Crystal Structure, Thermal Expansion and Electrical Conductivity of $\text{Y}_{0.8}\text{Ca}_{0.2}\text{Fe}_{1-x}\text{Mn}_x\text{O}_{3+\delta}$ ($0 \leq x \leq 1.0$)

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(Received August 23, 2001)

ABSTRACT

The crystal structure, thermal expansion and electrical conductivity of the solid solutions $\text{Y}_{0.8}\text{Ca}_{0.2}\text{Fe}_{1-x}\text{Mn}_x\text{O}_{3+\delta}$ ($0 < x < 1.0$) were investigated. All compositions had the GdFeO_3 -type orthorhombic perovskite structure with trace amounts of a second phase present in case of $x = 0.8$ and 1.0 . The lattice parameters were determined at room temperature by using X-ray powder diffraction (XRPD). The pseudo-cubic lattice constant decreased with increasing x . The average linear thermal expansion coefficient (α_{av}) in the temperature range from 673 to 973 K showed negligible change with x up to $x = 0.4$. The thermal expansion curve for $x = 1$ had a slope approaching zero in the temperature range from 648 to 948 K. The calculated activation energy values for electrical conduction indicate that conduction occurs primarily by the small polaron hopping mechanism. The drastic drop in electrical conductivity for a small addition of Mn ($0 < x < 0.2$) is caused by the preferential formation of Mn^{4+} ions (rather than Fe^{4+}) which act as carrier traps. This continues till the charge compensation for the divalent ions on the A-site is complete. The results indicate that with further increase in manganese content (beyond $x =$

0.4) in the solid solutions, there is an increase in excess oxygen and consequently, a small increase in Mn^{4+} ions which are charge compensated by the formation of cation vacancies.

1. INTRODUCTION

Doped perovskites have been extensively used as cathode materials for solid oxide fuel cells (SOFC) /1/. Strontia-doped lanthanum manganite has been the preferred material because of its high electrical conductivity and good stability in the applicable temperature (1173 to 1273 K) and oxygen partial pressure range (P_{O_2} from 0.21 to 1 atm) /2/. However, it has been found that $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ reacts with yttria-stabilized zirconia (YSZ) electrolyte to form $\text{La}_2\text{Zr}_2\text{O}_7$ during cell fabrication and operation /3,4/. The lanthanum dizirconate has poor electrical conductivity and hence degrades the cell performance over extended periods of operation. Furthermore, the thermal expansion mismatch between $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ and YSZ needs to be reduced /5/.

Rare-earth orthoferrites with perovskite structure display mixed ionic and electronic conductivity and are

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useful for SOFC electrodes [6,7]. The orthoferrites of the composition $Y_{1-x}Ca_xFeO_3$ have been investigated in order to explore the possibility of their application as an electrode material for solid oxide fuel cells [8,9]. It has been found that the coefficient of thermal expansion for calcia-doped $YFeO_3$ closely matches that of yttria-stabilized zirconia. However, the electrical conductivity is rather low ($\sim 10 \text{ S cm}^{-1}$) at about 1273 K. Attempts have been made to partially replace iron with cobalt in order to enhance the electrical conductivity [10]. Manganese when present as the B site element of ABO_3 type perovskites is known to impart high electrical conductivity to the oxide [11]. An attempt has therefore been made in this study to progressively replace the iron with manganese and investigate the resulting structural, thermal and electrical changes. Both pure and doped rare-earth manganites exhibit a high concentration of defects in the oxygen sublattice that involves both oxygen deficit at low P_{O_2} , and oxygen excess at high P_{O_2} . The oxygen non-stoichiometry on the oxygen-excess side decreases by doping with alkaline earth elements.

2. EXPERIMENTAL

$Y_{0.8}Ca_{0.2}Fe_{1-x}Mn_xO_3$ powders with manganese content ranging from $x = 0$ to 1.0 were synthesized by the glycol-nitrate synthesis route [12]. The different compositions were synthesized using yttrium nitrate (99.9 % pure, Indian Rare Earths), ferric nitrate, calcium nitrate and manganous acetate (analytical reagent grade, S. D. Fine Chemicals, India) as the starting materials, and ethylene glycol (extra pure grade) as the reducing agent and polymeric carrier. Used for the synthesis of all the above compositions was a glycol to nitrate molar ratio of 0.42.

The desired amounts of yttrium nitrate, ferric nitrate, calcium nitrate, manganous acetate and ethylene glycol were dissolved in a minimum amount of water in order to form a transparent, red, homogeneous solution. The process was carried out in a cylindrical crystallization dish over a hot plate at full power until a combustion reaction was initiated. The combustion reaction was accompanied by rapid and self-sustaining rise in

temperature. The exothermicity of the combustion reaction increased with Mn content, and for $x > 0.6$ a red glow along with swelling of the reaction mix were noticed. The resulting brown powder was calcined in air at 1023 K for 3.6 ks and then crushed in an agate mortar. The crushed powders were mixed with about 3% polyvinyl alcohol binder and passed through a 60 mesh sieve to form free flowing granules. The granules were uni-axially pressed into bar shaped compacts. All the compacts were sintered in a super-kanthal furnace for 7.2 ks at 1723 K. The dimensions of the sintered bars were approximately 3 mm x 3 mm x 50 mm.

The bulk density of the sintered bars was determined by Archimedes' liquid displacement technique using distilled water as the medium. The same bars were used for the measurement of thermal expansion. Thermal expansion measurements were conducted during heating from 373 K to 1273 K in air at 0.067 K/s using a horizontal quartz dilatometer.

The electrical conductivity was measured by the four-probe D. C. method on sintered bars of approximate dimensions 3 mm x 3 mm x 12 mm that were cut by a diamond saw from the longer samples used for thermal expansion studies. The measurements were performed upon heating from 323 K to 1173 K in air at a rate of 0.05 K/s. Platinum paste was painted on the square cross sectional edges of the sample and along one of the rectangular edges (separated by a distance L) to form current and voltage electrodes, respectively. The sample was heat treated at 1373 K for 3.6 ks to ensure good bonding between the electrodes and the sample. Two platinum wire contacts were made at the rod edges (by spring loading) to act as current contacts, and two voltage contacts were made with platinum wires connected to the voltage electrodes using silver paste. The sample was placed in a horizontal tube furnace. The voltage (V) between the two inner electrodes and the current (I) through the sample were recorded at each temperature. The electrical conductivity σ was calculated by the equation

$$\sigma = LI / VA \quad (1)$$

where A is the electrode area.

The crystal structure at room temperature was determined by X-ray powder diffraction (XRPD) on a JEOL diffractometer using Cu K α radiation. The diffractometer was operated at 30 kV and 20 mA in the scanning range $20^\circ < 2\theta \leq 80^\circ$. The powder for XRPD was calcined at 1723 K for 10.8 ks in air. The unit cell parameters were determined from the XRPD data by using a least squares refinement computer program (HOCT).

3. RESULTS AND DISCUSSION

3.1 Structural Study

The XRPD patterns of the oxides $\text{Y}_{0.8}\text{Ca}_{0.2}\text{Fe}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0) are shown in Fig. 1. While the oxide samples with $x = 0, 0.2, 0.4$ and 0.6 were single phase, those with $x = 0.8$ and 1.0 showed traces of a second phase. The second phase present in the high manganese compositions used in this study was identified as hexagonal YMnO_3 . It has been reported that almost pure hexagonal YMnO_3 coexists with the solid solution $\text{Y}_{1-y}\text{Ca}_y\text{MnO}_3$ for $0.25 \geq y \geq 0.05$ [13]. The major phase in all the samples was indexed on the orthorhombic perovskite (GdFeO_3 -type) structure

Fig. 1: X-ray powder diffraction patterns of $\text{Y}_{0.8}\text{Ca}_{0.2}\text{Fe}_{1-x}\text{Mn}_x\text{O}_3$. Peaks corresponding to the second phase (hexagonal YMnO_3) are identified by ●

/14/ with space group $Pbnm$. In the GdFeO_3 structure, each cell of dimension $a \times b \times c$ is built up of four small distorted perovskite unit cells. In the ideal situation the small unit cell is cubic with a lattice parameter α_p , then $a = b = \sqrt{2} \alpha_p$ and $c = 2 \alpha_p$, which implies that $a = b = c/\sqrt{2}$. However, the small unit cell is distorted in order to accommodate for misfit in ionic sizes and electronically induced deformations. This gives rise to two types of orthorhombic structures; the O-type is characterized by the relationship $a < c/\sqrt{2} < b$ and the O' - type by $c/\sqrt{2} < a \leq b$. A buckling of the network of octahedra corresponding to co-operative rotation about a 110 axis leads to the O - type orthorhombic structure. The O' - type orthorhombic structure is a variant with more severely distorted octahedral environment and is caused by the Jahn-Teller effect of Mn^{3+} which manifests as an extension of the octahedra in one direction in the a-b plane. The lattice parameters, the unit cell volume and the structure type of the compounds examined are listed in Table 1. The variation of a , b and $c/\sqrt{2}$ with x is shown in Fig. 2. It is apparent that beyond $x = 0.4$, b increases and c decreases rapidly until there is a transition from the O-type structure to the O'-type structure when x exceeds 0.8.

Fig. 2: The lattice parameters (a , b , $c/\sqrt{2}$) of $\text{Y}_{0.8}\text{Ca}_{0.2}\text{Fe}_{1-x}\text{Mn}_x\text{O}_3$ as a function of x

Table 1
Phase symmetry, lattice parameters, unit cell volume and type of orthorhombic structure
of the solid solutions $Y_{0.8}Ca_{0.2}Fe_{1-x}Mn_xO_3$

Composition (x)	Phase symmetry	a (Å)	b (Å)	c (Å)	V. (Å ³)	c/√2 (Å)	Relation between a, b and c/√2	Type of orthorhombic structure
0	orthorhombic	5.30158	5.59160	7.60238	225.37	5.37651	$a < b < c/\sqrt{2}$	O-type
0.2	orthorhombic	5.30336	5.55103	7.59035	223.45	5.36800	$a < b < c/\sqrt{2}$	O-type
0.4	orthorhombic	5.29955	5.55339	7.56394	222.61	5.348932	$a < b < c/\sqrt{2}$	O-type
0.6	orthorhombic	5.28353	5.59672	7.52603	222.55	5.32251	$a < b < c/\sqrt{2}$	O-type
0.8	orthorhombic	5.28140	5.62926	7.48061	222.40	5.29039	$a < b < c/\sqrt{2}$	O-type
1.0	orthorhombic	5.28359	5.66365	7.42566	222.21	5.25153	$c/\sqrt{2} < a < b$	O'-type

The pseudo-cubic lattice constant (a'), which represents the lattice parameter of a cubic unit cell containing one ABO_3 unit, can be defined as:

$$a' = (V/z)^{1/3} \quad (2)$$

where V is the volume of the unit cell, and z is the number of ABO_3 units in one unit cell of the crystal ($z = 4$ for an orthorhombic unit cell of the $GdFeO_3$ type). Figure 3 is a plot of a' as a function of Mn content (x). It is evident from the plot that a' decreases with the increase in x . Since Fe is being substituted by Mn in this case, the dependence of a' on x is governed by the mixed valence states of iron and manganese. In order to assess the valence states of iron and manganese in $Y_{0.8}Ca_{0.2}Fe_{1-x}Mn_xO_3$, the defect chemistry of the solid solutions must be considered.

The introduction of Ca^{2+} acceptor dopant in Y^{3+} sites of $YFeO_3$ at high oxygen partial pressures and low temperatures is electronically compensated by the formation of Fe^{4+} cations (holes) [8], according to the reaction:

Fig. 3: Pseudo-cubic lattice constant (a') as a function of x

where Y^X and Fe^X are Y^{3+} and Fe^{3+} cations respectively, on regular sites, Ca' is a Ca^{2+} cation on a

Y^{3+} lattice position and $Fe^\bullet$ is a Fe^{4+} cation on a Fe^{3+} position in the perovskite lattice (Kröger-Vink notation).

The electro-neutrality condition is given by

$$[Ca_Y'] = [Fe_{Fe}^\bullet] \quad (4)$$

Square brackets [] represent the concentration of the defect species within them. At relatively low partial pressures of oxygen and at high temperatures, there is a tendency for oxygen vacancy formation, and this happens by the reduction of Fe^{4+} cations to Fe^{3+} cations.

The electro-neutrality condition is then given by

$$[Ca_Y'] = [Fe_{Fe}^\bullet] + 2[V_O^{\bullet\bullet}] \quad (6)$$

Usually, both $Fe_{Fe}^\bullet$ and $V_O^{\bullet\bullet}$ coexist, and their relative concentrations depend on oxygen partial pressure (P_{O_2}), temperature and the extent of Ca doping /15/. The oxygen vacancy is enhanced by decreasing P_{O_2} and increasing temperature and Ca doping /16/.

It is known in the case of strontium-doped lanthanum perovskites that the ferrite has a greater tendency for oxygen deficiency than the manganite /17,18/. This in turn indicates that Mn^{4+} is more stable to reduction than Fe^{4+} (Eqn. 5). Therefore, when Mn is substituted on the B-site, the charge deficiency on the A-site caused by Ca doping is electronically compensated largely by the formation of Mn^{4+} in preference to Fe^{4+} ions. Since the ionic radius of Mn^{4+} is smaller than that of Fe^{4+} (Table 2), a' (pseudo-cubic lattice constant) decreases rapidly with increasing x for $0 < x < 0.4$. At $x = 0.4$ most of the charge deficiency caused by Ca doping on the A-site is compensated by the Mn^{4+} ions. As x increases further, Fe^{3+} is progressively replaced by Mn^{3+} ions until $x = 1.0$. It is well known that when the concentration of Mn^{3+} cations is large in a mixed manganite perovskite, a distortion of the lattice takes place as a result of the strong orbit-lattice interaction of these ions (cooperative Jahn-Teller effect) /19/. The Jahn-Teller effect of Mn^{3+} is manifested

Table 2

Coordination number (CN) and ionic radii of cations in the perovskite lattice /26/

Cation	Coordination number	Ionic radius (Å)
Y^{3+}	12	1.180
Ca^{2+}	12	1.340
Fe^{3+}	6	0.645
Fe^{4+}	6	0.585
Mn^{3+}	6	0.645
Mn^{4+}	6	0.530

by the increase of the lattice parameter b and decrease in c (Fig. 2) with x , particularly beyond $x = 0.4$. Since the ionic radii for Fe^{3+} and Mn^{3+} are very close, decrease in a' for $0.4 < x < 1.0$ is not expected. However, oxygen nonstoichiometry of this solid solution increases with manganese concentration. In air the samples contain excess oxygen. The close-packed ABO_3 perovskite structure cannot accommodate the excess oxygen as an interstitial ion because of its large radius. Therefore, the excess oxygen can only be considered in terms of a Schottky-type disorder, which involves the formation of cation vacancies:

The defect reaction causing oxygen nonstoichiometry in the oxygen-excess regime can be written as

Thus, with increasing manganese concentration in the solid solution, there is an increase in excess oxygen and, consequently, slightly more Mn^{4+} ions for charge compensation.

The gradual decrease in a' in Fig 3 for $x > 0.4$ is probably a reflection of the small increase in Mn^{4+} ions caused by increase in oxygen nonstoichiometry with x .

Table 3
Sintering temperature, bulk density (d), theoretical XRPD density (d_{th}) and d/d_{th} (%)
of the solid solution $Y_{0.8}Ca_{0.2}Fe_{1-x}Mn_xO_3$

Composition (x)	Sintering Temperature (K)	Bulk Density, d (gm cm ⁻³)	XRPD Density, d_{th} (gm cm ⁻³)	d/d_{th} (%)
0	1723	4.92	5.44	90.4
0.2	1723	5.11	5.44	94.0
0.4	1723	5.17	5.45	95.0
0.6	1723	5.39	5.45	99.0
0.8	1723	5.39	5.43	99.2
1.0	1723	5.32	5.40	98.5

3.2 Density

Relatively dense samples, with density greater than 90 % of the theoretical value, are required for the measurement of thermal expansion coefficient and electrical conductivity. Theoretical density can be calculated using the expression

$$d_{th} = \frac{zM}{0.6023V} \quad (9)$$

where M (in atomic mass units) is the mass of one formula unit, z is the number of such chemical units in one unit cell of the crystal, and V (in Å³) is the volume of the crystalline unit cell as determined by XRPD ($V = abc$ for the orthorhombic unit cell). For the GdFeO₃-type structure $z = 4$. The possible departures from stoichiometry have not been taken into account in calculating M .

The sintering temperature, the measured sintered density (d), the theoretical XRPD density (d_{th}), and the ratio d/d_{th} (%) are summarized in Table 3.

3.3 Thermal Expansion

Linear thermal expansion characteristics of $Y_{0.8}Ca_{0.2}$

$Fe_{1-x}Mn_xO_3$ ($x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0) obtained during heating from 373 to 1273 K in air are shown in Fig. 4. Since the thermal expansion curves cannot be

Fig. 4: Linear thermal expansion curves for $Y_{0.8}Ca_{0.2}Fe_{1-x}Mn_xO_3$ in air

Table 4
Coefficients of the derivative polynomial for the thermal expansion of $Y_{0.8}Ca_{0.2}Fe_{1-x}Mn_xO_3$

Composition (x)	Coefficients ⁺				
	B_1	B'_2	B'_3	B'_4	B'_5
0	-1.6006×10^{-4}	9.2513×10^{-7}	-1.7885×10^{-9}	1.4737×10^{-12}	-4.3892×10^{-16}
0.2	-8.0926×10^{-5}	4.7542×10^{-7}	-8.8477×10^{-10}	7.0152×10^{-13}	-2.0063×10^{-16}
0.4	-1.2864×10^{-5}	1.1957×10^{-7}	-2.4038×10^{-10}	2.1252×10^{-13}	-6.7623×10^{-17}
0.6	-3.2293×10^{-5}	1.9358×10^{-7}	-3.6875×10^{-10}	2.9486×10^{-13}	-8.1404×10^{-17}
0.8	-1.1574×10^{-4}	6.8824×10^{-7}	-1.4289×10^{-9}	1.2462×10^{-12}	-3.8469×10^{-16}
1.0	-2.3581×10^{-5}	1.8024×10^{-7}	-4.1521×10^{-10}	3.7446×10^{-13}	-1.1431×10^{-16}

+ Defined by equation (11).

represented adequately by a one or two straight-line segments, a fifth degree polynomial was used for curve fitting. The polynomial is of the form:

$$\frac{\Delta l}{l} = Y = B_0 + B_1T + B_2T^2 + B_3T^3 + B_4T^4 + B_5T^5 \quad (10)$$

where T is the absolute temperature and B_0, B_1, B_2, B_3, B_4 and B_5 are constants, specific to each composition. The thermal expansion coefficient (TEC) denoted by α is given by the slope of the curve and hence for any temperature T can be expressed as the derivative of equation 10;

$$\alpha = \left| \frac{dY}{dT} \right| = B_1 + B'_2T + B'_3T^2 + B'_4T^3 + B'_5T^4 \quad (11)$$

The values of constants B_1, B'_2, B'_3, B'_4 and B'_5 for different compositions are tabulated in Table 4. The mean linear thermal expansion coefficient (TEC) values (α_{av}) calculated from the thermal expansion curves in the temperature range from 673 to 973 K for different

values of x are shown in Table 5. It is apparent from the table that α_{av} decreases very little with x up to $x = 0.4$. In this composition range α is almost independent of temperature. Thereafter, the average value of TEC decreases rapidly with increasing x .

The thermal expansion curve for $x = 1$ shows negligible increase in the temperature range from 648 to

Table 5
Average linear thermal expansion coefficients (TEC) of $Y_{0.8}Ca_{0.2}Fe_{1-x}Mn_xO_3$ calculated from the thermal expansion curves in the temperature range from 673 to 973 K

Composition (x)	Average Linear TEC (α_{av}) [K ⁻¹ x 10 ⁻⁶]
0	10.78
0.2	10.47
0.4	10.02
0.6	4.61
0.8	1.95
1.0	0.35

948 K. It has been shown that in Ca-doped $YMnO_3$ an increase of the temperature above the ambient leads to a continuous change in the structure from the O' to the O-type, characterized by a rapid increase of the lattice parameter c /13/. This is accompanied by a decrease of the lattice parameter b and an increase in a . For $x = 1$, the increase in c and a is possibly balanced by the decrease in b in the temperature range from 648 to 948 K thus contributing to the extremely low TEC. As x decreases the lattice distortion caused by the Jahn-Teller effect decreases resulting in a progressively lower tendency for b to decrease with increase in temperature. This results in an increase in the TEC with decreasing x .

3.4 Electrical Conductivity

In Fig. 5 the logarithm of the product of electrical conductivity in air and absolute temperature ($\log \sigma T$) of the solid solution $Y_{0.8}Ca_{0.2}Fe_{1-x}Mn_xO_3$ ($0 < x < 1.0$) is plotted as a function of the reciprocal temperature in the range from 323 to 1173 K. For each sample, the

Fig. 5: The variation of $\log \sigma T$ as a function of the reciprocal of absolute temperature for $Y_{0.8}Ca_{0.2}Fe_{1-x}Mn_xO_3$ in air

conductivity increased with temperature in the entire range.

The conductivity behavior for $x = 0$ has been described by the small polaron hopping mechanism /8/. In the doped samples, Ca_Y' is electronically compensated by the formation of $Fe_{Fe}^{\bullet}$ according to Eqn. 3. The temperature dependence of electrical conductivity through the small polaron mechanism can be expressed by

$$\sigma = \frac{C}{T} \exp(-E_a / kT) \quad (12)$$

in which E_a is the activation energy for hopping conduction, k is the Boltzman constant, T is the absolute temperature, and C is the pre-exponential factor that contains several constants like the number of charge carriers and the average distance between the B cations. Therefore the plots in Fig. 5 should show a straight line behavior if conduction takes place by the small polaron hopping mechanism. A change in slope is noticed in the temperature range from 548 to 598 K for $x = 0$. The change in slope is probably related to antiferromagnetic to paramagnetic transition. A similar change in slope has been reported in undoped and Ca-doped $YFeO_3$ at 640 K /8,20/.

There is a drastic drop in the electrical conductivity at all temperatures when x is increased from 0 to 0.2. This is indicated by the minimum at $x = 0.2$ in the logarithmic plot of conductivity as a function of x (Fig. 6). A similar behavior has been documented in the $La(Cr,Mn)O_3$ /21,22/ and $Pr(Co,Mn)O_3$ /23/ perovskites. Mn possesses a lower small polaron site energy than Fe and hence when present in small concentration, acts as a trap to temporarily immobilize the charge carriers. The presence of such traps drastically reduces the electrical conductivity. As x increases further, the Mn^{3+} / Mn^{4+} ratio increases and hopping conduction is initiated in the Mn sub-lattice thereby resulting in a gradual increase in the electrical conductivity.

Table 6 lists the mean values of E_a calculated using simple linear regression, from the slopes of the plots in Fig. 5. The values obtained seem to be quite reasonable for a small polaron hopping mechanism /24/. It may be observed that the maximum activation energy is obtained for $x = 0.2$ in the temperature range from 848

Fig. 6: Logarithmic plot of electrical conductivity of $Y_{0.8}Ca_{0.2}Fe_{1-x}Mn_xO_3$ at various temperatures, as a function of x , in air

Table 6
Activation energies for the electrical conductivity of
 $Y_{0.8}Ca_{0.2}Fe_{1-x}Mn_xO_3$

Composition (x)	Temperature range (K)	E_a (eV)
0	323 – 548	0.323
	598–1173	0.161
0.2	323 – 848	0.416
	848 – 1173	0.579
0.4	323 – 1173	0.316
0.6	323 – 923	0.262
0.8	373 – 398	0.258
1.0	323 – 923	0.236

to 1173 K. This energy is associated with the energy required for a small polaron at a Mn site to hop to a neighboring Fe site /21/. The small increase in slope at temperatures beyond 923 K for the curve corresponding

to $x = 0.6$ may be attributed to the ability of carriers to occasionally pass through the energetically higher Fe sites, rather than having to go around them as would be required if the carriers were strictly confined to Mn sites /22/. The curve for $x = 0.8$ shows a deviation from the straight line behavior in the temperature range from 423 to 898 K. Seebeck coefficient data for $La_{0.9}Sr_{0.1}Cr_{0.2}Mn_{0.8}O_3$ /22/ indicates that there is generation of charge carriers in approximately the same temperature range. It is possible that a similar phenomenon results in the deviation from the straight line behavior. The curve for $x = 1$ shows a steep increase in slope at around 923 K. The conduction type for $Y_{0.7}Ca_{0.3}MnO_3$ is known to change from p to n at about 973 K with the transition point shifting from lower to higher temperatures with decreasing calcia content /25/. Hence, the change in slope at 923 K may be attributed to the change in the type of conduction.

4. CONCLUSION

Investigations were carried out on the structural, thermal and electrical properties of the oxides $Y_{0.8}Ca_{0.2}Fe_{1-x}Mn_xO_{3+\delta}$ ($0 < x \leq 1.0$). While the oxides with $x = 0, 0.2, 0.4$ and 0.6 were single phase, those with $x = 0.8$ and 1.0 showed traces of a second phase, which was identified as hexagonal $YMnO_3$. The pseudocubic lattice constant was found to decrease with increasing x .

The thermal expansion curves could be fitted with a fifth degree polynomial. The mean linear thermal expansion coefficient (TEC) values (α_{av}) for the temperature range 673 to 973 K showed negligible decrease with x up to $x = 0.4$. Thereafter, α_{av} decreased rapidly with increasing x . The thermal expansion curve for $x = 1$ had a slope approaching zero in the temperature range from 698 to 948 K. A possible explanation for this is that the increase in lattice parameters c and a is balanced by the decrease in b .

Electrical conduction takes place primarily by the small polaron hopping mechanism in these oxides. The drastic drop in electrical conductivity when x increases from 0 to 0.2 is a consequence of the preferential formation of Mn^{4+} to compensate for the A-site charge deficiency. Manganese possesses lower small polaron

site energy than Fe and hence acts as a charge carrier trap when present in low concentration, thereby lowering the conductivity.

The replacement of Fe with Mn in $Y_{0.8}Ca_{0.2}FeO_3$ results in a reduction in electrical conductivity. Hence these compounds are unlikely to find application as electrode materials in solid oxide fuel cells.

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