Synthesis and Characterization of Pyrochlore Oxides Bi₂MM'O₇ (M : Yb, Nd, Sm; M' : Sb, Nb, Ta)

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Abstract

Oxide compounds $Bi_2MM'O_7$ (M: Yb, Nd, Sm; M': Sb, Nb, Ta) have been synthesized by using solid state reaction. As a tool for predicting their stability, a stability field diagram for pyrochlore has been made. All the prepared oxides have a yellow color, except for M = Nd which is grey. Crystal structure types have been determined using powder X-ray diffraction. Single phase pyrochlore was obtained for Bi_2SmSbO_7 , while for Bi_2NdSbO_7 a distorted pyrochlore was obtained. Ideal pyrochlores with small amount of $Bi_{1.5}Yb_{0.5}O_3$ were obtained in Bi_2YbSbO_7 . For Bi_2MNbO_7 , (M: Yb, Nd, Sm) series the obtained phases were a mixture of ideal pyrochlore and small impurities of β -Nb₂O₅. For Bi_2MTaO_7 (M: Yb, Nd, Sm) series in addition to ideal pyrochlore as major phase, a small amount of $MTaO_4$ (M: Yb, Nd, Sm) rutile phase were obtained using the constructed structure map and the lattice energy arguments.

Keywords : pyrochlore, rare-earth oxide, bismuth oxide, X-ray diffraction, solid state reaction.

1. Introduction

Oxide materials with pyrochlore structure have a large number of applications, such as ferroelectric materials, ferromagnetic materials and ionic conductors^{1,2)}. Pyrochlores containing bismuth, such as $Bi_2Ru_2O_7$, have been used as heterogenic catalyst in a process like oxidative coupling of methane, propylene ammoxidation, and hydrocarbon oxidation; other such as $Bi_2Sn_2O_7$, has been used as a sensor and electrode material for oxygen reduction³⁾.

Pyrochlore oxide with general formula of A₂B₂O₇ tolerates wide range of A and B cations. A refers to a large cation with ionic radii of ~1 Å, which could be a monovalent alkaline ion, divalent alkaline earth ion, trivalent lanthanide or post transition cation such Bi³⁺ or Pb²⁺. B cations usually have ionic radii of ~0,6 Å and could be a tetravalent, pentavalent or hexavalent transition or post transition metal ion. It has been observed at a number occasion that inert pair cation, such Bi³⁺, which occupies A site drive a small structural distortion. The ideal structure of pyrochlore is a cubic, Z = 8, space group Fd3m. A cations, which occupy Wyckoff site 16(d), coordinated to eight oxygens, six at equidistant and two of them at shorter distant. Considering only the shortest distant A cations formed a linear chain of A₂O similar to that of Cu₂O. B cations, which occupies 16(c) site, bonded to six O, formed a trigonal antiprism BO_6 . These trigonal antiprism BO_6 share their vertices formed a B_2O_6 network which has a channel through [111] direction. Pyrochlore structure could be regarded as interpenetration of these two network, Figure 14. In some cases, pyrochlore with relatively large cation (~ 1 Å) occupies B site could be prepared, for example Bi₂YNbO₇ and Bi₂LuNb'O₇⁵⁾.



Figure 1. Pyrochlore structure could be regarded as interpenetration of these two network A_2O' (large darker spheres are A cations and small white spheres are O') and B_2O_6 (represented by the edge and vertices sharing octahedral network B cation in the centre of octahedral while O at the vertices of the octahedral).

One of the tools to predict the synthesis possibility of a materials with a certain composition is a structure map. A structure map is a plot which describes stability of phases as a function of a structural features, such as ionic radii^{2,6)}.

This paper describes synthesis of novel pyrochlore which has Bi^{3+} in A site and rare earth metals (Yb, Nd and Sm) in B site. A structure map is constructed as a preliminary step to predict the synthesis possibility of those pyrochlores.

2. Experiments

As a preliminary study preceding the synthesis, a structure map of pyrochlore was made. The map was constructed by plotting the ionic radii of A and B cations. This map could be regarded as a revision for previous map²) by adding several new pyrochlores, mainly from Subramanian⁵. About 400 known pyrochlores were included in the map. The pyrochlores were classified

according to the number of A and B cations. Simple pyrochlores contains single A and B cation, which could be $A_2^{2+}B_2^{5+}O_7$ or $A_2^{3+}B_2^{4+}O_7$. From literature reports the number of pyrochlore with formulae of $A_2^{3+}B_2^{4+}O_7$ outnumber those of the $A_2^{2+}B_2^{5+}O_7^{-2,5)}$. This could be explained simply as a consequence of relatively large number of A^{3+} and B^{4+} cations have ionic radii that fit the pyrochlore lattice. Ionic radii for A and B cations were obtained from Shannon⁸).

Pyrochlore oxides $(Bi_2MM'O_7 (M : Yb, Nd, Sm; M' : Sb, Nb, Ta))$ were synthesized using a solid state reaction using the oxides component Bi_2O_3 , Yb_2O_3 , Nd_2O_3 , Sm_2O_3 , Sb_2O_5 , Nb_2O_5 and Ta_2O_5 in the stoichiometric amount. The mixture was homogenized using mortar and pestle with a small amount of acetone. Subsequently the mixture was transferred into an alumina crucible. The crucible then was heated to 500 °C for 24 hours, 600 °C for 24 hours and 700 °C for 24 hours until no further changes in the X-ray powder diffraction patterns. Cell parameter determination of the product was carried out using Le Bail method implemented in Reitica⁹.

3. Results and Discussion

In addition to simple pyrochlores given at the previous map^{2} , pyrochlores with more complex stoichiometry, including non-stoichiometric pyrochlores such as pyrochlore with O vacancies were also known. In this work, we limited the map to pyrochlore oxides with composition of A₂(BB')O₇ and (AA')(BB')O₇, in addition to simplest pyrochlore A₂B₂O₇. For pyrochlores with more than one cation, ionic radii were taken as an average of ionic radii of the component with their stoichiometries as a weighting factor. The range of ionic radii ratio of the observed pyrochlores is given in the Table 1. The resulted structure map is given in Figure 2. The pyrochlore that will be synthesized, i.e. Bi₂MM'O₇(M : Yb, Nd, Sm; M' : Sb, Nb, Ta) is in the constructed structure map, with the r_A/r_B ratio of 1,44 – 1,59. Thus it can be predicted that the aimed pyrochlore oxides should be stable or could be synthesized.

Table 1. The r_A/r_B range of the observed pyrochlores

No.	Pyrochlore	$r_{\rm A}/r_{\rm B}$
1.	$A_2^{2+}B_2^{5+}O_7$	1,6 - 1,948
2.	$A_2^{3+}B_2^{4+}O_7.$	1,392 - 1,887
3.	$A_2(BB')O_7$	1,337 - 1,85
4.	(AA')(BB')O ₇	1,36 - 1,976



Figure 2. Pyrochlore structure map (\bullet : ambient and \blacktriangle : high pressure synthesis).

All the oxides obtained from the solid state reaction were light yellow in color, except for M = Ndwhich was grey in color. The ionic radii ratio, the average of ionic radii of B site cations and the structure of the obtained phases are given in Table 2. Single phase pyrochlore was obtained for Bi₂SmSbO₇. For Bi₂NdSbO₇, a distorted pyrochlore was obtained. Ideal pyrochlores with small impurities of rutile phase MTaO₄ or β -Nb₂O₅ were obtained for others. Powder diffraction patterns for Bi₂SmSbO₇, Bi₂NdSbO₇ and Bi₂(YbTa)O₇ are given in Figure 3. The refined cell parameter obtained for Bi₂SmSbO₇ was a = 10.819(4) Å, whilst for Bi₂NdSbO₇ 7a = 4.247(2), c = 10.779(4) Å.

No.	Pyrochlore	r_A/r_B	r _B (Å)	Phase(s)
1.	Bi ₂ (YbSb)O ₇	1.594	0.734	$\mathrm{IP} + \mathrm{Bi}_{1.5}\mathrm{Yb}_{0.5}\mathrm{O}_3$
2.	Bi ₂ (NdSb)O ₇	1.478	0.792	Distorted pyrochlore
3.	Bi ₂ (SmSb)O ₇	1.502	0.779	IP
4.	Bi ₂ (YbNb)O ₇	1.552	0.754	$IP + \beta - Nb_2O_5$
5.	Bi ₂ (NdNb)O ₇	1.442	0.812	$IP + \beta - Nb_2O_5$
6.	Bi ₂ (SmNb)O ₇	1.462	0.799	$IP + \beta - Nb_2O_5$
7.	Bi ₂ (YbTa)O ₇	1.464	0.754	$IP + YbTaO_4$
8.	Bi ₂ (NdTa)O ₇	1.552	0.812	$IP + NdTaO_4$
9.	Bi ₂ (SmTa)O ₇	1.464	0.799	$IP + SmTaO_4$

Table 2. Ionic radii ratio, the average of ionic radii of B site cations and the structure of the obtained phases of the synthesized pyrochlores.



Figure 3. Powder diffraction pattern for (a) Bi_2SmSbO_7 , (b) Bi_2NdSbO_7 and (c) $Bi_2(YbTa)O_7$, (*) represents $YbTaO_4$.

It is interesting to note that the series of Bi_2MSbO_7 (M : Yb; Sm, Nd) were obtained as an ideal pyrochlore and a small amount of $Bi_{1.5}Yb_{0.5}O_3$ phase, pure ideal pyrochlore, and a distorted pyrochlore, respectively. This could be explained in term of ionic size of M cation in B site. As shown in Table 2, the ionic radii of Yb < Sm < Nd. The perfect fit could be obtained for M = Yb and Sm. For M = Nd, the distortion in pyrochlore structure was driven by the larger size of Nd than those that normally occupy the site of ideal pyrochlore. The distortion driven by large cation in B site is well documented as has been observed in several pyrochlores⁵⁾. A small amount of $Bi_{1.5}Yb_{0.5}O_3$ present in Bi_2YbSbO_7 could be due to the small heating loss of Sb_2O_3 , among Bi_2O_3 , Yb_2O_3 , and Sb_2O_3 , Sb_2O_3 has greater heating loss tendency as its melting point is significantly lower that the other two oxides⁷).

The cell parameter of Bi_2SmSbO_7 (10.819(4) Å) is larger than cell parameter of Sm_2SmSbO_7 (10.720 Å). This is in agreement with the larger ionic radii of Bi^{3+} (1.31 Å) than Sm^{3+} (1.22 Å)⁸⁾. Cell parameters of Bi_2NdSbO_7 are a = 4.247²⁾, c = 10.779(4) Å. A comparison to an analogous distorted pyrochlore could not be made, due to lack of data available. However from the cell volume these are within the expected values for pyrochlore oxides.

The coexistence of pyrochlore and β -Nb₂O₅ or rutile phase of the type MTaO₄ presumably due to the similarity of their lattice energy. The similarity in lattice energy of the pyrochlore Bi₂MSbO₇ and rutile MSbO₄ could be explained by the fact that rutile phase has similar octahedral network, i.e. it consist of infinite array of MO₆ octahedral.

Lastly, all above observations could be put together using the constructed structure map. The constructed structure map predicted that all the oxides have pyrochlore structure. These were confirmed, although for some composition, presumably due to the similar lattice energy the co-existence of other phases were also observed.

Conclusions

The new structure map which include larger number of pyrochlores as an improvement of previous structure map has been constructed. From the structure map the oxides $Bi_2MM'O_7$ (M : Yb, Nd, Sm; M' : Sb, Nb, Ta) were predicted to have pyrochlore structure. The synthesis attempts of these oxides resulted in:

- 1. single phase pyrochlore for Bi₂SmSbO₇
- 2. a distorted pyrochlore for Bi₂NdSbO₇
- an ideal pyrochlores with small amount of Bi_{1.5}Yb_{0.5}O₃ for Bi₂YbSbO₇,
- an ideal pyrochlore and small impurities of β-Nb₂O₅ for Bi₂MNbO₇
- an ideal pyrochlore as major phase small MTaO₄ rutile phase for Bi₂MTaO₇

All these structures confirmed the prediction of the constructed structure map. The co-existence of other phases presumably due to the similar stability energy.

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