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Point defect parameters in β-PbF_2 revisited

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Abstract

The defect parameters in β-PbF_2 that have been determined to date from the association and extrinsic regions of the isobaric conductivity plot as well as from conductivity measurements under various pressures, are studied. We find that, in the low temperature range where bulk elastic and expansivity data are available, the defect volumes scale linearly with the defect enthalpies with a slope which is governed by bulk qualities. A deviation from linearity is observed in the high temperature range from which the relevant parameters for the anion Frenkel formation process are deduced.

Keywords: Frenkel defects; Defect volumes; Fluorites; Conductivity

1. Introduction

The major reason for the interest on the fluorite-structured materials during the last three decades has been the discovery that these systems exhibit superionic conductivity at high temperature. Here we focus on one of them, i.e., β-PbF_2, which is probably the most prominent fluoride superionic conductor because of its low transition temperature (≈700°K) and high ionic conductivity ($\sigma = 1\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at 800°K) (e.g., see Refs. [1,2]). This has been the subject of a large number of investigations. Among these studies, Figueroa et al. [3] have made low temperature dc-conductivity measurements under various pressures on PbF_2 either pure or doped with various alkali metals. At their lower temperatures of these measurements at which the conductivity is due to free vacancies thermally dissociated from the electric dipoles consisting of the impurity and the fluorine vacancy (created for reasons of charge compensation), the activation volume υ^{act} is given by:

$$\upsilon^{\mathrm{act}} = 1/2\ \upsilon^{\mathrm{a}} + \upsilon^{\mathrm{fm}} \tag{1}$$

where υ^{a}, υ^{fm} are the volumes that correspond to the association process and the free (fluorine) vacancy motion, respectively. Moreover, Figueroa et al. [3] made dielectric relaxation measurements at various pressures, which give the volume $\upsilon^{\mathrm{m,b}}$ for the (re)orientation process of the above dipoles. All these volumes determined for all the alkali ions Li^+, Na^+, K^+ and Rb^+ have been found to be positive. In addition, Figueroa et al. [3] noticed that the ratio of the activation volumes to the activation energies (which are, in fact, activation enthalpies designated hereafter with h^{act}), is the same for all dopants. An explanation on this important experimental finding was then proposed by Lazaridou et al. [4], based on an early model termed cBΩ model, that will be summarized later. In accordance with this explanation, the ratio $\upsilon^{\mathrm{act}}/h^{\mathrm{act}}$ should *solely* be governed by macroscopic properties of the bulk solid. Actually, it was shown [4] that the migration enthalpy ($h^{\mathrm{f,m}}$) and volume ($\upsilon^{\mathrm{f,m}}$) for the free (f) fluorine vacancy motion, as well as the corresponding quantities $h^{\mathrm{m,i}}$, $\upsilon^{\mathrm{m,i}}$ for the fluorine interstitial (i) migration, which have been determined from earlier conductivity measurements [5,6] under pressure, exhibit ratios $\upsilon^{\mathrm{f,m}}/h^{\mathrm{f,m}}$ and $\upsilon^{\mathrm{m,i}}/h^{\mathrm{m,i}}$ that are not only equal to those $\upsilon^{\mathrm{act}}/h^{\mathrm{act}}$ found by Figueroa et al. [3] but also equal to the value predicted by the cBΩ model. In the meantime, however, new conductivity measurements in β-PbF_2 appeared [7] which lead to values of the ratio υ/h for the defect migration as well as for the anion Frenkel defect formation processes. It is therefore of interest to investigate whether these new data –and hence the totality of data observed to date – result in values consistent with the behavior expected on the basis of the cBΩ model. This constitutes the main objective of the present paper.

The variation of the pressure (P) affects the formation Gibbs energy, g^{f}, as well as the migration Gibbs energy, g^{m}, of defects

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in solids. The defect volumes for the formation process (υ^{f}) and migration process (υ^{m}) are defined as [8]:

$$\upsilon^{\mathrm{f}} = \frac{\mathrm{d}g^{\mathrm{f}}}{\mathrm{d}P}|_T \quad \text{and} \quad \upsilon^{\mathrm{m}} = \frac{\mathrm{d}g^{\mathrm{m}}}{\mathrm{d}P}|_T \tag{2}$$

where T denotes the temperature. When both processes, i.e., formation (f) and migration (m) are operating, the experimental results are described in terms of an activation Gibbs energy g^{act}, on the basis of which an activation volume is defined:

$$\upsilon^{\mathrm{act}} = \frac{\mathrm{d}g^{\mathrm{act}}}{\mathrm{d}P}|_T \tag{3}$$

If experiments refer to migration (m) of a bound (b) defect, e.g., the case of the (re)orientation of electric dipoles consisting of an aliovalent impurity and a neighboring (bound) vacancy or interstitial, the results are described in terms of an activation energy $g^{\mathrm{act,b}}$ which is associated with an activation volume $\upsilon^{\mathrm{m,b}} \equiv (\mathrm{d}g^{\mathrm{m,b}}/\mathrm{d}P)_T$ for the (re)orientation process. In the vast majority of the experiments studying the pressure variation of either the dc ionic conductivity or the diffusion coefficients in various materials υ^{act} was found to be positive. The same holds for the $\upsilon^{\mathrm{m,b}}$ values obtained from electrical relaxation measurements under various pressures. However, some noticeable exceptions have been reported, in which negative activation volumes have been found [9–12]. This case is of particular importance since it provides the basis for the explanation [8,13,14] of the generation of low frequency electric signals that are observed before earthquakes [8,15–18].

The present paper is organized as follows: In Section 2 we briefly summarize the cBΩ model, whereas its application to the data of β-$\mathrm{PbF_2}$ is discussed in Section 3. Finally, in Section 4, we present our main conclusion.

2. The model that interconnects the defect Gibbs energy with the bulk properties

The defect Gibbs energy g^i is interconnected with the bulk properties of the solid through the relation [8,19–21]:

$$g^i = c^i B\Omega \tag{4}$$

where the superscript i refers here to the defect process under consideration, i.e., $i=f$ and m for the formation and migration, respectively. Concerning the symbols, B is the isothermal bulk modulus, Ω the mean volume per atom and c^i is dimensionless which can be considered – to the first approximation – independent of temperature and pressure. By differentiating Eq. (4) with respect to pressure, we find that the volume $\upsilon^i = (\mathrm{d}g^i/\mathrm{d}P)_T$ is given by:

$$\upsilon^i = c^i\Omega\left(\frac{\mathrm{d}B}{\mathrm{d}P}|_T - 1\right) \tag{5a}$$

or, equivalently

$$\upsilon^i = \frac{g^i}{B}\left(\frac{\mathrm{d}B}{\mathrm{d}P}|_T - 1\right) \tag{5b}$$

Similarly, by differentiating Eq. (4) with respect to temperature we find the entropy $s^i = -(\mathrm{d}g^i/\mathrm{d}T)_T$. We then insert this result as well as Eq. (4) into the relation $h^i = g^i + Ts^i$ which finally gives for the enthalpy h^i:

$$h^i = c^i\Omega\left(B - T\beta B - T\frac{\mathrm{d}B}{\mathrm{d}T}|_{\mathrm{P}}\right) \tag{6}$$

Thus, taking the ratio of Eqs. (5a), (5b) and (6), we get:

$$\frac{\upsilon^i}{h^i} = \left(\frac{\mathrm{d}B}{\mathrm{d}P}|_T - 1\right) \Big/ \left(B - T\beta B - T\frac{\mathrm{d}B}{\mathrm{d}T}|_{\mathrm{P}}\right) \tag{7}$$

Whenever the temperature is small and $Ts^i << h^i$, Eq. (7) can be approximately written as:

$$\frac{\upsilon^i}{h^i} \approx \frac{1}{B}\left(\frac{\mathrm{d}B}{\mathrm{d}P}|_T - 1\right)$$

which is reminiscent of an equation obtained in Ref. [22] that was derived, however, on a different basis [8], i.e., the dynamical theory of defect migration in solids. The validity of Eqs. (4) and (7) has been checked for various processes in a variety of solids [8,20,21]. The same procedure can be also applied to mixed ionic solids since their B-values used in Eq. (4) can be estimated from the corresponding B-values of the pure constituents [23]. Furthermore, we note that Eq. (4) has been recently found of value for the behavior in the formation of Schottky defects in high T_{c}-superconductors [24] as well as for the temperature dependence of the viscosity of glass forming liquids as we approach the glass transition [25,26].

3. Investigation of the compatibility of the parameters from conductivity measurements under pressure with the cBΩ model

Eq. (7) indicates that for a given host crystal the ratio υ^i/h^i should be the same irrespective of the process and the kind of the dopant and that its value is solely determined by the bulk properties. In Fig. 1, we plot the experimental values of υ^i versus h^i from various sources as follows: First, four points (solid dots) correspond to the association parameters from the conductivity studies of Figueroa et al. [3] in β-$\mathrm{PbF_2}$ doped with Li, Na, K and Rb (see their Tables III and IV), whereas two other points obtained by the same authors in two undoped samples $\mathrm{P_1}$ and $\mathrm{P_2}$. Second, three points (open, full and inverted triangle) correspond to the (free) fluorine vacancy migration parameters, as they have been reported by Oberschmidt and Lazarus [5], Samara [6] and Murin et al. [7], respectively. Third, two points (solid and open square) show the (free) fluorine interstitial migration parameters reported by Samara [6] and Murin et al. [7], respectively. Finally, the two remaining points (full and open diamond) correspond to the values deduced for the anion Frenkel formation process by Oberschmidt and Lazarus [5] and Murin et al. [7], respectively.

An inspection of this figure reveals that all the points, except of the two ones that correspond to the formation process, lie more or less on a straight line, as they should in accordance with the cBΩ model. In the same figure, for the sake of comparison,