Effect of strontium impurity ions on conductivity of KBr: Sr

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The study on ionic conductivity versus reciprocal temperature of pure KBr and KBr crystals doped with 0.075, 0.35 and 0.75 mole % strontium has been carried out in as-grown quenched from elevated temperatures (200, 300 and 400 °C) and deformed by different percentages. The plots exhibit three well-known regions as I, II and IV (extrinsic regions). But the region IV is not shown in the plots. 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, the association of strontium ion with cation vacancy in the lattice of KBr crystals are calculated. The values are compared with previously reported values. Further the variation in conductivity is 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 a form of defects; introduction of fresh dislocations etc.

1 Introduction

During the recent years considerable attention has been devoted to the process of impurity precipitation in alkali halide crystals doped with various types of impurities especially from experimental stand-point. Electrical conductivity technique has been successfully exploited in such studies11. The existence of precipitation in NaCl, KCl etc., has been studied by several workers in various techniques like optical and electron microscopy, light scattering, hardness studies, etc11. Although, a large amount of work has been reported on pure and doped KBr crystals in as-grown state only11 and most of the work has been explained on the basis of lattice defects and proposed various defect models which were predominant in transport property. So far, no serious attempt has been made to study the effect of Sr2+ impurity ion in KBr crystals (whether they favour formation of precipitates or not). So, in the present paper, an attempt has been made to study the transport properties of KBr: Sr2+ crystals in as-grown state, quenching from elevated temperature and deformed at different percentages. An attempt is also made to study the effect of quenching and deformation effect on impurity ions and conductivity process. A complete study of conductivity properties in KBr crystals doped with Sr2+ is likely to provide a considerable information about the nature of Sr2+ ion in host matrix.

2 Experimental Details

Single crystals of pure KBr and KBr containing 0.075, 0.35 and 0.75 mole % of strontium were grown in our laboratory by Czochralski technique using analar grade materials as starting materials. The actual concentration of Sr-doped KBr crystals was estimated by using inductively coupled plasma (ICP) emission spectroscopy method. All the crystals used in the present investigation were grown under identical conditions.

The sample crystals platelets of dimensions approximately 5×5×2 mm were used for measuring electrical conductivity. The samples are annealed at 200, 300 and 400 °C for 4 to 6 hr and suddenly quenched to room temperature by pouring the sample on metal plates. The electrical conductivity of all the samples were obtained by usual dc methods, by measuring currents with the help of Keithely current meter.

3 Results

The ionic conductivity (σ) versus reciprocal temperature (T) plots for pure KBr and KBr crystals
containing 0.075, 0.375 and 0.75 mole % of Sr$^{2+}$ are shown in Fig. 1. The plots of log $\sigma T$ versus $10^4/T$ are divided into four regions as I, II, III and IV according to Dreyfus & Nowick: region I for intrinsic conductivity where Schottky defects are dominant, region II for free vacancy conduction, region III for association of divalent impurity with cation vacancies and region IV for impurity precipitation.

In the present work, the conductivity measurements are made up to 575 °C only. The intrinsic region I is not observed in this temperature range. The conductivity of pure KBr and doped KBr; Sr$^{2+}$ crystals is shown in the Fig. 1. As concentration of Sr impurity increases, the conductivity also increases up to 0.375 mole %. On further increasing the concentration of impurity ion in the host lattice matrix, the conductivity decreases in extrinsic associated region III. The variation of conductivity in this region is explained on the basis of formation of aggregation of complexes.

In extrinsic unassociated region II, the conductivity entirely depends on thermally generated vacancies which is independent of concentration of impurity vacancies. The thermally generated vacancies entirely depend on thermal history of the sample. In the present investigation, when the dopant concentration increases; the conductivity behaviour in region II becomes anomalous. The slopes are no longer reproducible and show pronounced curvatures towards the temperature axis for the doped crystals. Similar type of behaviour is explained by Laredo & Dartyge in NaCl: Sr$^{2+}$ system. The corresponding activation energy values are compared with previously reported values on an alkaline impurity ions as shown in Table 2. From the above calculated values, enthalpies of formation of cation vacancy; the association of strontium ion with a cation vacancy are calculated. The values are shown in Table 1.

Fig. 2 shows the conductivity-reciprocal temperature plots of KBr crystals doped with 0.75 mole % Sr$^{2+}$ in as-grown state and quenched state (quenched from elevated temperatures 200, 300 and 400 °C). As the samples are quenched from 200 °C the conductivity initially decreased in lower temperature but increased in higher temperature. When the samples are quenched from 300 °C the conductivity increased in lower and higher range of 1/T while slightly decreased in value at higher temperatures in extrinsic associated region. However, as the samples are quenched from 400 °C, the conductivity decreased in extrinsic associated region III. The variation of conductivity in region II is going to be explained on the basis of formation of vacancy clusters which go on getting created and destroyed.

Fig. 3 shows the conductivity and reciprocal temperature plots of KBr: Sr of 0.75 mole % crystals (as-grown and deformed by 1%, 2% and 3%). As deformation percentage gradually increases up to 2% the conductivity increases. With further increase in deformation percentage beyond 2% the conductivity decreases. The corresponding activation energies are evaluated and shown in Table 1. The increase in conductivity is going to be explained on the basis of introduction of cation vacancies and decrease in conductivity is going to

| Table 1 — Activation energy parameters for KBr crystals doped with strontium |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| S.No | Crystal | Region I | Region II | Region III | Region IV | $E_a$(eV) | $E_i$(eV) |
| 1 | KBr (Pure) | 0.80 | 1.08 | - | - | 0.80 | 0.56 |
| 2 | KBr + 0.075 mole % Sr$^{2+}$ | - | 0.80 | 0.99 | - | 0.80 | 0.38 |
| 3 | KBr + 0.375 mole % Sr$^{2+}$ | - | 0.82 | 0.94 | - | 0.82 | 0.24 |
| 4 | KBr + 0.75 mole % Sr$^{2+}$ | - | 0.88 | 0.98 | - | 0.88 | 0.20 |
| 5 | KBr + 0.75 mole % Sr$^{2+}$ Quenched from 200 °C | - | 0.81 | 0.99 | - | 0.81 | 0.28 |
| 6 | KBr + 0.75 mole % Sr$^{2+}$ Quenched from 300 °C | - | 0.87 | 1.01 | - | 0.87 | 0.28 |
| 7 | KBr + 0.75 mole % Sr$^{2+}$ Quenched from 400 °C | - | 0.86 | 0.98 | - | 0.86 | 0.24 |
| 8 | KBr + 0.75 mole % Sr$^{2+}$ deformed 1% | - | 0.79 | 0.99 | - | 0.79 | 0.40 |
| 9 | KBr + 0.75 mole % Sr$^{2+}$ deformed 2% | - | 0.82 | 0.93 | - | 0.82 | 0.24 |
| 10 | KBr + 0.75 mole % Sr$^{2+}$ deformed 3% | - | 0.82 | 0.97 | - | 0.82 | 0.30 |
be explained by introduction of fresh dislocations.

4 Discussion

The ionic conductivity in alkali halide crystals is known to be mainly due to migration of cation vacancies. The previous works by Rolfe\textsuperscript{13}, Grunding\textsuperscript{14}, and Beamount & Jacobs\textsuperscript{15}, have shown that the contribution due to anion vacancies becomes significant at higher temperatures in KCl and KBr. This is mainly due to higher ionic radius of anions.

Generally, when KBr crystals are doped with compound of divalent impurity ion like SrBr\textsubscript{2}, SrBr\textsubscript{2} is dissociated and enters the crystal matrix as Sr\textsuperscript{2+} and Br\textsuperscript{1−}. When Sr\textsuperscript{2+} enters the host crystal matrix, it substitutes a positive ion K\textsuperscript{+} and for charge

![Graph](image-url)
compensation a positive ion vacancy is created in its nearest neighbourhood at one of the eight corners. The Sr\(^{2+}\) ion behaves as positive site and the positive ion vacancy site behaves as a negative site when these two are not a part, there will be a tendency for them to get paired up resulting in neutral impurity-vacancy (I-V) dipole, since the dipole is formed only when they are close to each other. As the concentration of impurity ion increases, more and more I-V dipoles are generated favouring formation of an aggregate of 2 or 3 dipoles\(^{18}\). On further increasing the concentration of impurity ion, there is a probability of precipitation. The effect of impurity concentration and quenching on conductivity of these crystals is discussed independently.

4.1 (a) Effect of Impurity Concentration

The conductivity temperature plots of pure KBr and strontium-doped KBr crystals are shown in Figs 1-3. The conductivity mechanism of pure crystals was discussed earlier by various
Before discussion of mechanism of conductivity in strontium-doped KBr crystals, we would like to discuss the formation of second order kinematic precipitation in the crystals. When the crystals are grown at higher temperatures and cooled down to room temperature at a constant rate, some part of impurity ions are in, favourable condition to form a second order precipitate. When the crystals are reheated, this second order phase, is re-dissolved in the temperature range 100-200 °C.

The strongest confirmation of this suggestion came from the other techniques\textsuperscript{12,17}. The formation of second order phase varies from sample to sample due to slight variation in cooling rate. So, it is very difficult to explain the region IV which is called as impurity precipitation region in conductivity plot.

The conductivity versus reciprocal temperature plots of Fig. 1, reveal that as the impurity concentration increases up to 0.375 mole %, the conductivity gradually increases. On further
increase in the concentration, the conductivity decreases. When strontium impurity ion concentration increases, it produces more and more vacancies and I-V dipoles. Due to this the conductivity increases in region III. On a further increase in concentration of Sr$^{2+}$ in host lattice, formation of nn-dipoles are favourable. Due to this, the concentration of cation vacancies are suppressed and consequently the conductivity decreases in the region III.

4.2 (b) Effect of quenching temperature on conductivity

In KBr crystals with 0.75 mole % to Sr$^{2+}$ (as-grown and quenched from elevated temperatures) the second order precipitation phase partly gets dissolved and Sr$^{2+}$ enters in the host lattice forming I-V dipoles in the crystal. These are not involved in the conductivity due to formation of (I-V) dipoles and due to formation of clusters of precipitation at low temperature. The concentration of cation vacancies are suppressed, consequently, the conductivity decreases in this region at low temperatures.

With further increase in temperature, the conductivity values gradually increase and tend to be the same as that of as-grown crystals because clusters of precipitation get dissolved producing more and more cation vacancies. Due to increase in cation vacancies the conductivity also increases. In extrinsic unassociated region the variation in conductivity is very visibly substantial, this is mainly due to creation and destruction of vacancy pairs and clusters which arise due to quenching.

4.3 (c) Effect of Deformation on Conductivity

The conductivity versus reciprocal temperature plots of KBr: Sr$^{2+}$ of 0.75 mole % doped crystals (as-grown and deformed at different percentages) are shown in Fig. 3. As the crystals are deformed up to 2%, there is an increase in conductivity compared to as-grown crystals. This means that, when the crystals are deformed, new cation vacancies are formed and these vacancies are stored in the crystals as a kind of defects which cannot take part in conductivity but are able to supply cation vacancies after thermal activation. Frohlich et al. 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 associate region-III.

At elevated temperatures and also at longer periods of annealing, the free cation vacancies get destroyed and created. This process favours formation of new kind of stable vacancy clusters of

<table>
<thead>
<tr>
<th>S.No</th>
<th>$E_w$ (eV)</th>
<th>$E_a$ (eV)</th>
<th>$E_{m+1/2E}$ (eV)</th>
<th>Sources</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>0.66</td>
<td>0.68</td>
<td>1.00</td>
<td>KBr:Pr (Radhakrishna &amp; Sharma$^{11}$)</td>
</tr>
<tr>
<td>2</td>
<td>0.67</td>
<td>0.60</td>
<td>0.97</td>
<td>KBr:Ca (Hoshino &amp; Shimoji$^{18}$)</td>
</tr>
<tr>
<td>3</td>
<td>0.65</td>
<td></td>
<td></td>
<td>KBr:Ca (Chandra &amp; Rolfe$^{18}$)</td>
</tr>
<tr>
<td>4</td>
<td>0.80</td>
<td>0.38</td>
<td>0.99</td>
<td>KBr: Sr$^{2+}$ (0.075 mole %)</td>
</tr>
<tr>
<td>5</td>
<td>0.82</td>
<td>0.14</td>
<td>0.94</td>
<td>KBr: Sr$^{2+}$ (0.375 mole %)</td>
</tr>
<tr>
<td>6</td>
<td>0.88</td>
<td>0.20</td>
<td>0.98</td>
<td>KBr: Sr$^{2+}$ (0.75 mole %)</td>
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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 samples. In the present investigation, when the dopant concentration increases, the conductivity behaviour becomes anomalous and the slopes are no longer reproducible. But the activation energy values are in good agreement with the values reported earlier$^{10,11,16}$. The anomalous behaviour is expected due to the fact that some of the free divalent cation vacancies are trapped at Dag paint which is used for good electrical contact. These trapped divalent cations give rise to the induced cation vacancies. Due to increase in free impurity induced cation vacancies, the conductivity increases anomalously in this region.
different sizes (possibly in the vicinity of Sr$^{2+}$ ions) or the vacancies themselves diffuse to the surface. Consequently the conductivity increases in extrinsic associate region$^9$ i.e., region--II.

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$^{19}$. Thus, the net concentration of cation vacancies decreases compared to 1% and 2% of deformation. Due to decrease in concentration of cation vacancies, the conductivity decreases in extrinsic associated region-III.

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