Ionic Conductivity of Lanthanum Fluoride

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The electrical conductivities of lanthanum fluoride single crystals containing from 0.02 to 0.15 mole percent calcium ion impurities were measured between 25° and 740° C. The intrinsic specific conductivity \( K \) in ohm\(^{-1}\)·cm\(^{-1}\) of lanthanum fluoride is

\[
K = \left( \frac{7 \pm 1 \times 10^5}{T} \right) \exp \left( \frac{-19000 \pm 300}{RT} \right)
\]

where \( T \) is the absolute temperature and \( R \) is the gas constant. The activation energies for the formation of Schottky defects and for the migration of fluoride ion vacancies are 46 and 7.6 kcal/mole (192 and 32 kJ/mole), respectively. Mechanisms are proposed for the fluoride ion conduction process in lanthanum fluoride.
IONIC CONDUCTIVITY OF LANTHANUM FLUORIDE

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SUMMARY

The electrical conductivities of lanthanum fluoride single crystals were measured between 25°C and 740°C. The experimental activation energies were calculated from the slopes of the plots of the logarithms of the products of the specific conductivity and the absolute temperature against the reciprocals of the absolute temperatures.

The specific conductivity $K$ in ohm$^{-1}$-centimeter$^{-1}$ of single crystals of lanthanum fluoride in the high-temperature intrinsic region is

$$K = \left(\frac{7\pm1\times10^5}{T}\right)\exp\left(-\frac{19100\pm300}{RT}\right)$$

where $T$ is the absolute temperature and $R$ is the gas constant. The following mechanism is proposed for the conductivity process for this region: (1) thermal formation of lanthanum and fluoride ion vacancies by the Schottky mechanism with an activation energy of about 46 kilocalories per mole (192 kJ/mole); and (2) migration of fluoride ions with a migration energy of about 7.6 kilocalories per mole (32 kJ/mole).

For the extrinsic region, the defects responsible for the conduction are formed by impurities. The following mechanism is proposed for the conductivity process for the straight line portion of this extrinsic region: (1) formation of fluoride ion vacancies by introduction of calcium ions into the lattice and (2) migration (with an activation energy of about 7.6 kcal/mole or 32 kJ/mole) of the fluoride ions through these vacancies.

At the lower portion of the extrinsic region, the activation energy increased. This increase is proposed to be a result of precipitation of the calcium ion impurities or of complexing of fluoride ion vacancies.
INTRODUCTION

Many of the previous investigations concerned with the ionic conductivity of solids have dealt with the halides of group IA (alkali metals) and IB (copper and silver) (ref. 1). All of these halides are cationic conductors. Group II fluorides have also been investigated (refs. 2 to 4). In contrast, these compounds are anionic conductors.

Lanthanum fluoride is of particular interest since its mechanism of conductivity may be representative of many ionic trivalent halides. Furthermore, the one previous investigation of its conductivity yielded some surprising results (ref. 5). For example, an experimental activation energy of only about 2 kilocalories per mole (8 kJ/mole) was reported for the data above 160° C. This energy is comparable with values for diffusional processes in the liquid state. The only other solid materials that have such low activation energies are certain silver compounds, α-silver iodide, (α-AgI), silver sulfur iodide (Ag₃S_I), or silver rubidium iodide (Ag₄RbI₅), in which the silver ion is mobile. For example, the activation energies for α-AgI (ref. 6) and Ag₄RbI₅ (ref. 7) are about 1.2 and 3.0 kilocalories per mole (5 and 13 kJ/mole), respectively.

The present investigation was undertaken to elucidate more fully the energetics and mechanisms for fluoride ion conduction. Measurements were made of the conductivities of lanthanum fluoride single crystals between 25° and 740° C. The activation energies and preexponential factors were calculated from the specific conductivities and their variations with temperature. Mechanisms consistent with the data are proposed for the conduction processes.

EXPERIMENT

Crystal Preparation

Three lanthanum fluoride single crystals (designated 1, 2, and 3) were obtained in sealed containers as 1-centimeter cubes from a commercial source. These crystals had been prepared by the Stockbarger technique (ref. 8). In this case, an atmosphere of gaseous hydrogen fluoride surrounded the crystals during growth. This atmosphere was used in an attempt to reduce the contamination of the crystals with oxide ions. Emission spectrographic analyses of crystals 1 and 3 are given in table I. The primary impurities in both crystals were calcium ions. Unfortunately, crystal 2 was inadvertently destroyed. Therefore, no analytical data could be obtained for crystal 2.

All manipulations of the crystals were carried out in a dry box that was continually purged with gaseous nitrogen obtained as boiloff from liquid nitrogen.
Any surface irregularities of the crystals were removed by grinding and polishing on fine emery paper. After the crystals were polished, they were colorless and transparent and contained no internal flaws visible to the eye. The dimensions of the crystals were determined with a micrometer.

Three methods were used to apply electrical contacts to the crystal faces in an attempt to minimize surface contact resistance. These methods were (1) sputtering with platinum, (2) sputtering with gold, and (3) painting with several thin coats of an emulsion of colloidal graphite in dry alcohol.

Temperature Control and Measurement

A three-heat-zone furnace was used. Each zone was controlled to $\pm 0.25^\circ C$ by means of a saturable-core reactor in conjunction with a proportional control unit. The temperatures of both electrodes were determined. These two temperatures usually did not differ by more than $0.2^\circ C$ to $0.4^\circ C$, and the temperature of the crystal was taken as the average of these readings. The measurements were made by means of platinum-platinum-13-percent-rhodium thermocouples that had been calibrated to provide an accuracy within at least $0.2^\circ C$ to $700^\circ C$.

Resistivity Measurements

Essentially, the same apparatus and procedure that had been used to determine the conductivities of the alkaline earth fluorides (refs. 3 and 4) were used in this study. The crystal was preheated to $100^\circ C$ to $250^\circ C$ in vacuum (mercury diffusion pump) for 4 to 8 hours in an attempt to remove oxygen, absorbed water, and other volatile contaminants, and then it was cooled slowly to room temperature. Helium gas that had been purified by passage over copper turnings at $375^\circ C$ was added slowly through two liquid-nitrogen traps to a system pressure of about 700 millimeters of mercury ($93 \text{ kN/m}^2$). Periodically, the system was reevacuated to counteract slight leakage or degassing of oxygen and water vapors.

Resistance measurements were made by the alternating-current method at 0.1, 1, 10, and 100 kilohertz with an impedance comparator bridge and standard resistors. The measured resistance of the crystal consists of two resistances in series: (1) the true crystal resistance and (2) the contact resistance at the crystal-electrode surface. This contact resistance is usually small depending on the type of electrode and the quality of the contact between the electrode and the crystal. This contact resistance was negligible for all the surface contacts below $550^\circ C$ at the higher frequencies of 1, 10, and
100 kilohertz. However, for 0.1 kilohertz, this contact resistance was 5 to 9 percent. Above 550°C, the contact resistance of the sputtered platinum and gold surfaces increased to such an extent that these contacts were completely unsatisfactory. The graphite surface coatings, on the other hand, were satisfactory to the highest temperature used (740°C). The reason for the increased contact resistance of the metal surfaces above 550°C is not known.

RESULTS

For each lanthanum fluoride crystal, the logarithms of the products of the specific conductivity and the absolute temperature were plotted against the reciprocals of the absolute temperatures. The plot for crystal 1 is shown in figure 1. The conductivity of the higher temperature region, designated as the intrinsic region I, is that for the "pure" crystal. This intrinsic conductivity can be expressed by an equation of the form

\[ \log K_I = \log \left( \frac{A_I}{T} \right) - \frac{\Delta E_I}{2.3026 RT} \]  

where

- \( K_I \) intrinsic specific conductivity, ohm\(^{-1}\)-cm\(^{-1}\)
- \( A_I \) intrinsic preexponential factor, ohm\(^{-1}\)-cm\(^{-1}\)
- \( T \) absolute temperature, K
- \( \Delta E_I \) intrinsic experimental activation energy, kcal/mole; kJ/mole
- \( R \) gas constant

The data for the intrinsic region for crystals 1 and 3 between about 380°C and 740°C are plotted in figure 2. The slope and intercept of this line were determined by the method of least squares from which the experimental activation energy, the preexponential factor, and their standard deviations were obtained. The specific conductivity of "pure" lanthanum fluoride can be expressed as

\[ K_I = \frac{7 \pm 1 \times 10^5}{T} \exp \left( - \frac{19 \pm 300}{RT} \right) \]  

In figure 1, the lower temperature region, designated as the extrinsic region E, is the impurity controlled region. If the number of free defects (formed by the impurities in the crystal) remains constant over this extrinsic temperature range, the data should
lie on one straight line. However, if the number of free defects decreases, the data for the entire extrinsic region may not lie on a single straight line but may curve below it at the lower temperatures. The plots for all three of the lanthanum fluoride crystals indicated that a decrease in the number of free defects does occur. An example of this decrease is shown in figure 3 for crystal 1. The curvature for crystal 1 is quite small above 120° C. Therefore, the data have been fitted to one straight line from 360° to about 120° C. Below about 120° C, the slope of the line increases. Similar results were obtained for crystals 2 and 3. For these cases, the data were fitted to one straight line between 500° and about 125° C for crystal 2 (fig. 4) and between 500° and about 175° C for crystal 3 (fig. 5). As for figure 2, the slopes of the straight line portion of these extrinsic regions were determined by the method of least squares. The values for the experimental activation energies, the preexponential factors, and their standard deviations are listed in table II. An average value of 7.6±0.2 kilocalories per mole (32 kJ/mole) was obtained for the activation energy in the extrinsic region.

The slopes for the lower portion of the extrinsic regions cannot be obtained with certainty. However, near room temperature the slopes do appear to reach a constant value, from which an apparent activation energy of about 10 kilocalories per mole (42 kJ/mole) was calculated.

Results obtained in a previous investigation (ref. 5) contrasted sharply with the present data for the intrinsic region. For example, an apparent activation energy of only about 2 kilocalories per mole (4 kJ/mole) was reported for the conductivity data above 160° C. On the other hand, the results of the previous and present investigations agreed more closely at lower temperatures. For example, the previous investigation reported an energy of about 11 kilocalories per mole (46 kJ/mole) near room temperature (ref. 5). This result compares favorably with the value of about 10 kilocalories per mole (42 kJ/mole) that was obtained in the present investigation.

**DISCUSSION**

Ions migrate through point defects in real crystals. The thermal formation of such point defects is believed to occur through the Schottky or Frenkel mechanism. The Schottky process (fig. 6(a)) involves movement of cations and anions from their normal lattice sites to the surface and leaves vacancies of both species. In the Frenkel process (fig. 6(b)), an ion moves from its normal site to an interstitial position and leaves a vacancy. Therefore, for the Schottky process, the bulk volume of the crystal expands faster than the unit cell volume as the crystal temperature increases. On the other hand, for the Frenkel process, these volume changes are comparable.
For lanthanum fluoride, nuclear magnetic resonance \( \left( ^{19}F \right) \) investigations show that fluoride ions are the migrating species (ref. 5). Further, since thermal expansion measurements (by dilatometer and X-ray diffraction) indicated that the bulk volume expanded faster than the unit cell volume, the thermal formation of point defects in lanthanum fluoride was assumed to occur primarily by the Schottky process (ref. 5).

The specific conductivity of lanthanum fluoride crystals \( K \) in ohm\(^{-1}\)-centimeter\(^{-1}\) is related to the total number of fluoride ion vacancies \( n_T \) and to their mobility \( \mu_F \) as follows:

\[
K = e n_T \mu_F
\]  

In the intrinsic region, the number of fluoride ion vacancies produced thermally \( n \) is greater than the number of those produced by impurities \( n_x \). Introducing the appropriate relation for \( n_T \) and \( \mu_F \) (ref. 9) into equation (3) gives

\[
K_I = e \left[ \gamma_B N \exp \left( \frac{\Delta E_F}{4RT} \right) \right] \left[ \nu \exp \left( \frac{-\Delta E_M}{RT} \right) \right]
\]

where

\[
\gamma_B \quad \text{correction factor for formation of defects}
\]
\[
N \quad \text{number of ions per cm}^3
\]
\[
\Delta E_F \quad \text{energy of formation, kcal/mole; kJ/mole}
\]
\[
R \quad \text{gas constant}
\]
\[
T \quad \text{temperature, K}
\]
\[
C \quad \text{correction factor for mobility of defects}
\]
\[
e \quad \text{electric charge}
\]
\[
\nu \quad \text{presentation frequency of fluoride ion at vacancy boundary (jump frequency), sec}^{-1}
\]
\[
a \quad \text{distance between adjacent positions in lattice, cm}
\]
\[
k \quad \text{Boltzmann constant}
\]
\[
\Delta E_M \quad \text{energy of migration, kcal/mole; kJ/mole}
\]

Equation (4) is rearranged to

\[
K_I = \left( \gamma B C \right) \left( \frac{N e^2 \nu a^2}{kT} \right) \left[ \exp \left( -\frac{\Delta E_F}{4RT} \right) \right] \left[ \exp \left( -\frac{\Delta E_M}{RT} \right) \right]
\]  

\[\text{(5)}\]
which reduces to

\[ K_I = \frac{A_I}{T} \exp\left(\frac{-\Delta E_I}{RT}\right) \]  

(6)

where \( A_I \) and \( \Delta E_I \) are the preexponential factor and the experimental activation energy for the intrinsic region, respectively. Equations (5) and (6) can be compared with equation (2), which describes the experimental results.

A value of 19.1 kilocalories per mole (80 kJ/mole) was obtained for the intrinsic activation energy for lanthanum fluoride. The migration energy of fluoride ion vacancies (discussed later in this section) is only about 7.6 kilocalories per mole (32 kJ/mole). Therefore, the energy of formation of the defects is \( \Delta E_F = 4 (\Delta E_I - \Delta E_M) = 46 \) kilocalories per mole (192 kJ/mole). For comparison, the energy for the formation of Schottky defects in sodium chloride is about 46 kilocalories per mole (192 kJ/mole) (ref. 10).

A value of about 3 was obtained for the correction factor \( \gamma_{BC} \) for lanthanum fluoride from the expressions for the intrinsic preexponential factor in equations (2) and (5). The values for the constants are \( N \), \( 1.8 \times 10^{22} \) centimeters\(^{-3} \); \( a \), \( 2.6 \times 10^{-8} \) centimeter (ref. 5); \( e^2 \), \( 2.56 \times 10^{-31} \) erg-second per ohm or \( 2.56 \times 10^{-38} \) joule-second per ohm; \( k \), \( 1.38 \times 10^{-6} \) erg per degree or \( 1.38 \times 10^{-13} \) joule per degree; and \( \nu \), \( 8 \times 10^{12} \) seconds\(^{-1} \).

The jump frequency \( \nu \), taken as the Debye frequency, was estimated from the Debye temperature (ref. 11). This small value for the correction factor \( \gamma_{BC} \) contrasts sharply with values that have been obtained for other solids. For example, Mott and Gurney suggested a value of about \( 10^4 \) for sodium chloride (ref. 9). A value of about 3 was estimated for the mobility correction factor \( C \) from the data in the extrinsic region (discussed later in this section). Therefore, the correction factor for the defect formation process \( \gamma_B \) was concluded to be essentially 1. This correction factor contrasts with values of about \( 10^3 \) suggested for \( \gamma_B \) for sodium chloride (ref. 9).

It should be pointed out that the experimental results obtained in this investigation for the intrinsic region differ significantly from the results of Sher et al. (ref. 5). As mentioned previously, they obtained a value for the apparent energy of activation of about 2 kilocalories per mole (8 kJ/mole) for the upper temperature range, which is in contrast to the value of 19.1 kilocalories per mole (80 kJ/mole) obtained in this work. The reason for this difference is not obvious.

In addition to thermal production of ion vacancies, fluoride ion vacancies can also be formed by impurities. Divalent cation impurities can produce fluoride ion vacancies, and tetravalent cations can produce fluoride ions in the interstitial sites (fig. 6(c) and (d)). For the lanthanum fluoride crystals used in this work, the production of interstitials by impurities was assumed to be negligible since tetravalent cations were not
detected in the analysis of the crystals. On the other hand, calcium ions were present as an impurity.

For the extrinsic region (impurity controlled region), the number of vacancies produced by the calcium ions \( n_x \) was much larger than those vacancies produced thermally. Therefore, for the straight line portion of the extrinsic region, the specific conductivity \( K_E \) in ohm\(^{-1}\)-centimeter\(^{-1}\) can be approximated from equation (4) as

\[
K_E = e n_x \frac{C e/\nu^2}{kT} \exp \left( -\frac{E_M}{RT} \right)
\]

This equation can be compared with the extrinsic preexponential factor and activation energy (given in table II) that describe the experimental results.

An estimate of the mobility correction factor \( C \) can be made from the preexponential factors and the various constants used before. About \( 3.6 \times 10^{18} \) and \( 2.7 \times 10^{19} \) fluoride ion vacancies per cubic centimeter were introduced into crystals 1 and 3, respectively, by the calcium ions. On this basis, a value for \( C \) of about 4 was obtained for crystal 1, and a value of about 2 was obtained for crystal 3. This difference in the value of \( C \) for the crystals is not significant. Accordingly, a value of 3 was assumed for the mobility correction factor. This value is of the same order of magnitude as that suggested for sodium chloride (ref. 9).

The experimental activation energy for the lanthanum fluoride crystals increased from 7.6 to about 10 kilocalories per mole (32 to 42 kJ/mole) for the temperature range below the straight line portion of the impurity controlled region. One could account for this apparent energy increase by assuming that the migration energy for fluoride ion vacancies increases with decreasing temperature in this region. This temperature dependence is not likely unless a change in the crystal lattice were to occur in this temperature range. Such is not the case. A more reasonable explanation is that the concentration of free fluoride ion vacancies, at these lower temperatures, decreases. This decrease in the number of free vacancies can arise by precipitation of the calcium ions or by complexing of vacancies. Both of these possibilities have been observed previously for alkali halides (ref. 12). For example, the presence of hydroxyl ions caused precipitation of magnesium ions, which had been added as a dopant to lithium fluoride (ref. 13). As a result, the apparent activation energy increased for the lower portion of the extrinsic region because of the removal of free lithium ion vacancies. A similar process may occur in lanthanum fluoride. If sufficient anions, such as hydroxyl or oxide ions, are present in the crystal, precipitation of the calcium ions may occur, which leads to an increased activation energy for the lower portion of the extrinsic region.

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Complexing may also cause the activation energy to increase. For example, at lower temperatures in sodium chloride crystals containing divalent cations such as Cd\(^{++}\), the sodium ion vacancies, which have a negative character, complex with the positive divalent cation of cadmium (ref. 14). This neutral complex will not contribute to the ionic conductivity. As a result, the conductivity decreases (as the number of free vacancies decreases) and this leads to an increase in the slope of the curve for the lower temperatures. A similar process may occur in lanthanum fluoride. Fluoride ion vacancies, having a positive character, may complex with a divalent anion to form a neutral species. Oxide ions, present in trace quantities, are the more likely source of such divalent anions. The complex may form as follows:

\[
(F_{\text{vacancy}}) + (O^-) \rightarrow (F_{\text{vacancy}} \cdot O^-)
\]  

Future experimental investigations with lanthanum fluoride crystals containing known quantities of oxide or hydroxide ions, halide ions, and cations with a valence other than +3 will contribute to further understanding of this complexing process.

**CONCLUDING REMARKS**

The mechanism for the conductivity of lanthanum fluoride single crystals in the intrinsic region was proposed as follows: (1) formation of fluoride and lanthanum ion vacancies by the Schottky mechanism and (2) migration of the fluoride ions through these fluoride ion vacancies. For the impurity controlled (extrinsic) region, the fluoride vacancies were formed by the introduction of calcium ions into the lattice. Migration occurred, as before, through these fluoride ion vacancies. Finally, at the lower temperature portion of the extrinsic region, precipitation of the calcium ions or complexing between the fluoride ion vacancies and anion species may occur.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, August 27, 1969,
120-34.
REFERENCES


TABLE I. - EMISSION SPECTROGRAPHIC ANALYSES OF LANTHANUM FLUORIDE (MOLE PERCENT)

<table>
<thead>
<tr>
<th>Element</th>
<th>Crystal</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Lanthanum</td>
<td>~0.02</td>
</tr>
<tr>
<td>Calcium</td>
<td>&lt;.007</td>
</tr>
<tr>
<td>Aluminum</td>
<td>(a)</td>
</tr>
<tr>
<td>Rare earths</td>
<td>(a)</td>
</tr>
<tr>
<td>Other</td>
<td>(a)</td>
</tr>
</tbody>
</table>

\(^a\text{Not detected.}\)

TABLE II. - CONDUCTIVITY OF LANTHANUM FLUORIDE IN STRAIGHT LINE PORTION OF EXTRINSIC REGION

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Activation energy, (\Delta E_E)</th>
<th>Preexponential factor, (A_E)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kcal/mole</td>
<td>kJ/mole</td>
</tr>
<tr>
<td>1</td>
<td>7.7±0.1</td>
<td>32±0.4</td>
</tr>
<tr>
<td>2</td>
<td>7.8±0.1</td>
<td>33±0.4</td>
</tr>
<tr>
<td>3</td>
<td>7.4±0.2</td>
<td>31±0.8</td>
</tr>
</tbody>
</table>
Figure 1. - Specific conductivity of lanthanum fluoride crystal 1.

Figure 2. - Specific conductivity of lanthanum fluoride in intrinsic region.
Figure 3. - Specific conductivity of lanthanum fluoride crystal in impurity region.
Figure 4. Specific conductivity of lanthanum fluoride crystal 2 in impurity region.

Figure 5. Specific conductivity of lanthanum fluoride crystal 3 in impurity region.
(a) Schottky formation in "pure" lanthanum fluoride crystal.

(b) Frenkel formation in "pure" lanthanum fluoride crystal.

(c) Fluoride vacancy formation by calcium fluoride.

(d) Fluoride interstitial formation by zirconium fluoride.

Figure 6. - Defects in lanthanum fluoride. (Sketches are only simple planar representations and are not intended to indicate structure of lanthanum fluoride.)
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—National Aeronautics and Space Act of 1958

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