Solution of exercises 06.05.2025

1. ***Write equations of reactions of incorporation of defects and corresponding mass constants assuming defect equilibrium.***

   a. Schottky defects in WO_3
   b. Frenkel-type cationic defects in Ta_2O_5
   c. Anionic Frenkel defects in MoO_3
   d. oxygen from atmosphere enters interstitial sites in Sr_2TiO_4
   e. Loss of Me in $Me^{+2}X^{-2}$ (Me evaporates)
   f. dissolution of CaO in HfO_2
   g. dissolution of Ta_2O_5 in $LaGaO_3$ - Ta goes to Ga sites
   h. dissolution of La2O3 in BaTiO3 Consider 3 possibilities (La goes to Ba sites, to Ti – sites or to both)

Solutions:

$$a)\ null \xleftrightarrow{WO_3} V_W^{''''''} + 3V_O^{\bullet\bullet} \qquad K_S = \left[V_W^{''''''}\right]\left[V_O^{\bullet\bullet}\right]^3$$

$$b)\ null \xleftrightarrow{Ta_2O_5} Ta_i^{\bullet\bullet\bullet\bullet\bullet} + V_{Ta}^{'''''} \qquad K_{CF} = \left[Ta_i^{\bullet\bullet\bullet\bullet\bullet}\right]\left[V_{Ta}^{'''''}\right]$$

$$c)\ null \xleftrightarrow{MoO_3} O_i'' + V_O^{\bullet\bullet} \qquad K_{AF} = \left[V_O^{\bullet\bullet}\right]\left[O_i''\right]$$

$$d)\ \frac{1}{2}O_2(\text{gaz}) \xleftrightarrow{Sr_2TiO_4} O_i'' + 2h \quad K = \left[O_i''\right]\left[h^{\bullet}\right]^2 p_{O_2}^{-1/2} = \left[O_i''\right]p^2 p_{O_2}^{-1/2}$$

$$\text{e) null} \xleftrightarrow{MeO} V_{Me}'' + Me(\text{gaz}) + 2h^{\bullet} + X_X \quad K = \left[V_{Me}''\right]\left[h^{\bullet}\right]^2 p_{Me} = \left[V_{Me}''\right]p^2 p_{Me}$$

$$\text{f)}\quad CaO \xleftrightarrow{HfO_2} Ca_{Hf}'' + V_O^{\bullet\bullet} + O_O^{\times} \quad K = \left[Ca_{Hf}''\right]\left[V_O^{\bullet\bullet}\right]$$

$$\text{g)}\quad Ta_2O_5 \xleftrightarrow{2LaGaO_3} 2Ta_{Ga}^{\bullet\bullet} + V_O^{\bullet\bullet} + 5O_O^{\times} + 2V_{La}''' \quad K = \left[Ta_{Ga}^{\bullet\bullet}\right]^2\left[V_O^{\bullet\bullet}\right]\left[V_{La}'''\right]^2$$

$$\text{h)}\quad La_2O_3 \xleftrightarrow{2BaTiO_3} 2La_{Ba}^{\bullet} + 2V_{Ti}'''' + 3V_O^{\bullet\bullet} + 3O_O^{\times} \quad K = \left[La_{Ba}^{\bullet}\right]^2\left[V_O^{\bullet\bullet}\right]^3\left[V_{Ti}''''\right]^2$$

ou

$$La_2O_3 \xleftrightarrow{BaTiO_3} La_{Ba}^{\bullet} + La_{Ti}' + 3O_O^{x} \quad K = \left[La_{Ba}^{\bullet}\right]\left[La_{Ti}'\right]$$

ou

$$La_2O_3 \xleftrightarrow{2BaTiO_3} 2La_{Ti}' + 2V_{Ba}'' + 3V_O^{\bullet\bullet} + 3O_O^{\times} \quad K = \left[La_{Ti}'\right]^2\left[V_O^{\bullet\bullet}\right]^3\left[V_{Ba}''\right]^2$$

2. Donor doping of $BaTiO_3$ can result in compensation with electrons or cation vacancies. Different possibilities will be explored in this exercises. In interior of the grains, where there is no atmospheric oxygen available, the compensation tends to be electronic, while at grain boundaries , where O is more readily available from the atmosphere, the compensation tends to be by cation vacancies.

Propose 3 possible reactions of $BaTiO_3$ doping with La, where La occupies sites of Ba. Use as reactants La_2O_3 + TiO_2 .

Solutions :

Variant 1: Consider a reaction with the electronic compensation

The compensation by electrons can be written as:

$$La_2O_3 + 2TiO_2 \overset{2BaTiO_3}{\rightarrow} 2La_{Ba}^{\bullet} + 6O_O + 2e' + \frac{1}{2}O_2(g)\uparrow + 2Ti_{Ti}$$

Variant 2: Consider a reaction with the compensation by Ba-vacancies

Compensation by Ba vacancies can be written as:

$$La_2O_3 + 3TiO_2 \overset{3BaTiO_3}{\rightarrow} 2La_{Ba}^{\bullet} + V_{Ba}'' + 3Ti_{Ti} + 9O_O$$

Variant 3: Consider a reaction with the compensation by Ti-vacancies

Compensation with Ti vacancies:

$$La_2O_3 + TiO_2 \overset{2BaTiO_3}{\rightarrow} 2La_{Ba}^{\bullet} + V_O^{\bullet\bullet} + Ti_{Ti} + V_{Ti}'''' + 5O_O\,)$$

Exercise 3.

The longitudinal piezoelectric response in the framework of the problem can be found as

$$d_{33} = \frac{\Delta L}{\Delta \mathrm{V}} = \frac{\varepsilon_3 \cdot L}{E_3 \cdot L} = \frac{\varepsilon_3}{E_3},$$

where ΔV is the change of voltage. To find the relation between ε_3 and E_3, we will use the constitutive equations at constant temperature:

$$D_i = \varepsilon_0 K_{ij} E_j + d_{ij}\sigma_j,$$
$$\varepsilon_i = d_{ji} E_j + s_{ij}\sigma_j.$$

Specifically, the equation for ε_3 has the following form:

$\varepsilon_3 = d_{j3}E_j + s_{3j}\sigma_j = d_{13}E_1 + d_{23}E_2 + d_{33}E_3 + s_{31}\sigma_1 + s_{32}\sigma_2 + s_{33}\sigma_3 + s_{34}\sigma_4 + s_{35}\sigma_5 + s_{36}\sigma_6$ In order to proceed, we apply symmetry restrictions for 4*mm* point group on the piezoelectric tensor ($d_{13} = d_{23} = 0$), and on the compliance tensor, which has the form (see Symmetry Tables)

$$s = \begin{pmatrix} s_{11} & s_{12} & s_{13} & 0 & 0 & 0 \\ s_{12} & s_{11} & s_{13} & 0 & 0 & 0 \\ s_{13} & s_{13} & s_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & s_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & s_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & s_{66} \end{pmatrix}.$$

Equation for ε_3 thus rewrites as follows:

$\varepsilon_3 = d_{33}E_3 + s_{13}\sigma_1 + s_{13}\sigma_2 + s_{33}\sigma_3$

Sample **I** is mechanically free, implying all $\sigma_i = 0$. Then, $\varepsilon_3 = d_{33}E_3$, and

$$d_{33}^{\text{free}} = \frac{\varepsilon_3}{E_3} = d_{33} = 86 \times 10^{-12}\ \frac{\mathrm{C}}{\mathrm{N}}.$$

Sample **II** is clamped in the x_1x_2 plane, implying $\varepsilon_1 = \varepsilon_2 = \varepsilon_6 = 0$, and free in other directions, implying $\sigma_3 = \sigma_4 = \sigma_5 = 0$. The constitutive equation for ε_3 is rewritten as

$$\varepsilon_3 = d_{33}E_3 + s_{13}(\sigma_1 + \sigma_2).$$

To find σ_1 and σ_2, we use the constitutive equations for $\varepsilon_1 = \varepsilon_2 = \varepsilon_6 = 0$, which must not change during the measurement. Applying considerations, similar to those formulated above, the equations for ε_1, ε_2 and ε_6 attain the following form:

$$\varepsilon_1 = d_{31}E_3 + s_{11}\sigma_1 + s_{12}\sigma_2 = 0,$$
$$\varepsilon_2 = d_{31}E_3 + s_{12}\sigma_1 + s_{11}\sigma_2 = 0,$$
$$\varepsilon_6 = s_{66}\sigma_6 = 0.$$

The third equation does not give any input to our problem. The solution of the first two linear equations gives:

$$\sigma_1 + \sigma_2 = -\frac{2d_{31}}{s_{11} + s_{12}} E_3.$$

Rewriting again the constitutive equation for ε_3, we obtain

$$\varepsilon_3 = d_{33}E_3 + s_{13}(\sigma_1 + \sigma_2) = \left(d_{33} - d_{31}\frac{2s_{13}}{s_{11} + s_{12}}\right)E_3,$$

$$d_{33}^{\text{sub}} = \frac{\varepsilon_3}{E_3} = d_{33} - d_{31}\frac{2s_{13}}{s_{11} + s_{12}} = 21.6 \times 10^{-12}\ \frac{\mathrm{C}}{\mathrm{N}}.$$

Thus, in samples **I** and **II** the difference between measured longitudinal piezoelectric responses is

$$\frac{d_{33}^{\text{free}} - d_{33}^{\text{sub}}}{d_{33}^{\text{free}}} = \frac{d_{31}}{d_{33}}\frac{2s_{13}}{s_{11} + s_{12}} = 0.75$$