

A Kröger-Vink Compatible Notation for Defects in Inherently Defective Sublattices

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ABSTRACT

Traditional Kröger-Vink (K-V) notation defines sites in ionic crystals as interstitial or belonging to host ions. It enables description and calculations of combinations of native and foreign defects, including dopants and substituents. However, some materials exhibit inherently disordered partial occupancy of ions and vacancies, or partial occupancy of two types of ions. For instance, the high temperature disordered phases of Bi_2O_3 , $\text{Ba}_2\text{In}_2\text{O}_5$, $\text{La}_2\text{Mo}_2\text{O}_9$, mayenite $\text{Ca}_{12}\text{Al}_4\text{O}_{33}$, AgI , and CsHSO_4 are all good ionic conductors and thus obviously contain charged point defects. But traditional K-V notation cannot account for a charge compensating defect in each case, without resorting to terms like “100% substitution” or “Frenkel disorder” – the former arbitrary and awkward and the latter inappropriate. Instead, a K-V compatible nomenclature in which the partially occupied site is defined as the perfect site, has been proposed. I here introduce it thoroughly and provide a number of examples.

Key words : Defects, Kröger-Vink notation, Disorder, Conductivity, Perovskite, $\text{Ba}_2\text{In}_2\text{O}_5$, $\text{Sr}_2\text{Fe}_2\text{O}_7$, $\text{Sr}_4(\text{Sr}_2\text{Nb}_2)\text{O}_{11}$, Bi_2O_3 , CsHSO_4 , AgI , $\text{Ca}_{12}\text{Al}_4\text{O}_{33}$

1. Introduction and Background

Aliovalent (or heterovalent) substitution is commonly used in order to achieve charge compensating point defects that can act as charge carriers in solid electrolytes and mixed conductors. Nevertheless, many good ionic conductors are pure, unsubstituted compounds and thus rely on intrinsic thermal disorder. Examples comprise cation conductors such as AgI , oxide ion conductors such as $\delta\text{-Bi}_2\text{O}_3$ and $\text{Ba}_2\text{In}_2\text{O}_5$, and proton conductors such as CsHSO_4 . They all have in common that the sublattice of the charge carrying species is not full. At a lower temperature the occupied and unoccupied sites are different, and the conductivity low, but at a “superionic” phase transition the sites become equivalent, so that a partial overall occupancy is realised. This results in a much higher conductivity.

Since there is no dopant, one may find it difficult to describe the defect structure of such compounds. There is intuitively a charged mobile defect, but what is the effective charge of the defect compensated by? Some will say that a defect notation is not required – the concept of disorder is enough. But the problem is that one is then unable to calculate how other defects behave and interact with the disordered sublattice as a function of temperature, component activity, or doping.

This article describes the situations at hand and some tradi-

tional ways of describing them. Most importantly, it then introduces a new subset of Kröger-Vink (K-V) nomenclature for inherently disordered sublattices that enables us to include them in defect chemical considerations. K-V nomenclature was carved out by Kröger and Vink^{1,2)} and denotes species and defects in crystalline lattices by a symbol with a subscript and a superscript; A_S^c . The main symbol A says *what* the species consist of; normally a chemical element formula or v for vacancy. The subscript S says *where* it is, that is, which lattice site it is on, normally again a formula for the chemical element occupying that site in the perfect crystal or i for interstitial site. The superscript c says *what charge* the species has. While this can be the real charge (denoted by a coefficient and + or -) the use of K-V notation especially emphasises the need and possibility to write the *effective charge*, i.e., the real charge of the species minus the real charge that the perfect crystal would have had in that location. Positive effective charge is denoted by dots, •, and negative by slashes, /. One may optionally assign effectively neutral charge by an “x”; x .

It may be noted that I have introduced lower case v and i for vacancy and interstitial, respectively, instead of the original uppercase versions V and I by Kröger and Vink, as this without any additional problems avoids confusion with vanadium, V , and iodine, I . For instance, defect chemical symbols in vanadium or iodine compounds would become ambiguous, and the case of vanadium iodide, e.g., VI_3 , would become hilarious with the use of the upper-case V and I . Lower-case v and i for the non-elemental items, the vacancy and the interstitial site, are thus used hereafter.

The extension of the K-V notation described here has been introduced previously by the author’s group for a few differ-

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ent cases of materials. These, and the references will be given under the examples of materials towards the end of this article.

2. Example of $\text{Ba}_2\text{In}_2\text{O}_5$ (or $\text{BaInO}_{2.5}$); traditional approaches

$\text{Ba}_2\text{In}_2\text{O}_5$ is an oxygen deficient perovskite ordered into the brownmillerite-structure at low temperatures. Around 930°C it disorders into the perovskite and the oxygen vacancy conductivity jumps two orders of magnitude. Rightfully, the vacancies do not move entirely freely – they are still interacting and moving probably quite correlated, and full mobility is attained only at somewhat higher temperatures – say 1300°C . But we shall for now neglect this complication that one always will have with such high defect concentrations, and see how we can envisage the defects that lead to the high conductivity.

The disordered phase has 5 oxide ions and 1 oxide ion vacancy sharing the same perovskite anion site. If this vacancy has the normal doubly positive effective charge and thus notation $v_o^{\bullet\bullet}$ one naturally asks – as we did above – what is the compensating negative effective charge? Two approaches are usually applied:

One could say that the disordering can be seen as an anion-Frenkel disorder, namely the formation of oxide ion vacancies and interstitials that has resulted in the disordered perovskite. While it is true that the ordered brownmillerite will display some anion-Frenkel disorder – placing interstitials in the ordered empty positions, compensated by vacancies in the regular sites – this can not be transposed to the new disordered structure. This is because the interstitials and vacancies cannot be taken to occupy only the respectively empty and regular sites of the brownmillerite, but now are distributed on all sites. Thus, the formation of the defective perovskite is not a formation of anion-Frenkel defects in the brownmillerite, but a phase transformation.

The other way is to acknowledge that the disordered perovskite is another phase than the brownmillerite, and to approach its defect chemistry by saying it is a 100% acceptor-doped oxide. It can be seen as for instance BaZrO_3 fully substituted with In^{3+} for Zr^{4+} , compensated by oxide ion vacancies. Or it can be seen as LaInO_3 fully substituted with Ba^{2+} for La^{3+} . The two dominating defect situations, $2[v_o^{\bullet\bullet}] = [\text{In}'_{\text{Zr}}] = \text{constant}$ or $2[v_o^{\bullet\bullet}] = [\text{Ba}'_{\text{La}}] = \text{constant}$, would both rationalise the high oxygen ion conductivity. They would also form basis for expanding the defect structures, for instance involving reduction or oxidation, or hydration. The problem is of course that it is not satisfying to have to define one of constituents – in this case one of the cations – as a defect when it obviously is not a defect. Also, it is unsatisfactory to have to define a mother structure – in this case for instance BaZrO_3 or LaInO_3 – which may be arbitrary. One may then of course have the freedom to look for a mother compound that possesses the same structure as the “100 % doped” compound of interest.

The third possibility – the new notation – circumvents the

problems of both the two above.

3. Example of $\text{Ba}_2\text{In}_2\text{O}_5$ (or $\text{BaInO}_{2.5}$); new nomenclature

In the new nomenclature we first of all acknowledge the disordered structure as a new structure – the disordering is a phase transformation. The disorder is thus part of the structure – a necessary part. Being disordered means in our context that a sublattice is occupied by more than one species. In the case of disordered $\text{Ba}_2\text{In}_2\text{O}_5$ they are oxide ions and vacancies on the oxide ion sublattice. Since the random occupancy of more than one species is the perfect state of the crystal structure, we now define it as such. For disordered $\text{Ba}_2\text{In}_2\text{O}_5$ the perfect oxide ion site is statistically occupied 5/6 with an oxide ion and 1/6 with a vacancy. We denote this site as a $\frac{5}{6}O$ site. We could also denote the site, for instance, $\frac{5}{6}O$ to simplify the writing, or $\frac{5}{6}O\frac{1}{6}v$ or $\frac{5O+1v}{6}$ to make it more general, but the first version, $\frac{5}{6}O$, will be used here for now.

Each oxide ion occupying the site to a degree of 5/6 has a formal charge -2, so that the $\frac{5}{6}O$ site statistically has a charge of $-2 \cdot 5/6 = -5/3$. This is now the averaged perfect charge of that site, and anything having that charge would be effectively neutral. However, no real species has that charge, of course, so that everything that may occupy that site will be effectively charged, i.e. defective: Both the oxide ion and the vacancy are now defects.

The oxide ion has a real charge of -2 so that its *effective* charge is now $-2 - (-5/3) = -1/3$. The oxide ion is thus denoted in the new expanded Kröger-Vink notation as $O_{\frac{5}{6}O}^{\frac{1}{3}}$.

The vacancy has a real charge of zero so that its *effective* charge is $0 - (-5/3) = +5/3$. The oxide ion vacancy is thus denoted in the expanded Kröger-Vink notation as $v_{\frac{5}{6}O}^{\frac{5}{3}}$.

One can *not* write a defect chemical equation for the formation of the two defects; they are native, or inherent.

One can, however, write an electroneutrality condition for the approximation that these two are the only predominant defects in the material:

$$\frac{1}{3}[O_{\frac{5}{6}O}^{\frac{1}{3}}] = \frac{5}{3}[v_{\frac{5}{6}O}^{\frac{5}{3}}] \text{ or } [O_{\frac{5}{6}O}^{\frac{1}{3}}] = 5[v_{\frac{5}{6}O}^{\frac{5}{3}}] \quad (1)$$

This was written following the normal approach to equalise all effectively positive and negative charges, namely to multiply the concentration of each defect type by its charge.

One can, furthermore, write a site occupancy sum. In terms of molar fraction for $\text{Ba}_2\text{In}_2\text{O}_5$, this reads:

$$[O_{\frac{5}{6}O}^{\frac{1}{3}}] + [v_{\frac{5}{6}O}^{\frac{5}{3}}] = 6 \quad (2)$$

The combination of Eqs. (1) and (2) is sufficient to describe the situation with these two defects, yielding $[O_{\frac{5}{6}O}^{\frac{1}{3}}] = 5$ and $[v_{\frac{5}{6}O}^{\frac{5}{3}}] = 1$.

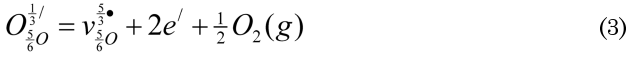
It is now straightforward to include more defects, write

defect formation equations, and expand the electroneutrality expression and, if necessary, the site occupation sum, as we shall exemplify briefly in the following.

4. Defect chemical reactions with $\text{Ba}_2\text{In}_2\text{O}_5$

4.1. Reduction and oxidation

Reduction of high-temperature disordered perovskite $\text{Ba}_2\text{In}_2\text{O}_5$ can now, in terms of oxygen ions and fully ionised vacancies be written as



and the equilibrium coefficient is accordingly

$$K_R = \frac{[v_{\frac{5}{6}O}^{\frac{5}{6}\bullet}][e']^2 p_{O_2}^{\frac{1}{2}}}{[O_{\frac{5}{6}O}^{\frac{1}{3}/}]} \quad (4)$$

It is natural to regard the defect electrons formed as reduced In states, e.g. In^{2+} . The total electroneutrality now reads

$$\frac{1}{3}[O_{\frac{5}{6}O}^{\frac{1}{3}/}] + [e'] = \frac{5}{3}[v_{\frac{5}{6}O}^{\frac{5}{6}\bullet}] \quad (5)$$

Under the assumption that electrons remain as minority defects we may regard the simplified limiting case

$$\frac{1}{3}[O_{\frac{5}{6}O}^{\frac{1}{3}/}] \cong \frac{5}{3}[v_{\frac{5}{6}O}^{\frac{5}{6}\bullet}] \quad (6)$$

and by inserting this into the equilibrium coefficient, we obtain

$$K_R = \frac{[v_{\frac{5}{6}O}^{\frac{5}{6}\bullet}][e']^2 p_{O_2}^{\frac{1}{2}}}{5[v_{\frac{5}{6}O}^{\frac{5}{6}\bullet}]} = \frac{[e']^2 p_{O_2}^{\frac{1}{2}}}{5} \quad (7)$$

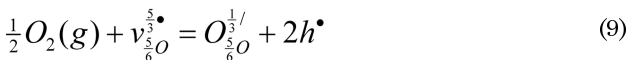
We may solve this with respect to the concentration of minority electrons and obtain

$$[e'] = (5K_R)^{\frac{1}{2}} p_{O_2}^{-\frac{1}{4}} \quad (8)$$

i.e., the $p_{O_2}^{-\frac{1}{4}}$ -dependency we are used to when fully ionised ionic defects of species in their normal oxidation states dominate, as in an aliovalently doped oxide.

If on the other hand, electrons become non-negligible in the electroneutrality, the full solution of Eqs. (2), (4), and (5) is required to obtain the defect structure. (The limiting case of dominating electrons and minority oxygen ions is not very relevant, as it would represent full destructive reduction of the oxide.)

The oxidation reaction is written



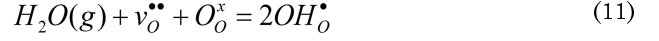
One may note that the sum of the reduction and oxidation reactions yields just the intrinsic ionisation of electrons

$$0 = 2e' + 2h^\bullet \text{ or } 0 = e' + h^\bullet \quad (10)$$

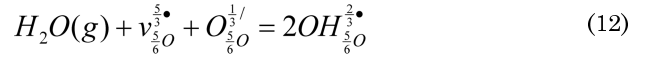
and does not contain an anion-Frenkel reaction, contrary to normal cases where these defects are not inherent.

4.2. Hydration

Materials with oxygen vacancies, e.g. introduced by acceptor dopants, may react with water vapour to fill the vacancies and replace their charges by protons in the form of hydroxide ions:



Disordered $\text{Ba}_2\text{In}_2\text{O}_5$ may also take up some water (although the reaction at such temperatures is driven far to the left) and then the reaction should be written



The equilibrium coefficient would be

$$K_H = \frac{[OH_{\frac{5}{6}O}^{\frac{2}{3}\bullet}]^2}{[v_{\frac{5}{6}O}^{\frac{5}{6}\bullet}][O_{\frac{5}{6}O}^{\frac{1}{3}/}]p_{H_2O}} \quad (13)$$

Assuming the hydroxide defects are in minority, and that the two native defects are dominating and constant, the concentration of hydroxide defects takes on a $p_{H_2O}^{\frac{1}{2}}$ dependency, as expected.

Should one imagine to increase the water vapour partial pressure such that the hydroxide defects become dominating, one gets as limiting electroneutrality

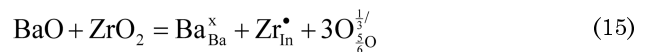
$$\frac{2}{3}[OH_{\frac{5}{6}O}^{\frac{2}{3}\bullet}] = \frac{1}{3}[O_{\frac{5}{6}O}^{\frac{1}{3}/}] \quad (14)$$

and in this situation the 6 oxygen sites are disorderly filled with 4 oxide ions and 2 hydroxide ions; with overall formula $\text{Ba}_2\text{In}_2\text{O}_4(\text{OH})_2$, or $\text{BaInO}_2(\text{OH})$. The disorder will in this case be taken on by the protons and such a phase should have considerable proton conductivity. Now, $\text{Ba}_2\text{In}_2\text{O}_5$ does indeed hydrate fully to $\text{Ba}_2\text{In}_2\text{O}_4(\text{OH})_2$ at around 300°C, but at these temperatures it is the ordered brownmillerite that is hydrated, and the hydrated oxohydroxide product is also ordered, and not very conductive.

4.3. Doping

The high-temperature disordered inherently oxygen deficient perovskite $\text{Ba}_2\text{In}_2\text{O}_5$ may be doped. Small doping levels should not affect the material much, since the inherent defect concentrations are so high. That is perhaps why it so easily accepts large dopant levels; the accompanying defects are not energy-demanding.

Zr can be substituted for In and then acts as a donor. In our new terminology with disordered $\text{Ba}_2\text{In}_2\text{O}_5$ as host compound, this is written



The electroneutrality becomes

$$\frac{1}{3}[O_{\frac{5}{6}O}^{\frac{1}{3}/}] = [\text{Zr}_{\text{In}}^\bullet] + \frac{5}{3}[v_{\frac{5}{6}O}^{\frac{5}{6}\bullet}] \quad (16)$$

For instance, at 50% substitution, we have one oxygen

vacancy and eleven oxide ions out of twelve positions; $\text{Ba}_4\text{In}_2\text{Zr}_2\text{O}_{11}$. At high doping levels, it gets the same whether one considers it to be Zr-doped $\text{Ba}_2\text{In}_2\text{O}_5$ or In-doped BaZrO_3 .

5. Diffusion and Conductivity

5.1. Transport in normal oxide with oxygen vacancies

In a normal oxide, self-diffusion or conductivity of oxide ions can take place by transport of ions through vacancy and interstitial mechanisms (in addition to interstitialcy mechanisms that we otherwise neglect in the following). The self-diffusion coefficient of vacancies is

$$\begin{aligned} D_{v_o^{**}} &= (1 - x_{v_o^{**}}) A s_{o-o}^2 \nu_o \exp \frac{\Delta S_m}{k} \exp \frac{-\Delta H_m}{kT} \\ &= (1 - x_{v_o^{**}}) D_{0,v_o^{**}} \exp \frac{-\Delta H_m}{kT} \end{aligned} \quad (17)$$

where x denotes site fraction, A is a constant, s_{o-o} is the jumping (oxygen-oxygen) distance, ν_o is the vibrational frequency, and ΔS_m and ΔH_m are the activation entropy and enthalpy of site exchange of a vacancy and ion, i.e. of migration. The pre-exponential of vacancy diffusivity is, from the above,

$$D_{0,v_o^{**}} = A s_{o-o}^2 \nu_o \exp \frac{\Delta S_m}{k} \quad (18)$$

The self-diffusion coefficient of oxide ions via vacancies in a normal case is correspondingly

$$\begin{aligned} D_{O^{2-}} &= x_{v_o^{**}} A s_{o-o}^2 \nu_o \exp \frac{\Delta S_m}{k} \exp \frac{-\Delta H_m}{kT} \\ &= x_{v_o^{**}} D_{0,v_o^{**}} \exp \frac{-\Delta H_m}{kT} \end{aligned} \quad (19)$$

and the ratio between the two is

$$\frac{D_{O^{2-}}}{D_{v_o^{**}}} = \frac{x_{v_o^{**}}}{1 - x_{v_o^{**}}} \quad (20)$$

In order to get numbers on transport of oxygen by a driving force, e.g. the oxide ion conductivity, one would have to consider *either* the transport of vacancies *or* the transport of ions, and get the same answer:

$$\begin{aligned} \sigma_{v_o^{**}} &= \frac{4e^2 c_o x_{v_o^{**}} D_{v_o^{**}}}{kT} = \sigma_{O^{2-}} = \frac{4e^2 c_o (1 - x_{v_o^{**}}) D_{O^{2-}}}{kT} \\ &= \frac{4e^2 c_o (1 - x_{v_o^{**}}) x_{v_o^{**}} D_{0,v_o^{**}}}{kT} \exp \frac{-\Delta H_m}{kT} \end{aligned} \quad (21)$$

where c_o is the volume concentration of (partially occupied) oxygen sites.

5.2. Transport in disordered $\text{Ba}_2\text{In}_2\text{O}_5$

For a disordered inherently deficient oxide, like $\text{Ba}_2\text{In}_2\text{O}_5$, we have defined both the oxide ion and the vacancy as defects. The diffusivity of a vacancy is

$$D_{\frac{5}{6}v_o^{**}} = x_{\frac{1}{6}O_{\frac{3}{6}O}} A s_{o-o}^2 \nu_o \exp \frac{\Delta S_m}{k} \exp \frac{-\Delta H_m}{kT}$$

$$= x_{\frac{1}{6}O_{\frac{3}{6}O}} D_{0,\frac{5}{6}v_o^{**}} \exp \frac{-\Delta H_m}{kT} \quad (22)$$

while the diffusivity of an oxide ion is

$$\begin{aligned} D_{\frac{1}{6}O_{\frac{3}{6}O}} &= x_{\frac{5}{6}v_o^{**}} A s_{o-o}^2 \nu_o \exp \frac{\Delta S_m}{k} \exp \frac{-\Delta H_m}{kT} \\ &= x_{\frac{5}{6}v_o^{**}} D_{0,\frac{5}{6}v_o^{**}} \exp \frac{-\Delta H_m}{kT} \end{aligned} \quad (23)$$

The ratio is – as before – the ratio between the fractions of the two species, in this case 5:1.

In expressing the conductivity, the charge transported by the process of migration is two, despite the defects' lower effective charges. This is because both species exchanged are defects with effective charge, unlike normal situations where all the effective charge is assigned one of the species.

Since both species are defined as defects, one might for a moment expect both to contribute to conductivity. However, just as in the regular case, a jump of a vacancy is also a jump of an ion, so we cannot add the two, but express the conductivity in terms of one or the other, and get the same result:

$$\sigma_{\frac{5}{6}v_o^{**}} = \frac{4e^2 c_o x_{\frac{5}{6}v_o^{**}} D_{\frac{5}{6}v_o^{**}}}{kT} = \sigma_{\frac{1}{6}O_{\frac{3}{6}O}} = \frac{4e^2 c_o x_{\frac{1}{6}O_{\frac{3}{6}O}} D_{\frac{1}{6}O_{\frac{3}{6}O}}}{kT} \quad (24)$$

In undoped $\text{Ba}_2\text{In}_2\text{O}_5$ the site fractions in the equations above can of course be simply set equal to 1/6 and 5/6.

Again, the result is not different from ordinary models or materials, but the use of the defect notation for disordered inherently defective lattices allows us to reach this conclusion and understand the situation properly.

6. Partial occupancy defects as ionised acceptors and donors

Charged defects based on partial occupancy that we have created and considered here – such as the $O_{\frac{3}{6}O}^{\frac{1}{6}\bullet}$ and $v_{\frac{5}{6}O}^{\frac{5}{6}\bullet}$ in high-temperature perovskite-structured $\text{Ba}_2\text{In}_2\text{O}_5$ – should be possible to regard as ionised acceptors and donors, respectively. This means that we may consider to reverse the ionisation and release one electron to the valence band or accept one electron from the conduction band to deionise the defects. These processes should normally involve whole, not fractional, electrons and holes. One might of course say that since we have created fractional occupancies as perfect entities, we could also consider fractional electrons. But the fractional occupant is only an imaginary species – something we never put into any chemical reaction, and so we will avoid doing redox reactions with fractional electrons. The deionisation of the above defects then can be written:



$$v_{\frac{5}{6}O}^{\bullet} + e' = v_{\frac{5}{6}O}^{\frac{1}{3}/} \quad (27)$$

The defect formed in the first case corresponds most closely to an O⁻ ion, the species we often associate with hole (p-type electronic) states in oxides. The latter two are reminiscent of singly ionised or unionised oxygen vacancies in normal defect chemistry – normal species to consider under very reducing or donor doped conditions.

In order to deionise the defects we need electronic defects from somewhere. Unless this is done by extreme conditions (reducing or oxidising) or by doping, it may be done by mutual deionisation of the two native defects. The first step would be

$$O_{\frac{5}{6}O}^{\frac{1}{3}/} + v_{\frac{5}{6}O}^{\bullet} = O_{\frac{5}{6}O}^{\bullet} + v_{\frac{5}{6}O}^{\frac{2}{3}\bullet} \quad (28)$$

whereafter the simplified electroneutrality would be

$$\frac{1}{3}[O_{\frac{5}{6}O}^{\frac{1}{3}/}] = \frac{2}{3}[O_{\frac{5}{6}O}^{\bullet}] + \frac{2}{3}[v_{\frac{5}{6}O}^{\frac{2}{3}\bullet}] \quad (29)$$

The second step would be

$$2O_{\frac{5}{6}O}^{\frac{1}{3}/} + v_{\frac{5}{6}O}^{\bullet} = 2O_{\frac{5}{6}O}^{\bullet} + v_{\frac{5}{6}O}^{\frac{1}{3}/} \quad (30)$$

with simplified electroneutrality

$$\frac{2}{3}[O_{\frac{5}{6}O}^{\frac{1}{3}/}] = \frac{1}{3}[O_{\frac{5}{6}O}^{\bullet}] + \frac{1}{3}[v_{\frac{5}{6}O}^{\frac{1}{3}/}] \quad (31)$$

In this case the electrons have relaxed so that two electrons populate the vacancy and these are taken from two oxide ions (to become O⁻ ions), leaving three ordinary oxide ions in the O²⁻ state.

This may not immediately be felt as useful, but provides an introduction to less ionised species and trapped electronic defects in a system with partial ionic occupancy.

7. Further examples

7.1. Other perovskites

An oxide like Sr₂Fe₂O₅ disorders in the same way as Ba₂In₂O₅ and attains an equally high oxide ion conductivity, and the same nomenclature applies.

Other inherently deficient perovskites have smaller vacancy contents. For instance, Sr₄Sr₂Nb₂O₁₁, Ba₄Ca₂Nb₂O₁₁, Ba₄In₂Zr₂O₁₁, and Ba₂La₂In₄O₁₁ have 11/12 occupied oxide ion lattices and are good oxide ion conductors when disordered at sufficiently high temperatures. Here, the electroneutrality reads

$$\frac{1}{6}[O_{\frac{11}{12}O}^{\frac{1}{6}/}] = \frac{11}{6}[v_{\frac{11}{12}O}^{\bullet}] \quad (32)$$

7.2. δ -Bi₂O₃

Bi₂O₃ represents an early and important example. In the disordered, cubic δ -phase the three oxide ions are spread over four sites, and in our new nomenclature the electroneutrality reads

$$\frac{1}{2}[O_{\frac{3}{4}O}^{\frac{1}{2}/}] = \frac{3}{2}[v_{\frac{3}{4}O}^{\bullet}] \quad (33)$$

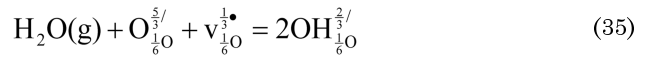
7.3. Mayenite, Ca₁₂Al₁₄O₃₃

Mayenite, Ca₁₂Al₁₄O₃₃, has a unit cell which can be expressed as (Ca₂₄Al₂₈O₆₄)⁴⁺ · 2O²⁻, where the first part is a lattice framework with 12 nano-cages, and the two so-called extra-framework oxide ions are randomly distributed in those nano-cages. Each nano-cage is somewhat elongated and contains two crystallographic positions for the oxide ion. However, it is reasonable to assume that only one oxide ion can be fitted in a cage at any time, and that the energy barrier between the two positions is small enough that the oxide ion is effectively delocalised over the two positions at elevated temperatures. In this way, each oxide ion occupies one out of 6 available cages.

The defect situation in mayenite can thus be described as one with an inherently deficient sublattice, namely the oxide ions in the extra-framework nanocages. In this, the site is denoted as one with 1/6 occupancy of oxide ions as the perfect state, consequently with a charge of -2/6 = -1/3. Occupied or empty cages have an effective charge relative to this. The electroneutrality in the pure, dry material then reads³⁾

$$5[O_{\frac{5}{6}O}^{\frac{5}{6}/}] = [v_{\frac{5}{6}O}^{\bullet}] \quad (34)$$

Mayenite has a strong tendency to become hydrated by replacing the oxide ions with hydroxide ions. In our notation the hydration reaction is written



The equilibrium constant is

$$K = [OH_{\frac{5}{6}O}^{\frac{2}{6}/}]^2 [O_{\frac{5}{6}O}^{\frac{5}{6}/}]^{-1} [v_{\frac{5}{6}O}^{\bullet}]^{-1} p_{H_2O}^{-1} \quad (36)$$

The new electroneutrality reads

$$2[OH_{\frac{5}{6}O}^{\frac{2}{6}/}] + 5[O_{\frac{5}{6}O}^{\frac{5}{6}/}] = [v_{\frac{5}{6}O}^{\bullet}] \quad (37)$$

and the site limitation is:

$$[OH_{\frac{5}{6}O}^{\frac{2}{6}/}] + [O_{\frac{5}{6}O}^{\frac{5}{6}/}] + [v_{\frac{5}{6}O}^{\bullet}] = 6 \quad (38)$$

It may be noted that the site sum of 6 enforces concentrations to refer to fractions of one formula unit mayenite Ca₁₂Al₁₄O₃₃, or molar fraction of the same. From these equations, the concentration of hydroxide ions as a function of water vapour partial pressure and temperature (via the equilibrium constant) can be derived:

$$[OH_{\frac{5}{6}O}^{\frac{2}{6}/}] = \frac{-6Kp_{H_2O} + 4\sqrt{(Kp_{H_2O})^2 + 5Kp_{H_2O}}}{4 - Kp_{H_2O}} \quad (39)$$

7.4. Other oxide classes

A number of other oxide systems are known where doping

seemingly is not necessary to create mobile ionic defects, and where inherent disordered partial occupancy is likely to be the proper description of the cause of the defect and transport. This comprises the perovskite-related $\text{Sr}_4\text{Fe}_6\text{O}_{13}$ and the analogues such as $\text{Sr}_4\text{Fe}_4\text{Co}_2\text{O}_{13}$ in which the 13^{th} oxide ion may be taken to be disordered over a number of sites.^{4,5)}

In the high temperature oxide ion conducting $\text{La}_2\text{Mo}_2\text{O}_9$, the conductivity is probably caused by the 9^{th} oxygen being disordered over a number of available partially occupied sites.

Lanthanum tungstate, $\text{La}_6\text{WO}_{12}$, exhibits native ionic and protonic conductivity depending on humidity and temperature,⁶⁾ and the conductivity seems not to be enhanced by acceptor doping and is thus possibly related to some of the oxide ions being disordered over a number of sites.

Lanthanum oxyborate, $\text{La}_{26}\text{O}_{27}(\text{BO}_3)_8$, is a system where one out of 28 oxide sites is unoccupied in a disorderly manner and it has been suggested that the proton conductivity measured when the material is hydrated is due to similarly disordered protons hosted over the same oxide ion sublattice.⁷⁾

7.5. Other classes of ionic conductors

Many of the early cation conductors may be described according to the proposed nomenclature. For instance, in the superprotonic phase of CsHSO_4 the proton is spread disorderly among the oxide ions of the sulphate groups, such that the electroneutrality reads

$$\frac{3}{4}[\text{H}_{\frac{1}{4}\text{H}}^{\frac{3}{4}\bullet}] = \frac{1}{4}[\text{V}_{\frac{1}{4}\text{H}}^{\frac{1}{4}}] \quad (40)$$

Silver iodide, $\beta\text{-AgI}$, transforms into $\alpha\text{-AgI}$ at around 147°C , a phase with high silver ion conductivity. The concept of silver ions disordered over a number of energetically equivalent sites was postulated in the mid-1930s by Strock^{8,9)} and Rahlfs,¹⁰⁾ although structural studies could confirm this only much later.

8. Systems with disordered occupancy by several occupants

For this class, we take a particular example to illustrate the case and raise a question of interest. $\text{Ba}_3\text{La}(\text{PO}_4)_3$ is a compound with the eulytite structure – in which the four cations, here three divalent Ba^{2+} and one trivalent La^{3+} , disorderly occupies the same site. The site is statistically occupied by $(3 \cdot 2 + 1 \cdot 3)/4 = 9/4 = 2\frac{1}{4}$ positive charges. In the new

nomenclature we might call it a $\frac{3\text{Ba}+1\text{La}}{4}^{\frac{9}{4}+}$ or $\frac{\text{Ba}_3\text{La}}{4}^{\frac{4}{9}+}$ or $\text{Ba}_{3/4}\text{La}_{1/4}^{\frac{9}{4}+}$ site, so that a Ba^{2+} or La^{3+} ion would be denoted, for instance, $\text{Ba}_{\frac{3\text{Ba}+1\text{La}}{4}}^{\frac{1}{4}}$ or $\text{La}_{\frac{3\text{Ba}+1\text{La}}{4}}^{\frac{3}{4}\bullet}$, respectively.¹¹⁾ We see that an abbreviation for the complex site expression can be useful in such cases. Thus, defining $M^{\frac{9}{4}+} = \frac{3\text{Ba}+1\text{La}}{4}^{\frac{9}{4}+}$ allows us to denote Ba^{2+} and La^{3+} as $\text{Ba}_M^{\frac{1}{4}}$ and $\text{La}_M^{\frac{3}{4}\bullet}$, respectively.

The electroneutrality reads

$$\frac{1}{4}[\text{Ba}_M^{\frac{1}{4}}] = \frac{3}{4}[\text{La}_M^{\frac{3}{4}\bullet}] \quad (41)$$

One can now in principle shift the ratio between the two cations and thereby achieve acceptor or donor doping, compensated by effectively positive or negative defects. For instance, it has been attempted to acceptor dope with an excess of Ba^{2+} to dissolve protons, in phosphates often represented as hydrogen phosphate defects on phosphate sites, with the new electroneutrality reading

$$\frac{1}{4}[\text{Ba}_M^{\frac{1}{4}}] = \frac{3}{4}[\text{La}_M^{\frac{3}{4}\bullet}] + [(\text{HPO}_4)_{\text{PO}_4}^{\bullet}] \quad (42)$$

Here we shall, however, turn to a different issue, specific to the concept of the new nomenclature: Assume the compound in question is perfectly stoichiometric, so that the electroneutrality Eq. (41) holds. Now, consider a minor concentration of additional defects formed by oxidation. The defects can, for instance, be oxygen interstitials and electron holes. If these were the only defects, we would, from ordinary defect chemistry, expect

$$p = 2[O_i^{\prime\prime}] \propto p_{\text{O}_2}^{1/6} \quad (43)$$

However, since the two defects of disordered Ba^{2+} and La^{3+} are dominating in numbers, one might also think for a moment that the holes end up as minor defects with the familiar $p \propto p_{\text{O}_2}^{1/4}$ dependency they attain when ionic defects rule. However, the two sets of defects are decoupled, the disordered Ba^{2+} and La^{3+} have no possibility to make small adjustments to buffer the uptake of oxygen, and Eq. (43) is correct. Should a misbalance be introduced into the $\text{Ba}^{2+}/\text{La}^{3+}$ ratio this will affect the other defects, however, and may make for instance oxygen interstitials dominating and holes minor, then with the $p \propto p_{\text{O}_2}^{1/4}$ dependency. All in all we learn that the notation for native disorder of cations allows a reasonable description of the individual effective charge of the cations, and to introduce non-stoichiometry of the cations as well as foreign cations, but that any charge imbalance introduced is normally “stiff”, like the balance between cation donors and acceptors in normal cases; the imbalance must be compensated, but it cannot adjust itself like a buffer. Exceptions may be found if the cations are in equilibrium with secondary phases or with the gas phase.

We may also mention that the two disordered cations will not give rise to a conductivity; they are disordered thermodynamically (location-wise), but not kinetically: Since there are intrinsically no cation vacancies, the cations are not as such free to move or exchange sites.

9. Is the new nomenclature useful for traditional doping?

Since a substitutional dopant partially occupies a sublattice, the use of the new nomenclature for partial occupancies can be applied also to traditional cases of dopants. Assume ZrO_2 is doped with 8 mol% Y_2O_3 . This gives 0.92 ZrO_2 and 0.08 Y_2O_3 , ending up with $0.92/1.08 \approx 0.85$ as the site fraction for Zr^{4+} ions and ca. 0.15 for Y^{3+} ions. The site

thus has an occupancy of $0.85\text{Zr}+0.15\text{Y}$ or $85\text{Zr}+15\text{Y}$ if one prefers, with an average charge of +3.85 per site. As we know, this nomenclature makes both the Zr and Y ions defective with respect to the partially occupied site. The two defects charge compensate each other, making the partially occupied lattice neutral – as required.

Since the partially occupied sublattice described in this way is effectively neutral, there is in principle no need to compensate it further by other defects. However, we know that Y doping is accompanied by a deficiency in the oxide ion sublattice, so that we may and should describe partial occupancy by ions and vacancies also here, but it will again represent a neutral state. The formula unit is then occupied by 1.925 oxide ions and 0.075 vacancies, so that each oxide ion site statistically is occupied by 0.9675 oxide ion and 0.0325 vacancy.

If one considers to vary the doping level, there seems to be little point in using this new nomenclature here; there seems to be no fixed perfect state of interest. However, one may note that the new nomenclature describes in a way a new perfect (minimum energy) state for each new overall composition $(1-x)\text{ZrO}_2 + x\text{Y}_2\text{O}_3$. If one keeps the doping level constant, on the other hand, the neutral partial occupancy of oxide ions and vacancies may be taken as a “perfect” starting point for defect reactions such as reduction/oxidation or hydration.

In a parallel to the mayenite case mentioned earlier, the new nomenclature corresponds to an effectively neutral cation sublattice and an effectively neutral anion sublattice, while the traditional notation represents an effectively charged (here negative – by the ionised acceptors) cation sublattice and correspondingly effectively charged (here positive – by the fully ionised oxygen vacancies) anion sublattice.

To conclude, it is possible, but in general not advantageous to use the new nomenclature of partial occupancy as an inherent property to describe aliovalently doped systems. On the contrary, it then just introduces generally awkward fractions and says little about the charged defects formed or the dominating electroneutrality. This repeats the main point of the nomenclature that its main applicability is to introduce defects appropriately in disordered systems where there at first sight seem to be no charge compensating defects.

10. Conclusions

A compatible extension of the Kröger-Vink nomenclature has been defined that allows the description and calculations of defect structure in inherently disordered, partially occupied sublattices. The nomenclature describes the average occupancy and average charge of a site as the normal

state. Any deviation from this – typically the real occupancy by an ion or vacancy – is then a defect. The system allows normal defect chemical reactions to be described and evaluated, without the need for unnatural or incorrect approaches that are otherwise required for the compounds in question. The new nomenclature has been illustrated by many example compounds.

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