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Cation Distribution and Interatomic Interactions in Oxides with Heterovalent Isomorphism: IV.[1] Temperature Dependence of Short-Order Parameters in the $YCaAlO_4$ Oxide

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Abstract—The degree of local ordering of Y^{3+} and Ca^{2+} cations in the stoichiometric $YCaAlO_4$ oxide was studied as a function of annealing temperature. The modulation of the Laue scattering background on the X-ray diffractograms of samples subjected to long-term calcination at 900, 110, 1300, and 1500°C was measured. The positive short-range ordering of Y^{3+} and Ca^{2+} decreases with increasing temperature. The temperature dependence of the degree of ordering is in a sufficiently good agreement with the results of calculations in the quasichemical approximation.

The short-range or positional ordering of cations in the structures of inorganic compounds with heterovalent stoichiometric isomorphism of atoms can efficiently decrease the probability of positively or negatively charged equilibrium composition fluctuations in crystal. Our previous data [1–3] on the short-range ordering of the isomorphous Ln^{3+} and Ca^{2+} cations in complex aluminates $LnCaAlO_4$ (Ln = Y, La, Nd, Gd, Ho, Er, Yb) led us to assume that La^{3+} and Ca^{2+} form stable at low temperatures cation pairs by filling neighboring square base–shared nine-coordinate oxygen polyhedra (Fig. 1). The degree of ordering was shown to depend both on effective cationic charges and on the number of unpaired *f* electrons in the lanthanide atom. The main result of the above studies was that the concept of disordered distribution of isomorphous atoms in crystal was replaced by the concept of disordered distribution of cation pairs, which refined the crystal-chemical model of oxides.

Here we report the results of studies on the dependence of the degree of short-range ordering of Y^{3+} and Ca^{2+} in the structure of the most stable oxide $YCaAlO_4$ on annealing temperature (900–1500°C). We studied polycrystalline samples of $YCaAlO_4$, prepared by conventional ceramic procedure as ~0.5-g pellets [1]. They were successively calcined for 100 h at 1500, 1300, and 1100°C, and for 150 h at 900°C, and then quenched at room temperature on a heavy brass plate. Complete cooling of the samples took several minutes. We believe that the distribution of isomorphous cations in the samples treated in such a way corresponds to the equilibrium distribution at the annealing temperature.

As in [1], we studied the short-range ordering of Y and Ca atoms in the approximation of the first nine cation coordination spheres. The lengths of the r_i vectors and the corresponding coordination numbers are given in Table 1. The closeness of r_1–r_3 and r_4–r_5 allows us to restrict our consideration to two combined spheres with the average radii $R_I = (r_1 + 4r_2 + 4r_3)/9$ and $R_{II} = (4r_4 + 4r_5)/8$ and to the coordination numbers 9 and 8. The short-range ordering factors are defined as $\alpha_i = 1 - P_{YCa}/C_{Ca}$, where P_{YCa} is the probability to find a Ca atom in the *i*th coordination

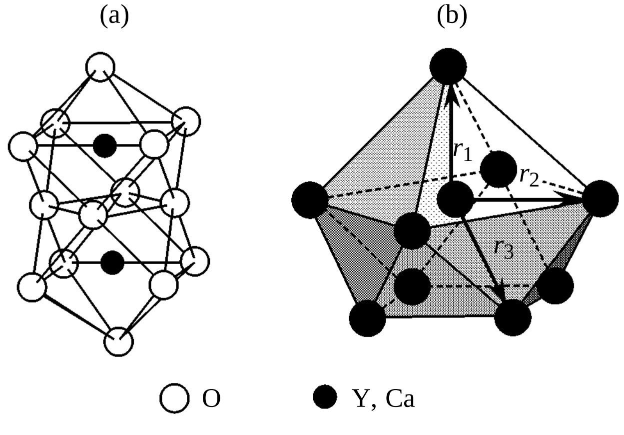

Fig. 1. Coordination polyhedra in the $YCaAlO_4$ oxide. (a) Oxygen surrounding of the Y^{3+}–Ca^{2+} cation pair in neighboring shared single-cap antiprisms and (b) vector radii in the first combined cation sphere.

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[1] For communication III, see [1].

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Table 1. Short-range ordering parameters α_i within two combined cation coordination spheres (radii R_I and R_{II}), rms deviations σ, and probabilities P_{YCa} for the $YCaAlO_4$ oxide as functions of annealing temperature

Temperature, °C	α_I	α_{II}	σ, %	$P_{YCa}(R_I)$	$P_{YCa}(r_I)$
900	–0.085	–0.076	3.6	0.542	0.883
1100	–0.080	–0.059	1.7	0.540	0.860
1300	–0.072	–0.046	1.6	0.536	0.824
1500	–0.065	–0.043	2.7	0.533	0.793

sphere of an Y atom, and $C_{Ca} = (1 - C_Y) = 0.5$ is the average concentration of Ca atoms in the compound ($\alpha_I > 0$ corresponds to a negative short-range ordering, i.e., short-range stratification, at $\alpha_I < 0$, a positive short-range ordering takes place, when contacts of different atoms are preferred).

In the approxomation of two coordination spheres and with regard to shifts of atoms in the first coordination sphere, the intensity of Laue background in electron units [4] is described by Eq. (1):

$$I_L = NC_YC_{Ca}(f_Y - f_{Ca})^2 \left\{1 + 9\alpha_I \frac{\sin(SR_I)}{SR_I} + 8\alpha_{II}\frac{\sin(SR_{II})}{SR_{II}} + 9\beta_I\left[\frac{\sin(SR_I)}{SR_I} - \cos(SR_I)\right]\right\}. \quad (1)$$

Here I_L is the intensity of Laue background; N is the number of pairs of the isomorphous Y and Ca atoms; C_Y, C_{Ca}, f_Y, and f_{Ca} are the concentrations and atomic amplitudes of Y and Ca; β_I is the shift parameter; $S = 4\pi\sin\theta/\lambda$ is the diffraction vector modulus; 2θ is the scattering angle; and $\lambda = 1.54$ Å is the wavelength of CuK_α X-ray radiation. For ordered arrangement of Y and Ca atoms the angular dependence of I_L oscillates about $(f_Y - f_{Ca})^2$, and in Eq. (1) the modulation is described by term (2):

$$\Sigma = 9\alpha_I\frac{\sin(SR_I)}{SR_I} + 8\alpha_{II}\frac{\sin(SR_{II})}{SR_{II}} + 9\beta_I\left[\frac{\sin(SR_I)}{SR_I} - \cos(SR_I)\right]. \quad (2)$$

The angular dependences of the experimental Σ value in the range $9° \le 2\theta \le 24°$ for samples subjected to long-term calcination at four temperatures are given in Fig. 2. The short-range ordering parameters α_I and α_{II}, obtained by fitting the calculated Σ to experimental over the entire angular range of measurements, are given in Table 1. These values show that over the entire experimental temperature range there is a positive short-range ordering of the isomorphous yttrium and calcium cations, namely, preferable contacts of unlike atoms. As temperature increases, the degree of ordering decreases but the probabilities of contacts of unlike atoms P_{YCa} always exceed the mean statistical value of 0.5. If we assume, as in [3], that the ordering by electrostatic interactions is the most efficient at the shortest r_1 distances, then the corresponding $P_{YCa}(r_I)$ values are greater than C_{Ca} by a factor of more than 1.5 (Table 1). In spite of the fact that the $P_{YCa}(r_I)$ values obtained under the above assumption may be slightly overestimated, we consider them to give

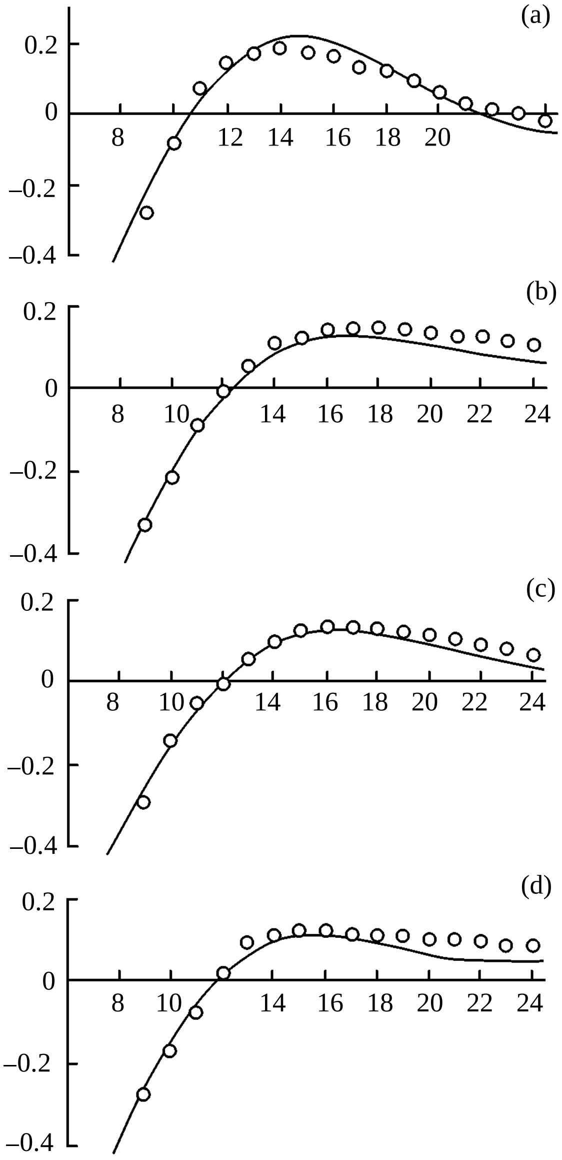

Fig. 2. Experimental and (solid line) calculated angular dependences of the modulating component Σ for the $YCaAlO_4$ oxide calcined at various temperatures. Temperature, °C: (a) 900, (b) 1100, (c) 1300, and (d) 1500.

Table 2. Interatomic distances in the first coordination sphere (Σ) for the $YCaAlO_4$ oxide at room temperature and 1000°C

Interatomic distance (Y,Ca)–(Y,Ca)	25°C		1000°C [5]
	[6]	[5]	
$1\times r_1$	3.368	3.376	3.435
$4\times r_2$	3.645	3.643	3.675
$4\times r_3$	3.640	3.631	3.665
$9\times R_I$	3.612	3.608	3.644

evidence for the real existence in the crystal of electrostatically linked pairs, which decreases the probability of formation of structural clusters with volume charges.

The fact that the degree of ordering decreases with increasing temperature is consistent with the data of Archaimbault *et al.* [5] who measured interatomic distances in $YCaAlO_4$ at room temperature and at 1000°C [5]. According to data in [5, 6] (Table 2), the most strongly lengthened on thermal expansion is the cation–cation distance r_1 which characterizes stability of the mixed-cation pair. Consequently, as temperature increases, the probability of contacts between unlike atoms decreases at all the distances, the greatest decrease corresponding to r_1.

The ordering of Y and Ca atoms results from different energies of interactions of homo- and heterocation pairs: Y–Y, Ca–Ca, and Y–Ca. The relationship between short-range ordering parameters and energy characteristics of ordering can be considered within the quasichemical approximation. In this case, only pair interactions of the nearest atoms are taken into account. The energies of these interactions are taken as parameters independent of temperature and of the local surrounding of the atoms. The main parameter is the interchange energy (the energy of replacement of 1 mol of heterocation pairs by 1 mol of homocation), $w = (U_{YY} + U_{CaCa})/2 - U_{YCa}$, where U_{ij} is the interaction energy of the *i*th and *j*th atoms. Within the limits of this approximation [4], Eq. (3) is valid.

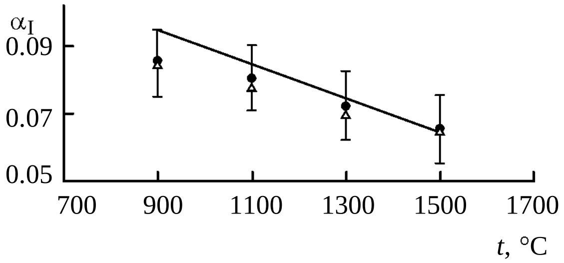

Fig. 3. Short-range ordering parameters α_I (circles) calculated from experimental data, (solid line) estimated in the quasichemical approximation, and (triangles) estimated with regard to the entropy factor.

$$\frac{\alpha_I}{(1-\alpha_I)^2} = C_Y C_{Ca}[e^{-2\omega/kT} - 1]. \qquad (3)$$

Using the interchange energy w of 1920 J/mol calculated for 1500°C by Eq. (3), we estimated α_I parameters for the other annealing temperatures. As seen from Fig. 3, the calculated data fairly fit the temperature dependence of the order parameters, calculated by Eq. (2). The observed discrepancy is associated with the known simplifications of the quasichemical approximation. The convergence can be improved by taking into account that the interchange energy is not an intrinsic but a free energy, i.e., $w = \Delta U - T\Delta S$. With regard to the entropy factor, a good convergence (Fig. 3) can be achieved at the following optimal values: ΔU 1210 J/mol and ΔS –0.4 J mol^{-1} K^{-1}.

Studies of segregation or ordering of isomorphous atoms in substitution solid solutions [4] showed that above the binodal in the single-phase region of the phase diagram these processes are often preceded by negative or positive short-range ordering, respectively, enhanced with decreasing temperature. In such cases it is appropriate to consider the short-range ordering as a precursor of the composition submicroheterogeneities arising on decomposition of the solutions and later developing into the final nucleation of equilibrium phases. From this point of view, compounds $LnCaAlO_4$ can be considered as analogs of equimolar solid solutions with an upper critical mixing point t_{cr} (for compounds this is the critical stability point). Then the fact that the degree of order in $YCaAlO_4$ increases with decreasing temperature points to metastability of the oxide, i.e., to its tendency to decomposition or transfer into another structural state. However, no decomposition is observed in this case, probably, by kinetic reasons or, more specifically, because of the low diffuse stability of linked Y–Ca cation pair at temperatures below 900°C. This conclusion is consistent with the results of our studies on the short-range ordering and decomposition of another oxide of the same series, $LaCaAlO_4$ [7–9]. The latter has a much higher t_{cr} than $YCaAlO_4$, i.e., above 1400°C, since $LaCaAlO_4$ intensively decomposes to $LaAlO_3$ and CaO in the range 800–1400°C. The reverse process, formation of the complex aluminate from the decomposition products, occurs only at $t >$ 1800°C. According to data in [9], the degree of ordering in $LaCaAlO_4$ obtained by the floating-zone method is higher than the degree of ordering in

$YCaAlO_4$ even at the lowest annealing temperature. In $LaCaAlO_4$, there is already an orientational ordering of heterocation pairs, resulting in enrichment of perovskite-like lattices close to {113} in the crystal structure by the same atoms. As the compound decomposes, these lattices develop into the final $LaAlO_3$ nuclei. Below 700°C we observed neither appreciable decomposition of $LaCaAlO_4$ nor aging effects in a single crystal stored at room temperature for more than fifteen years. These observables we also explain by the low diffusion mobility of La–Ca pairs.

We thus can conclude that in the $YCaAlO_4$ oxide a short-range ordering of isomorphous cations takes place. As the annealing temperature decreases, the degree of ordering increases. This suggests metastability of the compound at low temperatures ($t_{cr} <$ 900°C). Here, like in $LaCaAlO_4$, electrostatically linked cation pairs are formed from yttrium and calcium located in neighboring base-shared oxygen antiprisms. As a rule, in high-melting oxides the diffusion mobility of atoms is low. In $YCaAlO_4$ it is even lower due to pair formation, and this “stabilizes” the structure at low temperatures. It is this property which makes compounds with heterovalent stoichiometric isomorphism of atoms significantly different from substitution solid solutions.

EXPERIMENTAL

The intensity of Laue background was measured in a vacuum chamber on a DRON-3 X-ray diffractometer by the Bragg–Brentano scheme with monochromatization of reflected beam. Scattering measurements, introduction of corrections, and calculation of short-range ordering parameters α_I and α_{II} were performed as described in [1].

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