Mössbauer Study of Tetragonal ZrO$_2$–Y$_2$O$_3$–Fe$_2$O$_3$ Solid Solutions


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Abstract—Tetragonal Zr$_{0.886}$Y$_{0.057}$Fe$_{0.053}$O$_{2-8}$ solid solutions prepared by calcining coprecipitated and successively precipitated hydroxide mixtures were studied by Mössbauer spectroscopy immediately after calcination and after long-term storage. The results indicate that the solid solutions prepared via coprecipitation and successive precipitation contain Fe$^{3+}$ in two (octahedral coordination) and three (octahedral, fivefold, and tetrahedral coordinations) inequivalent sites, respectively. Partial Fe$^{3+}$ substitution for Y$^{3+}$ is shown to prevent or substantially slow down the low-temperature structural degradation of stabilized zirconia.

INTRODUCTION

The ZrO$_2$–Y$_2$O$_3$–Fe$_2$O$_3$ system is of great practical importance in the development of high-strength ceramics [1, 2] and solid electrolytes [3–6]. Partial Fe$^{3+}$ substitution for Y$^{3+}$ in ZrO$_2$–Y$_2$O$_3$ ceramics makes it possible to markedly reduce their sintering temperature [3, 5] and, accordingly, to obtain a fine-grained microstructure, which is essential for achieving high mechanical strength. ZrO$_2$ and Y$_2$O$_3$ are known to form oxygen-deficient substitutional solid solutions (the excess negative charge resulting from Y$^{3+}$ substitution for Zr$^{4+}$ in ZrO$_2$ is compensated by oxygen vacancies) [7, 8].

There are a number of reports [6, 9, 10] that the ZrO$_2$–Fe$_2$O$_3$ system contains no solid solutions, whereas Teterin et al. [11] and Berry et al. [12] hold that ZrO$_2$ dissolves a small amount of Fe$_2$O$_3$. According to Neumin et al. [6] and Karavaev et al. [10], ZrO$_2$–Y$_2$O$_3$ solid solutions dissolve Fe$_2$O$_3$ and Sc$_2$O$_3$, and the solubilities of these additives correlate with the content of the stabilizing oxide Y$_2$O$_3$. This correlation can be understood in terms of oxygen vacancies (variation in their concentration) in ZrO$_2$-based solid solutions and the formation of impurity–vacancy defect complexes [10]. The nonlinear temperature variation of the electrical conductivity of ZrO$_2$-based solid solutions was interpreted by Kotlyar et al. [13] as being due to the interaction between oxygen vacancies and solute cations. The interaction between lattice defects and nearest neighbors of stabilizer cations in ZrO$_2$-based solid solutions was studied in [12–17]. Only a limited number of such studies have been reported for Fe-containing systems [11, 12, 18].

Mössbauer studies of the ZrO$_2$–Fe$_2$O$_3$ system were reported in [11, 12]. According to Teterin et al. [11], the products of thermal transformations in this system are α-Fe$_2$O$_3$, ZrO$_2$, Fe$^{3+}$ in a superparamagnetic state, and Fe$^{3+}$ ions dissolved in zirconia. In our opinion, the Mössbauer parameters of the resonance doublets for the Fe$^{3+}$-containing phases were determined in that study inaccurately, since they were not checked by calibration, and the assignment of the resonance absorption doublets is debatable. The Mössbauer results reported by Berry et al. [12] indicate that the Fe-containing cubic ZrO$_2$ phase formed at 770 and 1020 K at certain Fe concentrations is represented by a quadrupole doublet close in parameters to that of high-spin Fe$^{3+}$ in distorted octahedral coordination. With increasing iron content and calcination temperature, the doublet gives way to a singlet, which may be due to phase transformations or changes in the coordination of Fe$^{3+}$. Berry et al. [12], however, did not specify the parameters of the paramagnetic component, which impedes interpretation of their results.

The lack of data on the defect structure and nature of ZrO$_2$–Y$_2$O$_3$–Fe$_2$O$_3$ solid solutions prompted us to undertake a detailed Mössbauer study of this system with the aim of gaining greater insight into the nearest neighbor environment of Fe$^{3+}$ and the interaction between the solute cations and oxygen vacancies. To
rule out the ambiguity associated with the presence of two or three phases in partially stabilized ZrO$_2$, it is reasonable to investigate stabilized ZrO$_2$ (single-phase solid solutions). In light of this, we studied single-phase samples of composition 0.94ZrO$_2$·0.03Y$_2$O$_3$·0.03Fe$_2$O$_3$, which were calcined at 1470 K. The samples were prepared by two procedures and had a tetragonally distorted fluorite structure [19].

Yttria-stabilized ZrO$_2$ is known to be prone to low-temperature structural degradation because of the tetragonal–monoclinic phase transformation [20]. It is, therefore, also of interest to examine the evolution of the fine structure of the Mössbauer spectrum during long-term storage (aging) of the material.

In this paper, we report a Mössbauer study of the tetragonal solid solution 0.94ZrO$_2$·0.03Y$_2$O$_3$·0.03Fe$_2$O$_3$ (Zr$_{0.886}$Y$_{0.057}$Fe$_{0.057}$O$_2$–$\delta$) before and after long-term storage, using samples prepared by two procedures.

**EXPERIMENTAL**

Zr$_{0.886}$Y$_{0.057}$Fe$_{0.057}$O$_2$–$\delta$ samples were prepared by calcining appropriate mixtures of ZrO(OH)$_2$, Y(OH)$_3$, and FeOOH precipitated from concentrated ZrOCl$_2$, Y(NO$_3$)$_3$, and Fe(NO$_3$)$_3$ solutions by adding aqueous ammonia. We used two procedures: coprecipitation and successive precipitation. In the latter case, Y(OH)$_3$ was precipitated after ZrO(OH)$_2$ and FeOOH coprecipitation. After washing with distilled water until the wash water was free of Cl$^-$ and NO$_3^-$, the precipitates were dried at 350 K and then calcined at 1470 K in a compartment furnace. The samples obtained by successive precipitation were characterized after calcination and after storage under atmospheric conditions for two years.

X-ray diffraction (XRD) measurements were made on a DRON 4-07 powder diffractometer (Co$K\alpha$ radiation, 40 kV, 18 mA). In phase analysis, we used JCPDS Powder Diffraction File data. Structural parameters were refined by the Rietveld profile analysis method, using the FullProf program. XRD patterns were run in the angular range $2\theta = 10^\circ$–$150^\circ$ in a step-scan mode with a step size $\Delta 2\theta = 0.02^\circ$ and a counting time of 10 s per data point. As external standards, we used SiO$_2$ (20 calibration) and Al$_2$O$_3$ (intensity standard [21]).

Mössbauer spectra were recorded at room temperature on an electrodynamic spectrometer at a constant acceleration. The gamma source used was $^{57}$Co in metallic Rh. In velocity calibration in the magnetic and extended-scale paramagnetic ranges, we used $\alpha$-Fe and sodium nitroprusside, respectively (the isomer shift relative to $\alpha$-Fe can be converted to that relative to sodium nitroprusside by adding 0.258 mm/s). In what follows, the isomer shifts in both ranges are specified relative to the respective standard.

Fe content was determined on a Pye Unicom SP 9 atomic absorption spectrophotometer ($\lambda = 248.3$ nm, spectral slit width of 0.2 nm, acetylene–air flame). Zr and Y were determined using the fluoride procedure [22]. In addition, Zr was determined as described in [23].

**RESULTS AND DISCUSSION**

XRD examination showed that the Zr$_{0.886}$Y$_{0.057}$Fe$_{0.057}$O$_2$–$\delta$ samples prepared via both coprecipitation and successive precipitation had a tetragonally distorted fluorite structure (sp. gr. P4/nmc, no. 137) (Fig. 1, Table 1). In addition, the samples con-

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**Fig. 1.** XRD patterns of Zr$_{0.886}$Y$_{0.057}$Fe$_{0.057}$O$_2$–$\delta$ samples prepared via (1) coprecipitation and (2) successive precipitation.