

ON SOME MIXED OXIDES IN THE SYSTEM CaO-CdO-Bi₂O₃-Nb₂O₅. CATION DISTRIBUTION IN A DISTORTED AURIVILLIUS STRUCTURE

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The crystalline structure of the mixed oxide CaCd₂Bi₂Nb₄O₁₅ has been refined starting from X-ray powder diffraction data and using the space group *A2₁am*. The real structure is very close to the proposed one but there are some differences that suggest further possibilities to improve the structural model.

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1. Introduction

The Aurivillius oxides of general formula (Bi₂O₂)[A_{m-1}(B)_mO_{3m+1}] have a structure that is usually represented by an intergrowth between (Bi₂O₂)²⁺ sheets and [A_{m-1}(B)_mO_{3m+1}]²⁻ pseudo-perovskite layers, with m the number of octahedra stacked perpendicular on the sheets. A is a mono-, di- or trivalent cation and B is a transition metal. These compounds have received increasing interest since their properties are suitable for a wide range of applications including medicine and health care [1].

The paper is a continuation of our previous studies concerning the synthesis and structure of some mixed oxides from the CaO-CdO-Bi₂O₃-Nb₂O₅ system and here we deal with the structure of an Aurivillius compound with m = 4 (CaCd₂Bi₂Nb₄O₁₅) [2-4].

2. Methods

The compound was sintered from the corresponding mixture of CaCO₃, CdO, Bi₂O₃ and Nb₂O₅ precursors by standard ceramic technology. The details concerning the synthesis were communicated elsewhere [2]. The polycrystalline samples were prepared for X-ray diffraction by standard metallographic technology. The diffractograms were obtained with a DRON 2.0 diffractometer, previewed with MoK α radiation. The structure was optimised by means of DICVOL [5], CELLREF [6] GRETEP [6] and an in house made software [3].

Our literature survey has found only a few papers describing the crystal structure for m = 4 Aurivillius phases (Bi₄BaTi₄O₁₅ as *I4/mmm* [7], Bi₅FeTi₃O₁₅ as *Fmm2* [8] and *A2₁am* [9], SrBi₄Ti₄O₁₅ [9, 10], PbBi₄Ti₄O₁₅ [10] and Bi_{2.5}Na_{2.5}Nb₄O₁₅ as *A2₁am* [11]).

Preliminary refinements performed for oxides from the CaO-CdO-Bi₂O₃-Nb₂O₅ system, in the space group *I4/mmm*, did not fit the experimental data since there are not enough degrees of freedom for the rotation of the NbO₆ octahedra [3, 12]. Newnham and co-workers [13] suggested since 1971 the orthorhombic space group *A2₁am* for even-layered Aurivillius terms. Therefore, also taking into account the chemical formula of our compound we decided to make the refinement of the atoms position based on the structure proposed by Borg et al. [11] for Bi_{2.5}Na_{2.5}Nb₄O₁₅.

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In our previous paper [4], the indexing of diffraction maxims was based on the assumption of one molecule per unit. Now according to the proposed model we have considered a much larger structure containing four molecules per unit cell. We also have to mention that the weak line with $d = 2.694 \text{ \AA}$ [4] was firmly assigned to the secondary phase BiNbO_4 . The parameters were firstly determined by means of DICVOL and subsequently they were refined using the CELLREF: $a = 5.2415 \text{ \AA}$, $b = 5.2507 \text{ \AA}$ and $c = 40.3273 \text{ \AA}$. Concomitantly, the Miller indices have been tested, checking the validity of the chosen model according to the rules of the allowed reflections for the proposed Aurivillius type structure (SG 36).

In order to obtain the cation distribution, the data were fitted by means of our software using the relation between the relative observed and calculated diffraction intensities:

$$\sum \left| \frac{I_{calc} - I_{obs}}{I_{calc}} \right|^2 = \text{minimum} \quad (1)$$

Table 1. The observed and calculated intensities for $\text{CaCd}_2\text{Bi}_2\text{Nb}_4\text{O}_{15}$.

No.	$d_{obs}(\text{\AA})$	$d_{calc}(\text{\AA})$	hkl	$I_{obs}(\text{a.u.})$	$I_{calc}(\text{a.u.})$
1	3.008	3.0165	0 1 11	100	100
2	2.605	2.6049	0 2 2	18.8	20.8
3	2.391	2.3887	1 1 13	5.70	6.30
4	2.130	2.1318	1 2 8	22.3	31.8
5	2.083	2.0753	2 0 12	6.60	7.20
6	1.851	1.8587	2 2 0	62.4	70.5
7	1.773	1.7495	0 3 1	4.00	4.60
8	1.579	1.5923	1 1 23	39.9	35.8
9	1.514	1.5161	3 1 11	12.3	13.1
10	1.370	1.3697	2 2 20	10.5	11.0
11	1.201	1.2014	0 2 30	7.40	7.90
12	1.173	1.1730	2 4 2	6.70	6.80
13	1.090	1.0896	4 2 14	2.00	2.10
14	1.042	1.0424	4 2 18	0.80	0.90

Table 2. Atomic coordinates and isotropic displacement parameters (\AA^2) of $\text{CaCd}_2\text{Bi}_2\text{Nb}_4\text{O}_{15}$.

Atom	Site	Occupancy	x	y	z	B
Ca/Cd	4a	0.7/0.3	0.0000	0.0880	0.0000	0.05
Ca/Cd	8b	0.15/0.85	0.0589	0.2470	0.0940	0.05
Bi	8b	1	0.4920	0.7300	0.21955	4.75
Nb(1)	8b	1	0.5000	0.8000	0.4600	2.25
Nb(2)	8b	1	0.5000	0.7800	0.34859	4.75
O(1)	4a	1	0.4900	0.3500	0.0000	0.05
O(2)	8b	1	0.2540	0.7700	0.6770	0.05
O(3)	8b	1	0.6800	-0.070	0.2410	0.05
O(4)	8b	1	0.7130	0.5300	0.4700	0.05
O(5)	8b	1	0.7300	0.9950	0.4510	0.05
O(6)	8b	1	0.4400	0.1870	0.0940	0.05
O(7)	8b	1	0.6800	0.3700	0.3500	0.05
O(8)	8b	1	0.7300	0.9200	0.3720	0.05

The cations Ca and Cd can occupy the 4a positions on the face Oxy taking into account the constraints imposed by the original model [11]. For the oxygen anions from the 4a positions have no constraints concerning the x coordinate.

During the refinement 36 positional parameters and 5 isotropic displacement parameters were varied. The molar distribution of Ca and Cd in the 4a and 8b sites were also varied in the final cycles of the refinement in order to determine the minimum of the relation (1). The performed calculations allowed the minimisation of the sum of relative square differences between the calculated and observed intensities down to the value of 0.12. Consequently, the calculated intensities show a quite good agreement with experimental data (see Table 1). The atomic coordinates and the isotropic displacement parameters are listed in Table 2.

3. Results and discussion

In the proposed crystal structure of CaCd₂Bi₂Nb₄O₁₅ is built up of (Bi₂O₂)²⁺ layers and (CaCd₂Nb₄O₁₃)²⁻ perovskite-like slabs with four two-dimensional corner sharing octahedral sheets along the c-direction. Selected bond lengths are shown in Table 3.

Table 3. Selected bonding distances for CaCd₂Bi₂Nb₄O₁₅ (Å).

(Bi ₂ O ₂) ²⁺ layer					
Bi-O(2)	3.215	Bi-O(3)	1.701	Bi-O(3)	2.420
Bi-O(2)	2.198	Bi-O(3)	2.585	Bi-O(3)	2.405
				Bi-O(7)	3.062
Perovskite layer					
Ca(1)-(O1)	3.006	Cd(2)-(O4)	3.354	Nb(1)-O(1)	1.636
Ca(1)-(O1)	2.914	Cd(2)-(O4)	3.071	Nb(1)-O(4)	1.833
Ca(1)-(O1)	2.300	Cd(2)-(O5)	2.821	Nb(1)-O(4)	2.347
Ca(1)-(O1)	2.951	Cd(2)-(O5)	2.436	Nb(1)-O(5)	1.603
Ca(1)-(O4)	1.954	Cd(2)-(O6)	3.259	Nb(1)-O(5)	1.835
Ca(1)-(O4)	1.954	Cd(2)-(O6)	2.022	Nb(1)-O(6)	2.283
Ca(1)-(O4)	1.759	Cd(2)-(O6)	2.362		
Ca(1)-(O4)	1.759	Cd(2)-(O6)	3.037	Nb(1)-O(2)	1.652
Ca(1)-(O5)	3.236	Cd(2)-(O7)	3.600	Nb(1)-O(6)	2.387
Ca(1)-(O5)	3.236	Cd(2)-(O7)	2.425	Nb(1)-O(7)	2.351
Ca(1)-(O5)	3.186	Cd(2)-(O8)	2.383	Nb(1)-O(7)	1.854
Ca(1)-(O5)	3.186	Cd(2)-(O8)	2.396	Nb(1)-O(8)	1.699
				Nb(1)-O(8)	2.318

Note: Ca(1) and Cd(2) denote the 4a and respectively 8b Wyckoff positions

The Bi atoms in the (Bi₂O₂)²⁺ layers do not retain the four-fold coordination geometry in this sample as for the *I4/mmm* prototype structure. There is one additional bond formed with an apex O(2) oxygen from the NbO₆ octahedra in the perovskite layer. The average bond length for the bonds that constitute the square pyramidal geometry is of 2.278 Å. The two remaining Bi-O(2) and Bi-O(7) distances of 3.215 and 3.062 Å may be considered as nonbonding according to the effective ionic radii.

The mean Nb-O bond lengths for the two sites are 1.923 and 2.044 Å, the second one being in very good agreement with the sum of their effective ionic radii (2.04 Å) [14]. However, if we consider the lengths of the individual Nb-O bonds we can assume that a fraction of the NbO₆ octahedra are connected on edges [15, 16]. On the other hand, bond valence sums calculated for the metal ions [17]

indicate an overbonding of Bi and Nb sites, which is partly in disagreement with the magnetic measurements [4].

4. Conclusions

The paper is the first one reporting a structure with $m = 4$ and the space group $A2_1am$ in the system $\text{CaO-CdO-Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5$. We consider that, in the limits of the measurement errors, the real structure is close to the one that we have tested here.

Despite the fact that there is a quite good fit between the experimental and calculated intensities of the diffraction spectrum, the cation distribution in our case suggests the presence of both corner and edge-shared NbO_6 octahedra. This fact is usually associated with polytype structures having mixed layers of octahedra. The results suggest the improvement of the proposed structure, a classical description of Aurivillius phases using a single space group being sometimes an approximation and has to be examined with care [18].

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