

DIELECTRICS

Effect of the Valence State of Ce Ions on the Phase Stability and Mechanical Properties of the Crystals of ZrO₂-Based Solid Solutions

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Abstract—The structure and mechanical properties of the crystals of solid solutions of zirconium dioxide, which are stabilized by yttrium and cerium oxides, have been studied. The electron paramagnetic resonance technique has been used to identify Ce³⁺ ions and to determine their relative concentration in the crystals. It is shown that the presence of Ce³⁺ ions in the crystals is the main factor responsible for their high fracture toughness. The annealings carried out during investigations, which lead to a decrease in the concentration of Ce³⁺ ions, show that a change in the valence state of cerium ions lowers the fracture toughness of the crystals.

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1. INTRODUCTION

Materials based on zirconium dioxide and stabilized by yttrium oxide are of considerable interest, because they possess a number of unique properties like high stability to abrasive wear and a low friction coefficient, as well as high resistance to acids and alkalis. Partly stabilized zirconium dioxide (PSZ) is a material of this type. PSZ crystals display a much lower degradation of mechanical properties than metals and structural ceramics in oxidizing media at high temperatures (up to 1400°C) [1]. Chemical and biological inertness, durability and high fracture toughness make PSZ crystals promising materials for use in medicine and engineering [2, 3].

Materials based on zirconium dioxide, mainly ceramics, have been known for a long time. The synthesis of crystalline materials using the technique of crystallization from the melt [4] makes it possible to obtain high-density solid materials with zero porosity and without a grain structure. Hence, PSZ crystals have higher frictional and strength characteristics as compared to familiar structural ceramic materials based on ZrO₂.

The phase composition, structure, and eventually mechanical properties of PSZ are also determined by parameters like the concentration and the type of the stabilizing oxide, which determine the concentration

of oxygen vacancies, as well as the technological conditions of synthesis.

Investigations of zirconium-dioxide-based materials stabilized by cerium oxide are of considerable interest because these materials are characterized by a high fracture toughness from 17 [5] to 35 MPa m^{1/2} [6].

However, in their strength characteristics like microhardness, Young's modulus, and flexural strength, these materials are inferior to zirconium-dioxide-based materials stabilized by yttrium oxide. One of the methods of optimizing mechanical characteristics of a material is the introduction of several stabilizing oxides, e.g., doping with yttrium and cerium oxides. For example, the mechanical properties of ceramic materials based on zirconium dioxide and doped simultaneously with Y₂O₃ and CeO₂ were studied in [7–9] as functions of the composition, grain structure, and conditions of synthesis.

The results of investigations of the mechanical properties of PSZ crystals doped simultaneously with yttrium and cerium oxides have been presented in [10, 11]. The values for microhardness (H_V) and fracture toughness (K_{Ic}) for a single sample of PSZ (whose chemical composition is not presented here) were found to be equal to (14.40–14.45) GPa and 11.43 MPa m^{1/2}, respectively [10]. It was also found