Electric field-modified segregation in crystal fibers of colossal magnetoresistive 'La
IND.0.7"Ca IND.0.3'Mn'O IND.3'
Electric field-modified segregation in crystal fibers of colossal magnetoresistive La$_{0.7}$Ca$_{0.3}$MnO$_3$

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**Abstract**

Manganites are materials with a high potential for applications in magnetic sensors, head-reading magnetoresistive hard disk, RAM memories and actuator devices, among others. Laser heated floating zone (LHFZ) growth of manganite fibers is a suitable technique to obtain high-quality crystals. In this study, an electric field was simultaneously applied to LHFZ in order to control the solidification morphology. Manganite fibers of La$_{0.7}$Ca$_{0.3}$MnO$_3$ composition were grown under an applied DC electric current density in the range 0–15.2 A/cm$^2$. At 11.4 A/cm$^2$ the solid/liquid (S/L) interface morphology changes from planar to cellular. The electric field promotes constitutional supercooling conditions by field-freezing the system, and the Ca effective segregation coefficient increasing from $k = 0.60$ towards the unity. At the same time, when the current density increases from 11.4 to 15.2A/cm$^2$, the intercellular spacing reduces from 22 to 11 $\mu$m.

**Keywords:**
A1. Interface shape
A1. Segregation
A2. LHFZ
B1. Manganites

1. Introduction

The colossal magnetoresistive (CMR) effect observed in perovskite-based manganese oxides (Ln$_{1-x}$A$_x$MnO$_3$, where Ln is a trivalent lanthanide and A is a divalent alkaline earth ion) has motivated an extensive study of these compounds [1–3]. Their electric and magnetic properties are mainly dependent on the Mn$^{4+}$/Mn$^{3+}$ ratio, which in turn is a function of the A-element concentration and also of the oxygen content. Of not less importance is the compositional homogeneity, whose study in single crystals allows a more complete understanding of the CMR effect nature.

Several groups have successfully grown manganese single crystals [4–8]. In particular, the laser heated floating zone technique (LHFZ) has been successfully applied for the growth of fiber-shaped La$_{0.7}$Ca$_{0.3}$MnO$_3$ single crystals [9]. The LHFZ technique, as a containerless method, is highly suitable for growing single crystals of materials with high melting points and aggressive melts, besides avoiding contamination from the crucible material. However, the strong segregation of the alkaline earth ions in these compounds has been pointed out as the main obstacle to obtaining good-quality single crystals from the melt. The samples obtained by Cardoso et al. [9] presented reasonable quality, although with a compositional gradient along the axis. In this way, the development of methods that allow controlling the segregation is highly desirable. Shulyatev et al. [8] showed that the distribution coefficient of Ca$^{2+}$ increases considerably in the reduced oxygen atmosphere.

An effective way to alter the thermodynamical conditions and growth dynamics is the application of an electric field during solidification. Conrad [10] published a comprehensive review on the microstructural changes induced by external electric fields. Carrasco et al. [11] proved the drastic change in phase development, microstructure and effective distribution coefficients in solidification of Bi–Sr–Ca–Cu–O superconductor fibers by LFZ modified by a DC electric field. Solidification conditions approximate to the equilibrium, namely the primary phase to crystallize,
is the equilibrium cuprate instead of the metastable one that develops in the conventional LFZ process. Moreover, thin, long and more aligned dendrites are favored. One of the major effects of the so-called electrical assisted laser floating zone (EALFZ) technique is the control of the effective distribution coefficients, $k$, that approximate to the equilibrium coefficient values, $k_0$, when the current is applied. Field-modified segregation was demonstrated in the single crystal fiber growth of Mn- and Cr-doped LiNbO$_3$ by an intrinsic interface electric field caused by the presence of high thermal gradients [12,13]. Feisst and Rauber [14] used an external electric field to show that $k$ of Cr$^{3+}$ in LiNbO$_3$ can exhibit an anomalous range of values beyond that expected between $k_0$ and the unity. The effect of external electric field on the stability of solid–liquid (S/L) interfaces was investigated by Warner and Verhoeven [15] upon solidification of Sn-Bi alloys. Chang et al. [16] showed the reduction of columnar/dendrite spacing by an external electric field upon the solidification of a Cu-5%Al alloy.

In this work, the application of an external DC electric field on the solidification of La$_{0.7}$Ca$_{0.3}$MnO$_3$ crystal fibers by LHFZ technique is studied. The changes in $k$ and morphology of the growing S/L interface effects were determined as a function of the electric current density. To our knowledge it is the first time that the influence of external electric field on the solidification of La$_{1-x}$Ca$_x$MnO$_3$ is reported.

2. Experimental procedure

Stoichiometric amounts of high-purity La$_2$O$_3$ (Puratronic 99.99%), CaCO$_3$ (Merck, Optipur), and MnO$_2$ (Puratronic 99.9%) powders were mixed with polyvinyl alcohol in aqueous solution to form a ceramic paste. Cylindrical source pedestals of 1.2 mm in diameter were prepared through a cold extrusion process. The directional solidification was performed in a conventional LHFZ system with a 125 W-cw CO$_2$ laser. Initially, fibers with 4 mm in length were grown at 1 mm/min solidification rate. The ending 2 mm of these fibers were used as seed and feed rods for growth under an applied electric field. The schematic of the experiment is shown in Fig. 1(a). The growth was carried out in upward direction with a fiber-pulling rate of 1 mm/min. The feed rate and the laser power were modulated by an automatic diameter control system. Both seed and feed rods were connected to a DC power source (15 V/1.5 A) using brass holders and copper wires, with the positive terminal at the seed. The electric current throughout the solidification interface was the control variable. In Fig. 1(b) it can be observed how the electric field is associated to the electric current flowing through the solidification interface. The length of feed+seed rods+growing fiber (L1+L2) and thermal gradient in them are the same, it is assumed that the resistive drop of the potential is approximately constant along the feed+seed rods as the growth occurs. So the electric field depends only on the current intensity, shown in Fig. 1(b). The maximum obtained current in the arrangement was of ~120 mA (15.2 A/cm$^2$) using the maximum voltage of the source. Although the fibers used as seed and feed rod presented low electric resistance, it is probable that a large part of the power was consumed at the electric contacts between the seed/seed rods and the brass holders.

Initial phase identification was carried out by powder X-ray diffraction (XRD) measurements of the crushed fibers. Microstructural and compositional analyses were performed in polished fibers and quenched molten zones using scanning electron microscopy (SEM) coupled with an electron probe microanalyzer (EPMA/EDS). Compositional profiles along the fiber axis were taken in 100 $\mu$m x 100 $\mu$m areas, at the centerline of the polished longitudinal section of the fibers. The solute concentration gradients in front of the S/L interface were estimated from EDS acquisitions within smaller 10 $\mu$m x 10 $\mu$m areas.

3. Results and discussion

The LHFZ growth of all La$_{0.7}$Ca$_{0.3}$MnO$_3$ fibers, independently of the applied current, was very steady concerning the geometry and volume of the molten zone. In Fig. 2 is shown the molten zone of a fiber grown under 11.4 A/cm$^2$ of applied electric current density.

With the application of an external electric field, the ions present in the liquid migrate with different drift velocities $R$ ($R = \mu E$, where $\mu$ is the ionic mobility and $E$ the electric field) towards the S/L interface, or from it, depending on polarity and on the ionic charge. So, assuming the presence of convection, there are two fluxes, one due to the rejection of solute (for $k_0 < 1$) by the advance of the S/L interface, and the other from the different mobilities of the ions under the electric field. The effect of these two fluxes reflects on $k$, the effective distribution coefficient value,
as given by the so-called modified BPS (Burton–Prim–Slichter) equation [17,18]:

\[
k = \frac{1 + R / R}{1 + [k_0(1 + R / R) - 1] \exp\left(-R \delta / D(1 + R / R)\right)}
\]  

(1)

where \( k = C_S / C_{BL} \) (\( C_S \) is the solid solute concentration at the interface and \( C_{BL} \) is the solute concentration in the bulk liquid), \( k_0 \) is the equilibrium distribution coefficient value (\( k_0 = C_S / C_L \), where \( C_S \) and \( C_L \) are the solid and liquid solute concentrations at the interface), \( R \) is the interface velocity and \( \delta \) is the diffusion layer thickness.

In order to survey the influence of an external electric field on \( k \), macrosegregation phenomenon was studied by measuring the axial compositional profiles. In Figs. 3(a–c) are plotted the correspondent profiles of fibers obtained with current densities of 0, 10.1 and 11.4 A/cm². The Mn/(La+Ca) ratio is slightly less than unity. This is attributed to Mn vaporization from the molten zone [7,8]. Despite this, the concentration of Mn ions is practically constant along the fiber axis in all conditions. Hereinafter, for sake of simplicity, only the segregation behavior of the Ca²⁺ ion is considered, since the La³⁺ ion behavior is the reverse. The measured \( k \) values for the Ca²⁺ ion, calculated from the ratio of Ca concentration in the solid and in the bulk molten zone, are given in Table 1. Additionally, the estimated \( k \) values from the fitting of data to Pfann’s equation [19], which gives the concentration profile along the fiber axis, are also presented:

\[
\frac{C}{C_0} = 1 - (1 - k) \exp(-kx/l)
\]

(2)

where \( x \) is the distance from the point at which the first solid froze, \( C \) is the solute concentration at \( x \), \( C_0 \) the initial concentration and \( l \) the length of the molten zone.

Measured and estimated \( k \) values agree quite well. Moreover, without applied current, the observed \( k \) of 0.60 is near that reported in literature for crystals grown by floating zone process [7]. The applied current has a net effect on \( k \), provoking an increase towards the unity value with increase of current density. The application of the electric field alters \( k \) by field freezing the system. Pfann and Wagner [17], however, cited that the increase of \( k \) towards the unity increases the chances of constitutional supercooling with concomitant effects such as cellular/dendritic breakdown of the planar interface. In Fig. 4(a–c) is shown SEM micrographs of the quenched interfaces for fibers grown with (a) 6.3, (b) 12.7, (c) 15.2 A/cm² of applied current density. For the selected pulling rate of 1 mm/min, all fibers grown in the range 0–10.8 A/cm² exhibit an S/L planar interface, as can be seen in Fig. 4(a). Disruption in the S/L interface stability occurs for an applied current density of approximately 11.4 A/cm² leading to a cellular morphology, as it can be seen in Figs. 4(b) (12.7 A/cm²) and (c) (15.2 A/cm²). The breakdown of the planar S/L interface is the outcome of constitutional supercooling conditions [20–22]. If the actual temperature is lower than the equilibrium solidification temperature, a driving force exists for the development of perturbations ahead of the S/L interface. Fig. 5 presents the detailed compositional profiles near the S/L interface of fibers.
grown without and with 11.4 A/cm² of applied current density. For
the latter, the steep concentration gradient in the boundary layer
ahead of the S/L interface that drives constitutional supercooling
conditions can be seen.

According to Eq. (1) and the results in Table 1, \( R' \) is positive in
the present case. This means the solute ions, in this case Ca²⁺,
move towards the S/L interface by the application of a DC current,
decreasing the segregation degree. Further current increase from
11.4 A/cm² until the maximum value reachable for our arrange-
ment of \( \sim 15.2 \) A/cm² did not show any appreciable change in \( k \)
value. This behavior is explained by the attainment of a Ca²⁺
saturation threshold for a current density of 11.4 A/cm². This
tendency turns improbable further accumulation of Ca²⁺ at the S/L
interface and incorporation in the solid, which is the only
possibility of having a \( k \) value higher than unity.

The relationship between the cell spacing and the applied
current density is shown in Fig. 6. For current densities from 11.4
to 15.2 A/cm² the spacing reduces from approximately 22 to
11 \( \mu \)m. The increase of the current density increases the instability
conditions and causes the intercellular spacing to reduce by a
branching mechanism in order to reduce the constitutional
supercooling condition, as can be seen when comparing Fig. 4(b)
and (c). When a DC electric current passes through the S/L
interface, the thermal and solute distributions are changed due to
Joule heating and Thomson effect. Chang et al. [23] postulated
that the electric conductivity difference between the solid and the
liquid raises the temperature at the dendrite tips, preventing their
advancing but at the same time, promoting the development of
newly protruding tips. By this, the amplitude and wave number of
protrusions simultaneously decrease and so the interface energy
is minimized when the electric current density is improved.

The microsegregation of Ca²⁺ inside the cell trunks could not
be quantified, although a higher concentration of Ca²⁺ in the
intercellular regions was verified. This can be seen by the darker
contrast in this region in Fig. 4(b) and (c). The hypothesis of a new
phase development between the cells could not be confirmed by
DRX analysis due to its very low volume.

### Table 1

<table>
<thead>
<tr>
<th>Current density (A/cm²)</th>
<th>0</th>
<th>10.8</th>
<th>12.7</th>
<th>15.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k = C_s/C_{BL} )</td>
<td>0.60</td>
<td>0.96</td>
<td>0.99</td>
<td>1.00</td>
</tr>
<tr>
<td>( k ) (by Eq. (2))</td>
<td>0.58</td>
<td>0.97</td>
<td>0.99</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Fig. 5. \( \text{Ca}^{2+} \) concentrations in solid and liquid near the S/L quenched interface for fibers obtained under applied current densities of (a) 0 and (b) 11.4 A/cm². (*These values are overestimated because they comprise EDS information from the electron interaction with the zone melt volume.*)
4. Conclusions

The influence of an external electric field has been experimentally investigated on the fiber growth of the La$_{0.7}$Ca$_{0.3}$MnO$_3$ compound by LHFZ. The applied electric field strongly modifies the effective distribution coefficient of Ca$^{2+}$ ions, from $k = 0.60$ to the unity under increasing current density. Thus, the application of an electric field can be used to decrease the macrosegregation phenomenon, even at low cooling rates. Additionally, starting from an applied current density of 11.4 A/cm$^2$, system field freezing takes place, promoting constitutional supercooling conditions that lead to a transition of planar to a cellular/dendritic S/L interface. Moreover, the minimization of the S/L interfacial energy leads to an intercellular spacing reduction from 22 to 11 $\mu$m when the current density increases from 11.4 to 15.2 A/cm$^2$.

Acknowledgments

The authors are thankful to the Brazilian agencies CAPES, CNPQ and FAPESP and Portuguese agency GRICES, for the financial support of this work.

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