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Cation Distribution and Interatomic Interactions in Oxides with Heterovalent Isomorphism: IX.[1] Complex Perovskites $A_2BB'O_6$ (A = Sr, Ba; B = Fe, Cr; B' = Nb, Ta)

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Abstract—A high degree of local order in the arrangement of isomorphous cations with a 3D character of ordering was found experimentally in complex stoichiometric oxides crystallizing in a random perovskite structure.

The structure of $A_2BB'O_6$ compounds which belong to the class of complex (double) perovskites can be presented in the form of apex-shared oxygen octahedra. Cations B and B' occupy centers of these octahedra between which cations A are located. It is accepted that the B^{3+} and B^{5+} cations occupy one common correct point system in disordered perovskites. In ordered structures, B^{3+} and B^{5+} are in neighboring positions of the first cationic coordination sphere. For years such compounds have attracted researcher's attention owing to their ferroelectric and piezoelectric properties [2].

We earlier revealed short-range orders of different types and degrees in the arrangement of isomorphous cations in stoichiometric layered oxides $LnCaAlO_4$ and $LnCaAl_3O_7$ (Ln is lanthanide) [3, 4], rutile-like oxides $AlSbO_4$, $CrSbO_4$, and $CrNbO_4$ [5, 6], and in $LiFeO_2$ (NaCl structural type) [6]. In the case of $LnCaAlO_4$ and $LnCaAl_3O_7$ in which there is the strongest anisotropy of the cationic environment of Ln^{3+} and Ca^+ (one cation in the first coordination sphere), mixed-cation Ln^{3+}–Ca^+ pairs electrostatically bound through an oxygen plane arise. They equiprobably occupy points of one common structural position. The probability of such pairing was 60–100%. In $AlSbO_4$, $CrSbO_4$, $CrNbO_4$, and $LiFeO_4$ we discovered almost fully ordered microdomains formed owing to the greater difference in the effective charges of cations with absolutely identical oxygen environments, which cannot equally compensate for the different charges of the cations. In the case of equiprobable distribution of cations, size distribution of positively or negatively charged structural clusters enriched by cations of the same type should exist. Therewith, strongly extended charged clusters may arise in the structure, which contradicts the electroneutrality of the crystal as a whole. Hence, at least the first cationic coordination sphere of the cation should include a cation with another charge. In the following we imply cationic coordination spheres, unless otherwise specified in the text.

In the present work we studied cation ordering in structures with isotropic distribution of differently charged cations over coordination spheres. We chose "disordered" complex perovskites Sr_2CrNbO_6, $Sr_2Cr\cdot TaO_6$, Sr_2FeNbO_6, Sr_2FeTaO_6, Ba_2FeTaO_6, and Ba_2FeNbO_6 as objects of study [7–11]. The formation of cation pairs, like in the layered oxides $LnCaAlO_4$ and $LnCaAl_3O_7$, is impossible in this case, because six equidistant cations are present in the first coordination sphere. Therefore, another type of ordering should be realized. Unlike the rutile-like oxides $AlSbO_4$, $CrSbO_4$, $CrNbO_4$, and $LiFeO_2$, where the difference in the formal charges of isomorphous cations, too, is two units, in the oxides in hand neighboring isomorphous cations are intervened by only one oxygen anion, rather than two or more. It is necessary to note that *d* elements whose atom occupy the same structural position can be in different oxidation states and, consequently, a significant charge redistribution between cations B and B' is probable. In particular, Bokov *et al.* [12] estimated the effective charges of the iron and niobium cations in Pb_2FeNbO_6 at +2.47 and +3.20, respectively.

According to published data, neighboring oxygen

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

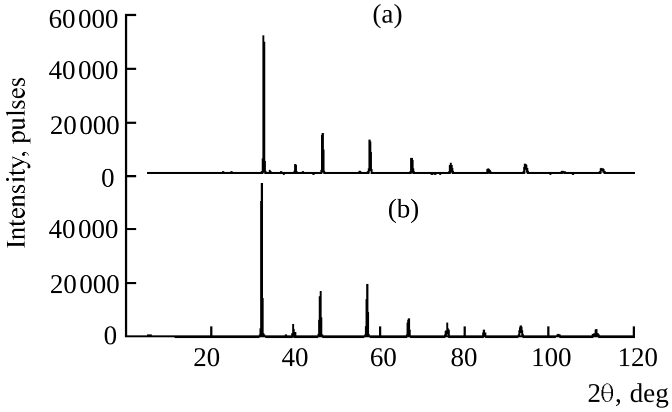

Fig. 1. X-ray diffraction patterns of (a) Sr_2CrNbO_6 and (b) Ba_2FeNbO_6. 2θ is scattering angle.

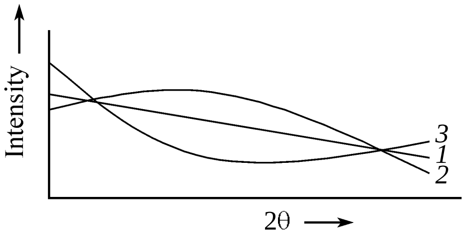

Fig. 2. Intensity of diffuse scattering in the (*1*) absence of ordering, (*2*) presence of short-range order, and (*3*) presence of short-range sheeting.

octahedra in fully ordered perovskite-like complex oxides containing B(III) and B'(V) cations are populated by differently charged cations [7–12]. Therewith, the crystal structure may remain cubic with a doubled unit cell parameter (8-fold increased volume) or acquire a tetragonal or trigonal distortion. Ordered and disordered perovskites $A_2BB'O_6$ and the probabilities of order–disorder transitions as a function of the ionicity and the difference in the ionic radii of cations B and B' have been considered in [12–14]. The authors hold the viewpoint that electrostatic interactions between isomorphous cations are the main reason for the ordering, while the difference in ionic radii is of secondary importance.

We synthesized six compounds from the $A_2BB'O_6$ series (A = Sr, Ba; B = Fe, Cr; B' = Nb, Ta), including all the four possible compounds with strontium and two with barium (Ba_2FeTaO_6 and Ba_2FeNbO_6). In all the cases, the X-ray diffraction data (the X-ray patterns for Sr_2CrNbO_6 and Ba_2FeNbO_6 are presented in Fig. 1) were identical to known structural data for compounds with disordered cation distributions in the crystal structures (perovskite structure, cubic symmetry, and space group *Pm*3*m*).

As before [3–6], the presence or absence of ordering of isomorphous atoms in the perovskite-like oxides under study was deduced from an analysis of the Laue background intensity, i.e. of diffuse X-ray scattering beyond Bragg structural maxima. The measurements were carried out in the $8° \le 2θ° \le 30°$ range. The resulting data were corrected for polarization and Compton scattering, and the intensity was brought to electron units. When short-range ordering takes place, the Laue background should initially increase, and in the case of short-range sheeting it should decrease. When both phenomena are absent, no modulations of the background take place (Fig. 2). The slope of the intensity curves and the observation of additional modulations depend on the degree of ordering and on the local structure distortions connected with displacements of atoms from the points of structural positions.

It was found out that diffuse scattering modulations are almost impossible to reveal experimentally in the presence of a heavy alkaline-earth metal cation, because the scattering volume of the sample is too small (scattering occurs almost exclusively from its surface). Therefore, with Ba_2FeNbO_6, we failed to reveal background modulations because of the smaller difference between the squared atomic amplitudes of the isomorphous iron and niobium cations as compared to Ba_2FeTaO_6.

The intensities of Laue background for five complex perovskites are presented in Fig. 3. The curves are similar to each other: first the scattering intensity increases and then decreases. The presence of a well-defined maximum near $2θ \sim 20°$ and the steep ascent of the initial background are indicative of a high degree of local ordering of isomorphous cations in the oxides under study. As shown in [3–6, 12], ordering arises mainly owing to electrostatic interactions through the oxygen environment of differently charged cations that should occupy contacting octahedra. In a cubic $A_2BB'O_6$ structure, there is a more uniform distribution of equidistant cations on spheres than in the rutile-type K_2NiF_4 and $LnCaAl_3O_7$ structures. Thus, six cations are located on the first cationic coordination sphere, twelve on the second, and eight on the third, and, therefore, we should not expect a selective electrostatic contact between one of the cations of the first sphere with the central cation. For this reason, bound mixed-cation pairs are impossible to form in complex perovskite-like oxides $A_2BB'O_6$. Short-range order parameters were calculated by the method of iterations and least squares within the limits of the first cationic sphere. The rms deviation σ of the calculated intensities from the experimental values was greater than 0.3, the greatest deviations being observed exactly in the vicinity of the diffuse maximum. Consecutive increase of the number of coordination spheres reduced σ, but resulted in physically meaningless values of short-range order parameters, when the number of cations on the sphere appeared greater that the corresponding coordination number, or the resulting data (for similar intensity curves) appeared contradictory. Therefore, we propose a qualitative consideration of the nature and degree of ordering, based on the following reasoning.

In the case of dominating electrostatic interactions in the structures of ionic compounds we should believe that B'(V) cations must be located mainly on the first cationic sphere of B(III) cations and, on the contrary, B(III) should be on the sphere of B'(V). In this way, a maximum distance between equally charged cations is attained, which effectively decreases the probability of formation of strongly extended charged structural clusters. Therewith, the structure can be distorted up to tetragonal or other symmetry because of the distortion of oxygen octahedra in the coordination sphere of isomorphous cations. Significant ordering gives rise to earlier forbidden structural maxima in the X-ray patterns. In our case, an almost full ordering of B(III) and B‘(V) cations is also possible. Thus, low-intensity broadened structural maxima in the position of the superstructural reflection 111 (2θ ~ 19°) for a perovskite with a doubled lattice parameter are present in the Xray patterns of Sr_2CrTaO_6, Sr_2CrNbO_6, and Sr_2FeTaO_6. The occurrence of this maximum points to a high degree of ordering of differently charged cations. As the samples are cooled, cation ordering occurs, when isomorphous cations occupy neighboring octahedra (Fig. 4). As a result, separate fine crystals pass in a completely ordered state. Such ordered perovskites were described earlier [7–14]. In the case of such ordering, the symmetry of the structure remains cubic, but it already belongs to the space group *Fm*3*m*.

Thus, in all the complex oxides studied we observe short-range ordering that effectively decreases the probability for formation of strongly extended charged structural clusters in the crystals. It is probable that at lower annealing temperatures the degree of ordering would increase up to a full order. Research in this direction will be continued.

EXPERIMENTAL

The oxides were synthesized by the ceramic technique in air at 1450°C within 10–30 h. For the strating reagent we used Cr_2O_3, Fe_2O_3, Nb_2O_5, Ta_2O_5, $SrCO_3$, and $BaCO_3$ taken in stoichiometric ratios. The charge was thoroughly mixed, pressed in tablets, and calcined in a silit oven. The isothermal mode of thermal treatment was maintained with an accuracy of ±2°C using a TP-403 high-precision program controller. The phase composition of the synthesized samples was controlled by X-ray diffraction in the $5° \le 2\theta \le 110°$ range (CuK_α radiation) using a PW-3020 Phillips Analytical X-ray diffractometer.

The intensity of diffuse scattering was recorded by the technique described in [3] on a DRON-3 diffractometer (CuK_α radiation) using a vacuum chamber.

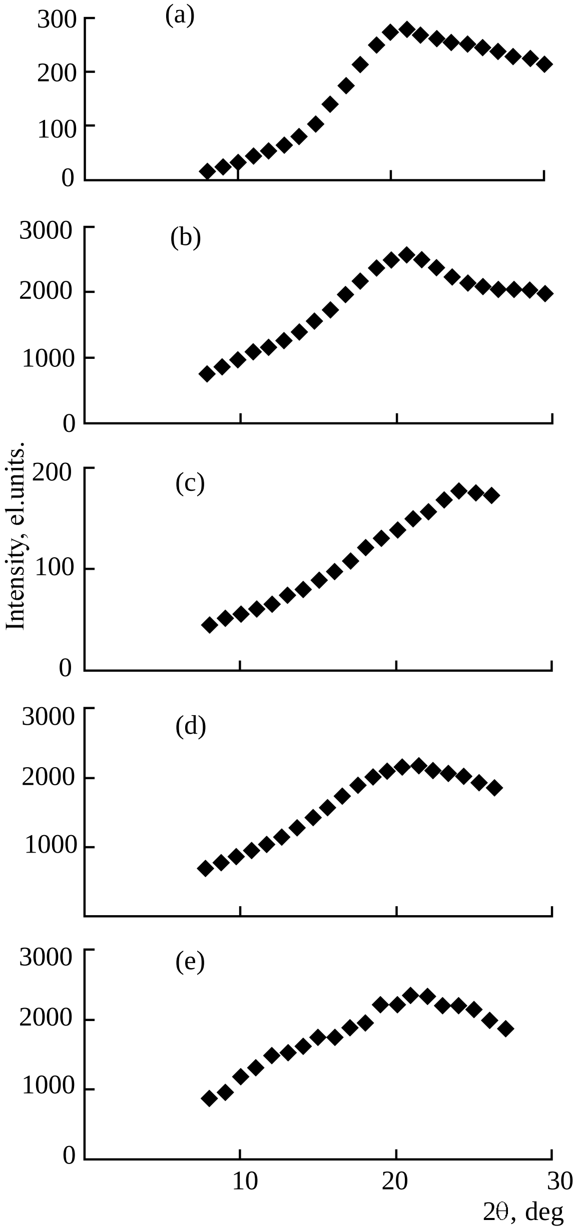

Fig. 3. Change in the intensity of Laue background as a function of scattering angle for oxides with a double perovskite structure. (a) Sr_2CrNbO_6, (b) Sr_2CrTaO_6, (c) Sr_2FeNbO_6, (d) Sr_2FeTaO_6, and (e) Ba_2FeTaO_6.

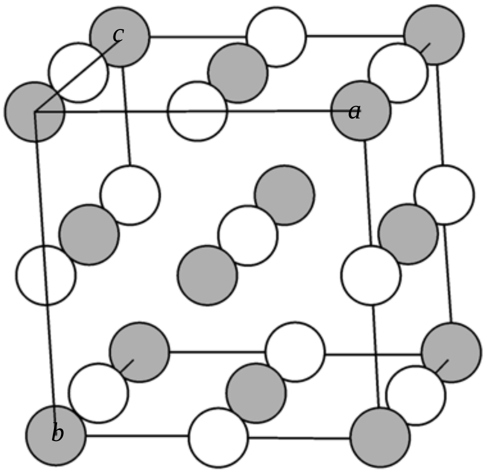

Fig. 4. Unit cell of ordered double perovskites and alternation of B(III) and B'(V) cations (colorless and gray circles, respectively).

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