Chapter 10
Zirconia

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Abstract Zirconia is a very important industrial ceramic for structural applications because of its high toughness, which has proven to be superior to other ceramics. In addition, it has applications making use of its high ionic conductivity. The thermodynamically stable, room temperature form of zirconia is baddeleyite. However, this mineral is not used for the great majority of industrial applications of zirconia. The intermediate-temperature phase of zirconia, which has a tetragonal structure, can be stabilized at room temperature by the addition of modest amounts (below \(\sim 8\) mol\%) of dopants such as \(Y^{3+}\) and \(Ca^{2+}\). This doped zirconia has mechanical toughness values as high as \(17\) MPa • m\(^{1/2}\). On the other hand, the high-temperature phase of zirconia, which has a cubic structure, can be stabilized at room temperature by the addition of significant amounts (above \(\sim 8\) mol\%) of dopants. This form of zirconia has one of the highest ionic conductivity values associated with ceramics, allowing the use of the material in oxygen sensors and solid-oxide fuel cells. Research on this material actively continues and many improvements can be expected in the years to come.

1 Introduction

Zirconia (\(ZrO_2\)) is an extremely versatile ceramic that has found use in oxygen pumps and sensors, fuel cells, thermal barrier coatings, and other high-temperature applications, all of which make use of the electrical, thermal, and mechanical properties of this material. Proof of the interest and usefulness of zirconia can be seen from the voluminous literature found on this material. This chapter is intended to provide a concise summary of the physical and chemical properties of all phases of zirconia that underlie the appropriate engineering applications.

The three low-pressure phases of zirconia are the monoclinic, tetragonal, and cubic, which are stable at increasingly higher temperatures. Calculated energy vs. volume data at zero absolute temperature confirms the higher stability of the monoclinic phase (Fig. 1). However, most engineering applications make use of the tetragonal and cubic phases, even though their stability at low temperatures is quite low. In fact, the engineering use of all three phases of zirconia in pure form is rare. Generally,
zirconia is doped with oxides such as $Y_2O_3$ that stabilize the high-temperature phases at room temperature. This has enormous consequences for both the mechanical and electrical properties of zirconia, even though the local atomic and electronic structure of Zr$^{4+}$ in all three polymorphs is for the most part dopant independent [3].

Doping of zirconia results in stabilization of the tetragonal phase at lower dopant concentrations (for mechanical toughness) or the cubic phase at higher dopant concentrations (for high ionic conductivity) at room temperature. The stabilization of the tetragonal phase at room temperature can result in the following common forms of

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**Fig. 1** Computed energy vs. volume data for cubic, tetragonal, and monoclinic phases from (a) Stapper et al. [1] and (b) Dewhurst and Lowther [2] (reprinted with permission)