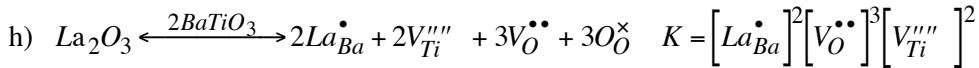
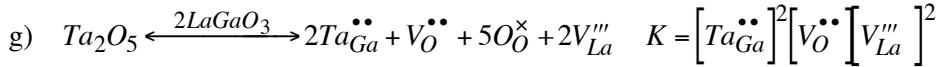
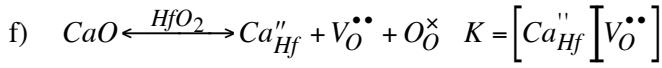
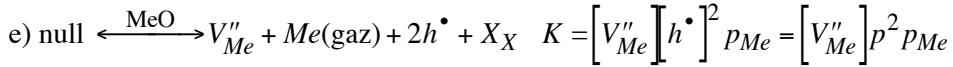
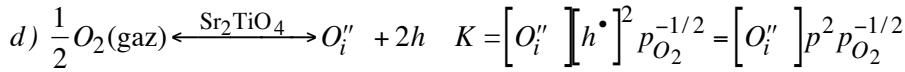
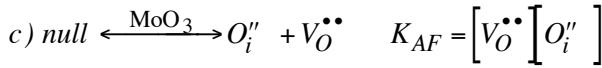
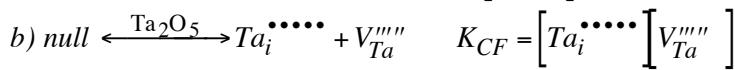
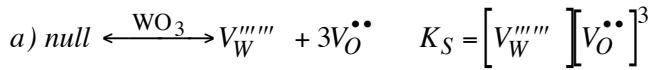


## Solution of exercises 06.05.2025

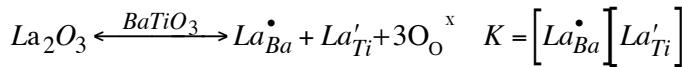
1. Write equations of reactions of incorporation of defects and corresponding mass constants assuming defect equilibrium.

- a. Schottky defects in  $\text{WO}_3$
- b. Frenkel-type cationic defects in  $\text{Ta}_2\text{O}_5$
- c. Anionic Frenkel defects in  $\text{MoO}_3$
- d. oxygen from atmosphere enters interstitial sites in  $\text{Sr}_2\text{TiO}_4$
- e. Loss of  $\text{Me}$  in  $\text{Me}^{+2}\text{X}^{-2}$  ( $\text{Me}$  evaporates)
- f. dissolution of  $\text{CaO}$  in  $\text{HfO}_2$
- g. dissolution of  $\text{Ta}_2\text{O}_5$  in  $\text{LaGaO}_3$  - Ta goes to Ga sites
- h. dissolution of  $\text{La}_2\text{O}_3$  in  $\text{BaTiO}_3$  Consider 3 possibilities (La goes to Ba sites, to Ti – sites or to both)

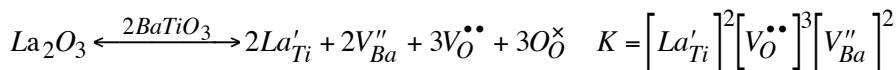
*Solutions:*



ou



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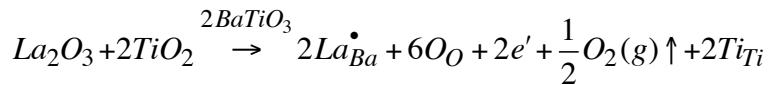


**2.** Donor doping of  $\text{BaTiO}_3$  can result in compensation with electrons or cation vacancies. Different possibilities will be explored in this exercises. In interior of the grains, where there is no atmospheric oxygen available, the compensation tends to be electronic, while at grain boundaries, where O is more readily available from the atmosphere, the compensation tends to be by cation vacancies.

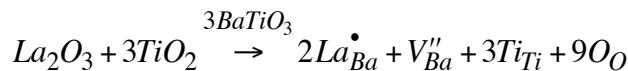
**Propose 3 possible reactions** of  $\text{BaTiO}_3$  doping with La, where La occupies sites of Ba. Use as reactants  $\text{La}_2\text{O}_3 + \text{TiO}_2$ .

Solutions :

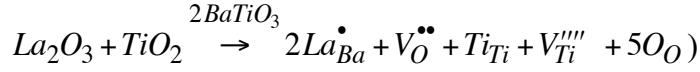
Variant 1: Consider a reaction with the electronic compensation  
The compensation by electrons can be written as:



Variant 2: Consider a reaction with the compensation by Ba-vacancies  
Compensation by Ba vacancies can be written as:



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



### Exercise 3.

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

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

where  $\Delta V$  is the change of voltage. To find the relation between  $\varepsilon_3$  and  $E_3$ , we will use the constitutive equations at constant temperature:

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

Specifically, the equation for  $\varepsilon_3$  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 4mm 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  $\varepsilon_3$  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

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

Sample **II** is clamped in the  $x_1 x_2$  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  $\varepsilon_3$  is rewritten as

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

To find  $\sigma_1$  and  $\sigma_2$ , 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  $\varepsilon_1$ ,  $\varepsilon_2$  and  $\varepsilon_6$  attain the following form:

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

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  $\varepsilon_3$ , we obtain

$$\begin{aligned} \varepsilon_3 &= d_{33} E_3 + s_{13} (\sigma_1 + \sigma_2) = \left( d_{33} - d_{31} \frac{2s_{13}}{s_{11} + s_{12}} \right) E_3, \\ d_{33}^{\text{sub}} &= \frac{\varepsilon_3}{E_3} = d_{33} - d_{31} \frac{2s_{13}}{s_{11} + s_{12}} = 21.6 \times 10^{-12} \frac{\text{C}}{\text{N}}. \end{aligned}$$

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

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