

Electrical conductivity and thermal stability measurements of a mixed perovskite oxide system

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For the mixed perovskite oxide system $(\text{Sr}_{0.8125}\text{La}_{0.1875})(\text{Zr}_{0.75}\text{Fe}_x\text{Ru}_{0.25-x})\text{O}_{3-\delta}$, electrical conductivities were measured in air as a function of temperature and Ru/Fe ratio. Liquidus and solidus temperatures were determined in air by the laser melting point measurement technique. The substitution of Ru for Fe was found to increase the electrical conductivity by over an order of magnitude while decreasing the solidus temperature of the Fe-rich solid solution by less than 10%.

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I. INTRODUCTION

As part of a larger study into potential candidate materials for improved electrodes in high-temperature power-generating systems based on magnetohydrodynamics (MHD), the electrical properties and thermal stability of the system $(\text{Sr}_{0.8125}\text{La}_{0.1875})(\text{Zr}_{0.75}\text{Fe}_x\text{Ru}_{0.25-x})\text{O}_{3-\delta}$ were investigated. The iron-rich end member of this solid solution system $(\text{Sr}_{0.8125}\text{La}_{0.1875})(\text{Zr}_{0.75}\text{Fe}_{0.25})\text{O}_{3-\delta}$, is one of two materials found from previous studies of the ternary system SrZrO_3 - $\text{SrFeO}_{3-\delta}$ - LaFeO_3 ,¹ which already comes fairly close to meeting many of the stringent requirements for power efficient and durable MHD electrodes. This is due to the perovskite structure of these compounds, which are quite refractory yet exhibit comparatively high electrical conductivities, two properties which tend to be mutually exclusive in most materials.

The present work attempted to improve further the electrical conductivity of this material without decreasing its thermal stability. The maximization of both electrical conductivity and thermal stability in one material for MHD electrodes had been attempted before in various ternary oxides, e.g., the spinels AB_2O_4 ,² and the perovskites ABO_3 ,^{1,3,4} in which more than one metal may be substituted on each of the A and B sites to form "solid solutions." This compositional flexibility makes these ternary oxide solutions highly versatile as engineering materials.

In $(\text{Sr}_{0.8125}\text{La}_{0.1875})(\text{Zr}_{0.75}\text{Fe}_x\text{Ru}_{0.25-x})\text{O}_{3-\delta}$, Sr and La occupy the A sites and Zr, Fe, and Ru occupy the B sites in the perovskite structure. The iron-rich end member is itself a compromise in properties between the highly refractory but electrically insulating SrZrO_3 and the more electrically conducting but lower-melting $(\text{Sr}_x\text{La}_{1-x})\text{FeO}_{3-\delta}$ perovskites. An attempt to improve further the properties of this material for MHD applications has been made here by substituting, in various amounts, Ru for Fe. An extrapolation of available electrical conductivity data for the perovskite solid solution $\text{LaFe}_x\text{Ru}_{1-x}\text{O}_3$,⁵ to higher temperatures suggested that the electrical conductivity of $(\text{Sr}_{0.8125}\text{La}_{0.1875})(\text{Zr}_{0.75}\text{Fe}_{0.25})\text{O}_{3-\delta}$ might be enhanced significantly by the substitution of Ru for Fe on the B sites in the perovskite structure. LaRuO_3 itself is interesting because

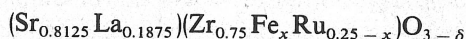
it is the only known example of an oxide formed from Ru^{+3} (Ref. 5) and is also the only $\text{A}^{+3}\text{B}^{+3}\text{O}_3$ perovskite oxide formed from a second-row transition-metal element. From the point of view of MHD, SrRuO_3 , which also exhibits the perovskite structure,⁶ is an attractive solid-solution end member because of its high thermal stability compared to that of its Fe counterpart $\text{SrFeO}_{3-\delta}$.

This article describes the results of electrical conductivity and thermal stability measurements performed in air as Ru content varied.

II. EXPERIMENTAL PROCEDURE

A. Fabrication and characterization of solid-solution samples

Six samples from the solid-solution system



were prepared with the nominal compositions given in Table I. Each of the six compositions was mixed from powders of SrZrO_3 ,⁷ SrCO_3 ,⁸ Fe_2O_3 ,⁹ RuO_2 ,¹⁰ and La_2O_3 .¹⁰ The processing of these powders included

- (i) firing them at 1550 °C for one hour in ZrO_2 crucibles open to the atmosphere,
- (ii) grinding to - 400 mesh (particle size less than 34 μ),
- (iii) isostatically pressing for one minute at 30 000 to 32 500 psi, and
- (iv) refiring in air for 1-3 h at temperatures of 1300-1350 °C.

A partial chemical characterization of the solid-solution system was obtained by neutron activation analysis of a number of representative solid-solution samples at various stages of fabrication. These measurements permitted the estimation of the losses of volatile components such as Ru and Fe during firing at high temperatures and the determination of the types and amounts of each impurity present.

B. Electrical conductivity measurements

The electrical conductivities of each of the six compositions were measured in air as a function of temperature using a standard four-point probe technique.

Samples measuring approximately $0.25 \times 0.25 \times 2$ cm

TABLE I. The dependence of the activation energy for electrical conduction on temperature and composition.

Sample number	Composition ^a (x)	E_a (eV)	Temperature interval (°C)
1	0.25	6.31×10^{-1}	872-1201
		1.63	1201-1576
2	0.20	7.41×10^{-1}	849-1051
		9.67×10^{-1}	1051-1423
		1.37	1423-1616
3	0.15	7.23×10^{-1}	860-1081
		8.36×10^{-1}	1081-1356
		9.92×10^{-1}	1356-1466
		1.98	1466-1494
4	0.10	5.48×10^{-1}	897-1260
		7.44×10^{-1}	1260-1379
5	0.05	3.62×10^{-1}	838-1166
		5.11×10^{-1}	1166-1329
6	0.00	2.53×10^{-1}	799-1156
		4.79×10^{-1}	1156-1293

^aComposition defined as $(\text{Sr}_{0.8125}\text{La}_{0.1875})(\text{Zr}_{0.75}\text{Fe}_x\text{Ru}_{0.25-x})\text{O}_{3-\delta}$.

were cut with a diamond saw from each of the six sintered bars. Pt wire leads were connected to the samples using Pt paste¹¹ and 0.0005-in. Pt foil. The variations in each of the two thicknesses across the length of the samples were no greater than 0.001 in., and the four interelectrode distances measured along the edges did not vary from one another by more than ~1%.

Samples were mounted onto a sample holder which served to position the samples and thermocouples within the furnace hot zone and facilitate the connection of sample current and voltage probes to the external circuitry during heating.

The temperature was monitored at each end of the sample at a position directly above the voltage probes by a Pt-10% Rh vs Pt thermocouple. The electrical apparatus for

conductivity measurements consisted of a voltage-stable solid-state 15 V source¹² dropped across a variable resistor (maintained at 9000Ω) in series with the sample. The sample current, voltage, and temperatures at each end were all measured with a digital multimeter.¹³ Ohmic behavior and lack of polarization (e.g., due to electrodes) were confirmed.

The electrical conductivity measurements were carried out in a vertical Mo wound resistance heating furnace. The temperature within the furnace was controlled to within 0.15% in the vicinity of the sample. No induced voltage from the Mo windings was detected in the measurement of either sample or thermocouple voltage.

In a typical experiment the sample was placed on the sample holder, positioned in the furnace, and heated to the maximum temperature of the experiment. It was then annealed for approximately 24 h. The anneal was terminated when the electrical conductivity had stabilized. Measurements were taken at intervals of 50 to 100 °C down to 800–900 °C. At each temperature, the sample was held for at least 1 h until the electrical conductivity had stabilized.

To check for any "hysteresis" in electrical conductivity which might, for example, arise from volatilization of one of the components in the sample, it was reheated and the electrical conductivity measured. Although the experiments lasted from one to two weeks, very little change in electrical conductivity with time was observed for any of the six samples. This is very encouraging from the point of view of MHD, since the amount of variation in electrical conductivity provides an indirect measure of long-term stability of the materials as high-temperature MHD electrodes.

C. Measurements of liquidus and solidus temperatures

The liquidus and solidus temperatures were determined in air for each of the six compositions by using a CO₂ laser beam¹⁴ as a heat source. The measurements were performed by aiming the beam onto the surface of a sample at a specified power intensity, recording the temperature attained at the surface with an optical pyrometer, quenching the sample to

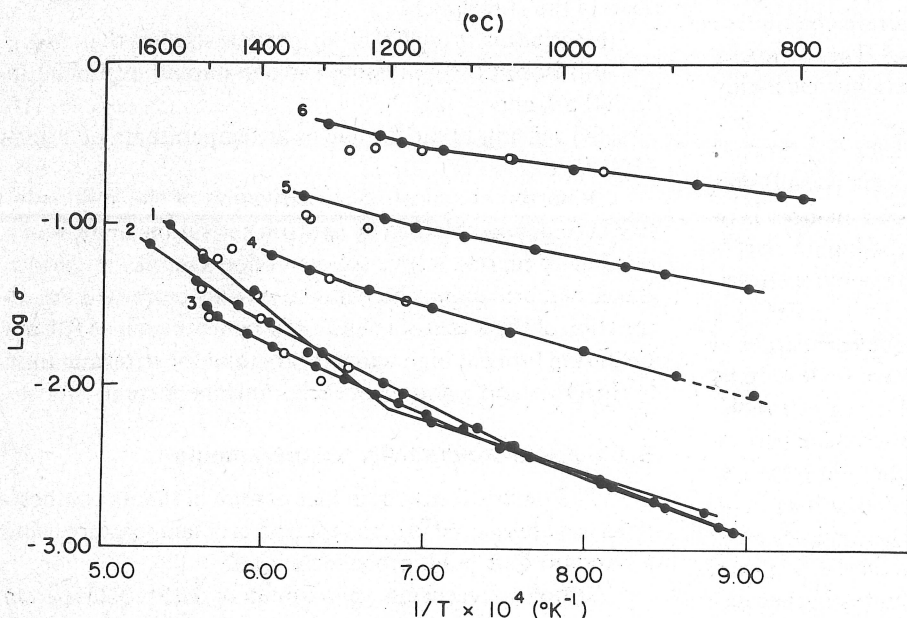


FIG. 1. The dependence of electrical conductivity on composition and temperature. Compositions are defined in Table I. Solid and open circles indicate measurements taken upon heating and cooling, respectively.

room temperature, and observing the resulting sample features under a stereoscope. The onset of the solidus is indicated by the appearance of a bumpy, shiny surface, whereas the liquidus is indicated by a smooth, glassy surface.

Temperatures were measured at the hottest portion of the sample visually with an optical pyrometer to within an estimated accuracy of $\pm 10^\circ\text{C}$ without any corrections made for emissivity. The liquidus temperature of 8 wt % Y-stabilized ZrO_2 (Ref. 15) obtained by this method (2535°C) agrees fairly well with the published values ($\sim 2750^\circ\text{C}$).¹⁶

The samples for these measurements consisted of very thin slabs $\sim 1\text{--}2$ mm thick, cut from the same six sintered bars with a diamond saw. A common firebrick served as a support for the samples during the measurements. To prevent the samples from reacting with the firebrick at the very high temperatures ($2000\text{--}2500^\circ\text{C}$), another slab of the same composition was placed directly under the sample as a protective substrate. Samples were heated slowly to temperature (~ 10 min.) to avoid excessive thermal shock.

III. RESULTS AND DISCUSSION

A. Electrical conductivity

The results of the electrical conductivity measurements are shown in Fig. 1 which plots $\log \sigma$ vs $1/T$. Transition temperatures were estimated by inspection, and the data were fit to two line segments about this temperature. The resulting high correlation coefficients r and low standard errors of estimate $S_{y,x}$ justified these choices of transition temperatures. The activation energies within each temperature interval and the transition temperatures are indicated in Table I. Previous work on the Fe-rich end member of this system has demonstrated that these temperatures correspond to phase changes.^{1,17} The variation of electrical conductivity with the Ru/Fe ratio at constant temperature is shown in Fig. 2.

In general, the electrical conductivity is found to increase with Ru/Fe ratio over a wide range of temperature and composition. Also, as the Ru/Fe ratio is increased, the electrical behavior changes gradually from an activated process characteristic of a semiconductor to a nonactivated process (almost like that of a metal), as seen in Table I. Similar changes in electrical conductivity with composition are also observed in the system $\text{La}(\text{Fe}_x\text{Ru}_{1-x})\text{O}_3$ as noted previously. However, in the system under study here, for certain temperature and composition regimes, the electrical conductivity decreases with small additions of Ru. As can be seen in Fig. 2, this behavior cannot be correlated with phase changes in the material.

B. Thermal stability and phase equilibria

On the basis of measurements of the liquidus and solidus temperatures (Sec. IIC), estimates of transition temperatures (Sec. IIIA), and reported phase equilibria for $(\text{Sr}_{0.8125}\text{La}_{0.1875})(\text{Zr}_{0.75}\text{Fe}_{0.25})\text{O}_{3-\delta}$ (Refs. 1, 17), a pseudo-binary phase diagram has been constructed and is shown in Fig. 3. In the high-temperature region, the open circles, closed circles, and open squares represent laser melting point

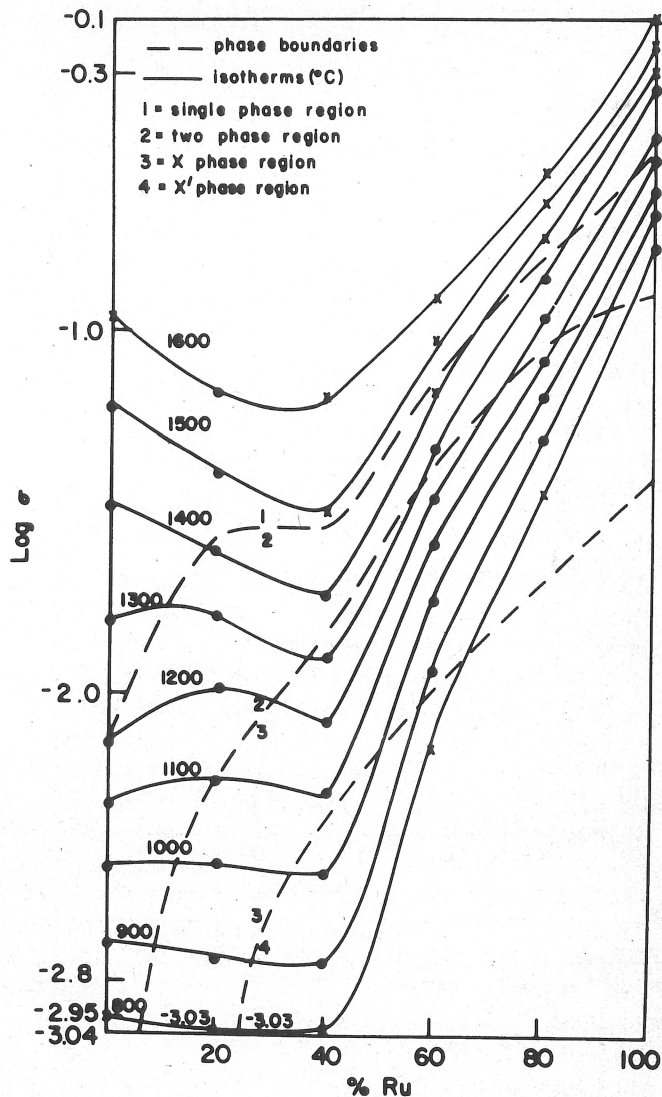


FIG. 2. Electrical conductivity isotherms showing the effect of Ru substitution for Fe.

measurements. X and X' represent unknown phases.

The substitution of Ru for Fe results in a relatively minor depression (less than 10%) of the solidus of the Fe-rich solid solution while the electrical conductivity increases dramatically (by a factor of 100 at $800\text{--}900^\circ\text{C}$). The substitution of Ru for Fe does not appear to give rise to new phases and eutectic-type behavior. However, at the low end of the temperature range studied, there is evidence for what could be either the onset of a new miscibility gap or an ordering of cations in one or more of the solid-solution phases. The latter is observed in other perovskite systems, for example, $\text{Ba}(B_{0.5}^{+3}\text{Nb}_{0.5}^{+5})\text{O}_3$, ($B^{+3} = \text{In}^{+3}, \text{Fe}^{+3}$ or any rare earth ion), $\text{RE}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ ($\text{RE} =$ any rare earth ion), and $A(B_{0.33}^{+2}\text{Nb}_{0.67}^{+5})\text{O}_3$ ($A = \text{Sr}, \text{Ba}$ and $B =$ any divalent ion).¹⁸⁻²⁰

IV. CONCLUSIONS

The system $(\text{Sr}_{0.8125}\text{La}_{0.1875})(\text{Zr}_{0.75}\text{Fe}_x\text{Ru}_{0.25-x})\text{O}_{3-\delta}$ deserves further investigation as a basis for high-tempera-

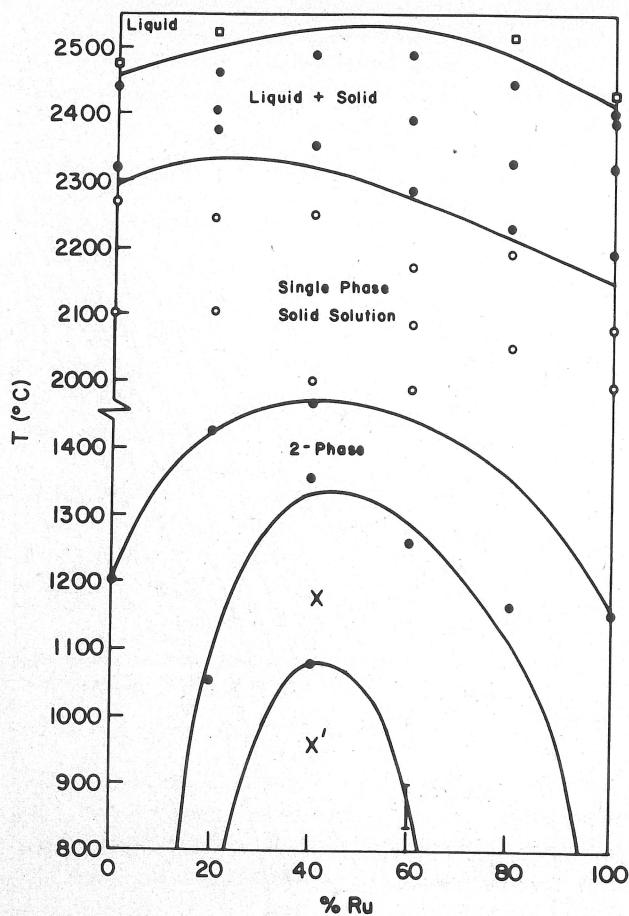


FIG. 3. Phase diagram of the pseudo-binary system $(\text{Sr}_{0.8125}\text{La}_{0.1875})(\text{Zr}_{0.75}\text{Fe}_{0.25})\text{O}_{3-\delta} - (\text{Sr}_{0.8125}\text{La}_{0.1875})(\text{Zr}_{0.75}\text{Ru}_{0.25})\text{O}_{3-\delta}$.

ture MHD electrode materials.

The electrical conductivity as measured in air from 800 to 1600 °C has been found to increase significantly with Ru concentration. Values approaching $1(\Omega \text{ cm})^{-1}$ at 1300 °C have been recorded. Substitution of Ru for Fe did not result in significant decreases in thermal stability.

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