

Interdiffusion under pressure in KBr–KCl single-crystals system

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Dependences of diffusion coefficients on pressure in the range from 1 to 6000 atm and at temperatures 450, 500, and 550°C in KBr and KCl single crystals were investigated by technique of sintering the compacts from KBr and KCl single crystals powder mixtures in the ratios providing 50 % KBr–KCl solid solution. Studying the kinetics of the solid solution formation was carried out by measuring the X-ray diffraction {200} intensity maxima depending on annealing time for the pure components. The obtained diffusion coefficient versus pressure dependences under the above-mentioned conditions indicate the observed diffusion coefficient decrease with increasing pressure (within this range) being caused by decreasing the equilibrium vacancies concentration under pressure.

Keywords: diffusion coefficient, alkali halide single crystals, powder sintering, pressure.

Исследована зависимость коэффициентов диффузии в монокристаллах KBr и KCl от давления в диапазоне (1–6000) атм и температурах 450, 500 и 550°C методом спекания порошковых прессовок из смеси порошков монокристаллов KBr и KCl в соотношении, дающем 50 %-ный твердый раствор KBr–KCl. Наблюдение кинетики формирования твердого раствора проводилось по измерению зависимости интенсивности дифракционных рентгеновских максимумов для чистых компонент типа {200} от времени отжига. Найден характер зависимости коэффициентов диффузии от давления при данных условиях, который указывает на то, что наблюдаемое уменьшение коэффициентов диффузии с ростом давления (в указанном диапазоне давлений) обусловлено уменьшением под давлением равновесной концентрации вакансий.

Взаємна дифузія під тиском у системі монокристалів KBr–KCl. *В.Г.Кононенко, В.В.Богданов, М.А.Волосюк, А.В.Волосюк.*

Досліджено залежність коефіцієнтів дифузії у монокристалах KBr і KCl від тиску в діапазоні (1–6000) атм і температурах 450, 500 і 550°C методом спікання порошкових пресувань з суміші порошків монокристалів KBr і KCl у співвідношенні, що дає 50 %-ий твердий розчин KBr–KCl. Спостереження кінетики формування твердого розчину проводилося за вимірюванням залежності інтенсивності дифракційних рентгенівських максимумів для чистих компонент типу {200} від часу відпалу. Знайдено характер залежності коефіцієнтів дифузії від тиску за даних умов, який указує на те, що зменшення коефіцієнтів дифузії що спостерігається із зростанням тиску (у вказаному діапазоні тиску) обумовлене зменшенням під тиском рівноважної концентрації вакансій.

1. Introduction

Materials obtained by powder sintering using ceramic crystal technology, powder metallurgy, and nano-technologies are widely applied [1–3]. In these technologies, the sintering processes are usually carried out at high temperatures and under high pressures. These are controlled by diffusion and plastic deformation processes.

Atomic thermal mobility induced by energy local fluctuations is the fundamental substance property which causes transport phenomena including diffusion determining various processes of influence on strength and durability of materials at any temperature [4–8]; the diffusion is in the basis of technologies for principally new materials production-nano-materials, amorphised metals, graphene, and hydrogen as fuel [9–13]. For determining the diffusion parameters under different conditions, besides experimental ones, the methods of molecular dynamics are widely used [14–19].

The objective of our work is studying the effect of hydrostatic compression on the diffusion mechanism and diffusion coefficient value in alkali halide (AH) single crystals KBr and KCl. The single crystals of this type are widely applied in laser, fiber optic, scintillation and other technologies; their working conditions by temperature and pressure being in the very broad range from the very low to the very high values close to the limit of material existing without destruction. At that the AH single crystals are convenient model objects.

2. Experimental

For solution of the mentioned problem, diffusion homogenization process of compact from 50 % mixture of KBr and KCl single crystal powders has been used. The system KBr–KCl forms a continuous series of solid solutions stable in the whole temperature range. The solid solution lattice parameter varies linearly from the value of pure KBr to the pure KCl one, i.e. is subjected to the Vegard rule.

Kinetics of interdiffusion through the boundary between contiguous powder particles of KBr and KCl single crystals was observed under varying the hydrostatic compression pressure and temperature. During the process, there took place the homogenization of the compact with formation of the 50 % KBr–KCl solid solution on account of diffusion counterblows of $\text{Br}^{(-)}$ anions into

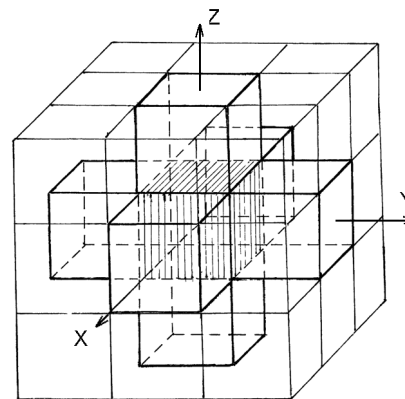


Fig. 1. Idealized calculation scheme of packing the powder particles as KBr and KCl single crystal cubic blocks alternating along X, Y, and Z axes and forming the spatial "chess board".

the KCl single crystal, and anions $\text{Cl}^{(-)}$ into the KBr one.

The experimental procedure was as follows. The KBr and KCl single crystals grown by the Kyropoulos method from the chemically pure raw material were taken in equal proportion, i.e. by 50 atomic percents of each type, fractioned, and in common (for better mixing) thoroughly grinded in a porcelain mortar to homogeneous state. The obtained mixture consisted of the powder particles with nearly cubic shape and the similar sizes (about 50 μm). This is connected with the fact that KBr and KCl single crystals possess both the cubic symmetry and isotropy of physical properties, while the surface energy of $\{100\}$ crystallographic planes has a sharp minimum in comparison with other planes. Thus, the crystals of alkali metal halides of NaCl type split easy by $\{100\}$ crystallographic planes.

The interdiffusion process is considered in the geometry of an idealized scheme (Fig. 1) where each powder particle is a cubic shape single crystal of A or B sort. At equal quantities of the both sorts of the particles and under ideal mixing, it can be assumed that each particle of the one sort is surrounded by six particles of another sort contacting by $\{100\}$ faces. The interdiffusion process takes place through the plane faces and, finally, the compact of KBr–KCl 50 % solid solution forms.

In connection with high absorbability of the single crystals (especially KBr), before compression of the samples, each portion of the powder mixture was annealed in the vacuum chamber [20] at $T = 300^\circ\text{C}$ directly in the mould without applying pressure dur-

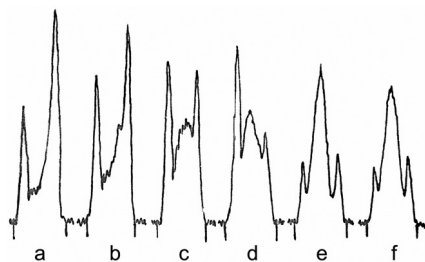


Fig. 2. Diffraction patterns obtained from the compacts of non-dehydrated powder mixtures compressed under different pressures, P , atm: a — 50, b — 200, c — 500, d — 1000, e — 2000, f — 5000. Temperature $T = 23^\circ\text{C}$; pressing time $t = 3$ min. Side maxima are (200) diffraction reflections from the pure components, the average maximum belongs to KBr–KCl 50 % solid solution.

ing 3 minutes, then the working pressure was applied, the chamber was heated to the working temperature and hold during the set time for diffusion annealing. The preliminary short annealing of the powder without applied pressure was necessary for dehydration of the powder surface from atmospheric moisture.

In the preliminary experiments it was established that if the non-dehydrated powder was compressed, then under pressure even at the room temperature ($T = 23^\circ\text{C}$) the homogenization process took place during short time interval (3 min.), the KBr–KCl 50 % solid solution formed, and the characteristic average maximum appeared in the diffraction pattern (Fig. 2).

From Fig. 2 it is seen that under these conditions, significant portion of the powder mixture quickly transforms into the solid solution state; the higher is the pressure, the more solid solution forms. Under pressure near 2000 atm., increasing of the formed solid solution quantity with pressure stops. This fact is apparently connected with depletion of water quantity adsorbed by the powder.

During the preliminary experiments, the minimum temperature ($T = 300^\circ\text{C}$) and the annealing time (≈ 3 min) were select so as the solid solution did not yet form, but moisture was removed.

The diffusion homogenization of the compacts was controlled by intensity variations of (200) diffraction lines from the KBr powder particles (angle $13^\circ30'$) and KCl (angle $14^\circ10'$). All measurements were carried out using X-ray diffractometer URS-50-IM with a copper anode, $\lambda_{\text{K}\alpha}\text{Cu} = 1.539 \text{ \AA}$. The homogenization process was

found to be slightly different on the surface and in the bulk; obviously that was connected with adsorption of some water on the surface of the compacts. For obtaining the reliable information about the diffusion processes within the compact bulk, its surface layer (about 1 mm depth) was removed by grinding after annealing before the X-ray diffraction studying.

By intensity variations of the selected (200) line for pure KBr and KCl depending on the diffusion annealing time, the features of the diffusion homogenization process can be established and diffusion coefficients calculated. The whole complex of measurements of the KBr and KCl (200) line intensities during homogenization of the powder particles mixture was realized at the following regimes: temperatures 550°C , 500°C , and 450°C ; annealing times at all temperatures and pressures $t = 0.5$ h, 1 h, 2 h, 3 h, 4 h, and 6 h; pressures $P = 1$ atm. and $(1, 2, 4, 6) \cdot 10^3$ atm. (at $T = 550^\circ\text{C}$); $P = 1$ atm. and $4 \cdot 10^3$ atm. (at $T = 450^\circ\text{C}$ and $T = 500^\circ\text{C}$).

3. Results and discussion

Results of measurements of KBr and KCl (200) diffraction line intensities depending on the diffusion annealing time t at temperature $T = 550^\circ\text{C}$ and under different pressures P are shown in Fig. 3a, b. It is seen from the figure, that homogenization process slows down as the pressure increases that is, obviously, connected with decreasing the diffusion coefficient under pressure increasing. Similar data have been obtained also at temperatures $T = 500^\circ\text{C}$ and 450°C . From comparison of the data it follows that temperature decreasing results in weakening the pressure influence on the diffusion coefficient.

By idealizing the situation, we consider the powder particles as KBr and KCl single-crystalline cube blocks alternating by three mutually perpendicular directions (along x , y , and z axes) (Fig. 1) forming the spatial "chess board". Such approach is conventional enough, because the cubes may have arbitrary orientation, not the same sizes, and not always regular alternation. However, taking into account that selected single crystals have cubic symmetry and isotropy of physical properties including bulk diffusion, and for calculation simplification we consider the chosen scheme justified.

If to solve the diffusion problem for such systems of cubes, then by comparing the calculation and experimental results it

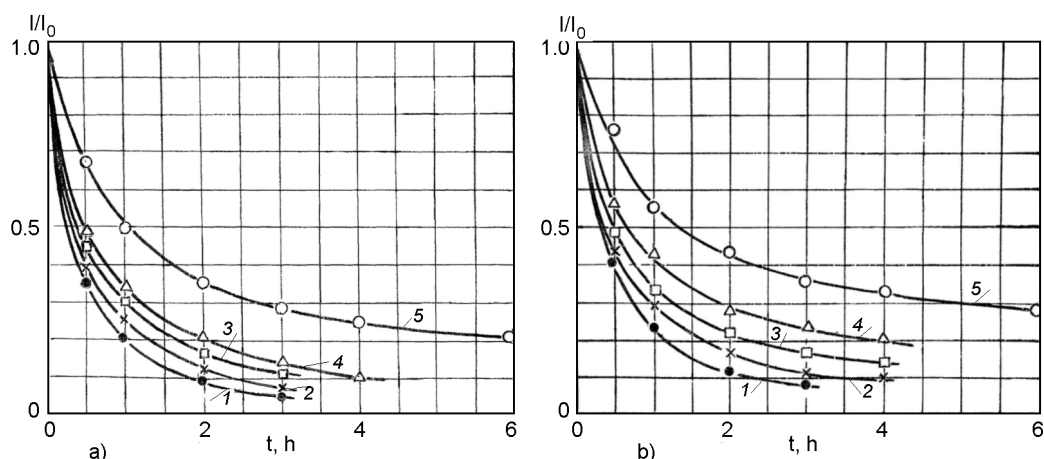


Fig. 3. X-ray diffraction line relative intensities depending on the diffusion annealing time: a) for KBr (200) line; b) for KCl (200) line at temperature $T = 550^{\circ}\text{C}$ and pressures P , atm: \bullet — 1, 2 — 1000, 3 — 2000, 4 — 4000, 5 — 6000.

could be possible, in principle, to determine diffusion coefficients controlling the diffusion homogenization process. The problem solution, on the one hand, is enough complex and cumbersome; on the other hand, if we are interested only in the effect of hydrostatic compression on the diffusion coefficient, we can limit ourselves by analysis of only the beginning stage of homogenization process, where the interaction of diffusion flows through different faces of an individual cube is yet small and negligible. Therefore, we apply the known solution of the problem on the diffusion through flat boundary into the infinite semi-space. From the solution it follows that the diffusion front of equal concentrations moves from the contact plane according to the equation [21, 22]:

$$x = \sqrt{Dt}, \tag{1}$$

where x is the diffusion front coordinate in the moment t (annealing time), D is diffusion coefficient. If size of the cubic crystals is a , the solution would be right in the case $x \ll a/2$.

A unit of volume of the compact contains $1/2 \cdot a^3$ KBr and KCl single crystals (particles). Intensity of the X-ray reflected signal depends on volumes of the pure components of KBr and KCl single crystals "caught the eye" of X-ray. Density of the particles (the number of particles in the volume unit) does not change with annealing, but volume of the pure phase in one particle changes: before annealing it is proportional to a^3 , while after annealing during t it being proportional to $(a - 2\sqrt{Dt})^3$. Therefore, intensity of the maximum in the t moment will be

$$I = \alpha(a - 2\sqrt{Dt})^3, \tag{2}$$

where α is proportionality factor (the experimental constant) taking into account also the number of particles got into the X-ray beam cross-section. The ratio of the maxima intensities after annealing, I , and before annealing, I_0 , will be

$$\frac{I}{I_0} = \frac{(a - 2\sqrt{Dt})^3}{a^3}. \tag{3}$$

Thus, relation (3) is the equation for the curves families shown in Fig. 3a and 3b, their parameters being diffusion coefficients in the KBr and KCl single crystals. So, the plots $(I/I_0)^{1/3}$ versus $t^{1/2}$ at different P would be linear, and by the angle of their slope it is possible to determine diffusion coefficients at corresponding P and T values by the equation:

$$D = \frac{a^2}{4} \left\{ \frac{d[(I/I_0)^{1/3}]}{d[t^{1/2}]} \right\}^2. \tag{4}$$

For $T = 550^{\circ}\text{C}$ these dependences are shown in Fig. 4a and 4b.

Similar dependences have been plotted also by the annealing results at $T = 500^{\circ}\text{C}$ and $T = 450^{\circ}\text{C}$, and pressures $P = 1$ atm. and $P = 4 \cdot 10^3$ atm.

Data on the diffusion coefficients in KBr and KCl single crystals at temperatures 550°C , 500°C and 450°C were calculated using plots of 4a and 4b type figures and equation (4), and tabulated in Table 1.

It is seen from Figs. 4a and 4b that as the pressure increases, the slopes of linear

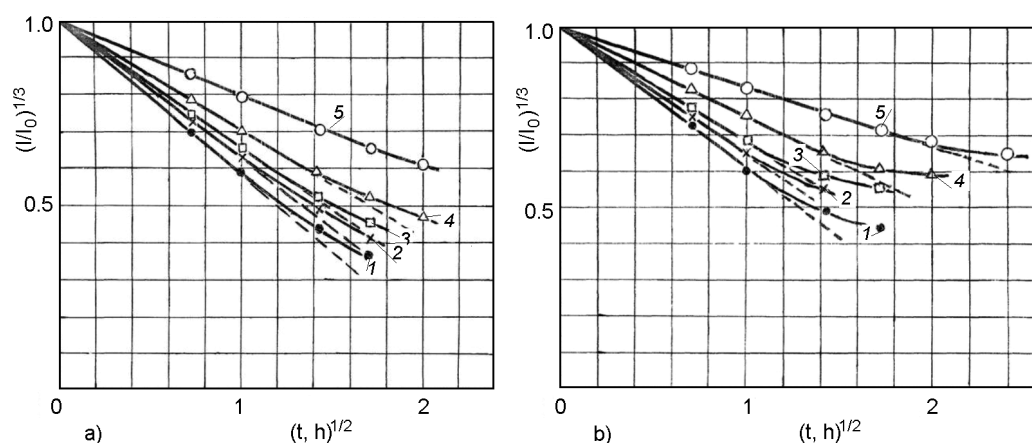


Fig. 4. Dependences $(I/I_0)^{1/3}$ versus $(t, \text{hours})^{1/2}$ for (a) KBr and (b) KCl (200) diffraction lines after annealing at $T = 550^\circ\text{C}$ under pressures P , atm: 1— 1, 2— 1000, 3— 2000, 4— 4000, 5— 6000.

Table 1. Diffusion coefficients in KBr and KCl single crystals

$T, ^\circ\text{C}$	Single crystal	Diffusion coefficients $D, 10^{-10} \text{ cm}^2/\text{s}$ under pressures P_{atm} and $P, 10^3 \text{ atm}$				
		P_{atm}	$P = 1$	$P = 2$	$P = 4$	$P = 6$
550	KBr	2.980	2.300	1.87	1.490	0.734
	KCl	2.680	2.127	1.794	1.085	0.510
500	KBr	0.646			0.409	
	KCl	0.554			0.287	
450	KBr	0.354			0.227	
	KCl	0.229			0.160	

Table 2. Interdiffusion coefficients in KBr and KCl single crystals

$T, ^\circ\text{C}$	Interdiffusion coefficients $D_{rel}, 10^{-10} \text{ cm}^2/\text{s}$ in KBr–KCl system under pressures P_{atm} and $P, 10^3 \text{ atm}$				
	P_{atm}	$P = 1$	$P = 2$	$P = 4$	$P = 6$
450	2.822	2.21	1.831	1.256	0.602
500	0.596			0.337	
550	0.278			0.188	

parts of the plots decrease which signifies decreasing the diffusion coefficient (see Table 1).

For practical purposes, e.g., for estimation of the formation time for the compact of homogeneous solid solution KBr–KCl, the interdiffusion coefficient D_{rel} is introduced by relation $D_{rel} = 2D_1D_2/(D_1 + D_2)$. Data on are given in Table 2.

In ionic crystals, the vacancy diffusion mechanism prevails, and the expression for diffusion coefficient in the pure ionic crystals can be written as [23]:

$$D = a_0^2 v \cdot \exp[-(\Delta F_v + 2\Delta F_m)/2kT], \quad (5)$$

where a_0 is lattice parameter; v is frequency at which atoms transit into new positions from the saddle point (its precise determination is difficult, therefore usually v is accepted equal to the Debye frequency [20]); ΔF_v is free energy need for formation of one pair of vacancies (anion and cation); ΔF_m is free energy for formation of activated complex (in connection with local variation of

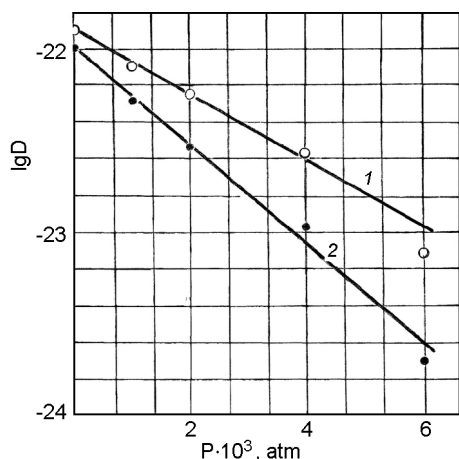


Fig. 5. Dependences $\ln D$ versus P obtained in experiments with $T = 550^\circ\text{C}$: 1 — for KBr single crystal; 2 — for KCl single crystal.

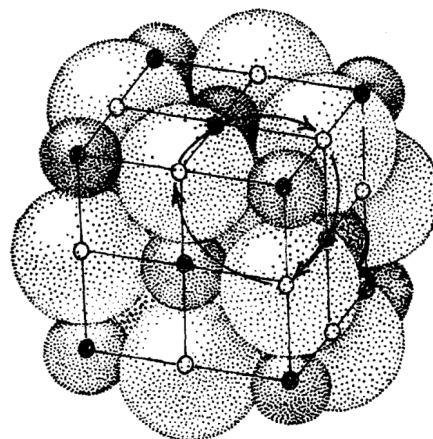


Fig. 6. Specifics of mutual arrangement of ions in NaCl-type ionic crystal: • — cations, ○ — anions; arrows indicate possible rotation of the ion group in planes parallel to $\{111\}$.

atomic and electron configuration), need for realization of each elemental diffusion act. Taking into account that in the isothermal process: $dF = -PdV$, the relation (5) is written as:

$$D = a_0^2 v \cdot \exp\left[-(\Delta V_v + 2\Delta V_m)P/2kT\right] = a_0^2 v \cdot \exp[-\Delta V_a P/2kT], \quad (6)$$

where P is pressure; ΔV_v is vacancy volume depending on the degree of relaxation of atoms surrounding the vacancy; ΔV_m is the volume of the activated complex, the value small enough comparing with volume \bar{V} per an atom (so, in gold [20], e.g., $\Delta V_m = 0.15\bar{V}$); the value $\Delta V_a = \Delta V_v + 2\Delta V_m$ is called the activation volume of transitional state.

From equations (5) and (6) it is seen that the first exponential factor in these relations determines the vacancy concentration at given temperature T and its dependence on pressure P .

According to (6) the plot $\ln(D)$ versus P should be a linear function as:

$$\ln D = \ln a_0^2 v - \Delta V_a P/2kT. \quad (7)$$

Using the data from Table 1 on the diffusion coefficients in the KBr and KCl single crystals at temperature 550°C and pressures from 1 atm. to $6 \cdot 10^3$ atm. the dependences $\ln(D)$ versus P were plotted and shown in Fig. 5.

The dependences $\ln D$ versus P are found to be close to linear. That means, in the studied pressure range, decreasing the diffusion coefficient is related indeed only with dropping vacancy concentration under

pressure (the first exponential factor in Eq. (5)). It is clear from physical point of view. Really, decreasing the free energy of the crystal under pressure can be achieved by reducing its volume by closure of the part of vacancies, i.e. dropping their concentration.

Differentiating equation (7) by pressure P , we obtain

$$\left. \frac{\partial \ln D}{\partial P} \right|_T = -\frac{\Delta V_a}{2kT}. \quad (8)$$

We use data of Fig. 5 and Eqs. (7), (8) for obtaining the values of activation volume ΔV_a under anions diffusion in the KBr and KCl single crystals. For the KBr single crystal, $\Delta V_a = 4.15 \cdot 10^{-29} \text{ m}^3$, while for KCl — $\Delta V_a = 6.43 \cdot 10^{-29} \text{ m}^3$. The volume of a unit cell per a molecule in the single crystals is following: for KBr, $\Delta V_m = 7.18 \cdot 10^{-29} \text{ m}^3$, and for KCl, $\Delta V_m = 6.23 \cdot 10^{-29} \text{ m}^3$.

Taking into consideration atomic radii for Br ($r_1 = 1.95 \text{ \AA}$), Cl ($r_2 = 1.81 \text{ \AA}$), and K ($r_3 = 1.33 \text{ \AA}$), we see that the anions occupy the largest part of the volume (about 60 ÷ 70 %) per one molecule in the crystalline lattice. The obtained value $\Delta V_a = 4.15 \cdot 10^{-29} \text{ m}^3$ for the KBr single crystal is practically similar to the volume of the anion vacancy having the value about $4.5 \cdot 10^{-29} \text{ m}^3$. In the KCl single crystal, the volume ΔV_a is found to be larger than the anion vacancy volume $3.86 \cdot 10^{-29} \text{ m}^3$. In order to explain this fact, let us specify the circumstances complicating the diffusion act in KCl in com-

parison with KBr. So, for the KBr single crystal, the experimental temperature is $0.819 T_m$ (550°C), while for KCl — this being $0.788 T_m$, i.e. somewhat lower, resulting in decreasing the fluctuations energy and their efficiency. Additionally, difference of the atomic radii between the anion and the cation in KBr single crystal is substantially larger than in KCl; so, there are more free space in KBr having the larger lattice parameter (as it is seen from Fig. 6), the fact facilitates an elementary diffusion act, that means the activation volume decreases.

More detailed analysis of the problem requires solution of a difficult quantum-mechanical task on the interaction of electron shells of the metal and halide ions in the ion crystal under pressure. From the experiments and calculations of [23] it follows that as the external pressure increases to more than hundreds of thousands atmospheres, there grows noticeably and quickly the potential barrier which an atom must overcome for going out of the lattice site. For this reason, we observe increasing the melting temperature, sharp dropping the vacancy concentration practically to zero (under pressures of hundreds of thousands and millions atmospheres). At that the vacancy mechanism of diffusion almost ceases, only the diffusion acts like collective rotations of atomic groups remain possible. In Fig. 6, for example, the possible fluctuation rotation of three anions within planes parallel to $\{111\}$ planes is shown. In this case, obviously, the linear behavior of $\ln D$ versus P plots will be broken.

The similar transition from individual jumps of atoms to collective moving of a number of atoms, sometimes, it is observed also under temperature variations [17].

4. Conclusions

The method has been presented for studying the interdiffusion kinetics in single crystals of KBr and KCl and for determination of diffusion coefficients in the components by using sintering the compacts of powder mixtures of the KBr and KCl single crystals in the ratio providing KBr–KCl 50 % solid solution, and by registration of evolution of X-ray diffraction $\{200\}$ peaks for pure components under different conditions of sintering: pressures from 1 to 6000 atmospheres and temperatures 450, 500, and 550°C .

The data have been obtained on the diffusion coefficients in the KBr and KCl single crystals under abovementioned experimental conditions, and it has been shown that in the range of the applied pressures, the diffusion coefficients decreasing is caused by reducing the vacancy concentration with pressure increasing. This is caused by the fact that in the alkali halide single crystals, the vacancy mechanism of diffusion dominates.

References

1. V.V.Skorokhod, *Poroshkova Metallurgia*, **9/10**, 42 (2014).
2. R.A.Andrijevsky, *Usp.Khim.*, **84**, 540 (2015).
3. R.A.Andrijevsky, *Usp.Fiz.Nauk*, **184**, 1017 (2014).
4. O.L.Khasanov, A.S.Dvilis, Z.G.Bakbayeva, *Methods for Compacting and Consolidation of Nano-Structural Materials and Products*, Tomsk Polytechnical University, Tomsk (2008) [in Russian].
5. P.A.Glebovsky, Yu.V.Petrov, *Phys.Solids*, **46**, 1021 (2004).
6. A.I.Slutsker, *Phys.Solids*, **46**, 1606 (2004).
7. A.I.Slutsker, *Phys.Solids*, **47**, 777 (2005).
8. V.L.Gilyarov, *Phys.Solids*, **47**, 808 (2005).
9. M.B.Belonenko, N.G.Lebedev, S.A.Sudorgin, *Zh.Tekhn.Fiz.*, **82**, 129 (2012).
10. Yu.M.Baykov, *Phys.Solids*, **52**, 1908 (2010).
11. A.V.Gapontsev, V.V.Kondratjev, *Usp.Fiz.Nauk*, **173**, 1107 (2003).
12. A.L.Bychkov, S.M.Korobeynikov, A.Yu.Ryzhkina, *Zh.Tekhn.Fiz.*, **81**, 106 (2011).
13. N.M.Vlasov, V.A.Zaznoba, *J.Techn.Phys.*, **79**, 49 (2009).
14. A.Yu.Kuksin, D.E.Smirnova, *Phys.Solids*, **56**, 1166 (2014).
15. Y.L.Jeyachandran, S.Venkatachalam, B.Karunakaran et al., *Mater.Sci.Eng.*, **27**, 35 (2007).
16. G.M.Poletayev, M.D.Starostenkov, *Phys.Solids*, **52**, 1075 (2010).
17. V.V.Alekseyenko, *Phys.Solids*, **50**, 1775 (2008).
18. E.G.Kharina, M.D.Starostenkov, G.M.Poletayev, R.Yu.Rakitin, *Phys.Solids*, **53**, 980 (2011).
19. Yu.I.Ustinovschikov, *Usp.Fiz.Nauk*, **184**, 723 (2014).
20. P.Shewmon, *Diffusion in Solids*, Metallurgia, Moscow (1966).
21. V.V.Bogdanov, *Diffusion in Crystals*, Kharkov National University named by V.Karazin, Kharkov (2006) [in Russian].
22. M.A.Volosyuk, A.V.Volosyuk, N.Ya.Rokhmanov, *Functional Materials*, **22**, 51 (2015).
23. Ya.B.Zeldovich, Yu.P.Raizer, *Physics of Blast Waves and High-Temperature Hydrodynamic Phenomena*, Nauka, Moscow (1966) [in Russian].