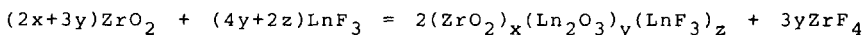


FORMATION OF THE STABILIZED ZIRCONIA WITH RARE-EARTH FLUORIDES AND ITS ELECTRICAL CONDUCTIVITY

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The new reactions with rare earth fluorides to prepare the stabilized zirconia and the electrical conductivity of it as the solid electrolyte have been examined by means of X-ray diffraction, DTA, EPMA and electrochemical methods. The eleven rare earth fluorides of YF₃ and SmF₃ through LuF₃ reacted with ZrO₂ to form the new type stabilized zirconias (LnFSZ) consisting of the ternary system of ZrO₂-Ln₂O₃-LnF₃



where x, y and z represent the stabilizing composition at which the homogeneous solid solution with the fluorite structure is formed, and $x + y + z = 1$. This reaction begins to take place at about 600 °C and is completed by firing at the temperature ranging from 1000 to 1300 °C for a few hours in an argon atmosphere. During the reaction, the weight loss was about 18 wt% at the maximum, which was found to be due to the sublimation of ZrF₄ resulting from the anion exchange reaction between LnF₃ and ZrO₂. This means that many defect sites of Zr⁴⁺, which Ln³⁺ can readily occupy to create the solid solution substitutionally, are formed in the ZrO₂ crystal as ZrF₄ goes out from the reaction system.

The electrical conductivities for LnFSZ are 10⁻⁴ Scm⁻¹ in the order of magnitude at 650 °C under around 10⁻⁷ atm oxygen which compares with that of YSZ or the other oxide stabilized zirconia. The maximum conductivity is obtained at the composition of the zirconium rich end of the homogeneous cubic for (ZrO₂)_x(Ln₂O₃)_y(LnF₃)_z at which the activation energy for the conductivity becomes minimum at that composition. The charge carrier in LnFSZ is proven to be mainly the oxide ion in spite of being the fluoride ion by the electrolysis method.

The electrical conductivity of the sintered sample of (ZrO₂)_{0.78}(Eu₂O₃)_{0.1}(EuF₃)_{0.12} prepared by hot-pressing at 1200 °C under 200 kgcm⁻² was measured to be 2.3x10⁻³ Scm⁻¹ at 700 °C by ac measurement, and its oxide ion transport number examined by the oxygen gas concentration cell method (¹⁸O₂:anode; 0.01 atm, cathode; 0.21 atm) is over 0.9 even at 450 °C.