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This Week's Citation Classic

 $Zr_{0.85}Ca_{0.15}O_{1.85}$ J. Amer. Ceram. Soc. 42:393-8, 1959. [Ceramics Division, Department of Metallurgy. Massachusetts Institute of Technology. Cambridge, MA]

Oxygen ion mobility in the cubic fluoritestructure phase having the composition $Zr_{0.85}Ca_{0.15}O_{1.85}$ has been directly determined by exchange measurements employing the stable isotope O^{18} and mass spectrometer analysis. Measurements of electrical conductivity have been carried out as a function of both temperature and oxygen pressure. Results indicate that the conductivity is wholly ionic with a transfer number near unity for the oxygen ion. [The *SCI*[®] indicates that this paper has been cited in over 210 publications.]

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This work was undertaken as part of a broader study of oxygen mobility in crystalline solids using oxygen isotope exchange^{1,2} for measuring diffusion coefficients and electrical conductivity transport numbers³ to derive ionic mobilities. The opportunity for diffusion measurements in lime-stabilized zirconia came partly from the availability of 100-micron-diameter spheres of this material prepared in conjunction with research on solid-state sintering.⁴ Thus, the particular research resulted from a confluence of the instrumentalities of material and method, focusing on a material with both scientific and technological interest.

Zirconium oxide stabilized in the cubic form by solid solution alloying first came to promi-

nence as an electrolytic conductor in the glow lamps invented by Walther Nernst and patented in 1899. Lamps using a ceramic oxide filament of about 85 wt% zirconia-15 wt% Y2O3 were manufactured by Westinghouse in the US and by the Allgemeine Elektrizitäts-Gesellschaft (AEG) in Germany. Nernst, already famous as a physical chemist, received a Nobel Prize for thermodynamics in 1920. In 1898 he sold his invention to the German AEG, reportedly receiving a million marks. He became a rich professor and indulged in a liking for sports cars and princely estates. The Nernst lamp was two to three times more efficient than the carbon filament; however, tungsten filaments were about three times more efficient than the ceramic Nernst glower. When tungsten filaments were introduced in 1906-1907, and particularly the drawn tungsten filament in 1911, all other lamp filaments, including the Nernst glower, were supplanted.

The ionic conductivity in cubic stabilized zirconia is higher than sulphuric acid, and it has been used as an electrolyte for fuel cells, batteries, oxygen sensors, and electrochemical research. As a result, the nature of the electrolytic conduction has been of considerable interest since the time of Nernst when ionic solutions were first being investigated.^{5,6} This paper was the first report of a direct and definitive measurement of the oxygen ion mobility and its relationship to high-temperature electrolytic conductivity and the oxygen ion vacancies in the cubic form of zirconium oxide.

Stabilized and partially stabilized zirconia have continued to be a subject of active research, not only for their electrical properties or as high-temperature refractories, but also for their mechanical properties, particularly in the partially stabilized form.^{7,8} It is not surprising that a fundamental determination of oxygen mobility in this material should be cited frequently.

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