

Synthesis of Novel Oxide Pyrochlores, $A_2BB'O_7$ ($A = \text{La, Nd}$; $BB' = \text{Pb, Sn, Bi}$), by Alkali Melt Route*

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Oxide pyrochlores of the formula $A_2BB'O_7$ ($A = \text{La, Nd}$; $BB' = \text{Pb, Sn, Bi}$) have been synthesized by a low-temperature ambient-pressure route employing KOH melts. All the compositions, including $\text{La}_2\text{Bi}_2\text{O}_7$ and its strontium-substituted derivatives, $\text{La}_{2-x}\text{Sr}_x\text{Bi}_2\text{O}_{7-\delta}$, are deeply colored insulators, confirming that a metallic ground state is not achieved for Pb(IV) and Bi(IV/V) oxides with the pyrochlore structure. © 1993 Academic Press, Inc.

Introduction

Perovskite oxides containing octahedral-site Pb(IV) and mixed-valent Bi are of special interest, exhibiting metallic (1) (e.g., BaPbO_3) and superconducting (2, 3) (e.g., $\text{Ba}(\text{Pb,Bi})\text{O}_3$ and $(\text{K,Ba})\text{BiO}_3$) properties. Unlike these materials, pyrochlore oxides containing Pb(IV) and Bi(V), $A_2\text{Pb}_2\text{O}_7$ ($A = \text{rare earth}$) and $AA'\text{PbBiO}_7$ ($A = \text{rare earth}$; $A' = \text{Ca, Sr, Ba}$), are colored insulators (4, 5), even though Pb(IV) and Bi(V) occupy octahedral sites and $(\text{PbBi})\text{O}_6$ octahedra share corners in the cubic pyrochlore ($Fd\bar{3}m$) structure just as in the perovskite structure. These pyrochlore oxides containing Pb(IV) and Bi(V) have been prepared at high pressures (3 kbar, 700–800°C) (4, 5). Here, we report the synthesis of several new and already known oxide pyrochlores containing lead, bismuth, and tin by a low-temperature ambient-pressure method employing alkali melts (6).

All the compositions investigated are insulating, including the newly synthesized $\text{La}_2\text{Bi}_2\text{O}_7$ and its strontium substituted derivatives $\text{La}_{2-x}\text{Sr}_x\text{Bi}_2\text{O}_{7-\delta}$. The results reinforce the earlier conclusion (7) that Pb(IV) and Bi(IV/V) oxides with the pyrochlore structure do not have a metallic ground state.

Experimental

$A_2BB'O_7$ ($A = \text{La, Nd}$; $BB' = \text{Pb, Sn, Bi}$) pyrochlores were synthesized by reacting stoichiometric mixtures of A_2O_3 and $\text{PbO}_2/\text{SnO}_2/\text{Bi}_2\text{O}_3$ in KOH melt at 300–450°C for several days. Typically, about 2 g of the oxide mixture and 50 g of fresh KOH in a high-alumina crucible were heated in an air oven to 300°C. A clear melt was formed initially from which solid product separated out after about 2 days. Reaction was continued for 2 more days under the same conditions, if necessary by adding another 5–10 g of KOH to the melt. The product was isolated from the cool, solidified melt by dissolving the alkali with distilled water, and was dried at 110°C in air. For bismuth-

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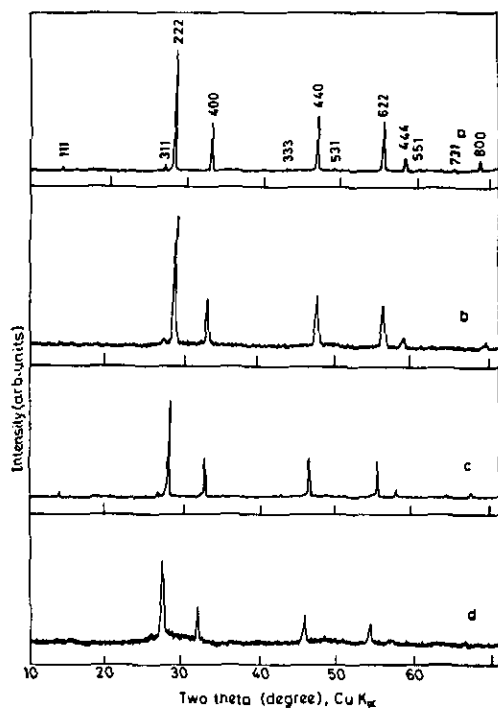


FIG. 1. X-ray powder diffraction patterns of (a) $\text{La}_2\text{Pb}_2\text{O}_7$, (b) $\text{La}_2\text{PbSnO}_7$, (c) $\text{La}_2\text{Pb}_{1.5}\text{Bi}_{0.5}\text{O}_7$, and (d) $\text{La}_2\text{Bi}_2\text{O}_7$.

containing compounds, we found that higher temperatures (400–450°C) were required to form the desired phase.

The product oxides were characterized by powder X-ray diffraction, infrared absorption spectroscopy, and chemical analysis of the oxygen content. Room-temperature electrical resistivity of the powder samples, pressed into cylindrical pellets, was measured by a two-probe method. The oxygen content due to higher oxidation states of Pb and Bi was determined by iodometric titration using KI.

Results and Discussion

We employed KOH melt as a reaction medium for the synthesis of Pb(IV)- and Bi(IV/V)-containing $A_2BB'O_7$ ($A = \text{La, Nd}$; $BB' = \text{Pb, Bi}$) pyrochlores, since molten al-

kali hydroxides are known to stabilize high oxidation states for metals such as copper and nickel (6, 8). First, we synthesized $\text{La}_2\text{Pb}_2\text{O}_7$ and $\text{Nd}_2\text{Pb}_2\text{O}_7$ by this method, which were earlier synthesized at high pressures. We could readily obtain single-phase materials of these pyrochlores by the KOH melt route (Fig. 1). The color, oxygen content, and lattice parameters of these pyrochlores (Table I) are in agreement with the data reported already for the same phases synthesized by the high-pressure route, indicating that Pb(IV) in these pyrochlores is stabilized at ambient pressure in the KOH melt. Next, we synthesized several new compositions of the $A_2BB'O_7$ type containing Pb(IV), Sn(IV), and mixed-valent Bi at the B site. In Table I, we list the data for the phases successfully synthesized by the KOH melt route. In Fig. 1 and Table II, we give the powder X-ray diffraction data for a few typical pyrochlores synthesized by this route.

We could readily synthesize $\text{La}_2\text{PbSnO}_7$ and $\text{Nd}_2\text{PbSnO}_7$, which are new pyrochlores containing Pb(IV) and Sn(IV) at the B site (Table I). The lattice parameters of these pyrochlores are intermediate between the values of the corresponding Pb(IV) and Sn(IV) analogs, as expected. $\text{La}_2\text{Pb}_{1.5}\text{Bi}_{0.5}\text{O}_7$ and $\text{La}_2\text{PbBiO}_7$ are two other new pyrochlores which we synthesized for the first

TABLE I
COMPOSITION, LATTICE PARAMETER, AND ELECTRICAL RESISTIVITY DATA FOR $A_2BB'O_7$ ($A = \text{La, Nd}$; $BB' = \text{Pb, Sn, Bi}$) PYROCHLORES

Compound	a (Å)	$\rho_{300\text{K}}$ (Ω cm)	Color	Oxygen content ^a
$\text{La}_2\text{Pb}_2\text{O}_7$	10.970(5)	1×10^7	Red	6.94
$\text{Nd}_2\text{Pb}_2\text{O}_7$	10.843(5)	$> 10^8$	Brown	6.97
$\text{La}_2\text{PbSnO}_7$	10.818(7)	3×10^7	Brown	6.99
$\text{Nd}_2\text{PbSnO}_7$	10.704(2)	$> 10^8$	Yellow	6.94
$\text{La}_2\text{Pb}_{1.5}\text{Bi}_{0.5}\text{O}_7$	10.959(7)	1×10^7	Brown	7.01
$\text{La}_2\text{PbBiO}_7$	11.005(7)	2×10^6	Brown	6.95
$\text{La}_2\text{Bi}_2\text{O}_7$	11.211(7)	1×10^7	Brown	7.10
$\text{La}_{1.5}\text{Sr}_{0.5}\text{Bi}_2\text{O}_7$	11.220(5)	1×10^5	Brown	6.61
$\text{La}_2\text{Sn}_2\text{O}_7$	10.714(7)	Very high	White	—

^a Determined by iodometry. The standard deviation in the oxygen content is within ± 0.03 .

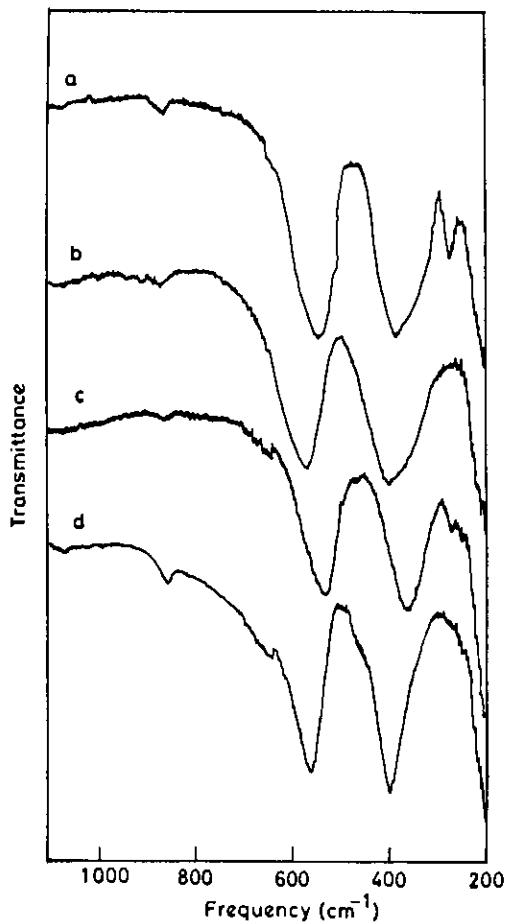


FIG. 2. Infrared absorption spectra of (a) $\text{La}_2\text{Pb}_2\text{O}_7$, (b) $\text{La}_2\text{PbSnO}_7$, (c) $\text{La}_2\text{Pb}_{1.5}\text{Bi}_{0.5}\text{O}_7$, and (d) $\text{La}_2\text{Bi}_2\text{O}_7$.

cm^{-1}) compared to those of $\text{La}_2\text{Pb}_2\text{O}_7$ (520 and 370 cm^{-1}). This shift is probably indicative of a greater covalency of Bi(V)-O bonds as compared to the Pb(IV)-O bonds.

In summary, we have successfully synthesized several oxide pyrochlores containing Pb(IV), Sn(IV), and Bi(IV/V) at am-

bient pressures by employing KOH melt as the reaction medium. None of the pyrochlore oxides investigated exhibits a metallic behavior. These oxides are expected to be potential catalysts for the direct conversion of methane to higher hydrocarbons via oxidative coupling (12).

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