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Relative Stabilities of Layered Perovskite and Pyrochlore Structures in Transition Metal Oxides Containing Trivalent Bismuth*

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In order to investigate the factors determining the relative stabilities of layered perovskite and pyrochlore structures of transition metal oxides containing trivalent bismuth, several ternary and quaternary oxides have been investigated. While d^0 cations stabilize the layered perovskite structure, cations containing partially-filled *d* orbitals (which suppress ferroelectric distortion of MO_6 octahedra) seem to favor pyrochlore-related structures. Thus, the vanadium analogue of the layered perovskite $Bi_4Ti_3O_{12}$ cannot be prepared; instead the composition consists of a mixture of pyrochlore-type $Bi_{1.33}V_2O_6$, Bi_2O_3, and Bi metal. The distortion of $Bi_{1.33}V_2O_6$ to orthorhombic symmetry is probably due to an ordering of anion vacancies in the pyrochlore structure. None of the other pyrochlores investigated, Bi_2NbCrO_7, Bi_2NbFeO_7, $TlBiM_2O_7$ (M = Nb, Ta), shows evidence for cation ordering in the X-Ray diffraction patterns, as indeed established by structure refinement of $TlBiNb_2O_7$. © 1985 Academic Press, Inc.

1. Introduction

Layered perovskite oxides have been investigated extensively in the literature; oxides of the Aurivillius family (*1, 2*) all possess the layered perovskite structure. Besides the layered perovskite structure, transition metal oxides containing trivalent bismuth are also known to adopt pyrochlore and other network structures (*3–6*). In this laboratory, we have investigated layered perovskites of the Aurivillius family and characterized a new homologous series of oxides based on recurrent intergrowth (*7*). We considered it important to investigate the relative stability of the layered perovskite and the pyrochlore structures for bismuth-containing transition metal oxides, in order to find the major factor determining the preference of one structure over the other. For this purpose, we have investigated the structures of several ternary and quaternary oxides in the systems Bi–V–O, Bi–*M*–Cr–O, Bi–*M*–Fe–O, and Bi–Tl–*M*–O (M = Nb or Ta). The study has revealed that pyrochlore phases are favored over the layered perovskite structures when the transition metal cations contain partially-filled *d* orbitals.

2. Experimental

Compositions in the Bi–V–O system were prepared by heating appropriate mixtures of Bi_2O_3, V_2O_3, and V_2O_5, in sealed, evacuated (~10^{-4} Torr) silica tubes at 1070 K for 1 week. $TlBiM_2O_7$ (M = Nb or Ta)

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were prepared by heating stoichiometric amounts of Tl_2CO_3, Bi_2O_3, and M_2O_5 at 1070 K in air for 4 days with intermittent grindings. The samples in Bi–Nb–Cr–O and Bi–Nb–Fe–O systems were similarly prepared from a mixture of oxides at 1270 K. Phases obtained were characterized by X-ray powder diffraction (Philips diffractometer, PW 1050/70). Magnetic susceptibility measurements were carried out on a Faraday balance between 15 and 300 K.

3. Results and Discussion

In the Bi–V–O system, our attempts to synthesize $Bi_4V_3O_{12}$ (analogous to $Bi_4Ti_3O_{12}$) invariably resulted in the formation of a pyrochlore phase; the phase is not cubic $Bi_2V_2O_7$ either. The pyrochlore phase in this system appeared to be defective, probably of the type $Bi_{1+x}V_2O_6$. We therefore reacted $Bi_{1+x}V_2O_6$ compositions corresponding to $x = 0.0, 0.33, 0.5$, and 1.00 in sealed silica ampoules. X-Ray diffraction revealed that a single phase was obtained only for $x \sim 0.33$. For $x = 0$, the composition contained a mixture of $BiVO_4$ and VO_2; for $x > 0.33$, bismuth metal was formed in addition to $Bi_{1.33}V_2O_6$. Chemical analysis of $Bi_{1.33}V_2O_6$ showed that all the vanadium was present in the 4+ state (total V = 21.8%; V^{4+} = 21.4%). A similar phase was obtained together with bismuth metal when $BiVO_4$ was reduced to $BiVO_3$ in a mixture of nitrogen and hydrogen (15 : 1 by volume) at 970 K in a thermogravimetric balance.

The X-ray powder diffraction pattern of $Bi_{1.33}V_2O_6$ (Table I) could be indexed on an orthorhombic cell with $a = 7.04(3)$, $b = 7.55(3)$ and $c = 10.70(2)$ Å. The diffraction pattern shows a strong resemblance to the pyrochlore pattern; the orthorhombic cell could be related to the cubic pyrochlore as follows:

$$\begin{pmatrix} a_o \\ b_o \\ c_o \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 0 \\ -\frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} a_c \\ b_c \\ c_c \end{pmatrix}.$$

Distortion of the cubic ($Fd3m$) pyroch-

TABLE I

X-RAY POWDER DIFFRACTION DATA OF $Bi_{1.33}V_2O_6$

Cubic $h\ k\ l$	Orthorhombic $h\ k\ l$	d_{obs} (Å)	I/I_o	d_{calc}[a] (Å)
1 1 0	0 1 0	7.6	10	7.6
	1 0 0	7.0	6	7.0
2 2 0	0 2 0	3.77	10	3.77
	2 0 0	3.52	10	3.52
3 1 1	0 1 3	—	—	3.226
	1 0 3			3.182
	1 2 1	3.150	25	3.177
	2 1 1	—	—	3.057
2 2 2	0 2 2	3.084	100	3.084
	2 0 2	—	—	2.941
3 1 2	1 2 2	2.800	5	2.820
	2 1 2	2.740	30	2.740
4 0 0	2 2 0	2.570	10	2.574
3 3 1	0 3 1	—	—	2.450
	1 2 3	2.436	15	2.433
	2 1 3	—		2.378
	3 0 1	—	—	2.292
4 2 0	1 3 0	—	—	2.370
	3 1 0	2.222	10	2.241
5 1 1	2 3 1	2.010	3	2.011
3 3 3	3 0 3	1.952	4	1.960
	3 2 1	1.940	10	1.958
4 4 0	0 4 0	1.880	10	1.888
	4 0 0	—	—	1.760
5 3 1	1 4 1	—	—	1.797
	4 1 1	—	—	1.692
4 4 2	0 4 2	—	—	1.780
	1 3 4	—	—	1.774
	3 1 4	1.722	3	1.718
	4 0 2	—	—	1.692
6 2 0	2 4 0	1.658	2	1.664
	4 2 0	—	—	1.595
5 3 3	0 3 5	1.642	10	1.631
	3 0 5	—	—	1.624
	1 4 3	—	—	1.581
	4 1 3	—	—	1.545
6 3 1	2 1 6	1.559	2	1.557
	4 1 3	1.546	8	1.545
6 4 2	2 4 4	—	—	1.413
	4 2 4	1.370	2	1.370

[a] $a = 7.04$, $b = 7.55$, and $c = 10.70$ Å.

lore ($A_2B_2X_7$) structure to lower symmetry is known to occur in defective pyrochlores; thus $PbTl_{0.9}Nb_2O_{6.45}$ is tetragonal ($P\bar{4}m2$) (*8*) and $(NH_4)Fe^{2+}Fe^{3+}F_6$ is orthorhombic (*Pnma*) (*9*). In both the cases, the distortion to lower symmetry arises from an ordering of anion vacancies in the pyrochlore structure. Beyerlein *et al.* (8) have shown that ordering of anion vacancies at 8*a* sites in the pyrochlore structure is associated with a displacement of the large *A* cations at 16*d* sites, which results in the appearance of cubic (420) and (640) reflections in the X-ray diffraction pattern; ordering of large *A* site ions is also revealed by the appearance of weak (110) reflection as seen in $PbTl_{0.9}Nb_2O_{6.45}$. In the pattern of $Bi_{1.33}V_2O_6$, we do see cubic (110) and (420) reflections [$(110)_c$ is split into $(010)_o$ and $(100)_o$ due to orthorhombic distortion] (Table I) indicating that the orthorhombic distortion of $Bi_{1.33}V_2O_6$ is probably due to an ordering of anion vacancies in the pyrochlore structure.

We have prepared charge-coupled pyrochlores $TlBiM_2O_7$ (M = Nb or Ta) and $Bi_2NbM'O_7$ (M' = Cr or Fe) containing multiply-substituted cations at A(16*d*) or B(16*c*) sites to examine the possibility of cation ordering in the absence of anion vacancies in cubic pyrochlores. While $TlBiNb_2O_7$ and $TlBiTa_2O_7$ are new pyrochlores reported for the first time, $Bi_2NbM'O_7$ is already known in the literature (*10*). We have found that $Bi_2NbM'O_7$ pyrochlores are favored over $Bi_7Nb_3M'_2O_{21}$ Aurivillius phases. All the four pyrochlore phases adopt cubic ($Fd\bar{3}m$) structures (Table II). Careful (slow) recording of the powder diffraction pattern of $TlBiNb_2O_7$ (Table III) showed no additional reflections other than those required for the $Fd\bar{3}m$ space group. Structure refinement of $TlBiNb_2O_7$ using X-ray powder diffraction intensities (*11*) established that cations at 16*d* sites are not ordered, the space group remaining $Fd\bar{3}m$. It is noteworthy that Pb and Tl atoms are ordered in $PbTl_{0.9}Nb_2O_{6.45}$ (*8*) while Bi and Tl are not ordered in $TlBiNb_2O_7$; A-site cation ordering in the pyrochlore structure appears to be associated with anion vacancy ordering. It is significant that while cubic $Pb_2M_2O_7$ (M = Nb or Ta) pyrochlores do not exist (12), $TlBiM_2O_7$ exist in the cubic pyrochlore structure.

TABLE II

UNIT CELL PARAMETERS OF BISMUTH-CONTAINING PYROCHLORES

Compound	a (Å)
Bi_2NbCrO_7	10.44
Bi_2NbFeO_7	10.53
$TlBiNb_2O_7$	10.70
$TlBiTa_2O_7$	10.77

TABLE III

X-RAY POWDER DIFFRACTION DATA OF $TlBiNb_2O_7$

$h\ k\ l$	d_{obs} (Å)	$d_{calc}{}^{a}$ (Å)	I_{obs}	$I_{calc}{}^{b}$
1 1 1	6.19	6.18	8	8
3 1 1	3.232	3.230	1	6
2 2 2	3.100	3.092	100	104
4 0 0	2.678	2.678	49	49
3 3 1	2.455	2.458	8	4
3 3 3	—	2.061	0	0
5 1 1	—	2.061	0	0
4 4 0	1.892	1.893	46	43
5 3 1	1.810	1.810	3	1
6 2 2	1.614	1.615	48	46
4 4 4	1.547	1.546	12	13
8 0 0	1.337	1.339	10	7
6 6 2	1.229	1.229	16	16
8 4 0	1.197	1.198	13	14

[a] a = 10.70 Å.

[b] I_{calc} corresponds to O(48*f*): x = 0.296(3) and the overall isotropic temperature factor B_o = 0.53(3), with all the other atoms occupying the fixed coordinates of the cubic pyrochlore structure (space group $Fd\bar{3}m$). The weighted residual factor, R_W = 8.8%.

$Bi_{1.33}V_2O_6$ is semiconducting and paramagnetic (μ_{eff} = 1.12 B.M.) above 120 K.

TABLE IV

STRUCTURAL DATA OF METAL OXIDES CONTAINING TRIVALENT BISMUTH

Compound	Structure	Space group	Nature of bismuth-oxygen polyhedron[a]	Nature of MO_6 octahedron[a]	References
Bi_2WO_6	$n = 1$ member of the Aurivillius family	$B2cb$	Bi is five-coordinated; four oxygens in Bi_2O_2 layer (Bi–O = 2.21, 2.28, 2.36, and 2.42) and the fifth one (2.49) from WO_6 octahedron	Distorted octahedron (1.69 × 2, 1.82 × 2, and 2.30 × 2)	*15*
Bi_3TiNbO_9[b]	$n = 2$ member of the Aurivillius family	$A2_1am$	Bi is eight-coordinated four oxygens (~2.29) from (Bi_2O_2) layer and four (~2.82) from the perovskite slab	Distorted octahedron (1.73, 1.77, 1.83, 2.20, 2.25, and 2.31)	*16*
$Bi_4Ti_3O_{12}$	$n = 3$ member of the Aurivillius family	Pc	Bi is eight-coordinated (2.29 × 4 and 2.72 × 4)	Distorted octahedron (1.75 × 2, 1.97 × 2 and 2.20 × 2)	*16*
$Bi_7Ti_4NbO_{21}$	*A* regular intergrowth of $n = 2$ and $n = 3$ members of the Aurivillius family	$I2cm$	—	—	*17*
$BiNbO_4$ (β)	$(NbO_4)_\infty$ octahedral sheets are held together by bismuth atoms	$P\bar{1}$	Bi has eight-coordination (square antiprism) (2.10, 2.30, 2.37, 2.59, 2.64, 2.74, 2.75, and 3.01)	Distorted octahedron (1.80, 1.87, 1.90, 1.97, 2.10, and 2.23)	*18*
$BiNbO_4$ (α)	Orthorhombic $SbNbO_4$ structure	$Pna2_1$	—	—	*18*
$Bi_3Ru_3O_{11}$	$KSbO_3$-related	$Pn3$	Two kinds of Bi; Bi_I is eight-coordinated (2.44 × 2 and 2.51 × 6) and Bi_{II} is nine-coordinated (2.21 × 3, 2.61 × 3, and 2.82 × 3)	Distorted octahedron (1.98 × 2, 1.89 × 2, and 2.03 × 2)	5
$Bi_2Rh_2O_{6.8}$	Pyrochlore	$Fd3m$	Bi is eight-coordinated (2.54 × 6 and 2.22 × 2)	Regular octahedron (1.97 × 6)	*19*
$BiCrWO_6$	Pyrochlore	$Fd3m$	Bi is eight-coordinated (2.59 × 6 and 2.10 × 2)	Regular octahedron (1.96 × 6)	*20*
$BiReO_4$	Corner-linked ReO_6 octahedra connected by Bi atoms	$Cmcm$	Distorted octahedron around Bi (2.26 × 2 and 2.42 × 4)	Distorted octahedron (1.87 × 2, 1.92 × 2, and 2.02 × 2)	*21*
$BiRe_2O_6$	Corner-linked Re_2O_{10} units connected by Bi atoms	$C2/m$	Distorted octahedron around Bi (2.12, 2.28, 2.29, 2.35, 2.72, and 2.82)	Distorted octahedron (1.92, 2.02, 1.97 × 2, and 1.98 × 2)	*21*

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[a] The values in parenthesis correspond to bond lengths in Å.

[b] Simultaneous substitution of Bi by Pb and Nb by W in Bi_3TiNbO_9 yields new phases $Bi_{3-x}Pb_xTiNb_{1-x}W_xO_9$ ($x = \frac{1}{3}, \frac{1}{2}, \frac{2}{3}$) which retain the $n = 2$ structure (*23*).

The reciprocal susceptibility-temperature plot shows that the magnetic moments order ferrimagnetically around 10 K. $AV^{4+}O_3$ (A = Ca, Sr) perovskites are Pauli paramagnetic metals (*13, 14*), but the $V^{4+}O_3$ framework in pyrochlore-related $Bi_{1.33}V_2O_6$ apparently does not favor itinerant d-electrons. $TlBiM_2O_7$ (M = Nb or Ta) is a pale yellow diamagnetic insulator, while Bi_2NbCrO_7 and Bi_2NbFeO_7 are paramagnetic insulators.

It is of interest to inquire why pyrochlore-related phases are stabilized in the Bi–V–O and Bi–Nb–Cr(Fe)–O systems instead of layered perovskites of the Aurivillius family, viz., $Bi_4V_3O_{12}$, $Bi_7Nb_3Cr_2O_{21}$, and $Bi_7Nb_3Fe_2O_{21}$. In Table IV we have listed structural data of important trivalent bismuth-containing transition metal oxides. From the table, we see that layered-perovskite phases are formed with d^0 cations such as Ti^{4+}, Nb^{5+}, and W^{6+}. In Bi_2WO_6, a $n = 1$ member of the Aurivillius family, $(Bi_2O_2)^{2+}$ $[A_{n-1}B_nO_{3n+1}]^{2-}$, bismuth is coordinated by five oxygens, four oxygens from the (Bi_2O_2) layer (Bi–O ~ 2.2–2.4 Å) and a fifth (Bi–O ~ 2.49 Å) from the WO_4 layer. In the higher members ($n \geq 2$) of the family, bismuth is surrounded by eight oxygens, four in the (Bi_2O_2) layer and four more from the perovskite slab at longer distance, completing a distorted cubic coordination around Bi^{3+}. Formation of weak bonds between bismuth in the (Bi_2O_2) layers and oxygens of the perovskite slab seems to be essential for the stabilization of Aurivillius phases. This stabilization is possible only in the presence of d^0 cations which permit ferroelectric distortion of the octahedra in the perovskite slabs. Furthermore, among the transition metal oxides containing bismuth, those with d^0 cations invariably crystallize in noncentrosymmetric structures at low temperatures, wherein the transition metal–oxygen octahedra are considerably distorted. Bismuth oxides containing d^n cations, on the other hand, adopt centrosymmetric structures where the metal–oxygen octahedra are more regular. (Distortion of transition metal–oxygen octahedra in $Bi_3Ru_3O_{11}$ and $BiRe_2O_6$ seems to be related to formation of metal–metal bonds.)

Hayashi *et al.* (*22*) have recently shown that in the series $Bi_3NbTi_{1-x}M_xO_9$ (M = Mo, Ru, Os, or Ir), the layered perovskite structure is destroyed beyond $x \sim 0.03$–0.05, stabilizing a pyrochlore structure. These results also clearly show that cations possessing outer d-electrons which suppress ferroelectric distortion of the MO_6 octahedra destabilize the layered perovskite structure. Thus, $Bi_4V_3O_{12}$ containing $V^{4+}: 3d^1$ does not exist in the Bi_2O_3–VO_2 system; instead a pryochlore-related phase is formed in the system. Similarly, $Bi_7Ti_{4.5}W_{0.50}O_{21}$ is formed in the layered perovskite structure (*7*), but similar phases containing chromium or iron, $Bi_7Nb_3Cr_2O_{21}$ and $Bi_7Nb_3Fe_2O_{21}$ do not exist.

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