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SOME STUDIES OF THE DEFECT STRUCTURE OF ALKALINE EARTH OXIDES (*)

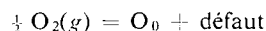
R. A. SWALIN

University of Minnesota, Minneapolis, Minnesota 55455, USA

Résumé. — Nous présentons une revue des travaux accomplis dans notre laboratoire sur SrO et BaO. Diverses expériences ont été conduites pour déterminer la structure des défauts.

Dans SrO, il semble qu'il existe des défauts de Schottky doublement ionisés à haute température, avec une énergie de formation de 3,7 eV. A la pression d'oxygène d'une atmosphère, un excès d'oxygène de quelques millièmes peut être incorporé dans le matériau. L'énergie d'activation de la diffusion du strontium à haute température est 4,61 eV.

Dans BaO, une concentration appréciable d'oxygène peut être incorporée à la pression d'une atmosphère d'oxygène (jusqu'à 1 %). La réaction qui se produit :



met en jeu une enthalpie de — 0,4 eV. Dans SrO cette enthalpie est + 1,0 eV. Dans BaO, le volume de la maille élémentaire augmente avec l'addition d'oxygène. A partir d'études de l'influence de la pression, les défauts semblent être ionisés une fois. L'énergie d'activation pour la diffusion du baryum à haute température est 4,0 eV. Des modèles possibles pour la structure du défaut sont suggérés.

Abstract. — A consolidated review of work performed in our laboratory on SrO and BaO is presented. Various experiments have been conducted in order to elucidate the defect structure of these alkaline earth oxides. The various experiments do not all combine neatly to yield a clean model of the defect structure. The situation for SrO is clearer than that for BaO, however.

In SrO, it appears most likely that Schottky defects exist which are doubly ionized at elevated temperatures. At one atmosphere oxygen partial pressure, excess oxygen to the extent of a few tenths of a percent can be accommodated in the material. Our data are compatible with a Schottky defect formation energy of 3.7 eV. The activation energy for strontium diffusion at high temperature is 4.61 eV.

In BaO, a significant concentration of excess oxygen can be incorporated in the material at a pressure of one atmosphere of oxygen. This concentration can approach one atomic per cent. The enthalpy associated with this incorporated in the following reaction.



is equal to — 0.4 eV. For SrO by comparison the enthalpy of the same reaction is + 1.0 eV. In BaO the volume of the unit cell increases with added oxygen. From pressure dependence studies, the defects appear to be unionized. The activation energy for barium ion diffusion at high temperature is 4.0 eV. Possible models of the defect structure are suggested.

1. Introduction. — Over the past decades considerable research has been performed on the alkali halides. As a result of this theoretical and experimental work, there is a considerable degree of understanding of the defect structure of these materials. Our understanding of the defect structure of oxides on the other hand is in a more primitive state. Experiments are often more difficult to perform on oxides because of their relatively high melting temperatures. Furthermore there is no generally available source of pure crystals with which to work. On the theoretical side there are

many perplexing aspects which indicate that the Born model coupled with additivity principles may not be applicable to oxide materials [1].

The alkaline earth oxides which crystallize with the NaCl structure are the structural analogues of the alkali halides and in principal should be the simplest oxides to understand. The series is MgO, CaO, SrO and BaO. In this series the melting point decreases monotonically from 3 073 K for MgO to 2 196 K for BaO. The deduced ionic cation size increases through the series until for BaO, the cation and anion sizes are about equal. From an experimental point of view, the materials become more difficult to handle as

(*) This research was supported by the National Science Foundation.

one moves through the series. SrO and BaO are quite hygroscopic and reactive with crucible materials. BaO is extreme in this regard since at elevated temperatures it appears to react chemically with virtually everything. From a practical point of view, it becomes difficult if not impossible to conduct experiments above 1700 K. As a result of these problems, most past work has been concentrated on MgO and CaO. Comparatively little work has been performed on SrO and BaO. In addition the large cation size of BaO in particular results in the existence of large interstitial sites in the crystal which would give rise in principle to some interesting types of defect structures. For these reasons, it was decided some years ago to begin a program of research activity in our laboratory on SrO and BaO. This program has involved several Ph. D. students and has resulted in several publications [2], [3], [4], [5]. For actual experimental results and design of experiments, the reader is referred to these references.

2. General experimental program. — Generally speaking a series of experimental properties has been determined over a range of oxygen partial pressure from 10^{-5} atm to one atm and homologous temperature (T/T_{mp}) from 0.55 to 0.75. The experimental properties investigated were electrical conductivity, cation self-diffusion coefficient, thermogravimetric analysis, room-temperature lattice parameter for quenched crystals and anion-cation ratio. In addition Pai and Sivertsen in our laboratory are presently studying the elastic moduli of BaO and SrO as a function of defect concentration. Substantial effort was made earlier to study oxygen self-diffusion in SrO by the isotope exchange method. This effort failed because of sample reactivity problems.

3. Summary of results for SrO [2], [3], [6]. — Electrical conductivity was investigated for single crystal and sintered compacts of 90 % theoretical density. The results indicated that the conductivity was dependent upon the oxygen partial pressure and varied exponentially with temperature. Several discrete regions with different activation energies were obtained. At low temperature the activation energy was 0.5-0.6 eV whereas at higher temperatures the energy increased to 1.6 eV. At low oxygen partial pressures and high temperatures a 3.0 eV region was observed. At all temperatures studied the conductivity of sintered compacts increased with oxygen partial pressure according to the equation

$$\sigma = \sigma_0 p_{O_2}^{1/n} \text{ (atm)} . \quad (1)$$

The term n was found to be in the range 4-5.

Thermogravimetric work was also performed on sintered compacts. The weight change upon changing the oxygen partial pressure from 5×10^{-5} atm to one atm exhibited the standard exponential temperature dependence namely

$$\Delta W = C \exp(-E/kT) \quad (2)$$

where E was found to be 1.0 eV. From the TGA work, an excess oxygen concentration of about $10^{20}/\text{cm}^3$ could be deduced upon a change in oxygen partial pressure from 5×10^{-5} atm to one atm.

One noticeable inexplicable characteristic associated with these studies is the rapid rate at which oxygen moved in and out of the crystals upon decreasing or increasing suddenly the oxygen partial pressure. For example, if the partial pressure was suddenly changed at say 1600 K, the sample re-equilibrated to the new weight value within a period of 5 to 10 minutes. If it is assumed that oxygen must diffuse into or out of the sample, a high oxygen diffusivity in the region of 10^{-5} - 10^{-6} cm^2/s must exist.

Room temperature lattice parameter measurements were obtained for SrO powder samples quenched from elevated temperatures where they were equilibrated at various oxygen partial pressures. No effect of oxygen partial pressure could be observed and the lattice parameter for all samples was found to be 5.1600 ± 0.0005 Å.

Cation diffusion coefficients were obtained for single crystals as a function of oxygen partial pressure and temperature [3]. Two discrete temperature ranges were obtained. Between 1475 K and 1720 K, the diffusivity followed the relation

$$D = 4.48 \times 10^{-4} \exp(-2.76 \text{ eV}/kT) \text{ cm}^2/\text{s} \\ (p_{O_2} = 2 \times 10^{-5} \text{ atm}) . \quad (3)$$

Between 1720 K and 1873 K, the highest temperature studied

$$D = 2.52 \times 10^2 \exp(-4.61 \text{ eV}/kT) \text{ cm}^2/\text{s} \\ (p_{O_2} = 2 \times 10^{-5} \text{ atm}) . \quad (4)$$

At elevated temperature, D varied with oxygen partial pressure according to the relation

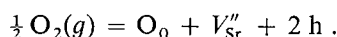
$$D \sim p_{O_2}^{1/n} \quad (5)$$

where $n = 6.2$. At lower temperatures, the dependence on oxygen partial pressure was absent.

Room temperature elastic constants are being obtained by Pai and Sivertsen on single crystal samples quenched from an elevated temperature. Values of C_{ij} are being obtained for samples near the stoichiometric composition and for crystals equilibrated at oxygen partial pressures of about one atm. The samples with excess oxygen are characterized by lower values of C_{ij} than samples closer to stoichiometry. For a crystal quenched from 1455 K under 0.95 atm of oxygen the values of C_{11} and C_{44} were lower by 1.7 % and 0.9 % respectively when compared with an as-grown crystal [6].

It is interesting at this point to examine the evidence provided as to the defect structure of SrO. The cation diffusion results are consistent with the existence of doubly ionized Schottky defects in SrO. According

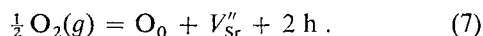
to this mechanism, excess oxygen is incorporated into the crystal according to a reaction of the type



The model of doubly ionized defects is compatible with the $1/6.2$ oxygen partial pressure dependence of D . The elastic constant data are also consistent with the existence of Schottky defects since the moduli would be expected to decrease upon the introduction of vacancies. According to this defect model, the high temperature diffusion region would be associated with intrinsically controlled defect concentration and the low temperature region would be associated with an impurity-controlled concentration of defects. The high temperature activity energy is accordingly given by

$$Q = \frac{\Delta H_{\text{defect}}}{3} + \Delta H_m \quad (6)$$

where ΔH_{defect} is the enthalpy associated with the reaction

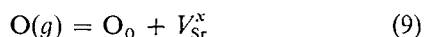


and ΔH_m is the activation enthalpy associated with the motion of a Sr cation into a neighboring vacancy.

The low temperature activation energy is given by

$$Q = \Delta H_m. \quad (8)$$

Appropriate substitution yields a value of the enthalpy associated with the formation of a neutral cation vacancy according to the relation



equal to about 2 eV. If one assumes for simplicity that the crystal is stoichiometric which of course is not true,

$$\Delta H_{\text{defect}} = \Delta H_s/2 \quad (10)$$

where ΔH_s is the Schottky defect formation energy. From our data ΔH_s is then calculated to be 3.7 eV. ΔH_m is equal to 2.8 eV.

The TGA and electrical conductivity results are not compatible with the numbers obtained from the diffusion experiments. Furthermore the large apparent diffusivity of oxygen into and out of the sample would tend to lend credence to an interstitial type mechanism for incorporation of excess oxygen. These results are compromised, however, by the fact that most of the resistivity work was done on sintered compacts and spurious results could have been obtained as a result.

4. Summary of results for BaO [4], [5]. — The results obtained for BaO contrast sharply with those for SrO. Thermogravimetric analysis of BaO powder obtained from decomposition of BaCO_3 indicate a significant absorption of oxygen into the crystal when the oxygen partial pressure is changed from 10^{-5} atm to one atm. For example at 1200 K, the sample weight increases by about 3 000 $\mu\text{g/g}$ when the oxygen

partial pressure is changed from 10^{-5} atm to one atm. Significantly the weight gain is proportional to $p_{\text{O}_2}^{1/2}$. Also it is interesting to note that the enthalpy change in equation

$$\left[\frac{\partial \Delta W}{\partial p_{\text{O}_2}^{1/2}} \right]_T = A \exp\left(-\frac{\Delta H}{kT}\right) \quad (11)$$

is equal to -0.40 eV. This enthalpy is presumably associated with the transfer of oxygen from the gas phase into the crystal and the reaction is exothermic instead of endothermic as is usually the case. The excess oxygen concentration in BaO may also be obtained directly from reaction of BaO with H_2O . The reaction yields a barium octahydrate and the oxygen excess is liberated as O_2 (gas) which may be collected. The excess oxygen concentration $[\text{O}_{\text{xs}}]$, determined in this way was determined for samples equilibrated at various elevated temperatures and was found to fit to the following type of equation

$$[\text{O}_{\text{xs}}]_{p_{\text{O}_2}=1\text{atm}} = A \exp(-\Delta H/kT). \quad (12)$$

The value of ΔH determined this way should in principle be the same as that obtained from the TGA analysis. The chemical reaction experimental data yielded a value of $\Delta H = -0.47$ eV which is in reasonable agreement with the TGA result of -0.40 eV.

The room temperature lattice parameter of BaO was found to vary significantly with amount of excess oxygen. For a sample annealed at 10^{-4} atm, the lattice parameter was equal to $5.5363 \text{ \AA}$ whereas at 0.7 atm the lattice parameter was equal to $5.5407 \text{ \AA}$. The volume of the unit cell was observed to vary linearly with $p_{\text{O}_2}^{1/2}$. This power dependence was the same as that observed from the TGA experiments. The experimental results indicate that about $3 \times 10^{20}/\text{cm}^3$ of excess oxygen was accommodated into the material and the unit cell expansion which accompanies this excess oxygen was about $0.5 \text{ \AA}^3$. The fact that both the weight gain and excess oxygen concentration are proportional to $p_{\text{O}_2}^{1/2}$ indicates that the defects formed are neutral in charge.

Cation self-diffusion measurements on single crystals yielded data which were similar in form to those for SrO. In the penetration plots, a near-surface region of about $30 \mu\text{m}$ existed in which the Ba activity decreased sharply. A more gradual decrease was then exhibited over a distance of $350 \mu\text{m}$. In analysing the data it was assumed that this narrow region was caused by the formation of a thin layer of some compounds such as hydroxide and that the data for the interior of the crystal represented true volume diffusion. When D values associated with these data were calculated and plotted as $\log D$ versus $1/T$, two regions were obtained as was the case for SrO. At high temperature (between 1470-1670 K) D was given by

$$D = 1.35 \times 10^4 \exp(-4.0 \text{ eV}/kT) \text{ cm}^2/\text{s}. \quad (13)$$

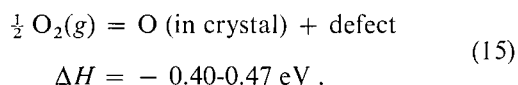
At low temperatures (1 220-1 370 K)

$$D = 1.2 \exp(-2.8 \text{ eV}/kT) \text{ cm}^2/\text{s}. \quad (14)$$

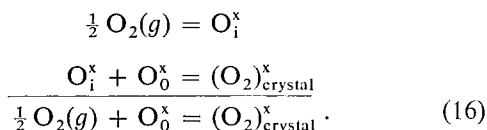
The data were found to be independent of oxygen partial pressure at all temperatures.

The various data for BaO do not combine simply to yield a model of the defect structure. If indeed the high temperature diffusion data represent an intrinsically controlled process, any ordinary defect model would predict a dependence of D in oxygen pressure. It might be tempting to conclude that the diffusion results were controlled by extrinsically controlled defects. This would explain the lack of dependence on oxygen partial pressure. On the other hand the TGA and lattice parameter data were obtained from samples treated in the same temperature region as the diffusion samples. They were characterized by significant changes in defect concentration. It is also possible that defects are intrinsically controlled but that diffusion occurs by some coupled mechanism which involves both Ba interstitials and Ba vacancies. Since the concentration of Ba_i^x would decrease linearly with $p_{\text{O}_2}^{1/2}$ whereas the concentration of V_{Ba}^x would increase linearly with $p_{\text{O}_2}^{1/2}$ the diffusion coefficient would be independent of oxygen partial pressure.

Another puzzling feature of both the TGA and chemical analysis results is the seemingly large tolerance of BaO for excess oxygen along with the negative enthalpy of incorporation. One expects normally to find a positive enthalpy although nothing, in principle, suggests that negative values are forbidden. The general reaction of interest is



One likely possibility for incorporation of excess oxygen is the formation O-O pairs in the crystals. Unlike the other alkaline earth oxides a stable peroxide, BaO_2 , exists in the Ba-O system. The tetragonal structure of BaO_2 is basically the same as that of BaO with tetragonal distortion to accommodate the formation of O-O pairs aligned in [100] directions. It seems possible that a principal mechanism of incorporation of excess oxygen in BaO is through the creation of O-O pairs. A possible reaction scheme is



Comparison of the unit cell dimensions of BaO_2 with BaO indicates that in BaO_2 a dilation of the BaO structure occurs in transforming to the BaO_2 structure and that the dilation is equivalent to $7.68 \text{ \AA}^3$ per O_2 pair. This agrees well with a value of $9.93 \text{ \AA}^3$ calculated from our direct excess oxygen measurements in conjunction with the lattice parameter work. Even if

excess oxygen is incorporated as O-O pairs according to the above reaction, D for Ba should vary with p_{O_2} if a vacancy mechanism for Ba diffusion is assumed and if the Ba vacancies are randomly distributed. This may be seen from the following relations

$$\text{nil} = \text{V}_{\text{Ba}}^x + \text{V}_0^x \quad K_1 = [\text{V}_{\text{Ba}}^x] [\text{V}_0^x] \quad (17)$$

$$\frac{1}{2} \text{O}_2(g) = \text{O}_i^x \quad K_2 = [\text{O}_i^x] / p_{\text{O}_2}^{1/2} \quad (18)$$

$$\text{O}_i^x + \text{O}_0^x = (\text{O}_2)_{\text{crystal}}^x \quad K_3 = \frac{[(\text{O}_2)_{\text{crystal}}^x]}{[\text{O}_i^x]} \quad (19)$$

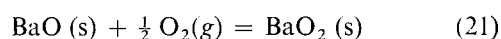
$$\text{O}_0^x = \text{O}_i^x + \text{V}_0^x \quad K_4 = [\text{V}_0^x][\text{O}_i^x]. \quad (20)$$

Upon appropriate substitution, one finds that

$$[\text{V}_{\text{Ba}}^x] \sim p_{\text{O}_2}^{1/2}$$

and then D_{Ba} should vary as $p_{\text{O}_2}^{1/2}$ if diffusion of barium occurs through a vacancy mechanism.

A possible explanation for the pressure independence of D_{Ba} would be the existence of microdomains of BaO_2 . If, for example, excess oxygen is not distributed randomly but instead is incorporated as clusters of BaO_2 , the remainder of the BaO could be essentially stoichiometric in composition. Diffusion of Ba through a vacancy mechanism would then be basically independent of oxygen partial pressure. Such a mechanism would account for the large excess concentration of oxygen permissible in BaO and could also account for the apparent negative reaction of oxygen incorporation since the enthalpy of formation of BaO_2 through the reaction



has been found to be negative [7].

No evidence exists for the existence of BaO_2 clusters, however, and such a proposal must be viewed as conjecture.

5. Comparison of results for alkaline earth oxides. —

A major problem in interpreting data for oxides is associated with the problem of impurities in the crystals. MgO has been examined by several investigators Harding and Price [8] recently studied diffusion in MgO and concluded that earlier work was dominated by controlled defects extrinsically. Their work was performed at elevated temperatures ($0.7 < T/T_{\text{mp}} < 0.8$) on pure crystals. From this work, it was deduced that the enthalpy of formation of Schottky defects in MgO is 3.8 eV and the enthalpy of motion of cations is 1.6 eV. The cation diffusion coefficient extrapolated to the melting point is $4 \times 10^{-7} \text{ cm}^2/\text{s}$. The activation energy for cation diffusion is 3.5 eV.

By comparison our results for SrO yields a high temperature activation energy of 4.6 eV. This would be associated with values of the enthalpy of Schottky defect formation and enthalpy of motion of 3.6 eV and 2.8 eV respectively. The diffusion coefficient

extrapolated to the melting point of $6.6 \times 10^{-7} \text{ cm}^2/\text{s}$ is close to that calculated for MgO.

For BaO, it is not reasonable to employ a simple Schottky mechanism for the sample studied. The cation self-diffusion coefficient extrapolated to the melting point is $7 \times 10^{-6} \text{ cm}^2/\text{s}$ which is an order of magnitude larger than the extrapolated values for MgO and SrO.

Examination of the values of activation energy and

enthalpy of motion for MgO, SrO and BaO in terms of phenomenological correlations such as dependence on melting point yields no simple relation as seems to be the case for alkali halides [9]. This lack of correlatability suggests either that the additivity rules which apply to alkali halides do not apply to oxides as suggested in reference 1 or that some of the data obtained for alkaline earth oxides are not characteristic of pure bulk material.

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DISCUSSION

F. BÉNIÈRE. — Are the diffusion coefficients as measured under oxygen pressure time dependent ?

R. A. SWALIN. — We have done a few studies in order to examine the time dependence of the diffusivity and D appears to be independent of the time of diffusion annealing. At the temperatures studied the samples appear to equilibrate with oxygen gas in a matter of minutes. The diffusion anneals on the other hand last for several days, generally.

L. W. HOBBS. — Have you looked for dislocations

in these materials after excess oxygen is absorbed ? One has here a situation like to that we have postulated in irradiated alkali halides where excess interstitial anions are accommodated by generation of Schottky pairs and nucleation of dislocation loops.

R. A. SWALIN. — No. It is an interesting idea and I hope someone does. We have looked at thin sections of SrO on electron microscope, but the material disintegrates slowly with accompanying generation of large voids. We assumed that oxygen was leaving the crystal and that vacancies generated formed voids.