Crystalline structure and electrical properties of $\text{Dy}_{1-x}\text{Ca}_x\text{MnO}_3$ solid solution

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Solid solutions corresponding to the $\text{Dy}_{1-x}\text{Ca}_x\text{MnO}_3$ system, $x=0.0$ to 0.60 have been studied. The powders were prepared by solid state reaction of the corresponding oxides and carbonates. Sintered bodies were obtained by firing between 1250 and 1450°C . All the compositions showed single-phased perovskite-type structure with orthorhombic symmetry and Space Group Pbnm. Increase of the CaO content leads to a monotonic decrease of the orthorhombicity factor b/a with the Ca^{2+} concentration up to $x=0.60$. All the solid solutions crystallised with the same O' -type orthorhombic perovskite structure such as pure DyMnO_3 . Electrical measurements have shown semiconducting behaviour for all the solid solutions. The room temperature conductivity increases monotonically with the CaO content. The $60/40$ Ca/Dy composition showed a high value of the electrical conductivity and a correlative very low value of the activation energy. Thermally activated small polaron hopping mechanism controls the conductivity of these perovskite ceramics.

Keywords: Perovskites, manganites, Crystalline structure, electrical conductivity.

Estructura cristalina y propiedades eléctricas de las soluciones sólidas $\text{Dy}_{1-x}\text{Ca}_x\text{MnO}_3$

Se han estudiado soluciones sólidas correspondientes al sistema $\text{Dy}_{1-x}\text{Ca}_x\text{MnO}_3$, $x=0.0$ a 0.60 . Los polvos cerámicos fueron preparados por reacción en estado sólido de los correspondientes óxidos y carbonatos. Los materiales cerámicos se obtuvieron por sinterización entre 1250° y 1450°C . Todas las composiciones fueron monofásicas y mostraron una estructura tipo perovskita, con simetría ortorrómbica y Grupo Espacial Pbnm. El aumento del contenido en CaO llevó a una disminución monótona del factor de ortorrómbicidad, b/a . Todas las soluciones sólidas cristalizaron con el mismo tipo de estructura perovskita ortorrómbica O' , como la del compuesto puro DyMnO_3 . Las medidas eléctricas mostraron comportamiento semiconductor en todas las soluciones sólidas. La conductividad a temperatura ambiente aumenta monótonamente con el contenido de CaO. La composición $60/40$ mostró un elevado valor de conductividad y un correlativo bajo valor de la energía de activación. Un mecanismo de salto térmicamente activado de pequeño polarón controla la conductividad de las perovskitas.

Palabras clave: Perovskitas, manganitas, estructura cristalina, conducción eléctrica

1. INTRODUCTION

The Rare Earth manganites have focused a great interest because of their electrical and magnetic properties such as semiconducting behaviour and magnetoresistive features. The most of the work has been devoted to the study of the properties of light RE manganites, particularly the LaMnO_3 compounds modified with Ba, Sr, or Ca, for use of these solid solutions as ceramic electrodes for Solid Oxide Fuel Cells (SOFC's) (1-3). More recently, the colossal magnetoresistive effect found in both single crystals and ceramic has been extensively treated by many authors (4). The Rare Earth (RE) manganites, REMnO_3 show, at room temperature, two different types of crystalline structure, depending on the ionic radius of the RE cation. Thus, the light, higher ionic radius RE manganites, from La^{3+} to Dy^{3+} crystallise with an orthorhombic, perovskite-type structure with a Space Group, (S.G.) Pbnm. The orthorhombicity factor, b/a , raises when the RE ionic radius lowers (5). The heavy, smaller ionic radius, RE manganites, (from Ho^{3+} to Lu^{3+} and the Y^{3+}) show a hexagonal-type structure, with a S.G. P_6cm (6) The change from perovskite-type structure to the hexagonal one is

caused by the presence of the Jahn-Teller-type cation Mn^{3+} , which induces a co-operative distortion on the octahedral coordinated B sites of the perovskite lattice. For the same reason, the manganite compounds with perovskite structure show a high orthorhombicity factor, i.e. a strong distortion when compared to another REMeO_3 , Me trivalent transition metal. The evolution of the Goldschmidt tolerance factor, t , i.e. the steric factor, plays a secondary role on the modification of the crystalline structure, as is proved by the existence of perovskite-type structure for all the series of compounds LnFeO_3 , ($\text{Ln}=\text{La}, \dots, \text{Y}$) (7), in which the Fe^{3+} cation has the same ionic radius that the Mn^{3+} one, and, therefore, the same tolerance factor, and other LnMeO_3 compounds with similar t values. In a strong correlation with the structural evolution, the electrical conductivity changes from the very high values measured on pure lanthanum manganites to that of the semi-insulator YMnO_3 compound (8). Therefore, it seems also to exist a correlation between the RE ionic radii and the electrical conductivity. On the other hand, the CaMnO_3 compound crystallises with a perovs-

kite-type structure, with a quasi-tetragonal, S.G. Pbnm O-type orthorhombic symmetry, with $a < c/\sqrt{2} < b$. The difference respect to the REMnO_3 compounds is the absence of Jahn-Teller Mn^{3+} cations in the lattice.

As was above indicated, the DyMnO_3 compound is a limit compound between the RE manganites with perovskite-type structure and those with hexagonal-type structure. The orthorhombicity factor is very high, 1.105, and its structure is O' -type, with $c/\sqrt{2} < a < b$. Its electrical conductivity is relatively low when compared to that of the La or Gd manganites. The substitution of Ca^{2+} for Dy^{3+} must lead to a modification of the valence state from Mn^{3+} to Mn^{4+} for valence equilibrium considerations, in a similar manner than that occurring in the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ system (9). This modification can induce variations on the crystalline structure and on the electrical behaviour.

The $(\text{La},\text{Me})\text{MnO}_3$, ($\text{Me}=\text{Ba},\text{Sr},\text{Ca}$), solid solutions have been extensively studied (10-12), while less work has been devoted to other light RE manganite systems, such as (Nd,Ca) , (13), (Sm,Sr) , (14), (Eu,Sr) (15) and (Gd,Sr) , (16) manganites. The scope of the present work is to study the formation of solid solution $\text{Dy}_{1-x}\text{Ca}_x\text{MnO}_3$, their crystalline features and their electrical conductivity behaviour.

2. EXPERIMENTAL METHODS

Pure DyMnO_3 and $\text{Dy}_{1-x}\text{Ca}_x\text{MnO}_3$ compositions with $x=0.15-0.60$ were prepared by solid state reaction of stoichiometric mixtures of reagent grade MnO , CaCO_3 , and Dy_2O_3 , all of them with submicronic particle size. The mixtures were homogenised by wet attrition milling using isopropanol as liquid medium. The dried mixtures were calcined at 1100°C for 2h with heating and cooling rates of $2^\circ\text{C}/\text{min}$. The calcined powders were remilled first by ball milling and after by attrition milling, to attain smaller particle size, dried, granulated, and isostatically pressed at 200 MPa. Granulometric analysis were carried out on the synthesised powders by means of laser counting, (Mastersizer model, Malvern Instruments, Ltd, U.K.) and BET techniques, (Quantachrome MS-16 model, Syosset, NY). Porosity measurements were performed by Hg intrusion techniques, (Micromeritics, Autopore II, 9215, Norgross, USA). Dilatometric essays were carried out on a Differential Dilatometer, (Netzsch, model 402/E7, Germany). Isopressed pellets were sintered between 1250 and 1450°C for several times, with a cooling rate of $2^\circ\text{C}/\text{min}$ for all the sintering runs. Apparent density was measured by water displacement. XRD analysis were performed both on the calcined powder and on the sintered samples using a D-5000 Siemens Diffractometer and CuK_α radiation. The powder was identified by scanning at a rate of $2^\circ 2\theta/\text{min}$, and the lattice parameters were calculated from the spectra obtained on the sintered and ground samples at a scanning rate of $1/4^\circ 2\theta/\text{min}$. Si powder was employed as an internal standard. The microstructure of the sintered ceramics was observed by Scanning Electron Microscopy (SEM), (Zeiss DSM 950, Oberkochen, Germany) on polished and thermally etched surfaces. Bar-shaped samples were electroded with silver paste. The electrodes were fired at 800°C for 1h. Four-point DC conductivity measurements were carried out on all the solid solutions between 25° and 700°C . For the measurements, a Constant Current DC power supply (Tektronix, model PS280) and a HP Multimeter (model 44201A), with $1\mu\text{A}$ DC current resolution were used. Activation energies were calculated from the corresponding Arrhenius plots. The Seebeck-

Coefficient measurements were made on cylindrical samples, 0.3 cm in diameter and 1.5 cm long, using quasi-conventional technique for a rapid and qualitative determination of the majority charge-carrier sign (17). For the measurements, two metal blocks containing the thermocouples held the sample. A heater on one block produced the temperature gradient in the sample. The thermoelectric voltage was measured between the same reference points.

The Goldschmidt tolerance factor, t , has been calculated using the ionic radii tabulated by Shannon (18), taking into account the oxygen co-ordination number of the cations and the existence of different valence states of the Mn cation, with different ionic radii, in the solid solutions. Mean ionic radius on A lattice sites has been used when two or more cations are present on that site.

3. RESULTS AND DISCUSSION

The apparent particle size, as measured by laser counting, not represented here, showed two maxima, one at $0.3\mu\text{m}$ and other at $2\mu\text{m}$, but this last size corresponds to that of aggregates. The BET measurements indicated specific surface area values of $\sim 4.5 \text{ m}^2/\text{g}$, which correlates well with an average particle size of $\sim 0.3 \text{ }\mu\text{m}$.

To establish the best conditions for sintering the ceramic materials, measurement of green porosity and dilatometric essays were performed. Figure 1 depicts the differential Hg intrusion against pore size curve for one of the solid solution composition, corresponding to $x=0.40$, which is representative of the behaviour of all compositions. It can be seen that there exists a majority porosity, which may be attributed to interagglomerate porosity for the region between 0.2 and $0.3 \mu\text{m}$, and a small amount of pores in the $0.004-0.02 \mu\text{m}$ region. This quasi-homogeneous distribution is reflected on the shrinkage rate curve, obtained by dilatometric measurement on the $x=0.40$

Figure 1. Pore sizes distribution in a green compact of isopressed $\text{Dy}_{0.60}\text{Ca}_{0.40}\text{MnO}_3$ powders

Figure 2. Shrinkage and shrinkage rate behaviour of $\text{Dy}_{0.60}\text{Ca}_{0.40}\text{MnO}_3$ green compacts during sintering

Figure 4. Developed microstructure of a $\text{Dy}_{0.60}\text{Ca}_{0.40}\text{MnO}_3$ sintered sample at 1375 °C for 2 h

Figure 3. Relative density of sintered $\text{Dy}_{0.60}\text{Ca}_{0.40}\text{MnO}_3$ compacts as a function of a) temperature, for 2h, and b) time, at 1375°C

Figure 5. X-Ray Diffraction patterns of several compositions of the $\text{Dy}_{1-x}\text{Ca}_x\text{MnO}_3$ solid solution

sample, (Figure 2), in which a single peak is observed. It can be appreciated that this peak appears at relatively high temperatures. This fact correlates well with the relatively high pore size of the majority porosity, with low surface energy. According to these results, isothermal sintering was conducted at temperatures near to that corresponding to the maximum shrinkage rate. Figure 3 shows the variation of the relative density against temperature, (a), for 2h, and time, (b) at 1375°C. Apparent density value of 98% D_{th} was attained at 1450°C, for 2h. Figure 4 shows the SEM micrograph of the polished and thermally etched surface of the sample $x=0.40$ sintered at 1375°C, for 2h. It can be seen that the microstructure is quite homogeneous, with an average grain size of $\sim 1.3 \mu\text{m}$.

Figure 5 shows the XRD patterns of samples from $x=0.15$, to 0.50. The diagrams were indexed on a perovskite-type unit cell with S.G. Pbnm, in a similar manner to that of pure DyMnO_3 . As can be seen, single perovskite phase has been formed in all cases. The observed modifications on the intensity and position of some peaks are due to the symmetry increase.

TABLE 1. LATTICE PARAMETERS OF THE $\text{Dy}_{1-x}\text{Ca}_x\text{MnO}_3$ SOLID SOLUTION.

% at Ca	a	b	c	b/a	V	$c^{1/2}$
15	0.5291	0.5701	0.7431	1.077	0.2241	0.5254
20	0.5292	0.5654	0.7451	1.068	0.2229	0.5269
25	0.5301	0.5622	0.7452	1.061	0.2221	0.5269
30	0.5303	0.5587	0.7454	1.054	0.2208	0.5271
40	0.5304	0.5559	0.7455	1.048	0.2198	0.5271
50	0.5307	0.5509	0.7457	1.038	0.2180	0.5273
60	0.5317	0.5473	0.7446	1.029	0.2167	0.5265

Table 1 shows the measured lattice parameters of the solid solutions. The incorporation of Ca cations causes a strong decrease of the b parameter, and a slight increase of the a parameter. As a consequence, the orthorhombicity parameter b/a lowers strongly. There is also a progressive decrease of the lattice volume i.e. the compactness grade of the perovskite lattice rises, in spite of the higher size of the Ca^{2+} cation against that of the Dy^{3+} one. Nevertheless, at opposite of that observed on other solid solutions in which the compactness of the crystalline lattice increases and the theoretical density raises, in the present case the theoretical density decreases with the Ca amount (Figure 6). The reason is the strong decrease on the molecular weight produced by the substitution of Ca for Dy. Figure 7 shows the variation of the lattice parameters as a function of the Ca amount; $c/\sqrt{2}$ has been represented in place of c. In such a representation is possible to appreciate that the perovskite lattice is, in all the cases, of type $c/\sqrt{2} < a < b$, i.e. O'-type orthorhombic lattice such as the pure Dy manganite.

Incorporation of Ca^{2+} to the DyMnO_3 leads to a change in the valence state of the Mn cation to equilibrate the electrical charge. Thus, it is possible to postulate the following formula to describe the solid solution composition

in the same way to that assigned to the $(\text{La,Ca})\text{MnO}_3$ solid solution.

Figure 8 shows the variation of the tolerance factor, as a function of CaO content. It can be appreciated that the t factor increases with the CaO amount. It is due to the increase of the average ionic radius on A sites, caused by the incorporation of Ca^{2+} ($r=1.26 \text{ \AA}$) substituting Dy^{3+} ($r=1.17 \text{ \AA}$) and the decreases of the average ionic radius on B sites, if it is supposed that a part of Mn^{3+} changes to Mn^{4+} , with a lower ionic radius. Nevertheless, the maximum t value, for $x=0.60$, remained below 0.90, and the perovskite structure is maintained as O'-type structure, with a relatively strong anisotropy. The reason can be attributed to the relatively low value of the mean ionic radius on site A, when it is compared, for example, to that of the Sr-Gd pair in the $\text{Gd}_{1-x}\text{Sr}_x\text{MnO}_3$ solid solution, in which t is near of 0.97 for $x=0.50$ and the structure is of O-type perovskite (16). In any case, the crystal lattice increases its symmetry when the CaO content raises, as can be seen on the figure 7 in which is possible to appreciate how the a and b lattice parameters approach their values between them, respect to the pure DyMnO_3 . The increase of the symmetry leads to the Mn-O-Mn angle to be closer to 180° and the decrease of the b lattice parameter is indicating a shortening of the Mn-O bond.

Figure 6. Theoretical density of the different $\text{Dy}_{1-x}\text{Ca}_x\text{MnO}_3$ solid solutions, calculated from the measured lattice parameters Figure 7. Lattice parameters of the $\text{Dy}_{1-x}\text{Ca}_x\text{MnO}_3$ solid solutions against Ca content Figure 8. Tolerance factor of the $\text{Dy}_{1-x}\text{Ca}_x\text{MnO}_3$ solid solutions

Figure 9 depicts the σT vs $1/T$ curves for some of the solid solutions. Table 2 shows the room temperature conductivity and the activation energy of the same samples. According to the obtained results, the conduction mechanism is via thermally activated small polaron hopping between Mn^{3+} and Mn^{4+} localised states. The electrical conductivity behaviour is similar to that described for other manganites with perovskite-type structure (8). It can be observed that the electrical conductivity increases monotonically with the CaO content. Taking into account that the conductivity depends primarily on the existence of Mn^{3+} - Mn^{4+} pairs, it could be expected the existence of a maximum in the conductivity for the 50/50 Dy/Ca composition. Kostoglou et al (16) found that this is the case in the $(\text{Gd},\text{Sr})\text{MnO}_3$ solid solution system, but its study was limited up to 50/50 composition. The same results were reported by J.A.M. van Roosmalen et al in the $(\text{La},\text{Sr})\text{MnO}_3$ system (19), also for 50 at% Sr as upper limit. In the present study, it has been found that the electrical conductivity continues its increasing for $x > 0.50$, despite the fact of the decrease of possible formation of Mn^{3+} - Mn^{4+} pairs. This monotonically increase agrees with that reported by Stevenson et al (20), which found that in the $\text{Y}_{1-y}\text{Ca}_y\text{MnO}_3$ solid solution, the conductivity increases also monotonically up to a Ca content of 60 at% and then decreases slightly only in the higher temperature region, showing a continuous decrease in the activation energy for compositions ranging from $y=0.30$ to $y=0.80$. Stevenson et al explained this behaviour assuming the existence of a thermally activated disproportionation process:

If it is assumed that Mn^{2+} does not participate in the conduction process, and calculating for each solid solution the proportion of the three cations, they led to relations between Mn^{3+} and Mn^{4+} for which Mn^{3+} amount remains almost constant while the Mn^{4+} increases, being always $\text{Mn}^{4+} > \text{Mn}^{3+}$ when the Ca content rises from $y > 0.30$ to 0.60. Therefore, the conductivity increases up to Ca amount of 0.60, and the majority charge carriers are electrons. This model could be applied to the present system, which is similar to that one, and therefore, could explain qualitatively the semiconducting behaviour.

The value of the E_a reported in (20) for the $y=0.60$ composition, 0.06 eV, agrees very well with the value measured for the same CaO amount in the present Dy-Ca system, see table 2. The low value of the activation energy can be attributed to the increase of the orbital overlapping between adjacent Mn^{3+} - Mn^{4+} cations (15,21), caused by the decrease of the lattice parameters and the increase of the symmetry, see above. The increase of the subsequent bandwidth results in the observed decrease of the activation energy. Values of conductivity $> 14,000 \text{ S}\cdot\text{m}^{-1}$ were measured at 700°C for samples with $x=0.50$ and $x=0.60$, which are of the same magnitude order than those measured on the well known $(\text{La},\text{Sr})\text{MnO}_3$ solid solutions, with equivalent divalent cation amount.

Figure 10 shows the Seebeck coefficients of the several compositions of the $\text{Dy}_{1-x}\text{Ca}_x\text{MnO}_3$ solid solution. Measured values correlate well with the proposed semiconduction mechanism of small polaron hopping. Typical values from 120 to $-50 \mu\text{V}/^\circ\text{C}$ have been determined. This fact corroborates the above statement about the contribution of Mn^{3+} - Mn^{4+} pairs to semiconducting mechanism. It is possible to see that the sign of charge carriers changes when the Ca amount is of 40 at%. In a first evaluation, the samples with $\text{Ca} \leq 0.50$ have a percentage of Mn^{3+} higher than that of Mn^{4+} , according to the

Figure 9. - Log σT vs $1/T$ for different $\text{Dy}_{1-x}\text{Ca}_x\text{MnO}_3$ solid solutions.

TABLE 2. ELECTRICAL CONDUCTIVITY AT ROOM TEMPERATURE AND ACTIVATION ENERGY FOR CONDUCTION FOR SEVERAL SOLID SOLUTIONS OF THE $\text{Dy}_{1-x}\text{Ca}_x\text{MnO}_3$ SYSTEM

% At. Ca	20	30	40	50	60
$\sigma (\text{Sm}^{-1})$ 25 °C	17.8	46.6	139.3	1079	3395
E_{ac} (eV)	0.190	0.160	0.140	0.11	0.06

Figure 10. - Seebeck coefficient vs temperature for different $\text{Dy}_{1-x}\text{Ca}_x\text{MnO}_3$ solid solutions.

formula [1]. Therefore, the predominant charge carriers are holes. For $\text{Ca} \geq 0.50$, the amount of Mn^{4+} is higher than the Mn^{3+} amount. As consequence, the predominant carriers must be electrons. The observed behaviour for these solid solutions, in which the sign change is displaced to lower values of the Ca/Dy ratio, agrees well with the results of Stevenson et al. who also found a charge carriers sign change for $y=0.40$, and corroborates the above statement.

4. CONCLUSIONS

The incorporation of Ca^{2+} cation as solid solution to the DyMnO_3 perovskite compound reduces the distortion degree of the crystalline lattice, but the O' -type structure remains, even at CaO contents >50 mol%. The compactness of the unit cell lattice increases with the increase of Ca amount, despite of the higher ionic volume of Ca^{2+} cation against that of Dy^{3+} one.

The solid solutions show semiconducting behaviour, and the conductivity is controlled by a thermally activated small polaron hopping mechanism. For $x>0.40$ a change in the charge carriers sign is observed, from p (holes) to n (electrons) carriers.

The conductivity increases and the activation energy for conduction decreases with the Ca amount. For $x=0.60$ very high conductivity, $\sim 3.400 \text{ S}\cdot\text{m}^{-1}$ at room temperature, and very low value of E_a , 0.06 eV , have been measured.

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