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Impurity vacancy Dipoles in alkali halides

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Abstract: Substitutional impurities, vacant lattice sites and the presence of interstitial atoms in a lattice are celled point defects. The formation of energy determines the concentration of the defects in the lattice whereas activation energy regulates the migration of the defects through the lattice. In a lattice MX, an increase in the concentration of M vacancies is associated with the corresponding increase in the concentration of either X vacancies or M interstitials or both, provided the charge neutrality is maintained. These vacancies and interstitial positions are recognized through Schottky and Frankel defects. In Schottky defects, equal numbers of cation and anion vacancies are produced whereas in Frankel defects equal number of Interstitials and vacancies of one component are created. The exact equalities of different defects apply only to an ideally pure stoichiometric material. A vacancy is created in the neighborhood of the aliovalent impurity ions just for the Sake of charge compensation. A coulombic attractive force between the impurity ion and the vacancy results in the formation of an impurity vacancy (IV) dipole.

Key Words: increase, concentration, M vacancies, associated, corresponding, either, interstitials.

With reference to impurity ion, the vacancy is located at one of the 12 equivalent orientation positions along the direction <110>. Such IV dipole after the application of the electric field, tries to align along the electric field direction. In the presence of an electric field, the energy of an IV dipole depends on its orientation. If the Electric field E is applied along one of the cube edges, out of the twelve equivalent orientations only three are observed to be in equivalent. Thus four positions are along the unpreferred direction and have an energy +eaE , four positions are perpendicular to E and have zero energy, end rest four positions are along the preferred direction and have energy -eaE. Here a and e represent the interatomic distance end electronic charge respectively. It is well known fact that anion cation vacancy pairs do not contribute to the electrical conductivity particularly because of the fact that they are electrically neutral. The same shall also be true for the IV dipoles. However, IV dipoles continuously change their orientations as a result of Jumps from one lattice position to the other. The Jumps mechanisms are ….

(1) 1 Jump: In this mode of Jumps, the vacancy jumps from one nearest neighbor (nn) site to another site keeping impurity ion at its centre. In such a jump, the direction of orientation changes by 60° and hence 1 jump is also known as (?/3)Jump.

(2) 2 Jump : In this mode of jump, the vacancy and impurity ion exchange their positions. In such a jump the direction of orientations changes by 180° and hence 2 Jump is also known as ? Jump.

(3) 3 Jump : There may be a strong attraction of the vacancy towards the impurity ions, which will cause the vacancy to come to an nn site only after few jumps from a next nearest neighbor (nnn) site. Jump processes via which a vacancy moves from an nnn site to an nn site are known as 3 Jump.

(4) 4 Jump : The vacancy may be loosely attached with the impurity ion,

consequently, It may have an appreciable chance of wandering off due to thermal chaos. Jump processes via which a vacancy moves from an nn site to an

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nnn site are known as 4 Jump. For an IV dipole due to impurity ion and vacancy at nn site 3 = 4 = 0, and hence we get only 1 and 2 Jumps.

The presence of IV dipole in a crystalline structure is generally detected through dielectric relaxation studies following procedures mentioned below:

(1) ac Bridge measurement: In this method dielectric constant and dielectric loss are measured as function of frequency and temperature.

(2) Isothermal Polarization Current Measurement: In this method fast polarization current at a fixed temperature is measured following sudden application of a static electric field.

(3) Ionic Thermo current Measurement: In this method the depolarization current due to frozen in IV dipoles is recorded as a function of temperature.

In a.c. bridge measurement the accuracy of the evaluated parameters depends on the extent to which the contribution of the conductivity is taken into account and also on the perfect contact of the sample with the electrode. In the isothermal fast polarization current measurement, the method in itself is technically typical and complicated. The ionic thermo current (ITC) technique proves to superior of these methods particularly because of its better sensitivity, accuracy and convenience. It is free from experimental problem of a.c. bridge measurement and technical complication of isothermal polarization current measurement. At the same time, the dielectric relaxation parameters can be analyzed easily following ITC technique. It can detect IV dipoles up to a fairly low concentration about 100 times less than that of lowest limit of a.c. bridge measurements. Furthermore it can resolve close overlapping relaxation processes with only slightly differring reorientation energies.

Summary of the review of the studied presented above will help in understanding the behavior of IV dipoles in alkali halides theoretically as well as experimentally.

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