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Synthesis and Electrical Properties of Perovskite Oxides, $LnB_{0.75}B'_{0.25}O_3$

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A series of ordered perovskite oxides of the type $Ln^{2+}_{0.75}B'^{6+}_{0.25}O_3$ (Ln = rare earth or Y; B = Mn, Fe, Co, Ni; B' = Mo, W, Re) has been synthesized and characterized by X-ray analysis and density measurements. Compounds with Ln = La are easily formed in all cases as single-phase materials and have either cubic or orthorhombic symmetry. When Ln = rare earth or Y, single-phase materials are formed only in the case of $LnFe_{0.75}Mo_{0.25}O_3$ and these possess an orthorhombic structure. All the phases tested are extrinsic semiconductors in the range of 25–350°C, with E_a ranging from 0.1 to 0.4 eV. Resistivity of the Ln(Fe, Mo)O_3 series of oxides increases from Ln = La to Ln = Lu. Ni-containing compounds are p type, while those containing Fe or Co in the B sites are n type.

Introduction

Oxide perovskites of the general formula, ABO_3, are a distinct class of compounds possessing interesting electrical, dielectric, and magnetic properties (*1, 2*). If the criteria of electrical charge neutrality and ionic radius tolerance factor are satisfied, complex oxides with the general formula $A(B_xB'_y)O_3$ with the perovskite-related structure can occur, and in fact, many compounds with $x, y = 0.67$, 0.33 and 0.50, 0.50 have been synthesized and reported in the literature (*1, 3, 4*). Examples of one series, $A(B_{0.75}B'_{0.25})O_3$, are relatively unknown; it was only recently that Boyer and Baud (*5*) reported the synthesis of compounds of the type $LaB_{0.75}B'_{0.25}O_3$ with the ionic valency pairs B, B' (+2, +6) involving Fe, Co, Ni and Mo, W, Re, respectively. They found that ordered perovskites form in the series. Torii and Matsumoto (*6*) independently reported the synthesis and electrical and magnetic properties of the compounds $LaNi_{0.75}B'_{0.25}O_3$, (B' = Mo, W). Since in the above series, the B element is a $3d$ transition metal, B' is an element of $4d$ or $5d$ series, and both B and B' can exhibit different valence states, interesting and unusual electrical and magnetic properties can be exhibited by the system. Many combinations of ionic valency pairs (B, B') with the lanthanide elements (Ln) to form $Ln^{3+}(B^{2+}_{0.75}B'^{6+}_{0.25})O_3$ perovskites exist, and we have tried some of them. Single-phase materials have been obtained in the following cases: La(B, Mo)O_3, B = Mn, Fe, Co, Ni; La(Ni, B')O_3, B' = W, Re; La(Co, W)O_3 and Ln(Fe, Mo)O_3, Ln = rare earth or Y. In this paper we report on the synthesis and characterization and electrical properties of the above compounds.

Experimental

High-purity starting materials were used: Ln_2O_3, 99.99% purity except for Ho_2O_3, which was 99.9% (Indian Rare Earths);

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Ln_2O_3, Ln = Eu, Er, Tm, Yb, and Lu, from American Potash Co. or Ventron, USA (99.99% pure); Mn metal, NiO, and MoO_3 (J&M, Specpure); ReO_3, 99.9% (Ventron, USA); and WO_3 (BDH, AR). FeO was prepared from Fe_2O_3 (99.9%) and Fe (J&M, Specpure) by reacting stoichiometric amounts of the reactants in an evacuated and sealed quartz tube at 900°C for 3 days and subsequent quenching. X Rays showed the product to be single phase and the composition ascertained from the lattice parameter (*7*) indicated it to be $Fe_{0.96}O$. CoO was prepared by heating Co_3O_4 (Fisher, USA, 99.9% pure) in vacuum (10^{-4} Torr) at 1000°C. X-Ray data revealed the product to be single phase and stoichiometric. MnO was prepared by the decomposition of Mn-nitrate in air to MnO_2 and subsequent reduction at 800°C for 4 hr in pure H_2. The purity of the phase was checked by X-ray diffraction. Pr_2O_3 and Tb_2O_3 were made from Pr_6O_{11} and Tb_4O_7 (99.9%, Indian Rare Earths) by H_2 reduction for 6 hr at 600 and 900°C, respectively (*8*). The constituent oxides in the stoichiometric proportion $(\frac{1}{2}\,La_2O_3+\frac{3}{4}BO+\frac{1}{4}B'O_3)$ were thoroughly ground in an agate mortar, pelletized, and sealed in evacuated quartz tubes. Experiments with ReO_3, which is extremely reactive in air and moisture, were done in a nitrogen-filled dry box. The quartz tubes containing the mixed oxides were then heated at 1000–1050°C for 1 or 2 days and then either gradually cooled or quenched. Preheating at temperatures of 600–700°C for 6–12 hr was always done before attaining the high temperatures, and this helped in obtaining single-phase materials. $LaNi_{0.75}Mo_{0.25}O_3$ and $LaNi_{0.75}W_{0.25}O_3$ were also synthesized by heating the respective oxides in air at 1350°C for 6–12 hr. X-Ray powder patterns (diffractometer and Debye–Scherrer camera) were taken with either Co or CuK_α radiation using a Philips unit. The lattice parameters were obtained by least-squares fitting procedures using computer programs. Powder densities were obtained at 25°C using dibromoethane or nitrobenzene liquid and a pycknometer. Polycrystalline pellets (2–3 mm thick, 1.25-cm diameter) were made by cold pressing in a die at 4–5 tons/cm^2 pressure. These were then sintered at 1100°C for 4–6 days in vacuum. Measurements showed that the pellets were 75–80% theoretically dense. Micrographic examination revealed the grain size to be 10–20 μm. Electrical resistivity (ρ) and Seebeck coefficient (α) data were obtained on the sintered pellets using an apparatus fabricated at our laboratory. A Systronics (India) LCR bridge (Q-meter) was used to measure two-probe resistivity (ac, 1 kHz) in the range of 25–350°C for all the compounds except $LaNi_{0.75}Mo_{0.25}O_3$. The latter compound exhibited a low resistivity at 25°C, and measurements were made by a four-probe van der Pauw technique in the range of 150–300 K. DuPont (USA) silver paint was used to make electrical contacts. Temperatures were measured with a calibrated Cr–Al thermocouple. Measurements of α were done in the range of 300–600 K. The principle used is based on the static method (*2, 9*) where different temperature gradients (ΔT) are created at both ends of the sample and stabilized around a mean temperature (T_m) and the corresponding Seebeck potentials (ΔE) are measured using a Philips GM 6020 dc microvoltmeter. Values of α are then obtained by extrapolating the ($\Delta E/\Delta T$) vs. ΔT plots to zero ΔT at the T_m, since by definition, $\alpha = (\Delta E/\Delta T)_{\Delta T\to 0}$. The sign of the cold junction was taken as the sign of α. ΔE values were measured with Pt leads, whereas ΔT and T_m were measured using calibrated Pt–13% Rh thermocouples.

Results and Discussion

$La(B_{0.75}B'_{0.25})O_3$ *Perovskites*

Lanthanum-containing compounds are formed easily under the preparative conditions employed. Well-defined single-phase materials were obtained in the following cases: La(B, Mo)O_3, B = Mn, Fe, Co, Ni; La (Ni, B')O_3, B' = W, Re; and La(Co, W)O_3. Optimum preparative conditions and the lattice parameters obtained are presented in Table I. Single-phase materials, however, were not obtained in the following cases: La(B, B')O_3, B = Mn, Fe and B' = W, Re; considerable amounts of the LaBO_3 perovskite and unreacted La_2O_3 were detected in the products formed after the heat treatment. These phases were not investigated further. The single-phase compounds are black in color and are stable in air and in the presence of moisture. Phases containing Mn, Fe, and Co, however, decompose at temperatures above 800°C when heated in air, and wet chemical analysis showed the presence of Mn^{3+}, Fe^{3+}, and Co^{3+} in the compounds. Iron-containing phases exhibited a color change from black to light brown. X-Ray diffraction data of the air-heated samples showed the presence of LaBO_3 (B = Mn, Fe, and Co) perovskite and La_2O_3 phases.

TABLE I

CRYSTAL AND ELECTRICAL DATA ON $LnB_{0.75}B'_{0.25}O_3$ PEROVSKITES

Compound	Lattice parameters[b] (Å)			ρ (Ω cm	
($LnB_{0.75}B'_{0.25}O_3$[a])	a	b	c	(50°C))	E_a (eV)
La(NiMo)O_3	7.868			1.6×10^0	0.11
	(7.868)				
La(NiW)O_3	7.884			4.0×10^4	0.40
	(7.888)				
La(NiRe)O_3	7.870			7.5×10^2	0.23
	(7.909)				
La(CoMo)O_3	5.554	5.590	7.958	1.2×10^3	0.22
	(5.573	5.573	7.922)		
La(CoW)O_3	5.586	5.628	7.983	8.3×10^3	0.33
	(5.614	5.614	7.972)		
La(MnMo)O_3	5.607	5.675	7.934	2.0×10^4	0.30
La(FeMo)O_3	5.594	5.636	7.940	3.1×10^2	0.14
	(5.583	5.583	7.929)		
Pr(FeMo)O_3	5.488	5.613	7.902	3.2×10^2	0.15
Nd(FeMo)O_3	5.471	5.619	7.861	3.8×10^2	0.19
Sm(FeMo)O_3	5.400	5.622	7.767	3.3×10^2	0.20
Eu(FeMo)O_3	5.374	5.633	7.708	5.0×10^2	0.20
Gd(FeMo)O_3	5.373	5.647	7.709	5.5×10^2	0.23
Tb(FeMo)O_3	5.368	5.641	7.699	1.1×10^3	0.23
Dy(FeMo)O_3	5.338	5.606	7.646	1.7×10^3	0.26
Ho(FeMo)O_3	5.324	5.593	7.632	6.9×10^3	0.30
Er(FeMo)O_3	5.287	5.611	7.618	7.2×10^3	0.30
Tm(FeMo)O_3	5.265	5.579	7.583	1.9×10^4	0.32
Yb(FeMo)O_3	5.252	5.543	7.554	2.1×10^4	0.37
Lu(FeMo)O_3	5.218	5.630	7.469	2.5×10^4	0.36
Y(FeMo)O_3	5.356	5.646	7.673	2.4×10^4	0.32

[a] Optimum preparative conditions: 1350°C, 6 hr in air for (Ni, Mo) and (Ni, W) phases; 1000°C, 6 hr and 1150°C, 12 hr in vacuum for (Ni, Re) phases; 600°C, 6 hr and 1100°C, 24 hr in vacuum for all others.

[b] For the cubic and orthorhombic phases; values in parentheses are from Refs. *5* and *6*.

We have indexed the La(Ni, B')O_3, B' = Mo, W, and Re, phases on the basis of an fcc structure. The lattice parameters for the Ni- and W-containing compounds agree very well with those reported by Torii and Matsumoto (*6*) and those of Boyer and Baud (*5*). Superlattice lines corresponding to $a \approx 7.9$ Å were clearly seen in the W compound but not in the Mo-containing compound. This might be due to the smaller difference in the X-ray atomic scattering factors between Ni^{2+} and Mo^{6+} than between Ni^{2+} and W^{6+} ions. Neutron diffraction experiments may reveal clearly the superlattice existing in these phases. Our value of a for $LaNi_{0.75}Re_{0.25}O_3$ is slightly smaller than that reported by Boyer and Baud (*5*). The ionic radii of Mo^{6+} and W^{6+} are identical (0.6 Å), whereas that of Re^{6+} is 0.52 Å (*10*). We would expect the a values of Mo and W compounds in $LaNi_{0.75}B'_{0.25}O_3$ to be identical and larger than the Re compound. However, our data show that a values follow the order, W-containing compound > Mo-containing compounds = Re-containing compounds. Reasons for this behavior are not known. Pycnometrically measured densities are in agreement with the values reported by Boyer and Baud (*5*) and give $Z = 4$ for the above phases. Boyer and Baud (*5*) indexed the La(Co, B')O_3, B' = Mo, W and La(Fe, Mo)O_3 phases on the basis of a tetragonal unit cell. Our results are in better agreement with the calculated d values and intensities of the observed X-ray diffraction pattern lines when we assume an orthorhombic unit cell (Fig. 1 and Table I) for the above phases and also for the La(Mn, Mo)O_3 phase.

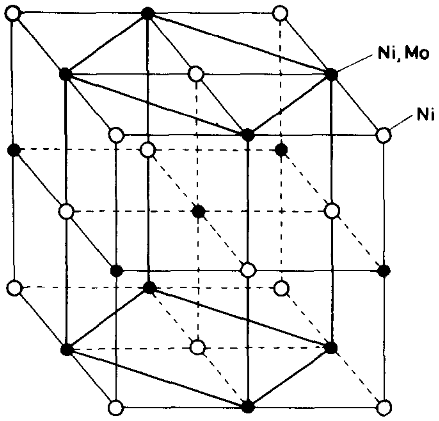

FIG. 1. Geometric connection between the fcc unit cell of $LaNi_{0.75}Mo_{0.25}O_3$ and the body-centered orthorhombic unit cell of $LaFe_{0.75}Mo_{0.25}O_3$. Only Ni and Mo ions are indicated. If we consider the small 1/8 cube, La ions are at the centers and O ions are at the edge centers.

Torii and Matsumoto (*6*) reported the magnetic susceptibility (χ) data on the La(Ni, Mo)O_3 and La(Ni, W)O_3 phases and showed that Ni exists in a 2+ state even though the effective magnetic moments, μ_{eff}, are slightly larger than the spin-only values (3.39 vs 2.83) and that the (Ni, W) phase is ferrimagnetic. Wet chemical analysis of La(Fe, Mo)O_3 showed that all the iron is present in a Fe^{2+} state. Room-temperature Mössbauer data also reveal the presence of only Fe^{2+} in this compound. Thus, the assumed valence states of the phases as written in $La^{3+}B^{2+}_{0.75}B'^{6+}_{0.25}O_3$ are fairly accurate. Detailed χ–T data on our samples are not yet available, but preliminary results show ferrimagnetism in La(Ni, Re)O_3 in addition to the La(Ni, W)O_3 phase.

Resistivity studies as a function of temperature show that all the La($B_{0.75}B'_{0.25}$)O_3 phases prepared as single-phase materials are semiconductors with energies of activation, E_a, obtained from Arrhenius plots (Figs. 2 and 3 and Table I), ranging from 0.11 to 0.40 eV, indicating an extrinsic behavior. Our results are in agreement with those of Torii and Matsumoto (*6*) on the La(Ni, B')O_3, B' = Mo, W phases. It is known that absolute values of resistivity obtained on powder compacted specimens are not very reliable due to complications arising out of porosity, grain boundary, and contact resistance effects, and hence the measurements are not as meaningful as those made on single crystals.

However, trends in the ρ–T and E_a data shown by a related series of compounds prepared and measured in pellet form under identical conditions are probably real and significant. We find that in the La(Ni, B')O_3 (B' = Mo, W, and Re) phases, ρ varies as Mo < Re < W, and in the La(B, Mo)O_3 (B = Ni, Co, Fe, Mn) phases, ρ varies as Ni < Fe < Co < Mn. It is possible that in Mo^{6+}-containing compounds, some of the sites are present as Mo^{5+} (and Ni^{3+}) and this mixed valence can give rise to a large conductivity. Similarly, the behavior of the La(B, Mo)O_3 series mentioned above is probably an indication of the ease of existence of B^{2+}, B^{3+} ions (e.g., Ni and Fe vs Co and Mn) in the material. The consistent semiconducting nature of all the phases shows that the d electrons of B^{2+} ions are localized. The conclusion that the extrinsic conduction in these compounds arises by the hopping of charge carriers from site to site (between B and B or B and B') is borne out by the Seebeck coefficient data (Fig. 4). The La(Ni, B')O_3 (B' = Mo, W, and Re) phases showed p-type behavior, while the

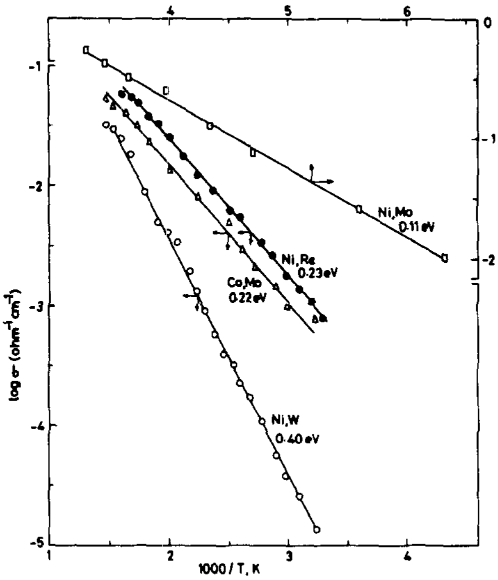

FIG. 2. Electrical conductivity vs $1/T$ plots for La$B_{0.75}B'_{0.25}O_3$ perovskites. Elements B, B' and E_a values are indicated.

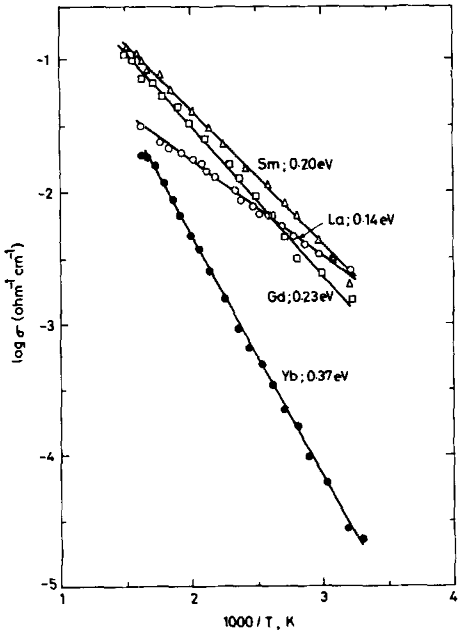

FIG. 3. Electrical conductivity vs $1/T$ plots for LnFe$_{0.75}$Mo$_{0.25}$O$_3$ perovskites. Elements Ln and E_a values are indicated.

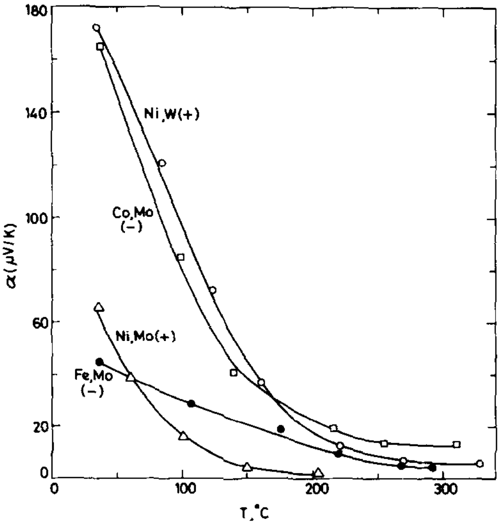

FIG. 4. Seebeck coefficient vs T plots for La$B_{0.75}B'_{0.25}O_3$ perovskites. Elements B, B' and the sign of α are indicated.

La(B, Mo)O_3 (B = Co and Fe) phases exhibited n-type behavior. The possibility of creation of anion vacancies in the compounds by the preparative technique employed (heating in evacuated tubes) is rules out because the La(Ni, Mo)O_3 phase synthesized by both the methods (see Experimental) showed identical α–T behavior, in addition to the consistency in the crystal and resistivity data. Values of α decrease rapidly with increases in temperature up to 200°C for all the compounds examined (Fig. 4) and level off to values ranging from 5 to 15 μV/K between 200 and 330°C. However, no change in sign of the charge carriers was noted in the compounds up to the maximum temperature (330°C) presently studied. A rapid decrease in α with increasing temperatures and a leveling off to smaller values at higher temperatures have also been noticed in LnCoO_3 (*11*) and Ln_2CuO_4 (*12*) oxides and are indicative of localized-collective transitions of the d electrons. It is possible that the La(BB')O_3 phases also exhibit similar collective electron behavior at temperatures above 350°C (~200°C for the La(Ni, Mo)O_3 phase) as shown by our α–T data. However, detailed studies by way of resistivity, χ, DTA, and heat capacity are needed to clarify this.

Ln(*Fe*$_{0.75}$*Mo*$_{0.25}$)*O*$_3$ *and Other Ln-Containing Perovskites*

Efforts were made to synthesize the corresponding rare earth- or Y-containing perovskites in place of La in the La(BB')O_3 phases. Single-phase materials were obtained only in the case of Ln(Fe$_{0.75}$Mo$_{0.25}$)O_3. In other cases (e.g., Ln = Nd, Gd; B = Ni, Co; B' = Mo, W) either the starting materials remained unreacted or highly impure phases were obtained under the preparative conditions employed. One exception is Ho(Mn$_{0.75}$Mo$_{0.25}$)O_3. Apparently, this phase seems to be formed as is revealed by a well-defined X-ray diffraction pattern, but the compound could not be indexed either as an orthorhombic or as a hexagonal (HoMnO_3 type (*13*)) lattice. Further measurements have not been made on this compound.

Ln(Fe, Mo)O_3 phases were indexed on the basis of an orthorhombic unit cell similar to the La-containing compound. Optimum preparative conditions and the least-squares-fit lattice parameters are given in Table I. The X-ray powder data on the Gd(Fe$_{0.75}$Mo$_{0.25}$)O_3 phase are presented in Table II. It should be pointed out that the Ln-containing phases involving heavy rare earths (Gd–Lu) showed a few unindexable medium- and weak-intensity X-ray diffraction pattern lines (Table II). Careful examination revealed that these extra lines do not correspond to an impurity phase (e.g., Ln_2O_3, FeO, Fe_2O_3, MoO_2, and MoO_3). It is

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR GdFe$_{0.75}$Mo$_{0.25}$O$_3$

hkl	*d* (Å) (obs)	*d* (Å) (calc)	Int (obs)
002	3.833	3.855	vw
111	3.452	3.475	w
—	3.226	—	m
—	3.147	—	m
020	2.811	2.824	w
112	2.726	2.739	vs
022	2.285	2.278	w
202	2.194	2.204	w
113	2.139	2.145	w
220	1.941	1.946	m
004	1.922	1.927	m
221	1.888	1.887	m
131	1.730	1.731	s
311	1.668	1.667	wb
—	1.643	—	w
132	1.612	1.613	w
024	1.592	1.592	w
312	1.561	1.561	s
133	1.463	1.461	w
041	1.392	1.389	w
224	1.370	1.370	m
400	1.344	1.343	w

possible that the heavy *Ln*-containing phases may adopt a monoclinically distorted orthorhombic lattice; however, the distortion must be smaller, since all the phases can be indexed fairly accurately on the basis of an orthorhombic unit cell. The phases are black in color, and heating in air above 800°C changes the color to light brown and leads to decomposition similar to the La(Fe, Mo)O_3 phase. An interesting feature of the *Ln*(Fe, Mo)O_3 oxide series is that the lattice parameters are of the same order as the corresponding lattice parameters in the orthorhombic *Ln*FeO_3 series, and further, while *a* and *c* exhibit a monotonic decrease with increasing atomic number of *Ln*, the *b* lattice parameter goes through a maximum at around Tb–Gd similar to *Ln*FeO_3 (*14*) and other $LnBO_3$ (B = Cr, Mn, Co, Ni, Ga) (*14, 15*) phases. In the semiconducting $LnFe_{0.75}Mo_{0.25}O_3$ phases, ρ increases (and also E_a) as we go down the *Ln* series (Table I and Fig. 3), indicating an increase in the covalency of the *Ln*–O bond and a decrease in the ionicity of the Fe–O and Mo-O bonds. A decrease in the probability of hopping of the charge carriers would be expected to accompany these changes in the bonding (*16, 17*). However, careful studies on single crystals are needed to establish the mechanism of conduction. Preliminary magnetic susceptibility data indicate that the *Ln*(Fe, Mo)O_3 (*Ln* = Gd–Lu) compounds are strongly magnetic at 25°C and probably exhibit a ferrimagnetic behavior. Detailed magnetic and Mössbauer studies on these materials are in progress and will be reported later.

Acknowledgments

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