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X-ray diffraction and structural ordering of B-cations in $A_2B'B''O_6$ double perovskites

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A method for quantitatively assessing the degree of structural ordering s from the intensities of superstructural X-ray diffraction reflections for double perovskites of the $A_2B'B''O_6$ type is analyzed. It is shown that the technique proposed in 1980 and still widely used cannot always give the correct result for the most practically important polar phases of perovskites described by non-centrosymmetric groups. Using the examples of Pb_2ScTaO_6 and Ca_2CrSbO_6, it is shown that the dependence of s on the probability of the lattice sites filling can be nonlinear, different for different XRD reflections, and at strong disorder, its values can differ by up to 10−50% from the value corresponding to the definition of its physical meaning.

Keywords: structural ordering, X-ray diffraction, oxides with perovskite structure.

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Electrically active oxides of the perovskite family (OPFs) ABO_3 and their solid solutions are widely used as a basis for materials and elements of electronic, mechanical, and acoustic devices, sensors, thermal imagers, and detectors. Practically important characteristics of materials may be adjusted by varying the degree of structural ordering s with the help of various processing methods and without changes to the chemical composition during synthesis. The value of s must be known both when obtaining the material and for theoretical analysis of the relationship between lattice ordering and its technically important characteristics.

Double OPFs of the $A_2B'B''O_6$ composition, where an ordered alternation of B cations of two types contributes to the emergence of polar atomic displacement systems in the A and O sublattices, are considered as classical objects for investigating the relation between s and macroscopic material properties. Depending on the technological conditions of preparation, some of them may exist in an ordered state, a disordered state, or in a state with an intermediate degree of structural ordering.

The method for quantitative assessment of ordering degree in $A_2B'B''O_6$ OPFs proposed in [1] relies on the concept of linear ordering of B-sublattice cations and simple relation

$$s = 2p - 1, \tag{1}$$

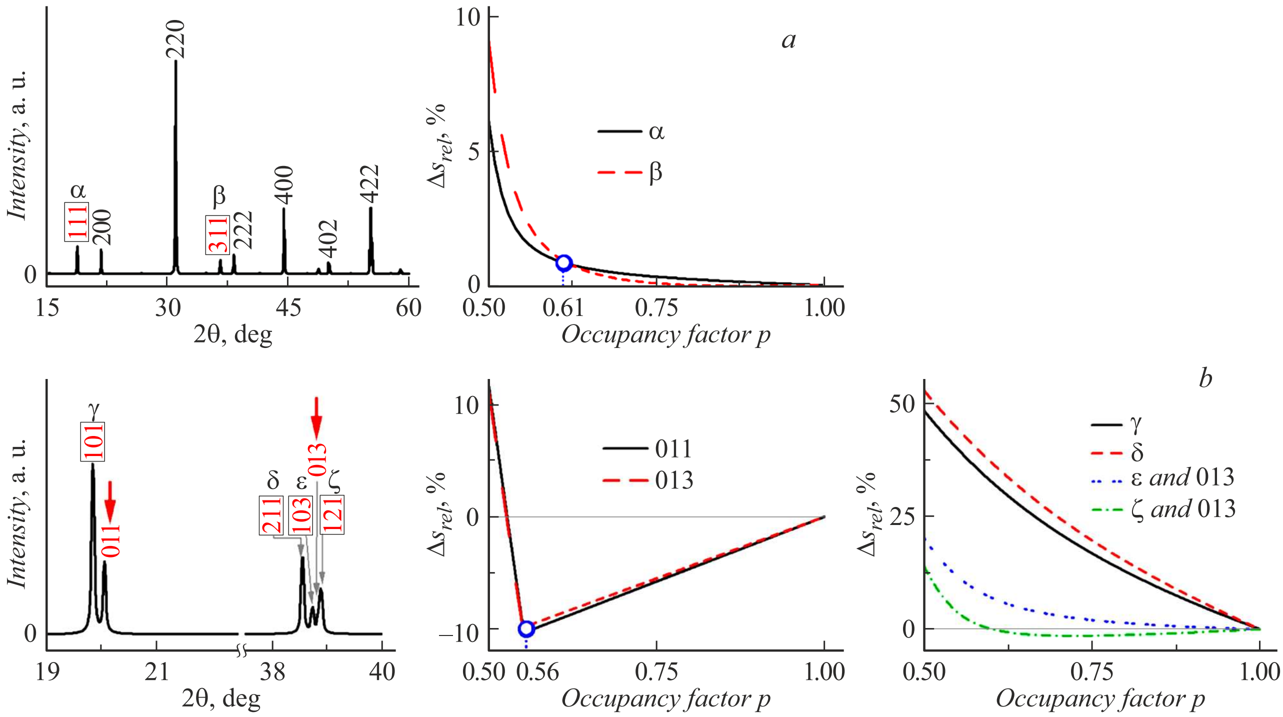
which determines physical meaning to s, associating this parameter with probability p of filling of $B1$ or $B2$ sublattice sites by an atom of one of the two types (B' or B''). This is not the only definition of s; an equivalent relation was proposed by Sakhnenko based on statistical concepts [2].

In (1), dependence $s(p)$ is linear and $0 \leqslant s \leqslant 1$, and it is sufficient to set the values of p within the $0.5 \leqslant p \leqslant 1$ interval. Quantity p in (1) belongs to the group of positional parameters of atoms (site occupancy factor, SOF) which are included in structural amplitudes $F(hkl)$ (i.e., in the intensity of X-ray diffraction reflections). This is the reason why X-ray diffractometry (XRD) is the most commonly used method to measure s.

Let us analyze in more detail the method [1] of determining s from XRD data by formula (1), which is still being used widely. It is assumed implicitly in this method that a correct value of parameter p for the compound under consideration is known for at least one of the octahedral sublattices; i.e., that a complete structural model with account for the space group, all systematic atomic displacements, and the SOF of all sublattices has been developed and applied. In practice, this implies that the result is known in advance. This approach also involves full-profile Rietveld analysis, which is labor-intensive and incompatible with the requirement of rapid evaluation of the results of routine synthesis. Therefore, the values of s are still being determined in practice from the reduced intensities of individual superstructural reflections, which emerge additionally as a result of a several-fold increase in the cell size (compared to the cubic perovskite cell with a lattice cell parameter of $\sim 4\,\text{Å}$), in accordance with the procedure proposed in 1980 [3]:

$$s^2 = \frac{(I_{ss}/I_m)_{meas}}{(I_{ss}/I_m)_{calc\,s=1}}. \tag{2}$$

To normalize the intensities (2) to an absolute scale, the measured $(meas)$ intensities of main (m) and superstructural (ss) reflections are divided by the corresponding calculated values for the structure with complete ordering $(calc\ s = 1)$. The matching of $(meas)$ and $(calc\ s = 1)$ intensity values implies complete structural ordering of the sample at $s = 1$. If the intensity of superstructural reflections is zero, structural ordering is lacking, and formula (2) yields $s = 0$.



X-ray diffraction patterns for Pb_2ScTaO_6 [4] (a) and Ca_2CrSbO_6 [5] (b) and dependences $\Delta s(p)$ for them. Miller indices of one reflection from the corresponding set (their full list is given in the text) are framed. Arrows indicate the positions of individual superstructural reflections for Ca_2CrSbO_6.

However, the outward simplicity and straightforwardness in use of relations (1) and (2) conceal the trivial fact that quantities p are not included explicitly in (2); i.e., the physical meaning of parameter s in (1) and relation (2) used for its experimental determination are based on different concepts. The problem of equivalence of definitions (1) and (2), which entails determining the relation between s and p in (2), thus becomes evident. This should allow one to evaluate correctly the error of method [3] in rapid determination of degree of ordering s and its physical meaning.

The relation of s with intensities I of XRD reflections is written as $I = GF^2$, where G is a factor depending exclusively on X-ray scattering angle θ and F is the structural amplitude depending on coordinates of atoms (xyz) and reflection indices (hkl):

$$F = \sum_j p_j f_j \exp\left(2\pi i \left(hx_j + ky_j + lz_j\right)\right), \qquad (3)$$

where p_j are the probabilities of filling of crystallographic sites and f_j are the atomic scattering functions. To obtain an explicit $s(p)$ dependence in (2), we consider the contribution of p to its components. When (3) is inserted into (2), it is easy to see that I_m for B-cations are independent of parameter p , since the structural data and the values of G are considered to remain the same within the entire interval of p values Thus, s depends only on ratio $(I_{ss})_{meas}/(I_{ss})_{calc\,s=1}$ (i.e., the corresponding F). Since experimental reflections may have close Bragg angles and overlap due specific features of the material structure, these contributions should be summed up in the expression for s:

$$s^2 = \sum(|F|^2_{ss})_{meas} \Big/ \sum(|F|^2_{ss})_{calc\,s=1}. \qquad (4)$$

Let us use (4) to verify the equivalence of application of approaches (1) and (2) in evaluation of the degree of ordering in $A_2B'B''O_6$. The structural data for Pb_2ScTaO_6 (PST), space group $R3$ (146) (rhombohedral axes) [4], and Ca_2CrSbO_6 (CCS), space group $P2_1/n$ (14) (unique axes b) [5], were used for this purpose. It is stated in [5] that Sb atoms occupy site $2b$ (1/2, 0, 1/2), which is not possible with such setup for this group. Since this is likely to be a typing error, positions $2c$ (1/2, 0, 1/2) were used to model the structure. To calculate s by formula (4), structural amplitudes F were taken in form (3), and f_j was determined in accordance with the well-known method [6] for Cu$K_{\alpha1}$ radiation. With the used radiation and lattice cell parameters, sets of unresolved or poorly resolved superstructural reflections with close Bragg angles may be observed. They were denoted by Greek letters. In the case of PST, these are 111 and $1\bar{1}1$ (set α) and 311, $3\bar{1}1$, $31\bar{1}$, and $3\bar{1}\bar{1}$ (β) (see panel a of the figure). Individual reflections were indicated in [5] for CCS: 011 and 013 (arrows in panel b of the figure). In addition, sets $\bar{1}01$, 101 (γ); $\bar{2}11$, 211 (δ); $\bar{1}03$, 103 (ε); and $\bar{1}21$, 121 (ξ) (see panel b of the figure) were found in the course of modeling the diffraction pattern. The last two sets (ε, ξ) are located close to or overlap with 013 (see panel b of the figure), making the calculations, which were performed for sets in the same way as for individual reflections, somewhat more complicated. The results of calculations are presented in the figure in the form of difference $\Delta s(p)$ between the values calculated with the use of (4) and specified by the representation of the physical meaning of s in (1).

The $\Delta s(p)$ dependences turned out to be different due to the fact that the mutual arrangement and/or overlapping of reflections are specified by individual structural characteristics of the material. In the case of PST, the error is $\sim 1\%$ within the $0.61 \leqslant p \leqslant 1$ range for sets α and β (see panel *a* of the figure). At $p < 0.61$, the error starts increasing and reaches $\sim 9\%$ at $p = 0.5$. The pattern in CCS is different: the error for reflections 011 and 013 reaches $\sim 10\%$ at $p = 0.5$ (see panel *b* of the figure). The error for sets may reach $\sim 12\%$ (ξ and 013) or $\sim 20\%$ (ε and $0\underline{1}3$). The deviation reaches its maximum for γ (reflections $\bar{1}01$, 101) and δ (reflections $\bar{2}11$, 211): $\sim 50\%$ at $p = 0.5$.

The deviation for dependencies $\Delta s(p)$ in the figure is maximized at complete disorder, which may be a consequence of distortion of oxygen octahedra. The relative contribution of ions from the *A* and O sublattices in the reflection plane, which initially featured *B* cations only, may change because of this. Thus, the contribution of *B* cations to this reflection decreases on approach to $p = 0.5$ (disorder), while the contribution from the *A* and O sublattices remains unchanged, which leads to a strong deviation of the values of s when this parameter is determined using (2).

A comparison of data for PST and CCS revealed that method (2) may yield different $s(p)$ dependences; at $p \sim 0.6{-}1$, the difference may be $< 1\%$, but it is also possible for it to reach 10% (see the figure). With strong disorder, the error of this technique may exceed 10% and, in certain cases, reach 50%.

In general, the root for the error is the linear $s(p)$ relation specified by the definition of s , which does not take into account the actual structural order of the material that is governed by complex structures and bonds of atoms (especially in the case of strong disorder).

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Conflict of interest

The authors declare that they have no conflict of interest.

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