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Structures in Superspace of Intergrowth Polytypoids $LaTi_{1-x}O_3$ and $(Ba_{1-4x}La_{4x})Ti_{1-x}O_3$ with x=1/5

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New Rietveld refinements of powder diffraction data of the cation deficient perovskite-related compounds mentioned in the title were performed in 4D using a recently proposed superspace model with discrete atomic occupation domains. The results confirm the validity and efficiency of the superspace description of these layered systems. The resulting 3D structure for $La_5Ti_4O_{15}$ corrects a previously reported model.

1. The structures of $La_5Ti_4O_{15}$ and $BaLa_4Ti_4O_{15}$ in superspace.

Layered structures necessarily have an average periodicity related with the interlayer distances. This is the basis for their description in superspace as modulated structures. The presence or not of a given atom according to the realization or not of a certain layer along the stacking periodic sequence is described in superspace through step-like (crenel) occupational modulation functions for each layer atom. This means that the atomic occupation domains are dense but discontinuous along the internal space, similarly as it happens in quasicrystals, and in contrast with "classical" modulated structures. Under these premises, many families of intergrowth polytypoids with so-called uniform layer sequences are bound to have very efficient superspace descriptions [1,2]. In particular, trigonal cation deficient perovskites $La_nTi_{n-m}O_{3n}$ (n≥4m; m≥1) $[LaTi_{1-x}O_3]$ [3] have been recently reanalyzed under this approach [4]. The modulation wave vector along the trigonal axis is given by $^{2(1+x)}/_3\,\mathbf{c}^*$. The whole homologous series can be described under a single superspace group $R'\bar{3}c1(00\gamma)00$. R' indicates a non-conventional centering ($^2/_3,^1/_3,0,^1/_3$). When described in the superspace, the variation of the structure as a function of composition reduces to a change of the wave vector (a strain of the superpace unit cell), a variation of the x_4 length of the occupation domain of Ti and slight changes in the displacive modulations. The proposed model is also valid for the related series $(Ba_{n-4m}La_{4m})Ti_{n-m}O_{3n}$ (n≥4m; m≥1)$[Ba_{1-4x}La_{4x}Ti_{1-4x}O_3]$[5].

Obviously, the superspace approach becomes specially important for long period intergrowths with complex fractions x, where the large unit cell makes difficult a conventional analysis. However, even for short period members, the use of a superspace description can be illuminating with respect to hidden correlations not described by the conventional space group symmetry and common to the whole family. Under this perspective, the structure of the $x=^1/_5$ members of the two series mentioned above have been reanalyzed by means of 4D superspace Rietveld refinements using JANA2000 [6]. The input powder diffraction data was previously used for conventional Rietveld studies of both compounds (X-ray data for $La_5Ti_4O_{15}$ [7], and both X-ray and neutron data for $BaLa_4Ti_4O_{15}$ [8]). Both compounds could be well refined within the superspace group mentioned above, and with the set of crenel atomic occupation domains described in ref. 4, confirming the proposed superspace model. Being a commensurate case, the best section perpendicular to the internal space for the refinement was $t=^1/_2$ or equivalent, which corresponds to a 3D $P\bar{3}c1$ space group [4]. The resulting 3D structure for $BaLa_4Ti_4O_{15}$ essentially coincides with that obtained by conventional means [8]. In the case of $La_5Ti_4O_{15}$, however, the resulting structure corrects the one previously reported[7]. The new one has significantly better confidence parameters (using the same data). The new structure is summarized in Table 1. Thus, the apparent exception to the general superspace model which the previously reported structural model represented [4] disappears. A projection x_3x_4 of the superspace description of $La_4Ti_4O_1$ is presented in Fig. 1.

Table 1: Structural parameters of $La_5Ti_4O_{15}$. Space group P-3c1. a= 5.57717(4)Å, c=22.0016(2)Å. Rietveld refinement. Rp=5.99%, Rwp=8.09%, R=4.05.

	x	*y*	*z*	*B*(Å^2)
La_1	0	0	$^1/_4$	0.00978(16)
La_2	$^1/_3$	$^2/_3$	0.64255(5)	0.00978(16)
La_3	$^1/_3$	$^2/_3$	0.46248(5)	0.00978(16)
Ti_1	$^1/_3$	$^2/_3$	0.3008(2)	0.0120(4)
Ti_2	0	0	0.40921(13)	0.0120(4)
O_1	0	0.555(2)	$^1/_4$	0.0051(10)
O_2	0.6769(14)	0.801(2)	0.3459(4)	0.0051(10)
O_3	0.3407(10)	0.2468(18)	0.4509(4)	0.0051(10)

The Ti vacant sites locate along the internal space, at the x_4 intervals where the misfit between the La domains corresponding to the three different kinds of layers, produces a "fault" in their cubic sequence. The fact that the vacant sites locate (for incommensurate compositions) in dense domains along the internal space, is directly related with the fact that the La vacancies distribute in real space in so called uniform sequences of vacant La-layers [2,4].

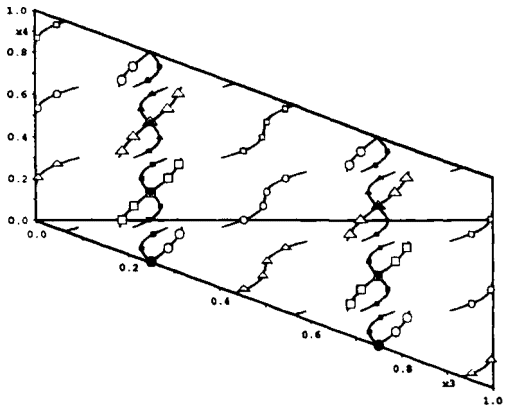

Figure 1: Superspace x_3x_4 projection of the structures of $La_5Ti_4O_{15}$. Commensurate physical points on the modulation functions corresponding to real cationic sites are indicated by empty symbols (large La, small Ti). Oxygen sites are represented by filled symbols. The three different symbols used (triangles, squares and circles) correspond to the three types (A B or C layers) of x,y coordinates of the projected atoms.

As observed in $La_9Ti_7O_{27}$[4], the slopes of the approximate sawtooth displacive modulations for both cations are such that they can be seen as forming in superspace a single average site with different periodicity than the one initially used in the superspace description. From this viewpoint the cations, distributed in Ba/La or Ti trigonal layers, stack along the z-direction according to an ACB... perfect sequence with an average periodicity different from that of the oxygens. This stacking produces an approximate bcc cubic cation lattice [5]. Hence, the two structures could be alternatively considered as composites with the cations and oxygens as two different modulated subsystems. The modulations of the Ba/La domains are particularly transportable from one system to the other, despite that bond valence calculations and the 3D refinement of the neutron data indicate that the Ba in this occupation domain is ordered and locates, mixed with La, only in the sites neighbouring the Ti vacant layer. Indeed, the main structural difference between the two compounds is clearly observed in the behaviour of the oxygens in this layer contiguous to the vacant Ti-layer. In the pure Lanthanum compound, this oxygen clearly breaks the saw-tooth behaviour maintained by all oxygens in the Ba/La compound. This represents a quite different coordination in the two compounds for the vacant Ti site and the corresponding La or Ba/La sites.

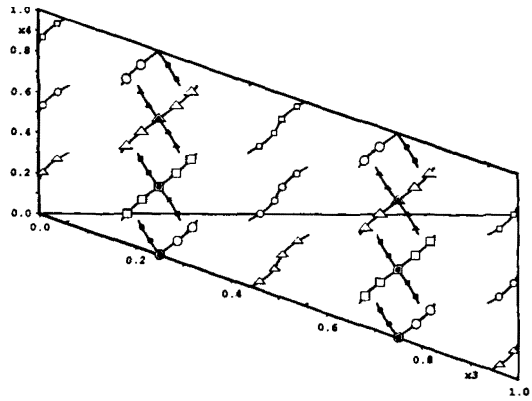

Figure 2: The same as Figure 1 for $BaLa_4Ti_4O_{15}$.

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