JOURNAL OF SOLID STATE CHEMISTRY **26**, 17–25 (1978)

Diffusion of Point Defects Participating in Solid-Phase Chemical Reactions (Trap Diffusion): Demonstration for the $Ti^{3+} \rightarrow Ti^{4+}$ Transition in Corundum

E. M. AKUL'ONOK,* V. Ya. KHAIMOV-MAL'KOV,*
Yu. K. DANILEIKO,† A. A. MANENKOV,† V. S. NECHITAILO,† AND
T. P. LEBEDEVA‡

** Institute of Crystallography of the Academy of Sciences of the U.S.S.R., Moscow, U.S.S.R.,† Lebedev Physical Institute, Academy of Sciences of the U.S.S.R., Moscow, U.S.S.R., and ‡ Moscow State University, Moscow, U.S.S.R.*

Received December 1, 1977

A problem of trap diffusion, that is diffusion of point defects in crystals participating in a solid-phase chemical reaction with motionless impurity ions, is solved. Time dependences of the reaction-front displacement, X_f, and its steepness, $(\partial C/\partial X)_f$ are determined analytically for $N_0 \ll C_0$ and numerically for all relations of N_0 and C_0

$$X_f^2 = 2\frac{N_0}{C_0}Dt; \qquad \left(\frac{\partial C}{\partial X}\right)_f = 0.3C_0^{3/2}\left(\frac{g}{D}\right)^{1/2},$$

where C_0 and N_0 are the initial concentration of impurity and the equilibrium defect concentration, respectively, D is a diffusion coefficient, and g is a chemical reaction constant. Dependence of X_f vs C_0 and t is confirmed for oxygen annealing of corundum crystals doped with titanium which, reacting with the point defects, changes its valency. The data are obtained for dependence of displacement X_f upon partial oxygen pressure and thermotreatment temperature as well as upon the sign of the constant electric field applied to the sample. From these data we conclude that the reaction of titanium impurity, changing from the three-valent to the tetravalent state at the activation energy of 80 ± 8.5 kcal/mole is due to anisotropic diffusion of charged aluminum vacancy and holes in the valence band. The diffusion coefficient for that process at 1500°C is estimated to be larger than 10^{-5} cm^2/sec. Using the trap-diffusion features, the concentration of optical centers of the 0.315-μm absorption band in ruby is also estimated.

Introduction

Many theoretical and experimental investigations are devoted to the problems of point defect diffusion in crystals. In most of them, different mechanisms of diffusion are considered for self or impurity atoms under forces caused by concentration gradients and mechanical stress as well as under an electric field (*1–3*). At the same time, in many cases (say, in impurity crystals) a diffusion of the intrinsic defects can be accompanied by their participation in solid-phase chemical reactions. As a result of the chemical reaction, diffused defects can leave a diffusion process either by modification in the course of reaction or by forming stable motionless associates with the reacting impurity. Such a process may play an important role not only in specially doped crystals but in many other cases, since a concentration of uncontrollable impurities in crystals can be an order of magnitude or more than the

0022-4596/78/0261-0017$02.00/0

concentrations of intrinsic defects. A similar "trap diffusion" accompanied by chemical reaction of a diffusing component with fixed impurity can take place in crystal growth and in crystal thermotreatment as well.

The aim of the present paper is a detailed investigation of trap diffusion including the theoretical consideration of the trap effect and its experimental confirmation in the diffusion process. As an example of such a process we choose the diffusion from a crystal surface of aluminum vacancies and valence band holes in corundum crystals on thermal treatment in an oxygen atmosphere. This thermal treatment process, as has been shown earlier (*4*), resulted in oxidation of titanium impurities (the $Ti^{3+} \rightarrow Ti^{4+}$ transition).

In this paper we demonstrate that the study of trap diffusion can be used as a new approach to investigation of point defects and solid-phase chemical reactions, which allows us to determine rather easily the activation energy and its dependence on the partial pressure of surrounding gases. In addition, in an appropriate experiment such important parameters as the diffusion coefficient and the equilibrium concentration of most defects, as well as the constant of the defect-impurity chemical reaction, can be found independently.

I. Theoretical Consideration of Trap Diffusion

In contrast to the usual diffusion, we shall consider a diffusion of point defects reacting with motionless impurity ions. This reaction results not only in the impurity state changing but also in the defects leaving the initial diffusion process. A diffusion process involving a second-order chemical reaction can be described by a one-dimensional rate equation for the defect N and impurity c concentrations

$$\begin{aligned} \frac{\partial N}{\partial t} &= D\,\frac{\partial^2 N}{\partial x^2} - gNc, \\ \frac{\partial c}{\partial t} &= -gNc \end{aligned} \qquad (1)$$

under the initial and boundary conditions

$$t=0; \quad N=0, \quad c=C_0, \quad x>0,$$

$$x=0; \quad N=N_0, \quad t>0,$$

where C_0 is the initial impurity concentration, N_0 is the equilibrium concentration of point defects on the sample surface, and D is the diffusion coefficient in the X-direction.

The first equation of system (1) is the Fick equation taking into account the leaving of the diffusing defects during the reaction. The second is a kinetic equation of the second-order chemical reaction.

By introducing dimensionless values

$$y=\left(\frac{gC_0}{D}\right)^{1/2} x; \quad \tau = gN_0t; \quad \beta = \frac{N_0}{C_0};$$

$$u=\frac{c}{C_0}; \quad v=\frac{N}{N_0}$$

and proceeding to a new function $\varphi(y, \tau)$ so that

$$u = \exp(-\varphi); \qquad v = \frac{\partial\varphi}{\partial\tau}, \qquad (2)$$

system (1) can be reduced to a dimensionless equation

$$\beta\frac{\partial\varphi}{\partial\tau} = \frac{\partial^2\varphi}{\partial y^2} - (1-e^{-\varphi}) \qquad (3)$$

under the initial and boundary conditions

$$\tau=0; \quad \varphi=0, \quad \partial\varphi/\partial\tau=0, \quad y>0,$$

$$y=0, \varphi=\tau, \quad \tau>0. \qquad (4)$$

From Eqs. (3) and (4) it is evident that the solution for φ, and, hence, for u and v according to Eq. (2) is determined by the three independent parameters

$$gN_0; \quad N_0/C_0; \quad (gC_0/D)^{1/2}.$$

Note that parameters N_0, D, and g, which characterize the trap diffusion of point defects, are usually unknown and their determination is of great physical interest for the elucidation of the nature of point defects and of the character of their interactions with the impurity. In the diffusion experiments a directly measured value is the impurity concentration $c(x,t)$ for any time $t > 0$. For this reason it is necessary to clear up the dependence $c(x,t)$ vs the given values N_0, D, g.

In typically realized situations (say, in the case of point defect diffusion in corundum crystals activated by Ti^{3+} ions) parameter $\beta \ll 1$. This leads to the fact that the distribution of the impurity concentration depends mainly on the two parameters gN_0 and $(gC_0/D)^{1/2}$ including three independent values N_0, D, g, owing to which their separate definitions become possible only when the relative error in the definition of the distribution of the impurity concentration $c(x,t)$ does not exceed β. β can be found, for example, while investigating $c(x,t)$ near the solid boundary, according to the formula

$$\beta = \frac{\partial^2}{\partial y^2}(-\ln u)|_{y=0} - (1-u)|_{y=0}.$$

By measuring the β value in this way, one can find an equilibrium concentration of point defects N_0, and consequently, the D and g parameters from the dependence $c(x,t)$. When the relative error of the impurity concentration distribution $c(x,t)$ becomes greater than β an independent definition of the absolute parameter values N_0, D, and g according to $c(x,t)$ becomes impossible and requires additional experiments to find any of the above values. However, in the absence of additional experiments, the investigation of the distribution of impurity concentration has a definite meaning, since it makes it possible to measure relatively the parameters N_0, D, and g.

Parameter β may be found, while studying diffusion in the matrix with decreased impurity concentration C_0, to be larger than the accuracy of the experimental definition of $c(x,t)$. Thus, the value of β affects considerably the character of the trap diffusion proceeding and the possibility of determination of the N_0, D, and g parameters by the distribution of the impurity concentration $c(x,t)$.

Let us consider in detail the case which is more often realized in practice, where $\beta \ll 1$. A complete analytical solution of Eq. (3) in the case of Eq. (4) is very difficult. However, a number of characteristics of the trap diffusion process can be found without calculating $\varphi(y,\tau)$. Such a characteristic is the experimentally measured value of the reaction-front displacement of point defects with impurity (the reaction front is determined from $\varphi = 1$, which corresponds to a drop of impurity concentration by a factor of e) as well as in the reaction-front steepness equal to the tangent of the slope angle of the $c(x,t)$ distribution at an inflection, where

$$\frac{\partial^2 c}{\partial x^2} = 0.$$

Proceedings in Eq. (3) to an equivalent integration equation, one can demonstrate that the displacement of the chemical reaction front (X_f) at $\tau \gg 1$ has the form

$$X_f^2 = 2\frac{N_0}{C_0}Dt. \qquad (5)$$

As is seen from Eq. (5), the displacement of the chemical reaction front for point defects with impurity obeys the diffusion law having a coefficient of the reaction-front displacement D_f equal to

$$D_f = 2\frac{N_0}{C_0}D. \qquad (6)$$

This coefficient by its essence is considerably different from the diffusion coefficient of point defects D by the fact that D_f depends on N_0 and C_0 concentrations. In the literature, this fact has not been given proper consideration, and the D_f parameter has been identified with a diffusion coefficient D(*4*). The above experiments (see below, Section III) have shown that the reaction front is displaced according to the diffusion law (Eq. (6)), $D_f \sim C_0^{-1}$ and, thereby, the coefficient D_f is shown experimentally to differ considerably from D.

The system of Eq. (1) has also been calculated at different ratios of N_0 and C_0 concentrations. It turned out that at both $N_0 < C_0$ and $N_0 > C_0$ the chemical reaction front for

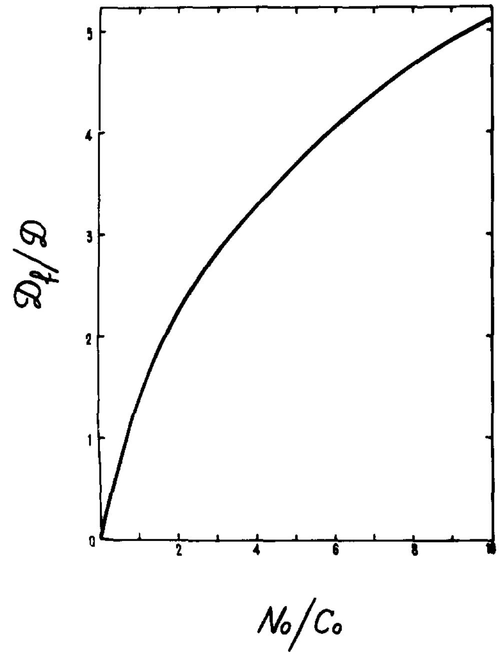

FIG. 1. Dependence of the reaction-front displacement coefficient on the ratio of equilibrium concentration of point defects to the initial impurity concentration.

point defects with impurity is displaced according to the diffusion law and the displacement coefficient of the reaction front has the form represented in Fig. 1. It is seen that at $N_0 \ll C_0$, $D_f \ll D$, and at $N_0 \gtrsim C_0$ the D_f coefficient can become greater than D, that is, owing to the chemical reaction proceeding on the "tail" of the distribution of the point-defect concentration in a solid volume. A possible definition of D and N_0 parameters in the study of D_f vs the impurity concentration is also seen from Fig. 1. In the region of $N_0 \ll C_0$ one could determine only the product of N_0D. Their separate measurements are possible only in the case when the C_0 concentration is so small that the difference of dependence $D_f \sim C_0^{-1}$ from the linear one, according to Eq. (6), can be fixed against the experimental errors. It actually corresponds to the case $C_0 \simeq N_0$. The results of analytical consideration and numerical calculations of the diffusion process for point defects reacting with impurity have shown that the reaction constant g can be calculated while measuring the reaction-front steepness at the inflection point ($\partial^2C/\partial x^2 = 0$). The front steepness at $\tau \gg 1$ turned out to vary slightly in its displacement, which is well illustrated by the curves of Fig. 2 at different values of the β parameter. With increasing β, the front steepness is seen to increase slightly, which can be explained easily from the analytical expression obtained from Eq. (3).

$$\left(\frac{\partial u}{\partial y}\right)_f \simeq 0.4(0.6 + \beta v|_{y=y_f})^{1/2}. \tag{7}$$

Proceeding in Eq. (7) to dimensional values at $\beta \ll 1$ we obtain

$$\left(\frac{\partial c}{\partial x}\right)_f \simeq 0.3C_0^{3/2}\left(\frac{g}{D}\right)^{1/2}. \tag{8}$$

Knowing C_0 and D from Eq. (8), one can estimate the constant of chemical reaction for point defects with impurity.

II. Experimental Methods

A diffusion of point defects reacting with impurity was investigated in corrundum crystals activated by titanium ions. Selection of this material is stipulated by the fact that at its thermotreatment in oxygen atmosphere one observes trivalent titanium ions oxidized to the tetravalent state (Ti^{4+}) (*4*). Besides, the regions with Ti^{3+} and Ti^{4+} have a well-distinguished boundary owing to Ti^{3+} absorption in the range of ~0.5 μm (*5*), which allows one to fix the displacement of the reaction front by optical methods.

In this work 16 × 12 × 6-mm samples were studied, whose optical axes are normal to the 16 × 12-mm side. The samples were grown both by the Verneil method and by horizontal crystallization in a molybdenum crucible. In the first case the density of basis dislocations was about 4×10^6 cm^{-2}, and in the second one, about 2×10^6 cm^{-2}. The total content of foreign impurities (excluding titanium) in the crystals grown by the Verneil method was about 1.5×10^{-3}%, but from the melt, about 1.5×10^{-2}%. The impurity content in samples

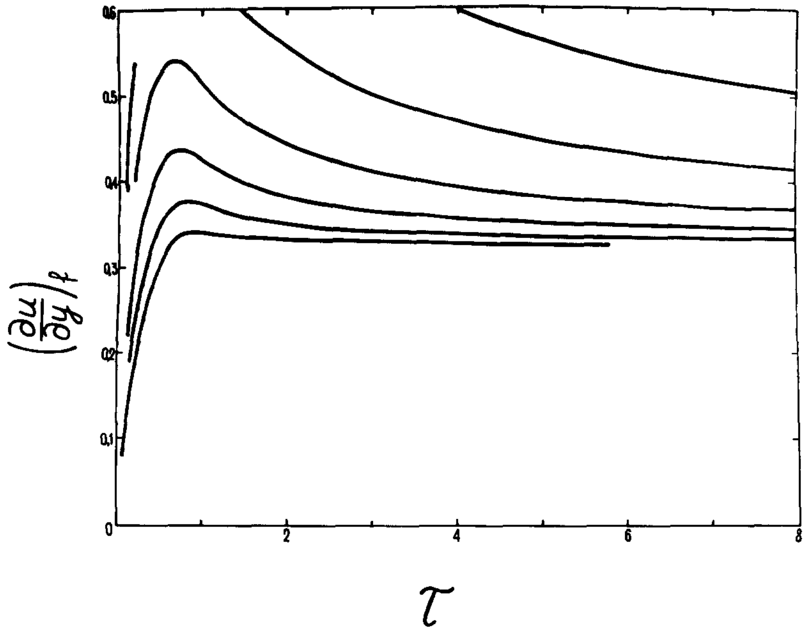

FIG. 2. Dependence of the reaction-front steepness on time at different parameter values β; for the curves from top to bottom $\beta = 0.1, 0.25, 0.5, 1, 2,$ and 4, respectively.

grown from the melt has been realized via increased content of iron (about $5 \times 10^{-3}\%$) and molybdenum (about $2.5 \times 10^{-3}\%$). The titanium content in the crystals varies from 4.10^{-3} to 2.3×10^{-2} in weight percent.

For the previous reduction of titanium impurity to the trivalent state the samples were thermotreated under vacuum (about 10^{-5} Torr) at 1800°C for 12 hr, which was enough for full conversion of the titanium impurity to the Ti^{3+} state in all the samples investigated. After annealing under vacuum the samples were placed in an oxygen furnace ($P_{O_2} = 1$ atm), whose temperature was controlled by a platinum–platinum–rhodium thermocouple in the sample location. After the allotted time of thermotreatment, the samples were taken out of the furnace. They were cooled and the distance was measured from the appropriate edge of the sample to the reaction front. Input and output times of the sample (only the temperature over 1000°C is taken into account) usually do not exceed 1–2% of the total time of thermotreatment and were always considered. A similar preliminary vacuum annealing was carried out when working out the temperature dependence of the reaction-front displacement at a fixed annealing time or dependence of the reaction-front displacement on partial oxygen pressure at a given temperature and time. In the last case, the furnace was blown off by a flux of helium and oxygen mixture. To make the mixture having small partial pressures of oxygen, we used helium with no more than $1 \times 10^{-4}\%$ oxygen. The reaction-front position was measured by scanning a narrow slit along the sample and by fixing the intensity of light passing through the crystal in the absorption band at about 0.493 μm. In such a case, the sample was placed in a special holder which was continuously moving in front of the photomultiplier slit (about 0.02 mm) whose signal was registered by a recorder. The sample was transilluminated by a monochromatic light beam ($\lambda = 0.5$ μm) with 4–8 angular minutes' divergence. The incident light was polarized to the extraordinary ray with greater absorption in the crystal. Because

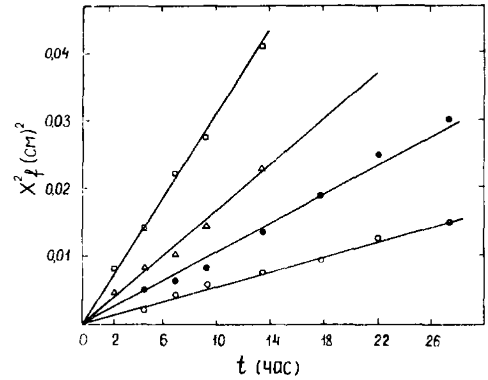

FIG. 3. Dependence of the square of the reaction-front displacement on the time of the crystal thermotreatment in an oxygen atmosphere; titanium contents in the samples: ○, 2.3 × 10^{-2}; ●, 1.13 × 10^{-2}; △, 0.72 × 10^{-2}; □, 0.4 × 10^{-2} wt%.

the reaction front in the diffusion process was not plane (because of the inhomogeneity of the titanium concentration) and its thickness did not exceed 5 × 10^{-2} cm, it was difficult to estimate the front steepness at scanning by narrow light beam. Therefore, all further measurements are referred only to the displacement of the reaction front. The experimental results were treated by the least-squares method.

III. Experimental Results and Discussion

Figure 3 represents the plots of the squares of the reaction-front displacement (X_f^2) depending on the time of treatment in an oxygen atmosphere for a sample with different initial weight concentrations of trivalent titanium—C_0. The oxygen pressure is 1 atm; annealing temperature, 1500°C. From the plots it is seen that dependences correspond to Eq. (5) for each concentration.

Qualitative dependence of the front displaced from the initial concentration of trivalent titanium can be observed from Fig. 4 which represents a sample with nonuniform titanium displacement after internal treatment in an oxygen atmosphere. From the photo, it is seen that trivalent titanium (dark regions) begins transforming into tetravalent (light regions) nonuniformly from the surface and more slowly in the regions with higher Ti^{3+} concentration (dark regions). Quantitative dependence of the reaction-front displacement on impurity concentration (see Fig. 5) can be obtained in Fig. 3 by calculating the tangents of the dip angles (D_f) for the straight line.

A linear character of this dependence corresponds to Eq. (6). The lower point of the straight line (Fig. 5) is taken from (*4*) for thermotreatment temperature of 1500°C. In

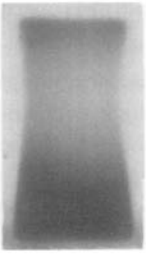

FIG. 4. Photo of a corundum crystal with nonuniform titanium impurity distribution after its thermotreatment in an oxygen atmosphere.

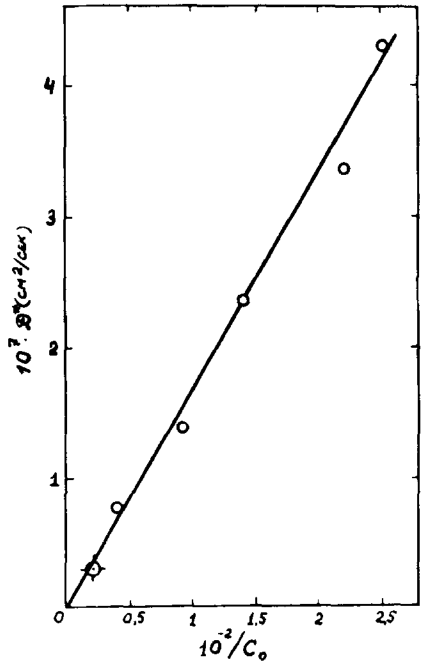

FIG. 5. Dependence of the coefficient of reaction-front displacement on the back value of the initial titanium concentration.

this work the samples were annealed in air; the titanium concentration was about 5 × 10^{-2} wt%, and the dislocation density was 10^{+5} cm^{-2}. The experimental results for the samples grown by various techniques with different chemical purities and dislocation densities indicate that the trap diffusion observed is proper.

Thus, the conformity of theoretically observed dependences points to the fact that the titanium oxidation process in corundum is determined by a trap-diffusion mechanism.

As mentioned above, the effect of trap diffusion can be used as a method of investigation of the proper diffusion process and solid chemical reactions. For example, at constant time and thermotreatment temperature the value of $X_f^2C_0$ for the present matrix will depend, according to Eq. (5), on the equilibrium defect concentration N_0. It makes it possible to judge by the X_f^2 value the change of dependence N_0, say, on the partial pressure of oxygen. In its turn, knowledge of this dependence allows one to fix the type of the equation of chemical reaction. Figure 6 represents the dependence $\sim\ln(X_fC_0^{1/2})$ on the logarithm of the partial oxygen pressure (P_{O_2}) at the temperature 1500°C. From the plot it follows that

$$(X_f^2C_0) \sim N_0 \sim P_{\mathrm{O}_2}^{(0.178\pm0.08)} \tag{9}$$

On the other hand N_0 vs P_{O_2} can be obtained directly from the equation of supposed solid-phase reactions. Naturally, the transformation of $\mathrm{Ti}^{3+}(\mathrm{Ti}_{\mathrm{Al}}^x)$ under thermotreating of the samples in an oxygen atmosphere can be explained as titanium oxidation in diffusion of aluminum vacancies (V_{Al}). In terms used by Kröger (*3*) one of the oxidation reactions in its detailed equilibrium can be represented in the form

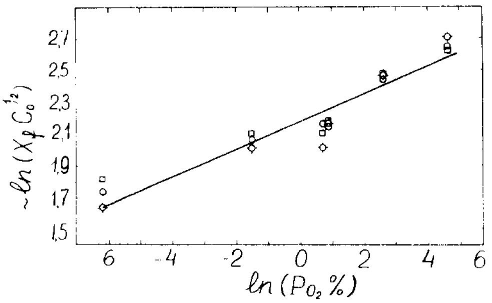

FIG. 6. Dependence of reaction-front displacement on the partial oxygen pressure while thermotreating the samples with different initial titanium concentrations.

$$\tfrac{1}{2}\mathrm{O}_2 \rightleftarrows \tfrac{2}{3}\mathrm{V}_{\mathrm{Al}}^x + \mathrm{O}_0^x, \tag{10}$$

$$\mathrm{V}_{\mathrm{Al}}^x \rightleftarrows \mathrm{V}_{\mathrm{Al}}^1 + h^1, \tag{11}$$

$$\mathrm{Ti}_{\mathrm{Al}}^x + h \rightleftarrows \mathrm{Ti}_{\mathrm{Al}}^{\bullet}. \tag{12}$$

From these equations, we see that the point defects directly oxidizing the titanium are the holes in the valence band h, and their concentration ($[h]$) is the value N_0. Using mass action and charge conservation laws from Eqs. (10) and (11), one can find that

$$[h] = K_1^{0.75}\,P_{\mathrm{O}_2}^{0.375} \tag{13}$$

where K_1 is the equilibrium constant. If we consider in Eq. (11) that the neutral vacancy ($\mathrm{V}_{\mathrm{Al}}^x$) decays not to single-charge ($\mathrm{V}_{\mathrm{Al}}^1$) but to a two- or three-charge vacancy, then for ($[h]$) we correspondingly obtain

$$[h] = 1.26K_2^{0.5}\,P_{\mathrm{O}_2}^{0.25} \tag{14}$$

and

$$[h] = 1.32\,K_3{}^{0.375}\,P_{\mathrm{O}_2}^{0.188}. \tag{15}$$

Comparing the degree dependences Eqs. (13), (14), and (15) obtained with the experimental dependences, one may conclude that titanium is oxidized with the diffusion of a triply charged aluminum vacancy.

Using laws of trap diffusion, one can also obtain the absolute impurity concentrations. Two different impurities of the same matrix are used to react with the same point defects. Then, from Eq. (5), knowing the absolute concentration of impurity (C_1), one may determine it in terms of the other (C_2) according to the formula

$$C_2 = X_1^2C_1/X_2^2, \tag{16}$$

where X_1 is the reaction-front position in a crystal with the first impurity, and X_2, in a crystal with the second impurity.

Concentration of centers with typical absorption in the range of 0.315 μm (*6*) has been estimated similarly for ruby crystals. These centers are formed on crystal annealing under vacuum and disappear in annealing in oxygen atmosphere (*7*). The conducted experiments have shown that oxygen annealing for these centers proceeds according to the laws of trap diffusion. From Eq. (16) it follows that thermotreatment under vacuum results in the appearance of the above-mentioned centers with a concentration of about 7.10^{-4} atm% (chromium concentration in ruby is about 5×10^{-2}). This estimation refers to a fixed sample, since the concentration of the centers observed is a structurally sensitive value.

Attention must be given to the temperature dependence of the reaction-front displacement. If in the ordinary vacancy diffusion a similar dependence makes it possible to estimate directly an enthalpy of vacancy displacement then, in this case, it is necessary to consider also an enthalpy of their formation. Naturally, the temperature dependence of X_f according to Eq. (5) will be determined by dependences of $D(T)$ and $N_0(T) \sim K(T)$, which are usually of an exponential character. If we assume that in the case of titanium oxidation N_0, according to Eq. (15), is proportional to $K_3^{3/8}$, then from the temperature dependence X_f (see Fig. 7) it follows that the energy of activation (80 ± 8.5 kcal/mole) is equal to ($\frac{3}{8} H_d + H_m$) where H_m is the enthalpy of defect displacement and H_d is the enthalpy of their formation.

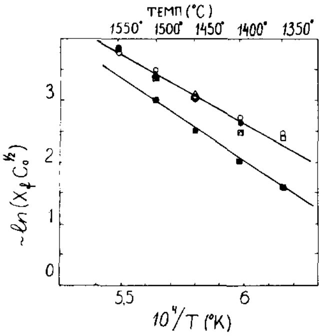

FIG. 7. Dependence of the logarithm of the reaction-front displacement on the back temperature at the treatment of the samples with the initial titanium contents: ○, 2.3×10^{-2}; ●, 1.13×10^{-2}; △, 0.72×10^{-2}; □,■, 0.4×10^{-4} w%, ■, in contrast to the others, refers to diffusion directed normally to the optical crystal axis.

As mentioned in the cases considered, separate determinations of parameters N_0, D, and g are difficult. However, these parameters can be estimated. Since the rule of trap diffusion and their concentration $\sim 7 \times 10^{-4}$ atm% is true for the color centers in ruby crystals, it follows from $\beta \ll 1$ that $N_0 \lesssim 10^{-4}$ atm% and $D \gtrsim 4 \times 10^{-5}$ cm^2 sec^{-1}. If we compare this estimation of D with the corresponding values of the self-diffusion coefficient of oxygen, 4×10^{-15}–4×10^{-14} cm^2 sec^{-1} (*8*), or aluminum, $\sim 10^{-12}$ cm^2 sec^{-1} (*9*), it becomes evident that the present process is not determined by the intrinsic ion diffusion. As mentioned, this process is not sensitive either, as identical results were produced for crystals grown by three different techniques, differing in content of foreign impurities and in dislocation density by an order of magnitude. Taking into consideration the above-mentioned information as well as the data on dependence of the reaction-front displacement on partial oxygen pressure, one can consider that the diffusion studied is determined by vacancy diffusion on aluminum with the holes in the valence band accompanying them. The fact that the vacancies and holes are separated spatially follows not only from the data on the degree dependence of oxygen partial pressure (Eq. (15)) but from the experiment on trap diffusion in a constant electric field. Figure 8 represents a photo of a sample on whose thermotreatment (12 hr in an oxygen atmosphere at 1500°C) the voltage of

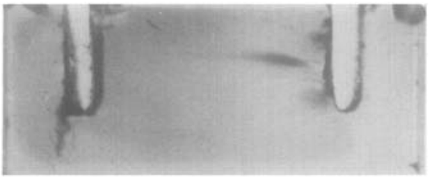

FIG. 8. Crystal photo after its thermotreatment in an oxygen atmosphere in a constant electrical field.

300 + 700 V was fed in platinum electrodes pressed into sample slots. From the photo, it is seen that the velocity of the reaction front of the transition $Ti^{3+} \rightarrow T^{4+}$ (light framing) displaced to the side of the positive electrodes is definitely larger then at the other sides. As in all the experiments above, the annealing of the present sample in vacuum reduces the initial valency of titanium without its redistribution; i.e., titanium electrolysis is not observed. From this it follows that diffusion of the negatively charged point defect (aluminum vacancy) is a "bottleneck" of the solid-phase reaction observed.

Conclusion

The theoretical analysis has shown that the diffusion process of point defects in impurity crystals is strongly affected by a chemical reaction of the defects with the motionless impurity. In this combined diffusion–reaction process the reaction-front displacement follows the diffusion law characteristic whose parameter is smaller by many orders of magnitude than the diffusion coefficient for defects.

Thermal treatment of titanium-doped corundum crystals in an oxygen atmosphere has been found to be subject to the trap diffusion characteristics. Careful measurements for the $T^{3+} \rightarrow T^{4+}$ transition-front displacement as a function of initial impurity concentration, partial oxygen pressure, temperature, and sign of the applied electric field have allowed us to determine a mechanism and the main properties of this solid-phase reaction. In particular, it has been shown that the $Ti^{3+} \rightarrow Ti^{4+}$ reaction occurring at an activation energy of (80 ± 8.5) kcal/mole is determined by anisotropic diffusion of spatially separated aluminum vacancy-hole associates. The diffusion coefficient of such an associate at the temperature of about 1500°C is larger than 10^{-5} cm^2 sec^{-1}. The concentration of impurity centers in ruby responsible for optical absorption at 0.315 μm has also been estimated: at a chromium concentration of 5×10^{-2}%, it was about 7×10^{-4}%.

Acknowledgments

The authors are greatful to K. P. Malakhova, L. N. Pashkovskaya, A. T. Kalachiov, and V. A. Pavlov for sample preparation and help in conducting the experiments.

References

1. J. R. MANNING, "Diffusion Kinetics for Atoms in Crystals," Van Nostrand, Princeton, N.J.,/Toronto (1968).
2. K. HAUFFE, "Reaktionen in und an festen Stoffen," Springer-Verlag, Berlin/Göttingen/Heidelberg (1953).
3. F. A. KRÖGER, "The Chemistry of Imperfect Crystals," North–Holland, Amsterdam (1964).
4. T. P. JONES, R. L. COBLE, AND C. J. MOGAB, *J. Amer. Ceram. Soc.* **52**, 331 (1969).
5. D. S. MCCLURE, *J. Chem. Phys.* **36**, 2757 (1962).
6. S. V. GRUM-GRZHIMYLO, L. B. PASTERNAK, D. T. SVIRIDOV, L. G. CHENTSOVA, AND M. A. CHERNYSHOVA, *in* "Spectroskopiya cristallov" (Proc. Materialy Simposiuma, Moscow, February 3–6, 1965), Nauka, Moscow (1966).
7. D. V. SANDREYEV, P. A. ARSENYEV, Z. G. MAREYEVA, A. A. MAYER, R. N. TOLCHISKY, AND V. L. FARSCHTENDIKER, *Kristall und Technik* **8**, 957 (1973).
8. Y. OSHI AND W. D. KINGERY, *J. Chem. Phys.* **33**, 480 (1960).
9. A. E. PALADINO AND W. D. KINGERY, *J. Chem. Phys.* **33**, 957 (1962).