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Journal of Solid State Chemistry 177 (2004) 2644–2648

JOURNAL OF SOLID STATE CHEMISTRY

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Modulated structure of the composite crystal $InCr_{1-x}Ti_xO_{3+x/2}$

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Received 17 December 2003; received in revised form 11 April 2004; accepted 14 April 2004

Abstract

Incommensurately modulated structure of the composite crystal $InCr_{1-x}Ti_xO_{3+x/2}$ was refined by the profile fitting of powder X-ray diffraction based on the four-dimensional superspace group. The crystal consists of two monoclinic subsystems mutually incommensurate in **b**. The first subsystem is the alternate stacking of an edge-shared InO_6 octahedral layer and a Cr/Ti triangle-lattice plane along $\mathbf{c}^*$. A sheet of oxygen atoms constructing the second subsystem is also extending on the Cr/Ti plane. The whole structure is the alternate stacking of an edge-shared InO_6 octahedral layer and a Cr/Ti–O plane, where displacive modulation of O ions is prominent. Metal ions on the Cr/Ti–O plane are surrounded by three or four oxygen ions on the plane and, in addition, two axial ones.

Keywords: $InCr_{1-x}Ti_xO_{3+x/2}$; Composite crystal; Incommensurate structure; Modulated structure

1. Introduction

In pseudoternary systems In_2O_3–TiO_2–A_2O_3 ($A=$Al, Ga, Cr, Fe) and In_2O_3–TiO_2-BO ($B=$Mg, Mn, Co, Ni, Cu, Zn), a large family with two types of layered structures was found and named Unison-X_1 [1–4]. Solution ranges were practically limited on the pseudo-binary line $InAO_3$–$In_2Ti_2O_7$ in the case of In_2O_3–TiO_2–A_2O_3. Generally, the phase formed in an A-rich region has an orthorhombic structure, and the other one in a Ti-rich region has a monoclinic. Both structures are closely related to each other and generally described as an alternate stacking of the InO6 octahedral sheet and the M–O plane along $\mathbf{c}^*$, where the M site is occupied by A or Ti. Stacking modes are, however, different between the two structures. Namely, the orthorhombic phase is approximated by the hexagonal symmetry [5], while the monoclinic one is by the rhombohedral [6]. Strictly, structures of both forms are more complicated because commensurate or incommensurate satellite-like spots were observed along $\mathbf{b}^*$ in diffraction patterns. A compositely modulated structure consisting of the two subsystems has been revealed by a superspace-group approach for orthorhombic $InFe_{1-x}Ti_xO_{3+x/2}$ [7]. The first subsystem contains the InO_6 octahedral sheet and metal atoms (Fe, Ti) on the M–O plane, while the second one consists of oxygen atoms on the M–O plane. Two subsystems have the same period in **a** and **c**, but a different one in **b**. Displacive modulations of atoms were prominent on the M–O plane. Recently, the structure of a commensurate phase of monoclinic $InFe_{1-x}Ti_xO_{3+x/2}$ ($x=2/3$) was refined by the conventional Rietveld profile fitting with a superlattice of $\mathbf{b}=3\mathbf{b}_{sub}$ [8]. Atomic arrangement on the M–O plane of the refined structure was similar to that seen in a part of the orthorhombic structure. In analogy with the orthorhombic form, monoclinic phases were supposed to have a compositely modulated structure consisting of the two subsystems, although modulated structures of incommensurate phases of the monoclinic type have never been clarified yet. In this study, the incommensurately modulated structure of monoclinic $InCr_{1-x}Ti_xO_{3+x/2}$ was refined by the $(3+1)$-dimensional superspace-group approach of powder X-ray diffractions. In addition, coordination character around the M site was compared with that of the orthorhombic form.

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doi:10.1016/j.jssc.2004.04.033

2. Experimental

In_2O_3, Cr_2O_3, and TiO_2 (99.9%) heated at 850°C for 1 day prior to reaction were mixed at a molar ratio of $In_2O_3:TiO_2:Cr_2O_3 = 3:4:1$ using an agate mortar for about 25 min in ethanol. The mixture was pelletized and heated at 1200°C in air for 2 days with a platinum crucible, then cooled to room temperature. After grinding, the sample was pelletized and heated at 1200°C for 2 days. Before and after heating the sample, we measured its weight carefully and did not detect the weight loss. Formation of the monoclinic phase was confirmed by the X-ray diffraction measurement.

Diffraction data for structure analysis were collected on a Rigaku Rad 2B diffractometer with graphite-monochromatized Cu$K\alpha$ radiation in a scan range of 20–120° at intervals of 0.02°. The structure was refined by the profile fitting using the program *PREMOS*91 [9]. Crystallographic data of $InCr_{1-x}Ti_xO_{3+x/2}$ $(x = 2/3)$ are given in Table 1. Two monoclinic unit cells with common a, c, and β are used for indexing reflections. The two subsystems are mutually incommensurate in $\mathbf{b}$. The superspace group of the overall structure is $C2/m(1, 1.345, 0)s0$, where modulation wave vector is $\mathbf{q} = \mathbf{a}^* + \mathbf{b}_2^* = \mathbf{a}^* + 1.345\mathbf{b}_1^*$. This superspace group can be converted to $B2/m(0, 0, 0.345)s0$ (No. 12.4) in *International Tables for Crystallography, Vol. C* [10] by $\mathbf{a}'^* = \mathbf{a}^*$, $\mathbf{b_1}'^* = \mathbf{c}^*$, $\mathbf{c}'^* = -\mathbf{b_1}^*$, $\mathbf{q}' = \mathbf{q}^i - \mathbf{b_1}^*$. A conventional basis ($\mathbf{a}^*$, $\mathbf{b}_1^*$, $\mathbf{c}^*$, $\mathbf{q}^i = \sigma_2\mathbf{b}_1^* = \mathbf{b}_2^*$) was used for the description of the structure, and symmetry operations are (0, 0, 0, 0; 1/2, 1/2, 0, 1/2) + x_1, x_2, x_3, x_4; $-x_1$, x_2, $-x_3$, $1/2+x_4$; $-x_1$, $-x_2$, $-x_3$, $-x_4$; x_1, $-x_2$, x_3, $1/2-x_4$. The indexing by $h\mathbf{a}^* + k\mathbf{b}_1^* + l\mathbf{c}^* + m\mathbf{b}_2^*$ showed systematic reflection conditions $h + k + m = 2n$ for $h\,k\,l\,m$ and $m = 2n$ for $0\,k\,0\,m$ (n: integer). Fractional coordinates for atoms in the jth subsystem are given by

$$u_j = u_{j0} + A_0 + \Sigma_{n>0}[A_n \cos(2\pi nt) + B_n \sin(2\pi nt)],$$

where $t = \mathbf{q}_j^i(\mathbf{n}_j + \mathbf{r}_j)$, $\mathbf{n}_j$ is the lattice vector, $\mathbf{r}_j$ the position of the basic structure ($a_j x_{j0}$, $b_j y_{j0}$, $c_j z_{j0}$), and A_0, A_n, and B_n are refined parameters. Restrictions for Fourier coefficients of modulation functions for atoms at special positions were obtained by programs *SPA* [11,12]. Fourier coefficients up to the fourth order have been taken into account for positional parameters, although coefficients higher than the second order of the oxygen atom in the first subsystem had no significant values and fixed to 0. Modulation of thermal parameters was considered for no atom. Similar scattering abilities of Cr^{3+} and Ti^{4+} made it difficult to refine occupation factors of Cr and Ti at the M site, which were fixed at 0.333 for Cr and 0.667 for Ti. To prevent improbable geometries, penalty function was imposed on O2–O2 distances less than 2.4 Å in the refinement.

Table 1
Crystallographic data for $InCr_{1-x}Ti_xO_{3+x/2}$ $(x = 2/3)$

Crystal system	Monoclinic
Superspace group	$C2/m(1, 1.345, 0)s0$
a (Å)	5.9269(2)
$b1$	3.3597(1)
c	6.3583(2)
$b2$	2.4984(9)
β (deg)	108.09642(3)
Z	2
R_{wp}	0.108
S	1.54

Table 2
Final structural parameters for $InCr_{1-x}Ti_xO_{3+x/2}$ $(x = 2/3)$

	x	y	z	B (Å^2)
Subsystem 1				
In	0	0	0	0.5
A_0	0	0	0	
A_1	0	0	0	
B_1	−0.024(1)	0	−0.007(2)	
A_2	0	0	0	
B_2	0	−0.012(7)	0	
A_3	0	0	0	
B_3	−0.006(7)	0	−0.005(6)	
A_4	0	0	0	
B_4	0	0.01(1)	0	
M (Cr/Ti)	0.5	0	0.5	0.5
A_0	0	0	0	
A_1	0	0	0	
B_1	−0.056(3)	0	−0.008(4)	
A_2	0	0	0	
B_2	0	−0.03(1)	0	
A_3	0	0	0	
B_3	−0.01(1)	0	−0.01(1)	
A_4	0	0	0	
B_4	0	−0.01(3)	0	
O1	0.38	0	0.16	1.0
A_0	0.011(3)	0	0.004(2)	
A_1	0	0.00(1)	0	
B_1	−0.032(6)	0	0.001(9)	
A_2	−0.01(2)	0	−0.02(1)	
B_2	0	0.02(3)	0	
Subsystem 2				
O2	0.25	0.25	0.5	1.0
A_0	0	0	0	
A_1	−0.145(5)	0	−0.012(7)	
B_1	0	0	0	
A_2	0	0	0	
B_2	0	−0.095(5)	0	
A_3	−0.004(7)	0	−0.01(2)	
B_3	0	0	0	
A_4	0	0	0	
B_4	0	0.06(3)	0	

Occupation ratio at the M site is fixed at Cr/Ti = 0.333/0.667.

3. Results and discussion

Final structural parameters and the profile fit are given in Table 2 and Fig. 1, respectively. The first

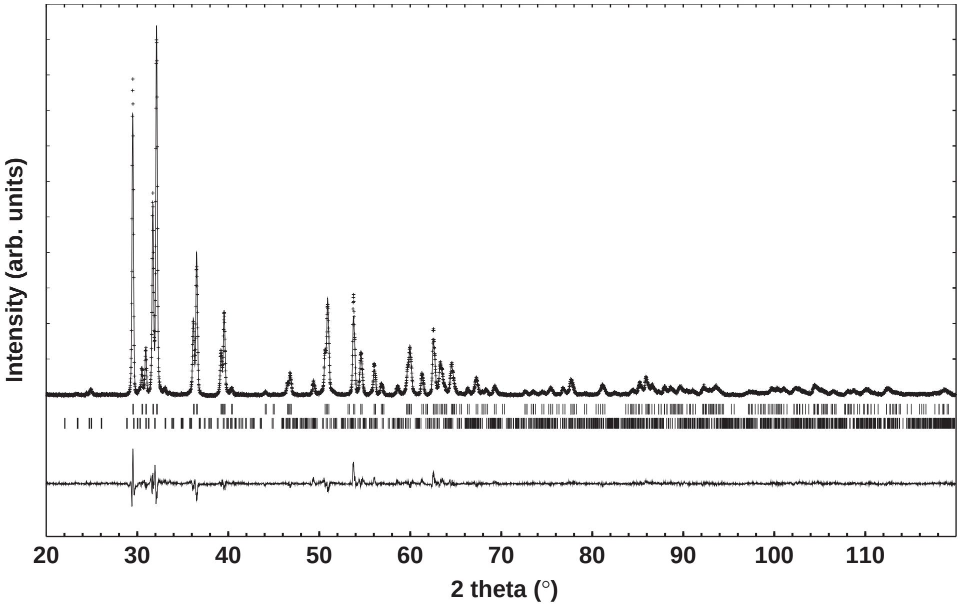

Fig. 1. Final Rietveld fit for $InCr_{1-x}Ti_xO_{3+x/2}$. Observed data are represented by +, and the calculated profile is by the solid line. Upper and lower ticks represent positions of main ($k = 0$ or $m = 0$) and satellite ($k \neq 0$ and $m \neq 0$) reflections, respectively. The difference plot is at the bottom.

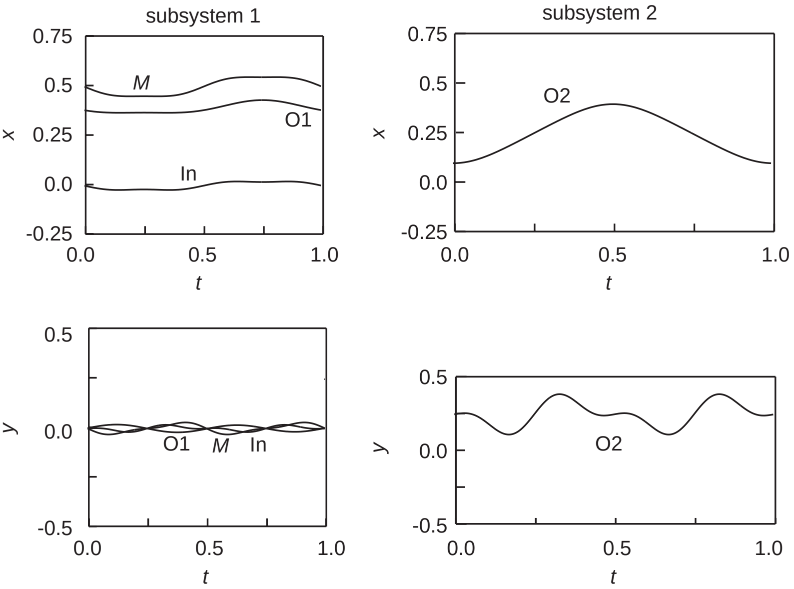

Fig. 2. Displacive modulation functions of x and y in $InCr_{1-x}Ti_xO_{3+x/2}$.

subsystem consists of In, Ti, Cr and a part of oxygen ions, O1, while the rest O atoms, O2, construct the second subsystem. The chemical composition of the composite crystal $InA_{1-x}Ti_xO_{3+x/2}$ is related to the ratio of cell dimensions of the two subsystem by $b_1/b_2 = 1 + x/2$ [8]. The relation is, however, not the case for the present crystal with $b_1/b_2 = 1.345$ and $1 + x/2 = 1.333$. One of the possible explanations for this discrepancy is the introduction of defects at oxygen sites, O1 and/or O2. Estimated vacant sites are only 0.36% (=(3.345−3.333)/3.345) of the total oxygen positions, which are too few to be considered in refinements and ignored in discussion hereafter. The first subsystem $InCr_{1-x}Ti_xO_2$ is the alternate stacking of an edge-shared InO_6 octahedral layer and a triangle-lattice plane of the M site occupied by Cr and Ti atoms along $\mathbf{c}^*$. The M and O1 atoms form a linear coordination O1–M–O1 nearly along $\mathbf{c}^*$. The second subsystem consists of an oxygen (O2) sheet extending on the M-site plane. The overall structure is characterized as an alternate stacking of the $InO1_6$ octahedral layer and the M–O2 sheet along $\mathbf{c}^*$.

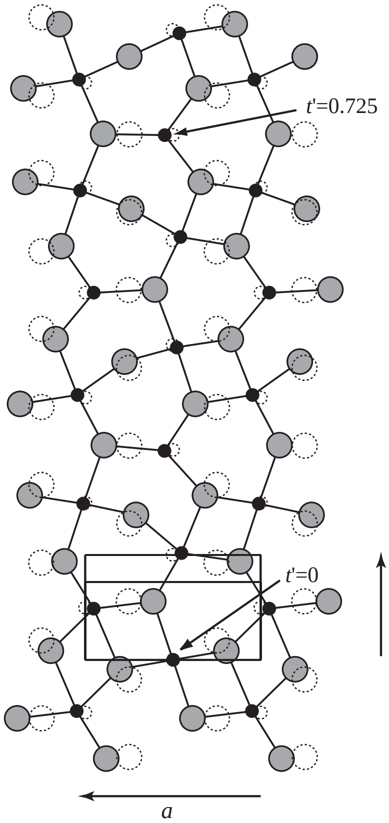

Fig. 3. Atomic arrangement in the slab around $z\approx 0.5$ in $InCr_{1-x}Ti_xO_{3+x/2}$. Small filled circles are M and large circles O2. Dotted circles represent the basic structure.

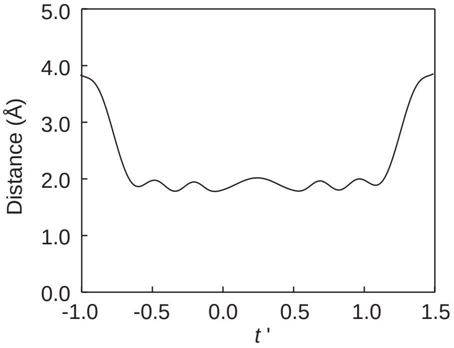

Fig. 4. M–O2 distance in $InCr_{1-x}Ti_xO_{3+x/2}$ as a function of $t'(=-\sigma_2 x_2 + x_4)$.

Displacive modulation functions for x and y are shown in Fig. 2. Similar to the orthorhombic form, prominent displacements are seen for the O2 atom because the triangle lattice of the M belonging to the first subsystem is on the same plane (Fig. 3). Modulation functions of the O2 atom are similar to those in the orthorhombic form. The interatomic distance between the M and the O2 is given as a function of $t'(=-\sigma_2 x_2 + x_4)$ in Fig. 4, which is not periodic because the two atoms belong to different subsystems. If the atoms suffer no modulation, the O2 ion is within 1.5 Å from the M site at around $t' = 0.25$, which is too short for a distance between a metal (Cr or Ti) and an oxygen ion considering ionic radii of 0.615 Å for Cr^{3+}, 0.605 Å for Ti^{4+} (in six coordination), and 1.40 Å for O^{2-} [13]. Actually in the modulated structure, the M–O2 distance always exceeds 1.8 Å.

The number of O2 atoms within a given distance from the M site is obtained from Fig. 5 which shows distances of O2 atoms from the M. If 2.1 Å is taken as a limit of M–O2 coordination, a metal ion with $t' = 0$ is coordinated by four O2 ions as indicated in Fig. 3. Total coordination number of this metal site is 6 including two M–O1 bonds approximately normal to the M–O2 plane. Another metal site around $t' = 0.725$ also shown in Fig. 3 is regarded as a 5-coordination site because only three O2 atoms are found within 2.1 Å. Thus, the coordination number for the M site is five or six, which are varied according to t', although the inclusion of an oxygen atom into the coordination may be arbitrary when the atom is at an intermediate distance from the metal site. Five-coordination ranges based on the limit M–O2 distance of 2.1 Å are shaded in Fig. 5, which are less than those in orthorhombic $InFe_{1-x}Ti_xO_{3+x/2}$ [7]. This is obviously because the basic period of the O2 lattice in $InCr_{1-x}Ti_xO_{3+x/2}$ is smaller than that in $InFe_{1-x}Ti_xO_{3+x/2}$ ($b_2 = 2.568(6)$ Å). Namely, O2 ions on the M–O2 plane are more dense in the former than the latter. The occupational ordering of metal ions at the M site, though unable to be refined as mentioned in the former section, should be associated with the variation of the coordination feature. Cr^{3+} ions in oxides are never seen in 5-coordination sites as far as we know, while the trigonal bipyramid around a Ti^{4+} ion is

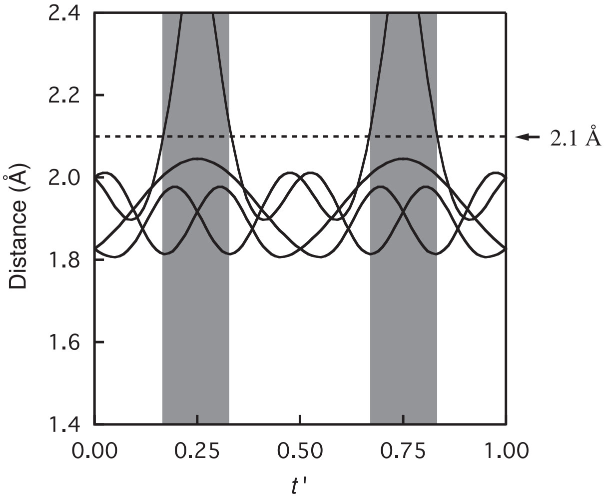

Fig. 5. Variation of the coordination feature of the M site in $InCr_{1-x}Ti_xO_{3+x/2}$ as functions of $t'(=-\sigma_2 x_2 + x_4)$. Five-coordination ranges based on the limit M–O2 distance of 2.1 Å are shaded.

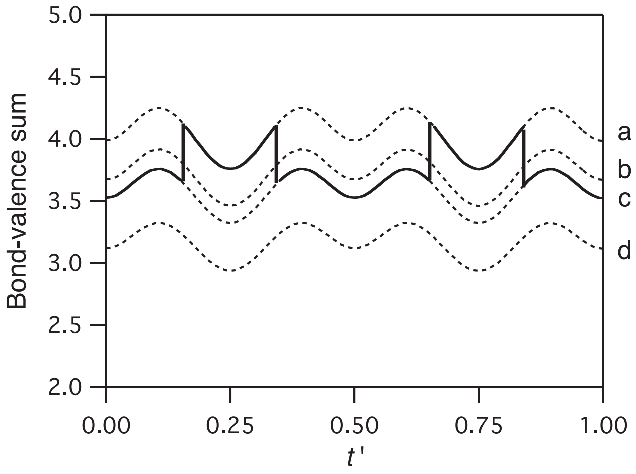

Fig. 6. BVS at the M site as a function of $t'(= -\sigma_2 x_2 + x_4)$. Broken lines are given by assuming the full occupation by Ti^{4+} (a), $Cr^{3+}/Ti^{4+} = 1/2$ (b), $Cr^{3+}/Ti^{4+} = 1$ (c), and the full occupation by Cr^{3+} (d).

observed in La_2TiO_5 [14] and In_2TiO_5 [15]. It can therefore be presumed that 5-coordination sites are occupied by only Ti^{4+} ions, and Cr^{3+} ions are limited in 6-coordination ranges of t' with an occupation ratio approximated to Cr/Ti = 1. According to this assumption, the bond-valence sum (BVS) at the M site was calculated to give the solid line in Fig. 6. Namely, a parameter $r_0 = r_0(\mathrm{Ti}^{4+}) = 1.815$ was used for full occupation of Ti^{4+} ions in $1/6 < t' < 1/3$ and $2/3 < t' < 5/6$, while composition-weighted mean for Cr/Ti = 1, $r_0 = [r_0(\mathrm{Cr}^{3+}) + r_0(\mathrm{Ti}^{4+})]/2 = (1.724 + 1.815)/2 = 1.7695$, was applied for $0 < t' < 1/6$, $1/3 < t' < 2/3$, and $5/6 < t' < 1$. The obtained BVS is roughly in agreement with the expected value, that should be 4 in $1/6 < t' < 1/3$ and $2/3 < t' < 5/6$, and 3.5 in $0 < t' < 1/6$, $1/3 < t' < 2/3$, and $5/6 < t' < 1$. However, this consistent result cannot be an evidence for the adequacy of the above assumption for the Cr/Ti ordering against t'. The BVS based on the Ti^{4+} ($r_0 = 1.815$) gives values roughly close to the ideal value, 4, and that based on the Cr^{3+} ($r_0 = 1.724$) is also close to the ideal one, 3, which are shown in Fig. 6 by dotted lines a and d for Ti^{4+} and Cr^{3+} ions, respectively. Consequently, the BVS based on any assumption for the Cr/Ti ratio always gives generally reasonable results. By assuming the constant ratio Cr/Ti = 1/2 (i.e., $r_0 = [r_0(\mathrm{Cr}^{3+}) + 2r_0(\mathrm{Ti}^{4+})]/3 = (1.724 + 2 \times 1.815)/3 = 1.7847$) over the all t', for example, the obtained BVS (the broken line b in Fig. 6) is close to 3.67. (It should be also noted that the BVS calculated by any Cr/Ti ratios is always a little higher at around $t' = 0.1$, 0.4, 0.6, and 0.9, but lower around $t' = 0.25$ and 0.75 than the ideal value, as is explicitly shown by four cases of dotted lines a–d in Fig. 6.) Thus, the BVS analysis is unfortunately of little use for considering the Cr/Ti ordering at the M site in the present structure. Such a situation is caused by the fact that Ti^{4+} and Cr^{3+} ions have similar ionic radii.

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