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New Ordering Scheme Based on the Partial Occupation of Prismatic Sites in a Monodimensional Sr−Rh−O System

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Monodimensional oxides have attracted particular attention by the community of material chemists because some of these oxides show spectacular anisotropy in their properties.[1] A structural family widely studied in recent years is that built up by the intergrowth of the Sr_4PtO_6[2] and 2H−$BaNiO_3$[3] structural types. Several general formulas have been proposed to denote this homologous series and general approaches to determine their structures have been reported. Particular attention should be given to the papers by Darriet and Subramanian,[4] Battle et al.,[5] Evain et al.,[6] and Zakhour-Nakhl et al.[7] On the basis of the structural units constituting these oxides, the general formula $(A_3B_2O_6)_\alpha(A_3B_3O_9)_\beta$ seems to be the most appropriate because it provides information in both symmetry and structure of each member of the series.[8]

Despite the variety of cations stabilizing such structures, all the phases belonging to this family show a common feature: they are formed by isolated chains constituted by alternating octahedral (Oh) and trigonal prismatic (TP) units leading to structures characterized by an a parameter related to a_{2H} by a $\sqrt{3}$ factor ($a \cong \sqrt{3}a_{2H}$) and a c parameter which depends on the Oh/TP ratio.

Surprisingly enough, only the $Sr_6Rh_5O_{15}$ compound reported by Claridge and zur Loye[9] escapes such general behavior. For this cationic ratio, the stabilization of the (6:5) structure must be expected. In such a structure, polyhedra rows are formed by four octahedra and one trigonal prism sharing faces. Among others, $Sr_6Co_5O_{15}$[10] and $Ba_6Ni_5O_{15}$[11] adopt this rhombohedral structure (space group $R32$). According to Claridge and zur Loye,[9] although $Sr_6Rh_5O_{15}$ is closely related to the above-mentioned Sr/Co and Ba/Ni oxides, to account for all the observed X-ray diffraction peaks, a doubling of the unit cell basis is proposed to arise from a distortion of the strontium chains.

When single crystals are not available, the combination of selected area electron diffraction (SAED) and high-resolution electron microscopy (HREM) is the most powerful tool to adequately characterize the structures of these monodimensional oxides. The aim of this paper is the microstructural characterization of a sample of nominal composition $Sr_6Rh_5O_{15}$ to show that the general features of the above-mentioned monodimensional oxides, even for the Sr:Rh = 6:5 ratio, are maintained. In addition, superimposed to the 6:5 basic cell a new ordering appears arising from occupied and unoccupied

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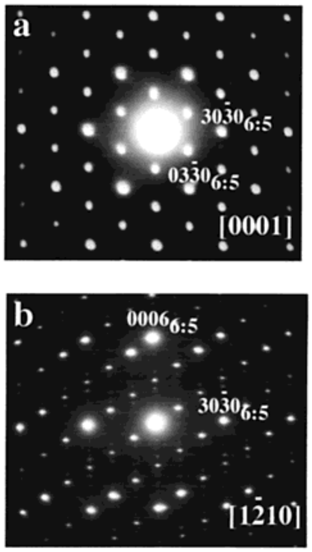

Figure 1. SAED pattern corresponding to the sample with nominal composition $Sr_6Rh_5O_{15}$ along (a) $[0001]_{6:5}$ and (b) $[1\bar{2}10]_{6:5}$.

prismatic sites.

Powder X-ray diffraction data of the so-formulated $Sr_6Rh_5O_{15}$ sample, prepared under the same conditions as those reported in ref 9, are apparently identical to that shown in Figure 1 of such a reference. Actually, with respect to the rhombohedral unit cell corresponding to the $A_6B_5O_{15}$ type, extra peaks can be observed. However, the SAED study clearly shows that superstructure spots cannot be indexed according to the unit cell proposed by Claridge and zur Loye.[9] Figure 1a shows the SAED pattern along $[0001]_{6:5}$ which corresponds to the basis of the unit cell of any rhombohedral term up to now reported, that is, $a = b \cong 0.96$ nm. No evidence of superstructure spots along a^* or b^* axes is seen. However, in the $[1\bar{2}10]_{6:5}$ reciprocal plane, a 5-fold superstructure along the c axis is clearly observed (Figure 1b). In fact, this would be the characteristic SAED pattern of the (6:5) phase if only the most intense reflections were considered. This can be observed by comparing such a pattern with that shown in Figure 3a of ref 12. The observed superstructure leads to a rhombohedral unit cell of parameters $a = a_{6:5}$, $c = 5c_{6:5}$, i.e., close to 0.96 and 6.5 nm, respectively.

The HREM corresponding to the $[1\bar{2}10]_{6:5}$ zone axis (Figure 2) reveals the origin of the superstructure spots along the c axis. At first sight, an apparently well-ordered material with d spacings of 1.30 and 0.84 nm along the c and a axes, respectively, is observed. As previously reported,[12] this is the information obtained by HREM for a (6:5) phase, where bright dots are associated with trigonal prisms. In fact, the (6:5) phase constitutes the basic unit cell of the new phase. Superimposed to the (6:5) basic contrast, fringes perpendicular to the c axis (marked with arrows in Figure 2) are also seen. They intersect the c axis of the new supercell at $^{1}/_{3}$, $^{2}/_{3}$, and 1. These fringes appear as a consequence of a contrast variation of the dots associated with trigonal prisms. This is better seen along the $[\bar{1}011]_{6:5}$ direction, where bright and less bright dots alternate following a 2:3 sequence. Such a variation could indicate the presence of unoccupied prisms. If this is true, a variation in the chemical composition with respect to the (6:5) phase must be present. Therefore, a careful compositional microanalysis was performed by EDS. More than 50 crystals were analyzed. All of them were homogeneous with a Rh/Sr ratio close to 0.75 quite far from 0.83 (corresponding to a (6:5) phase). These results confirm the presence of Rh unoccupied sites in the new superstructure.

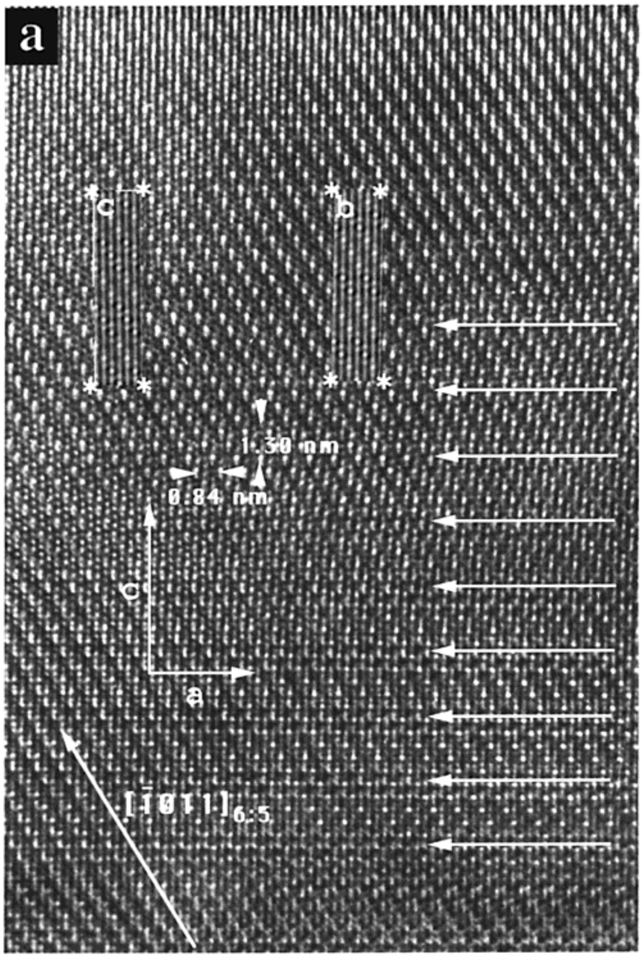

Figure 2. (a) Corresponding HREM image along $[1\bar{2}10]_{6:5}$. (b) Calculated image for a $Sr_{30}Rh_{22}O_{75}$ composition. (c) Calculated image for a $Sr_{30}Rh_{23}O_{75}$composition.

The most plausible model of Rh atoms ordering in the TP sites is schematically represented in Figure 3, in a $[1\bar{2}10]_{6:5}$ projection. Such a model accounts for the structural data obtained from the HREM and SAED results. Actually, the observed 5-fold superstructure of the (6:5) basic unit cell is generated as a consequence of the ordered distribution of both occupied and unoccupied trigonal prisms in a sequence 3:2 following the $[\bar{1}011]_{6:5}$ direction. Such distribution preserves both the rhombohedral symmetry and the $R32$ space group according to SAED results.

If the 3:2 sequence corresponds to three vacancy sites (represented by squares in Figure 3) alternating to two occupied ones (represented by circles), the Sr:Rh = 30:22 (i.e., Rh/Sr = 0.73) ratio is attained, whereas a Sr:

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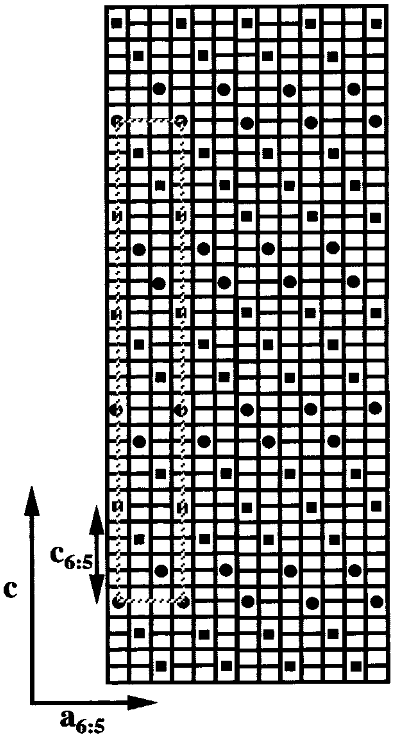

Figure 3. Schematic representation of an ordered distribution of Rh metal in the TP sites following a 3:2 sequence in a $a_{6:5}$, $5c_{6:5}$ rhombohedral unit cell.

Rh = 30:23 ratio (i.e., Rh/Sr = 0.76) corresponds to three occupied trigonal prisms (which in this case would be represented by squares) and two empty sites. In both cases, the resulting Sr:Rh ratio is very close to the 0.75 experimental value. According to that, the chemical composition for the new phase could be either $Sr_{30}Rh_{22}O_{75}$ or $Sr_{30}Rh_{23}O_{75}$. Both structures can be derived from the (6:5) type by removing the Rh atoms occupying two or three of every five trigonal prisms. The polyhedra sequence constituting every isolated row corresponds to [4Oh:1TP:4Oh:*1ETP*:4Oh:*1ETP*:4Oh:1TP:4Oh:*1ETP*], for $Sr_{30}Rh_{22}O_{75}$, and [4Oh:*1ETP*:4Oh:1TP:4Oh:1TP:4Oh:*1ETP*:4Oh:*1ETP*], for $Sr_{30}Rh_{23}O_{75}$, where *1ETP* stands for an empty trigonal prism.

From the ideal atomic coordinates corresponding to the above stacking sequences we have performed a calculation of both images and SAED patterns along the $[1\bar{2}10]_{6:5}$ projection. The calculated images for both $Sr_{30}Rh_{22}O_{75}$ (Figure 2b) and $Sr_{30}Rh_{23}O_{75}$ (Figure 2c) fit quite nicely to the experimental one for $\Delta t = 3$ nm, $\Delta f = -70$ nm. This is not surprising because the general structural features are identical for both 3:2 sequences. In the same way, the information given by the calculated SAED patterns (Figure 4a,b) is not conclusive because only very small differences in the superstructure spot intensities can be appreciated. In fact, an intermediate situation can also be considered because a mixed distribution of both sequences along the $[\bar{1}011]_{6:5}$ direction (marked with an arrow in Figure 2) preserves the 5-fold superstructure clearly observed along the *c* axis.

The difference between the three possibilities resides in the Rh oxidation state. Actually, a 30:23 cationic ratio should correspond to $Sr_{30}Rh^{IV}{}_{21}Rh^{III}{}_{2}O_{75}$, whereas a 30:22 ratio accounts for $Sr_{30}Rh^{IV}{}_{20}Rh^{V}{}_{2}O_{75}$. A small amount of Rh(V) is not surprising because conclusive evidence for the existence of such an oxidation state has been reported on Sr_2ARhO_6 (A = Li, Na) prepared at ambient pressure.[13] Finally, the intermediate situation $Sr_{60}Rh^{IV}{}_{45}O_{150}$ corresponds to all Rh in the IV oxidation state. To elucidate the real stoichiometry, an EPR study is in progress. Preliminary results indicate that only Rh(IV) can be clearly detected but the small amount of either Rh(V) or Rh(III) corresponding to the above compositions (in any case lower than 3.5%) cannot be discarded.

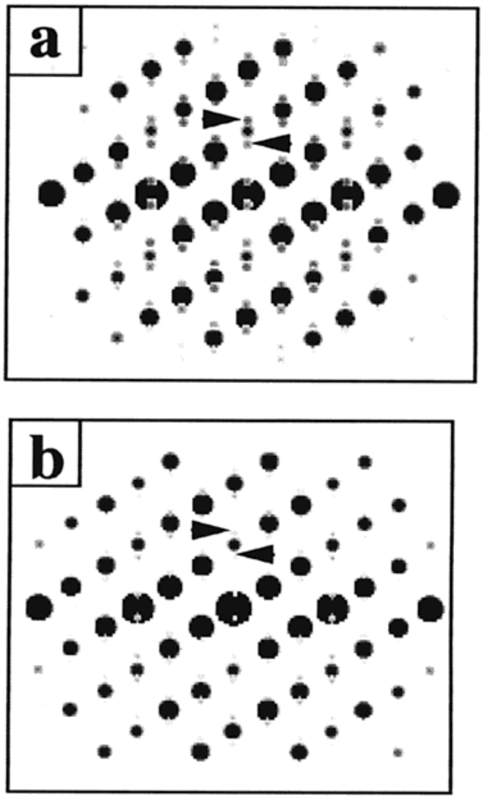

Figure 4. (a) Calculated SAED pattern for a 30:22 ratio along $[1\bar{2}10]$ for $\Delta t = 9$ nm. (b) Calculated SAED pattern for a 30:23 ratio along $[1\bar{2}10]$ for $\Delta t = 9$ nm.

The presence of unoccupied trigonal prisms in these phases is not surprising. In fact, void trigonal prisms (TPs) randomly distributed have been reported in the Sr–Ni–O system for the (4:3)[14] and (9:7)[15] phases. An ordered distribution is found in $Sr_4Ru_2O_9$ where all TPs are empty.[16] $Sr_{30}Rh_{22}O_{75}$ is the first example showing an ordered distribution of both unoccupied and occupied TPs in such a way that the essential structural features of the (6:5) phase are maintained. Preliminary results, which will be reported in due course, show that the presence of empty TPs is the rule rather than the exception in other related monodimensional phases of the A–Rh–O system (A = Ba, Sr).

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