575°C only.

The ionic conductivity of pure KCl crystals is shown in figure 1. The conductivity was studied over the temperature range 200–575°C; the plots exhibited three regions IV, III and II according to Dreyfus and Nowick (1962). The slopes of three regions IV, III and II gave activation energies of 1·98, 1·11 and 0·73 eV, respectively. These values are found to be in good agreement with the values reported earlier (Nadler and Rossel 1973; Niizeki *et al* 1989; Saibabu 1995).

The conductivity vs reciprocal temperature plots of KCl crystals doped with different concentrations of gadolinium impurity ions are also shown in figure 1. The plots exhibit three regions as pure KCl crystals. The region IV corresponds to the impurity precipitation region. In this region, it is very difficult to explain the variation of conductivity with increase in percentage of gadolinium ion because the formation of second order precipitate is a kinetic process that depends upon the rate of cooling. In the present studies, as concentration of impurity ion increases up to 0·3 mol%, the conductivity increases in low temperature and show a peculiar anomalous increase in conductivity compared to pure KCl crystals. But as temperature increases further, the conductivity varies in extrinsic associated and unassociated regions (i.e. regions III and II, respectively). In case of 0·5 mole% crystals, the conductivity was totally suppressed in extrinsic associated and unassociated regions as compared to pure KCl crystals. The increase in conductivity is explained on the basis of formation of more and more (*I*–*V*) dipoles and the decrease in conductivity is explained on the basis of formation of dimers, trimers etc.

The quenching and annealing effects on conductivity and variation in conductivity are explained on the basis of dissolution of dimers and trimers and formation of clusters and clusters of precipitation etc.

The effect of plastic deformation on conductivity and variation in conductivity is explained on the basis of creation of fresh cation vacancies, introducing distortions as digs and jogs etc.

Rare earth impurities like samarium, europium, neodymium, gadolinium etc can be introduced into the alkali halide crystal matrix as divalent or trivalent or higher oxidation state ions, depending mainly on the tempera-

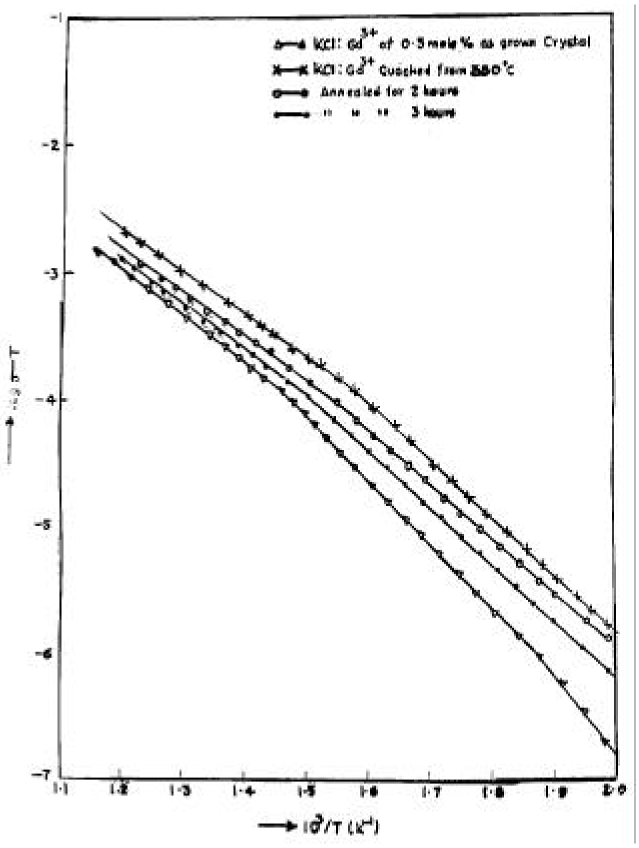


Figure 3. Conductivity vs temperature plots of KCl crystals doped with 0·5 mol% of Gd^{3+} ion of quenched sample and annealed at different timings.

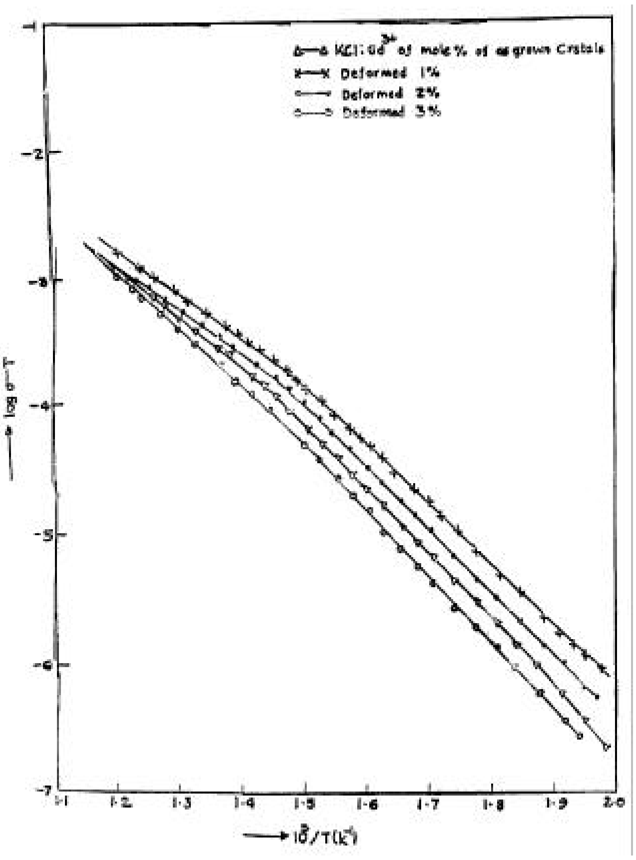
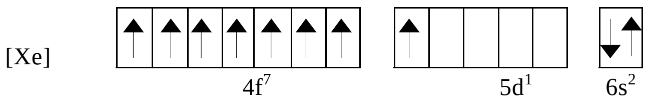


Figure 4. Conductivity vs temperature plots of KCl: Gd^{3+} of 0·5 mole% crystals of as grown and deformed at different percentages.

ture at which the addition of impurity is made. The presence of either form is confirmed by optical absorption and fluorescence measurements. The trivalent form occurs when alkali halide crystals are grown from aqueous solutions composed of alkali halide and rare earth halides (Gruen *et al* 1956; Prizbram 1975; Beniere and Rokbani 1977). It will occur if the dry mixture of the two salts is pulverized and pressed, to form a pellet. The trivalent form occurred on the sintered mixtures just before melting points. But once the mass was melted and single crystals were grown, only divalent form appeared (Gruen *et al* 1956; Narasimha Reddy *et al* 1979, 1982; Vijayan and Murthy 1988; Narasimha Reddy and Subba Rao 1989; Vasanth Kumar 1997). But here the question is whether the gadolinium ion exists either in trivalent or divalent state. So that in the present investigation an attempt is made to explain nearly the nature of existence of gadolinium ion in various conditions.

The atomic number of gadolinium is 64. The electronic configuration is [Xe] $4f^7 5d^1 6s^2$. Thus in gadolinium outer most orbital, the *f*-sub shell is half filled and attains the more stable state and *s*-orbital is totally filled and *d*-orbital is filled with only one electron by following Pauli's principle.

The electronic configuration is shown below



This is in unstable state and when three electrons are removed from the outermost orbital the stable state results. Actually when the *f* subshell is empty (f^0), half filled (f^7) or fully filled (f^{14}), the lanthanides approach stability. The explanation of oxidation state on the basis of filling of *f* subshell is of dubious validity. The existence of the various oxidation states is best interpreted based on highly complicated thermodynamic and kinetic considerations like ionization, enthalpies, enthalpies of sublimation of metals, lattice energies and so on. Based on thermodynamic and kinetic consideration, magnetism, spectra and transition of electrons in *f* transition, it has been confirmed that the gadolinium exists only in Gd^{3+} state, but not in Gd^{2+} state. If the Gd^{2+} exists in + 2 state, it has to show colour but it is actually colourless (Therald 1956; Mackay and Ann Mackay 1969; Albert and Wilkinson 1988). But in some of the earlier studies it has been shown that divalent gadolinium exists as dichloride or di-iodide, by the reaction of the metals with the fused trihalides. But this divalent gadolinium is much less stable and there is no existence of divalent state.

Further sesqui chlorides of unique type is also possible to form by Gd, Gd_2Cl_3 or $[Gd_4^{6+}\ (Cl^-)_6]_n$, consisting of infinite chains of metal atoms in octahedra sharing opposite edges, with chlorine atoms located over triangles formed by three Gd atoms. These halides can be reduced at 800°C to GdCl, which is much less stable (Therald 1956; Mackay and Ann Mackay 1969). From the above discussion it is clear that the gadolinium ion exists in trivalent state only and not in divalent state or mono valent state. A conclusive way of ascertaining the existence of Gd^{3+} is to check the EPR of KCl: Gd crystals.

It is ascertained by the previous investigation that in alkali halide like KCl crystals doped with alkaline earth metals like Ca^{2+}, Sr^{2+}, Ba^{2+} etc ions enter the crystal matrix by substituting a K^+ ion and creates a positive ion vacancy in its nearest neighbourhood for charge compensation (Dubrie *et al* 1971; Nadler and Rossel 1973; Saibabu 1995). The substituted ion behaves effectively positive and the positive vacancy site behaves as effectively negative, when these are not apart, then there will be a tendency for them to get paired up resulting in a neutral impurity-vacancy [*I*–*V*] dipoles. Similarly when KCl crystals are doped with $GdCl_3$ impurity ion, the $GdCl_3$ is dissociated and enter in the crystal matrix as Gd^{3+} and Cl^-. When Gd^{3+} enters the host crystal matrix, it substitutes a K^+ ion and for charge compensation two positive ion vacancies are created in its nearest neighbourhood (Dubrie *et al* 1971; Nadler and Rossel 1973; Saibabu 1995). Actually two positive ion vacancies are created in the vicinity of gadolinium ion which is surrounded by six cations. Here the [*I*–*V*] dipoles are formed only when the effectively positive ion and positive ion vacancy sites are close to each other for charge compensation of excess positive ion vacancies, some of nearest chlorine ions move away from its regular lattice site and form the anion vacancies (Schottky defect) in the nearest neighbourhood of positive ion vacancies in KCl. The positive ion vacancy site behaves effectively negative, similarly, the anion vacancy site behaves effectively positive. The formed positive and negative vacancies can form vacancy–vacancy pairs via coulombic interaction (Beniere and Rokbani 1977), resulting in more and more [*I*–*V*] dipoles. These [*I*–*V*] dipoles are favourable to formation of *nn* and *nnn*-dipoles as reported earlier in alkali earth metal doped alkali halide crystals (Dubrie *et al* 1971) and more and more vacancy–vacancy pairs are created. These vacancies are favourable in formation of large aggregation of non-interacting clusters. These [*I*–*V*] dipoles and vacancy pairs are not involved in conductivity. The effects of impurity concentration, quenching and annealing and deformation on conductivity are discussed independently.

4.1 *Effect of impurity concentration*

The conductivity vs $10^3/T$ plots of pure KCl and gadolinium doped KCl crystals are shown in figure 1. The conductivity mechanism of pure crystals was discussed earlier by various investigators (Nadler and Rossel 1973; Buniya 1977; Acuna and Jacobs 1980; Saibabu 1995).

Before discussing the mechanism of conductivity in gadolinium-doped KCl crystals, we would like to discuss the formation of second order kinematic precipitation in the crystals. When the crystals were grown at higher temperatures and cooled down to room temperature at a constant rate, some part of impurity ions were in favourable condition to form a second order precipitate when the crystals were reheated. This second order phase was redissolved in the temperature range 100–200°C. The strongest confirmation of the suggestion came from the other techniques like TGA, DTA etc (Dreyfus and Nowick 1962; Saibabu *et al* 2002). The amount of second order phase thus formed varied from sample to sample due to variations in cooling rate. So it is very difficult to explain the region IV which is called as impurity precipitation region or impurity segregate region in the conductivity plot.

At low temperature, the conductivity of KCl crystal doped with 0·1 and 0·3 mole% gadolinium shows peculiar behaviour as shown in figure 1. Initially the conductivity increases at low temperature compared to pure KCl crystals. As the temperature increases, the conductivity decreases in extrinsic associate region [region III]. Here the conductivity increases at low temperatures because the low-temperature measurements need much more time and the kinetics of precipitation are rather slow. The precipitates reach equilibrium state faster on increasing (dissolution of the precipitates) rather than on decreasing (precipitation) temperature. These kinetics are controlled by the diffusion coefficient of impurity (Beniere and Rokbani 1977). Fortunately, the present system is rather favourable by the fast diffusivity of gadolinium.

Another possibility is, the host material whatever the back ground divalent impurity ions it contains, also favours the formation of second order precipitate along with doped impurity ion. When the temperature raises gradually at low temperature, the dissolution of impurity precipitation of doped ions is faster than the background impurity ions, so that the conductivity shows anomalous behaviour. Here the second order precipitate region [region IV] and the extrinsic associated region [region III] are very difficult to discriminate.

As the temperature is raised gradually, the second order precipitate dissociate and enter the crystal lattice and produce more and more vacancies in the extrinsic associate region [region III] and favour the formation of [*I*–*V*] dipoles and vacancy–vacancy pairs. Already some of the impurity ions entered the lattice at the time of growth only, so that it forms more and more dipoles and favour the formation of *nn*-dipoles and *nnn*-dipoles as well as vacancy pairs as reported earlier (Dubrie *et al* 1971). Due to formation of *nn*- and *nnn*-dipoles as well as vacancy–vacancy pairs, the concentration of cation vacancies are suppressed. Consequently the conductivity increases at low temperature and decreases as temperature raises in extrinsic associated region (region III).

As the concentration of impurity ion increases to 0·5 mol% gadolinium in KCl crystal, the conductivity plots exhibit exactly three prompt regions (regions IV, III and II) with well distinguished slopes. The conductivity decreases in extrinsic associated region [region III] mainly due to large aggregates of [*I*–*V*] dipoles and vacancy pair clusters. When the large aggregates and vacancy pair clusters are formed, the concentration of cation vacancies are suppressed. Consequently the conductivity decreases.

In region II [extrinsic unassociated region], the conductivity is independent of dopant concentration. The conductivity is mainly due to the thermally generated vacancies. The thermally generated vacancies entirely depend on thermal history of the sample. But the conductivity also varies in this region [extrinsic unassociated region], compared to pure KCl crystal. Here the main possibility is that the thermally generated vacancies go on creating and destroying (Saibabu 1995; Saibabu *et al* 2002) so that the conductivity varies in all samples, but the activation energy values are nearly equal for all samples.

4.2 *Effect of quenching and annealing*

The thermal treatment of quenching plays a vital role on the electrical and mechanical properties of alkali halides. In the present studies of Gd^{3+} of 0·5 mole% doped KCl crystals, the samples were quenched from 100°C and 350°C, the conductivity increased compared to as grown crystals as shown in figure 2. The increase in conductivity is explained on the basis of dissolution of higher aggregation.

As the samples are annealed at 100°C, certain part of aggregation dissociate and form the isolated Gd^{3+} and cation vacancies. When the annealed samples are quenched suddenly to room temperature, due to time lag, these Gd^{3+} and cation vacancies exist as isolated Gd^{3+} and isolated cation vacancies. Due to increase in concentration of cation vacancies, the conductivity also increases in region III [extrinsic associated region].

When the crystals are annealed at 350°C the higher aggregates dissociate to a maximum extent and form more and more isolated Gd^{3+} and cation vacancies. Due to increase in concentration of cation vacancies, the conductivity increases in extrinsic associated region [i.e. region III].

When the crystals are annealed at 500°C, the higher aggregates are totally dissociated and give more and more isolated Gd^{3+} and cation vacancies. When the crystals are suddenly quenched to room temperature, conditions are favourable for the formation of precipitate of Gd^{3+} vacancy clusters. Due to formation of precipitation and clusters, the cation vacancies are suppressed. Due to suppression in concentration of cation vacancies, the conductivity decreases compared to as grown crystals in extrinsic associated region [i.e. region III].

In case of extrinsic unassociated region [region II], the conductivity is actually independent of impurity concentration. The conductivity is mainly due to thermally generated vacancies. But here the conductivity also increases for quenched samples of 100°C and 350°C. This is expected due to some of the non-interacting vacancy clusters formation at the time of quenching. These non-interacting vacancy clusters are dissociated at higher temperature. Due to increase in dissociated vacancies as well as thermally generated vacancies, the conductivity increases in this region. Further in case of quenched samples from 500°C, the conductivity is suppressed compared to as grown crystals, which retain cluster of precipitation.

The quenched samples are, once again annealed at 358°C and the conductivity measurements were made. The conductivity is shown in figure 3. As the annealing time increases, the conductivity of quenched Gd^{3+} of 0·5 mole% of KCl crystals decreases and lie in a state of intermediate between as grown and quenched states. This is mainly due to association of more and more [*I*–*V*] dipoles, which result in large aggregates. Due to formation of complexes, the concentration of cation vacancies decreases and conductivity is suppressed in extrinsic associated region (region III).

The variation in conductivity in extrinsic unassociated region is mainly due to thermally generated vacancies and is independent of concentration of dopant, annealing temperature and time. The variation in conductivity in extrinsic un-associated region is already explained when dealing with the effect of concentration.

4.3 *Effect of deformation on conductivity*

The conductivity vs reciprocal temperature plots of KCl: Gd^{3+} of 0·5 mole% doped crystals (as grown and deformed at different percentages) are shown in figure 4. As the crystals are deformed to 1%, there is an increase in conductivity compared to as grown crystals. This means that, when the crystals are deformed, the vacancy–vacancy pairs dissociate as well as new cation vacancies are formed and these vacancies are stored in the crystal as a kind of defects, which cannot take part in conductivity but are able to supply cation vacancies after thermal activation. Frohlich *et al* (1971) discussed the formation mechanism of these defects, which are said to be vacancy clusters. The clusters are destroyed in the annealing process but a part of clusters consists of vacancies, which have been formed during deformation. Therefore, conductivity is increased by the additional cation vacancies, which are originated during deformation process. Hence, deformation generates cations, which in turn create excess conductivity in the extrinsic associated region III.

As the deformation percentage increases up to 3%, more and more cation vacancies are produced which are stored in a kind of defects. Further, it produces fresh dislocations in the crystal matrix, simultaneously which are invariably charged. During the conductivity measurements, the free cation vacancies may get trapped near the core of these dislocations (Saibabu *et al* 2002). Thus, the net concentration of cation vacancies decreases compared to 1% of deformation. Due to decrease in concentration of cation vacancies, the conductivity decreases in extrinsic associated region III.

At elevated temperatures and also for longer periods of annealing, the free cation vacancies get destroyed and created. This process favours formation of new kind of stable vacancy clusters of different sizes (possibly in the vicinity of Gd^{3+}) or the vacancies themselves diffuse to the surface. Consequently the conductivity increases in extrinsic unassociated region i.e. region II (Frohlich *et al* 1971; Saibabu *et al* 2002).

5. Conclusions

The pure KCl and KCl crystals doped with 0·1, 0·3 and 0·5 mol per cent gadolinium were grown by using melt technique. The conductivity measurements were made up to 575°C in as grown state, quenched, annealed and deformed samples. The variation in conductivity is explained on the basis of formation of *I*–*V* dipoles, non-interacting vacancy clusters, impurity precipitations, and introduction of fresh dislocations in the crystal matrix. Further an attempt is also made to exploit the gadolinium ion existing in + 3 state rather than + 2 state as reported earlier. Further investigations can be made to study the nature of Gd^{3+} by using experimental techniques like EPR, thermoluminescence, microhardness etc.

Acknowledgements

The authors are grateful to Prof. P D Townsend, Department of Physics and Astronomy, University of Sussex, Brighton, UK and Prof. A D P Rao, Department of Physics, Andhra University, Visakhapatnam, for their useful suggestions, discussion and constant encouragement.

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