Indian Journal of Pure & Applied Physics
Vol. 40, December 2002, pp. 862-866

Study of ionic conductivity in KBr: $(CrO_4)^{2-}$ crystals

G Saibabu[1], N Vasanth Kumar[2], A Ramachandra Reddy[3] & D Srikanth[3]

[1]Department of Physics, Railway Junior College, Kazipet, Warangal 506 003

[2]Bharath Sanchar Nigam Limited, Warangal

[3]Department of Physics, Regional Engineering College, Warangal 506 009

Received 12 April 2002; revised 6 August 2002

The ionic conductivity of pure KBr and KBr crystals doped with chromate anion has been measured in the temperature range of 200–600 °C. In pure KBr crystals, large contribution to conductivity by cation vacancies has been observed at higher temperatures. Ionic conductivity measurements are made on pure KBr crystals and KBr crystals doped with 0.25, 0.5 and 0.75 mole % of chromate anion in as-grown state. Further, the effects of quenching and annealing on conductivity of KBr crystals doped with 0.75 mole % chromate ion are measured. The conductivity versus temperature plots show that, as concentration of impurity anions increases, the conductivity decreases in extrinsic associated region. As the concentration increases to 0.75 mole %, the conductivity increased to high value compared to 0.5 mole %. But, it is less than that of pure crystals. The extrinsic un-associated region shows a slight variation in conductivity but, tends to be same that of as-grown pure KBr crystals. The variation in conductivity of doped KBr crystals are explained on the basis of formation of complexes with background impurities, formation of neutral pairs, introduction of fresh dislocations, etc. The variation in conductivity due to quenching and annealing is explained on the basis of dissociations and aggregation of complexes, vanishing of newly introduced dislocations, etc. The corresponding activation energy values are evaluated.

1 Introduction

Most of the recent works have been dealing with lattice defects in alkali halide crystals doped with divalent cations[1,2,3] and to a much lesser extent with anions[4,5]. The nature of lattice defects can be studied by using various techniques like, ionic conductivity, thermally stimulated de-polarization currents, etc. Among these techniques, ionic conductivity is one of the convenient methods to provide valuable information on the state-of-point defects, nature of impurity precipitate and complexes.

Ionic conductivity as a function of temperature has been carried out by a number of workers on alkali halide crystals doped with divalent cation impurities[1,3] and, to a much less extent, on divalent anions[5,6]. The effect of quenching-induced changes on conductivity of cation-doped crystals has been investigated by a number of workers[3,7,8]. Specially, the conductivity on potassium bromide crystals doped with cation has been reported by a number of workers[3,7,9]. A very little work has been reported on KBr crystals doped with anions[6]. Particularly, KBr crystals doped with chromate ion was studied by various workers on optical and spectroscopical properties[10]. But, no attempts have been made on the study of ionic conductivity of KBr crystals doped with chromate anion. So, in the present paper, an attempt has been made to study the effect of chromate ion in KBr crystals using ionic conductivity method. An attempt is made to evaluate the activation energies for migration of an anion vacancy, the formation of separate pair of Schottky vacancies or I-V dipoles and, dissolution of impurity ion in host lattice. A plausible mechanism is suggested to explain the variation of conductivity in the present system.

2 Experimental Details

Single crystals of pure KBr and KBr crystals doped with 0.25, 0.5 and 0.75 mole % of potassium chromate were grown by using melt technique in air. The starting materials used for the growth of the crystals were Sarabhai, Merck analar grade KBr salt and potassium chromate salt. The weighted salts were ground separately to form fine powder and then mixed to get homogenized mixture. The mixed salt was taken in a platinum crucible and kept in the furnance in a zone, where the temperature is uniform.

Slowly, the temperature of the furnance was increased above the melting point of the host material. The melt was kept at a temperature of 100 to 125 °C above the melting point, for four to five hours, to ensure a steady temperature. The temperature of the melt brought to below 50 °C of melting point of host material, at the rate of 5 °C per hr and further the temperature decreased at a rate of 50 °C per hr. The samples were ground once and the growth process was repeated. When the melt was brought to room temperature, small cracks were observed and the sample broke into pieces. A fine shape of the crystals of about 2 × 2 × 0.4 cm dimensions were achieved. They were annealed at 600 °C for four to five hours and cooled to room temperature at the rate of 20 °C per hr. After annealing of the crystals, the presence of potassium chromate was analysed by chemical reaction method. The optical absorption spectra showed similar peaks as reported earlier[10].

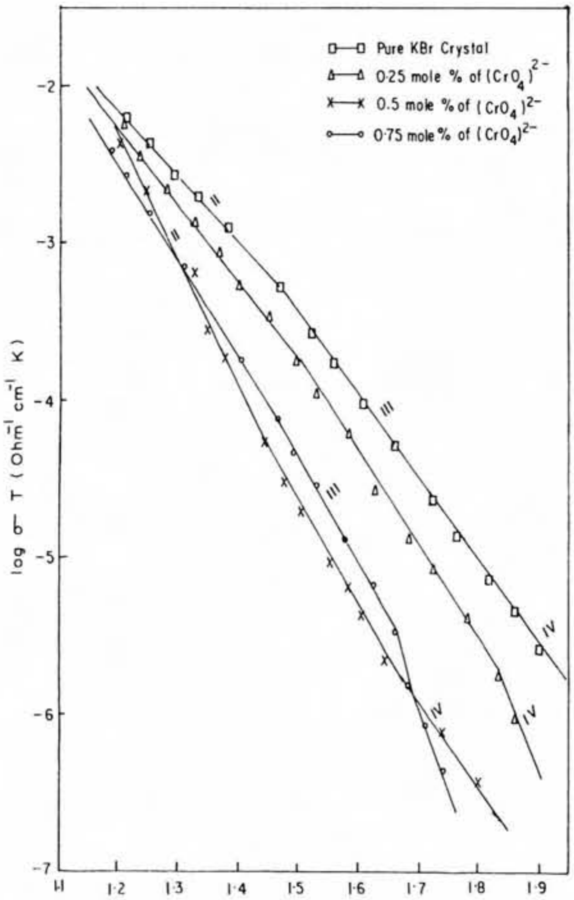

Fig. 1 — Conductivity versus temperature plots of pure and $(CrO_4)^{2-}$-doped KBr crystals of different concentrations

The dc conductivity of samples was measured in the temperature range 200 to 600 °C. For measuring the conductivity, a two-probe conductivity cell was used. The cell consists of two copper electrodes. The sample mounted in between the electrodes are kept in a furnace. For measuring the current, a potential difference of 1.5 volts (dry battery) applied in between the electrodes. The current was measured by using a cary 401 electrometer. The temperature of the sample was measured with a chromel–alumel thermocouple. The samples were annealed at high temperature of 600 °C for 3 hr and suddenly quenched to room temperature by pouring the sample on metal plate. Further, the quenched samples were once again annealed at 500 °C temperature for 2 hr and brought to room temperature slowly by decreasing the temperature at the rate of 30 °C per hr. The conductivity of quenched and annealed samples were measured at identical conditions.

3 Results and Discussion

The results of the ionic conductivity of pure KBr and KBr crystals doped with chromate ion, in different percentages are shown in Fig. 1. These are plotted as log σT versus $10^3/T$. The domains of conductivity plots of intrinsic and extrinsic regions have been marked as regions I, II, III and IV according to Drefus & Novick[3,5,7]. In the present study, the plots show only regions II, III and IV. Neither for grown crystals nor for quenched or annealed samples the region I is shown.

In the present study, when the KBr crystals doped with 0.25, 0.5 mole % of chromate ion, the conductivity decreased in extrinsic associated and un-associated regions. When the dopant concentration increases from 0.5 to 0.75 mole % the conductivity increases in extrinsic associated and un-associated regions. Particularly, in un-associated region, the conductivity tends to be same as that of the pure KBr crystals.

Fig. 2 depicts the conductivity of KBr: $(CrO_4)^{2-}$ crystals of 0.75 mole % of as-grown crystals, quenched from 600 °C and annealed at 500 °C for 2 or 3 hr. From the plots, it is clear that, as the samples are quenched from higher temperature, the conductivity increases compared to as-grown crystals. The annealed crystals conductivity lies in intermediate state of pre-quenched (as-grown) and quenched crystals in extrinsic associated region. The conductivity also varied in extrinsic un-associated region. But, as the temperature of the sample increases, the conductivity tends to be same as that of the pre-quenched samples. The corresponding activation energies, of each region of different samples are shown in Table 1.

Table 1 — Activation energies of pure KBr and doped KBr crystals

Sample	Activation energies for different regions (ev)			
	I	II	III	IV
KBr (Pure)	-	0.86	1.03	-
KBr +$(CrO_4)^{2-}$ (0.25 mole %)	-	0.91	1.17	1.98
KBr + $(CrO_4)^{2-}$ (0.5 mole %)	-	1.18	1.35	1.8
KBr +$(CrO_4)^{2-}$ (0.75 mole %)	-	1.11	1.23	2.14
Quenched	-	0.91	1.11	2.47
Annealed	-	1.00	1.18	2.57

In alkali halide crystals, ionic conductivity is mostly due to the migration of cation vacancies at lower temperatures. At high temperatures, the conductivity is due to migration of cations as well as anions. The mobility of anions are lesser than the cations due to higher ionic radius. The mobility of anion is negligible at lower temperatures.

The ionic conductivity of pure KBr crystals is shown in Fig. 1. The conductivity of pure crystals was measured only up to 575 °C. The plot exhibits only the prominent regions as II, III and IV regions. The conductivity mechanism of different regions was discussed by various investigators[1,3,5,7]. The conductivity plots of log σT versus $10^3/T$ of KBr:$(CrO_4)^{2-}$ also depicts three regions for pure crystals. When the crystals are doped with gradually increasing concentration of dopant, the conductivity first decreases and then increases, but always remains lower than that of pure crystal. The variation in conductivity can be explained as follows.

It is ascertained by various investigators[5,10] that, impurity anion $(CrO_4)^{2-}$ admixture enters in the KCl lattice, substitutionally, in the Cl^- site. In the same manner, the chromate ion enters in the KBr crystal matrix, substitutionally, in the Br^- site. Due to aloivalent impurity; the extra charged negative defect is introduced to keep the crystal electrically neutral. The negative defect (or) the anion vacancy is favourable in the formation of vacancy not exactly in its surroundings[11]. But, in case of divalent cation-doped crystals, the cation vacancies are favourably formed in its surroundings[3,7,12]. This anion vacancy effectively behaves as a positive one. Similarly, the background impurity like Me^{2+} (Ca^{2+} and others) present in the host material produces positive ion vacancies for charge compensation. These positive ion vacancies behave effectively as negative. These two defects form as a neutral pair. These neutral pairs do not contribute to conductivity. Further, $(CrO_4)^{2-}$ ion forms complexes with background impurities of Me^{2+}. These complexes are also not involved in the conductivity[5].

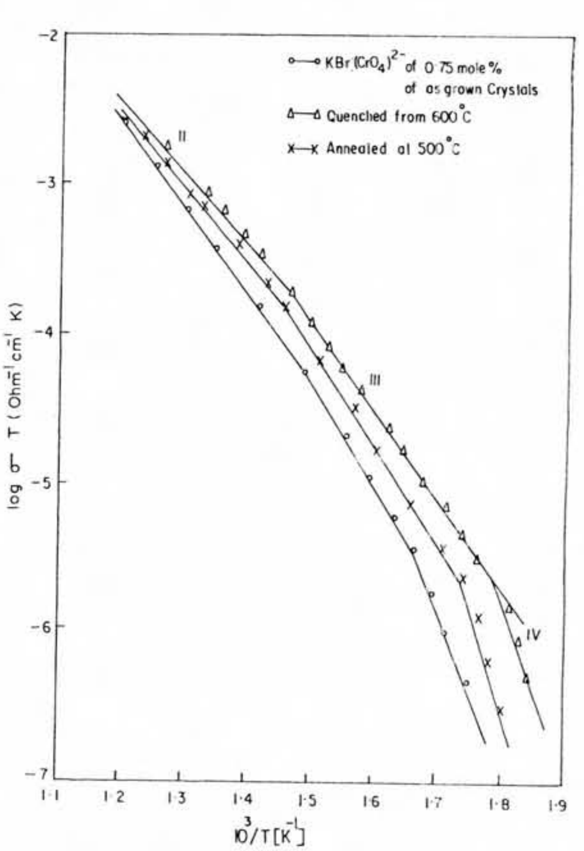

Fig. 2 — The conductivity versus temperature plots of KBr crystals doped with 0.75 mole % of chromate ion of as-grown, quenched and annealed crystals

3.1 Effect of impurity concentration on conductivity

In general, when alkali halides like, KBr crystals are doped with impurity admixture, K_2CrO_4, the impurity admixture appears as a second-order phase on the surface of the crystals. When conductivity was measured at gradually increasing temperature, then, the second-order impurity precipitate dissociated as cations and anions and entered into the crystal. Due to the motion of cations and anions, a small current flows in the crystal. In the log σT versus ($10^3/T$) plot, it appeared as region IV. The region IV is called anomalous precipitate region (or) extrinsic segregated region. In this region, it is very difficult to explain the variation of conductivity with the increase in percentage of dopant concentration (or) anions because, the formation of second-order precipitate depends upon the rate of cooling.

With further increase in temperature, the impurity anion enters into the crystal matrix and substitutionally occupies in Br site. According to earlier discussion, more and more extra negative defects are introduced in crystal matrix which are occupying not exactly in the nearest neighbourhood[11].

These negative defects behave effectively positive. Similarly, due to the presence of background impurity like, Me^{2+}(Ca^{2+} and others) in host material, positive ion vacancies are produced for charge compensation. These positive ion vacancies behave as effectively negative. The effectively positive and negative charge carriers behave as neutral pairs due to coulombic interaction forces. These pairs are not involved in the conductivity, i.e., the concentration of Schottky vacancies are suppressed. As the $(CrO_4)^{2-}$ concentration increases up to 0.5 mole %, more and more neutral pairs are formed. Due to this, the conductivity decreases in extrinsic associated region (region III) as compared to pure crystals.

Further increase in concentration of chromate to 0.75 mole %, the conductivity lies in between that of pure KBr crystals and 0.5 mole % chromate-doped crystals. The increase in conductivity of 0.75 mole % of $(CrO_4)^{2-}$ in KBr is mainly due to introduction of fresh dislocations in the crystals as a result of higher ionic radius (3Å) of $(CrO_4)^{2-}$ that produces certain local stress in its surroundings. These fresh dislocations possess a property to attract the solute atoms[13,14]. These solute atoms can easily move and settle down in a position of low potential energy. As the temperature increases, more and more solute atoms prefer to move to a position of low potential energy, due to increase in thermal energy and attracting dislocations. Due to this, the conductivity gradually increases, in extrinsic associated region or region III. Here, the possibility of other mechanism is, as the temperature increases, the dislocations also try to move in the crystal matrix. Due to motion of these dislocations, conductivity may enhance further.

3.2 Effect of quenching and annealing on conductivity

The thermal treatment of crystals plays a vital role on their electrical and mechanical properties. In the present studies, $(CrO_4)^{2-}$ of 0.75 mole % doped crystals were quenched from 600 °C in air. The conductivity of these crystals are greater than as-grown crystals. The increase in conductivity is explained on the basis of dissolution of Me^{2+}–$(CrO_4)^{2-}$ complexes.

When $(CrO_4)^{2-}$ doped KBr crystals are annealed at higher temperature, the Ca^{2+} $(CrO_4)^{2-}$ (or) Me^{2+}-$(CrO_4)^{2-}$ complexes are dissociated as Me^{2+} and $(CrO_4)^{2-}$ ions. These ions are randomly distributed in the sample, when the crystals were quenched to room temperature, the $(CrO_4)^{2-}$ is unable to join with the impurity ion, due to shorter time available to move to the nearest neighbour position of Me^{2+} site. Due to formation of isolated Me^{2+} and $(CrO_4)^{2-}$, the concentration of cation vacancies and anion vacancies is increased. Due to increase in concentration of cation vacancies, the conductivity increases in extrinsic associated region (region III)[5].

In case of extrinsic un-associated region at low temperature range, the conductivity also varies. This is mainly due to thermally-generated vacancies, which are frozen in the form of clusters. These clusters are dissociated with increase in temperature and destroy themselves and maintain the vacancies concentration of as-grown crystals. So, the conductivity tends to be same as that of as-grown samples in region–II (Refs. 5,7).

The quenched samples are, once again, annealed at 600 °C and the conductivity is shown in Fig. 2. The conductivity of annealed sample lies in intermediate state of as-grown and quenched crystals states. This is mainly attributed to association of complexes with background impurity like Ca^{2+} ions, once again. Due to formation of complexes, concentration of cation vacancies decreases and conductivity is suppressed in extrinsic associate region (region III).

In extrinsic un-associated region, the conductivity is mainly due to thermally-generated vacancies and it is independent of impurity dopant concentration. The conductivity remains as that of grown crystals.

Acknowledgement

The authors wish to thank Prof P D Townsend, Department of Physics and Astronomy, University of Sussex, Brighton, UK, Prof M N Chary, Prof U V Subba Rao and Dr K Narsimha Reddy, Department of Physics, Osmania University, Hyderabad, for their useful suggestions, discussions and constant encouragement in bringing out this paper. One of the authors (GSB), wishes to thank, CPO South Central Railway, Hyderabad and Sr DPO (SC Division), Secunderabad, for their constant encouragement in bringing out this paper.

References

1 Kessler A, *Phys Status Solidi* (*a*), 131 (1992) 235.

2 Suzynska M & Cappelletti R, *Acta Phys Sol A*, 80 (1991) 129.

3 Saibabu G, Vasanth Kumar N, Srikanth D & Ramachandra Reddy A, *Indian J Pure & Appl Phys*, 40 (2002) 290.

4 Prakash J, *Phys Status Solidi* (*b*) 135 (1986) 7741.

5 Saibabu G, *Phys Status Solidi* (*a*), 17 (1998) 17.

6 Saibabu G, Srinivas G, Dayanand C & Salagram M, *Proceedings of International Workshop on Solid State Materials*, Malaysia, 1991, pp. 49-54.

7 Saibabu G, PhD thesis, Osmania University, Hyderabad, India, 1995.

8 Chadwick A C, *Radiat Eff Defects Solids*, 121 (1992) 619.

9 Cook J S, Dryden J S, Ferguson J & Gwan P B, *J Phys C*, 19 (1986) 4999.

10 Jain S C & Warrier A V R, *Optical behaviours of materials*, (Ed) Kasturi L Chopra (Thomson Press, India), 1973, pp. 233–253.

11 Demyanenkoyu P T, Syaschenko & Eerlan E M, *Fiz Tverd Tela*, 12 (1970) 3124.

12 Alybokov A A, Toichiew N & Akchalov S H, *Phys Status Solidi* (*b*), 109 (1982) 295.

13 Cottrell & Bilby B A, *Proc Phys Soc B*, 62 (1949) 49.

14 *Solid state physics*, (Ed) Ryogo Kubo, University of Tokyo & Takeo Nagamiya, Osaka University, (McGraw-Hill Book Co), 1968, pp. 764-768.