

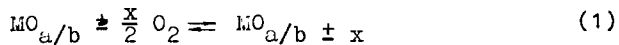
THE APPLICATION OF DILATOMETRY FOR STUDIES  
OF NON-STOICHIOMETRIC DEFECTS IN OXIDES

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ABSTRACT

The paper presents the experimental and theoretical foundations for uses of dilatometry to determine the type of non-stoichiometric defects, the mean volume taken up by a defect, and the contribution to the entropy of defect formation due to vibration. An analytical relationship between the type of defect and the changes in the relative density is given and the formula relating the volume of defect to the contribution to the entropy of its formation due to vibration is derived.

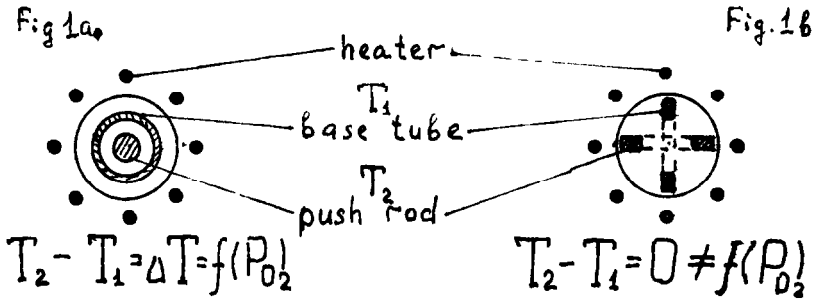
$\text{MO}_{a/b}$  oxide, when heated, invariably changes its composition according to the reaction



where  $a$  and  $b$  are the stoichiometric coefficients,  $x$  is the value of a deviation from stoichiometry.

With the change in the composition, non-stoichiometric defects which affect the ion and electron processes in crystals, form in the ion and electron subsystems. This suggests that the way to understand the distinctive features of the oxide chemistry lies through the study of the ion type non-stoichiometric defects. At present the thermal methods of analysis are not of wide application for studies of the non-stoichiometry phenomenon, although they have the important advantage of making it possible to investigate the change in the crystal parameters right in the defect formation while the equilibrium conditions are being established at high temperatures and at the predetermined partial oxygen pressure. The change in the oxide composition will be followed by the changes in the crystal mass ( $\Delta m$ ), volume ( $\Delta V$ ), and density ( $\Delta d$ ), with the behaviour of these relationships dependent on the type and concentration of the defects formed in the process. Therefore, dilatometry and TGA look promising for the study of defect formation. TGA has been mentioned as a promising method in /1/, whereas a dilatometer was used for the defect studies only

by Deportes et al. (e.g. /2/) who investigated the relationship between the change in the volume and the quantity of electricity passed through at high T and low  $P_{O_2}$  assuming this relationship to be responsible for the concentration of non-stoichiometric defects. The above authors did not alter the oxide composition by changing the oxygen partial pressure because the conventional design of the dilatometer used by the authors failed to provide identical thermal conditions for its push rod and base tube as shown in Fig. 1a.



Clearly such a design is of limited usefulness for studies of non-stoichiometric defects. The dilatometer design featuring the push rod and base tube made as U-shaped frames fully identical in form is free from this disadvantage. With this design, the temperature distribution obtained suggests that the dilatometer chamber pressure change will not produce linear changes within the system because of identical thermal conditions in the dilatometer push rod and base tube /3/, Fig. 1b. Such a design of the dilatometer is suited for the non-stoichiometric studies in oxides and primarily to determine the predominant type of defects. As shown in /1/, departures in the oxide from stoichiometry give rise to vacancies in the anion and cation sublattices or to the interstitial anion or cation arrangement. No interpretation of the defect concentration as a function of the oxygen partial pressure within the framework of the quasi-chemical approximation method can supply the unambiguous answer on the predominant type defects  $[O_1]$  or  $[V_M]$ ,  $[V_O]$  or  $[M_1]$  unless added information is available. The type of defect can be determined precisely by measuring the change in the oxide relative density against departures from stoichiometry.

This can be shown analytically. It is common knowledge that

$$\Delta d/d = \Delta m/m - \Delta V/V \quad (2)$$

Assuming that there is no interaction between the defect, we can derive relationships between the change in the relative density and the type of defects formed in the oxide when departures from stoichiometry occur. These relationships are represented analytically and graphically in Fig. 2, each type of defect possible fitting its slope angle. The notation used in Fig. 2 is as follows:  $w_{M_i}$ ,  $w_{V_1}$ ,  $w_{V_M}$ ,  $w_{M_1}$ ,  $w_{V_0}$  is the volume of a structure element denoted by Kröger's symbols,  $U_f$  is the volume of a unified formula unit,  $A$  is the number of vacant interstices,  $y$  is the number of formula units in a structure cell.

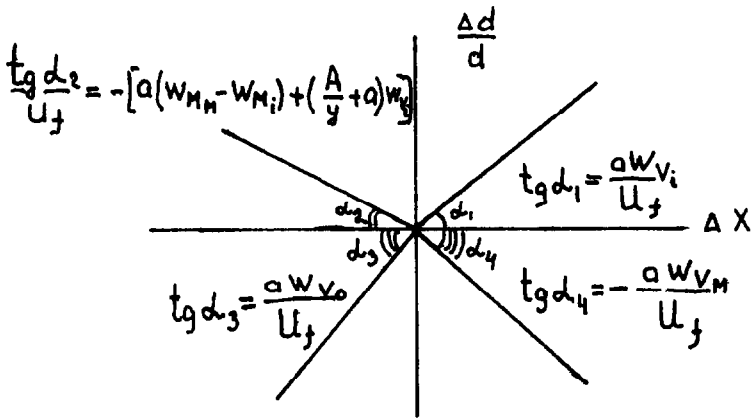


Fig 2

Hence, we can determine unambiguously the type of non-stoichiometric defects by studying the changes in the volume and mass with deviations from the oxide stoichiometry, and a correlation between the changes in the defect concentration and their associated changes in the volume obtained for the same crystal make it possible to estimate the mean volume per defect. Within the framework of a quasi-harmonic approximation, this quantity provides a means for changing to the energy characteristic of an individual defect, that is, to the vibration contribution to the entropy of formation

$$\frac{\Delta S_{\text{vibr}}}{k} = \frac{3z \cdot N \cdot E \cdot w}{t \cdot C_V} \quad (3)$$

where  $C_V$  is the heat capacity,  $z$  is the number of neighbours surrounding the defect,  $E$  is the coefficient of volume expansion,  $t$  is the isothermal compressibility,  $w$  is the mean volume per defect,  $N$  is the number of atoms in the crystal under study, and

k is the Boltzmann constant.

Fig. 3 shows the relationships between the changes in the relative density, volume, and coefficients of thermal expansion versus departures from stoichiometry at 1600 K for single crystals of  $0.9 \text{ Zr}(\text{Y}_2\text{O}_3)\text{O}_{2-x}$ .

As illustrated in Fig. 3, at the first stage of the lattice reduction vacancies are formed in the anion sublattice, which is attended by a decrease in density and an increase in volume. However, as defects build up to  $x = 10^{-3}$  atomic fractions, interaction starting between the defects results in the crystal compression. In this case, the coefficient of thermal expansion does not change, indicates that the invariable structure over the whole compositions range under consideration. It is easy to calculate that the mean volume per defect is  $10 \text{ \AA}^3$  and the vibration contribution to the entropy of formation is 4 entropy units.

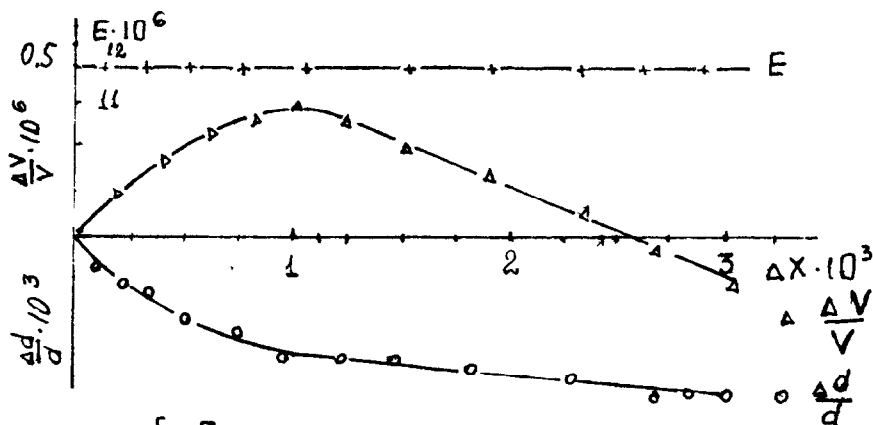


Fig. 3

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