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Iron–Zirconium Oxides: An Investigation of Structural Transformations by X-Ray Diffraction, Electron Diffraction, and Iron-57 Mössbauer Spectroscopy

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Zirconium dioxide and some iron–zirconium oxides have been prepared by the calcination of precipitates. The results show that the incorporation of Fe^{3+} within the tetragonal zirconium dioxide structure at moderate temperatures (ca. 500°C) stabilizes the cubic modification and inhibits its transformation to the monoclinic phase. The stabilization of the cubic structure is associated with the presence of interstitial Fe^{3+} ions and oxygen vacancies. Calcination of the cubic iron-containing zirconium dioxide at 1000°C induces conversion to the monoclinic zirconium dioxide and a partial segregation of iron from the structure to form iron(III) oxide which probably contains zirconium. Pure tetragonal zirconium dioxide was found to undergo a transformation to the monoclinic structure when exposed to the electron beam of the electron microscope. In contrast the cubic iron–zirconium oxides remained stable in the electron beam. © 1989 Academic Press, Inc.

Introduction

Pure zirconium dioxide can be crystallized with either cubic, tetragonal, or monoclinic structure. The cubic polymorph adopts the calcium difluoride fluorite structure in which the zirconium cations are coordinated by eight oxygen ions while the tetragonal phase may be regarded as a slightly distorted fluorite array from which the diffraction patterns are indexed to a face-centered tetragonal cell. The monoclinic polymorph, which is sometimes referred to as the Baddeleyite structure, contains zirconium ions in sevenfold coordination with oxide ions (*1*).

The monoclinic form of zirconium dioxide is usually found at room temperature and at ca. 1200°C undergoes a reversible martensitic phase transformation to a high-temperature tetragonal phase (*2*) which cannot be retained by quenching and is converted (*3*) to the monoclinic structure at ca. 900°C. The tetragonal phase remains unaltered by thermal treatment until ca. 2400°C when it transforms to the cubic phase which is stable to the melting point at ca. 2700°C (*4*).

A low-temperature tetragonal phase, reported to be identical to the high-temperature tetragonal structure, can be formed at room temperature by adding aqueous am-

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monia to a zirconium(IV) oxychloride solution and heating the resulting gel, described as zirconium hydroxide, at 110°C and subsequently at 500°C (*5*). Other workers have reported (*6*) that the low-temperature tetragonal phase of zirconium dioxide can also be formed by heating a zirconium(IV) hydroxide gel at 290°C. This tetragonal phase is reported to be converted at temperatures between 350 and 600°C to the monoclinic polymorph. More recently (*7*) a zirconium oxide gel dried in air at 110°C and heated *in vacuo* at 350°C has been described as transforming to the tetragonal phase.

Although the stabilization of the cubic phase of zirconium dioxide by the addition of various main group-, transition,- or lanthanide-metals has been considered in the past (*8*), the determination of the limits of solubility of iron and the effects on the structural properties of zirconium dioxide have received less attention. We therefore initiated a comprehensive investigation of zirconium oxides and iron–zirconium oxides to clarify some of the uncertainties concerning the nature of phases which can be formed by the calcination of precipitates. In particular it was our intention to examine the stabilization of the cubic form of zirconium dioxide by the incorporation of metal ions in the tetragonal zirconium(IV) oxide structure. However, after the submission of our manuscript a description of cubic zirconium dioxide containing 2.5 to 40 at.% Fe^{3+} prepared by codecomposition of iron(III) nitrate and zirconyl nitrate was reported (*9*). Although the most recent report (*9*) covered some of the territory examined by ourselves we have amended our original manuscript and we report here on our studies of zirconium dioxide formed by the calcination of precipitates. In particular we focus attention on the tetragonal modification of zirconium dioxide, which can be transformed to a cubic phase at low temperatures by the incorporation of iron, and on the stability of this phase. We also report on the iron-containing monoclinic modification of zirconium dioxide, since up to 20 mole% iron(III) oxide has been reported to be soluble in the monoclinic zirconium dioxide lattice (*10*) and more recent work (*11*) has described the coexistence of zirconium-substituted iron(III) oxide with iron-substituted zirconium hydrate gel when iron-rich coprecipitates are heated at 80°C. We also describe the results of some preliminary studies of the stability of tetragonal zirconium dioxide and its iron-doped analog in the electron beam of an electron microscope.

Experimental

Iron–zirconium oxides with compositions ranging between 0 and 95% iron (mole% of total metal content) were prepared by precipitation techniques. Aqueous ammonia (10%) was added dropwise to stirred aqueous solutions of iron(III) nitrate and zirconium(IV) nitrate containing the required concentrations of the metal ions until pH 7.0 ± 0.2 was attained. The resulting precipitates were removed by filtration, washed with water, dried in air at 120°C (24 hr), ground, and calcined in air at temperatures between 250 and 1000°C (24 hr).

X-ray powder diffraction data were recorded with a Philips PW 1050/70 diffractometer using Cu$K\alpha$ radiation. X-ray powder diffraction photographs were obtained with a Debye–Scherrer camera using the Straumanis method of film loading.

Electron diffraction and energy-dispersive X-ray analysis (EDX) was performed with a Philips EM400T transmission electron microscope operating at 100 kV interfaced to an EDAX 9100/60 X-ray analysis system.

^{57}Fe Mössbauer spectra were recorded at 298 K with a microprocessor-controlled Mössbauer spectrometer using a 25 mCi $^{57}Co/Rh$ source. The drive velocity was calibrated with a ^{57}Co/Rh source and a natural iron foil absorber. All the spectra were computer fitted and the ^{57}Fe Mössbauer chemical isomer shift data were calculated relative to metallic iron.

Results and Discussion

The phases identified by X-ray powder diffraction in the iron–zirconium–oxygen system as functions of iron content and the calcination temperature of the precipitates are summarized in Fig. 1. Although more detailed studies are required to define the phase boundaries with accuracy the results summarized in Fig. 1 do show that the incorporation of iron within the tetragonal zirconium dioxide structure gives rise to a cubic modification of zirconium(IV) oxide and that the temperature of the cubic to monoclinic martensitic phase transformation in the iron-containing zirconium dioxide prepared by precipitation methods is dependent on the iron content of the mixed oxide.

The initial precipitates may be envisaged

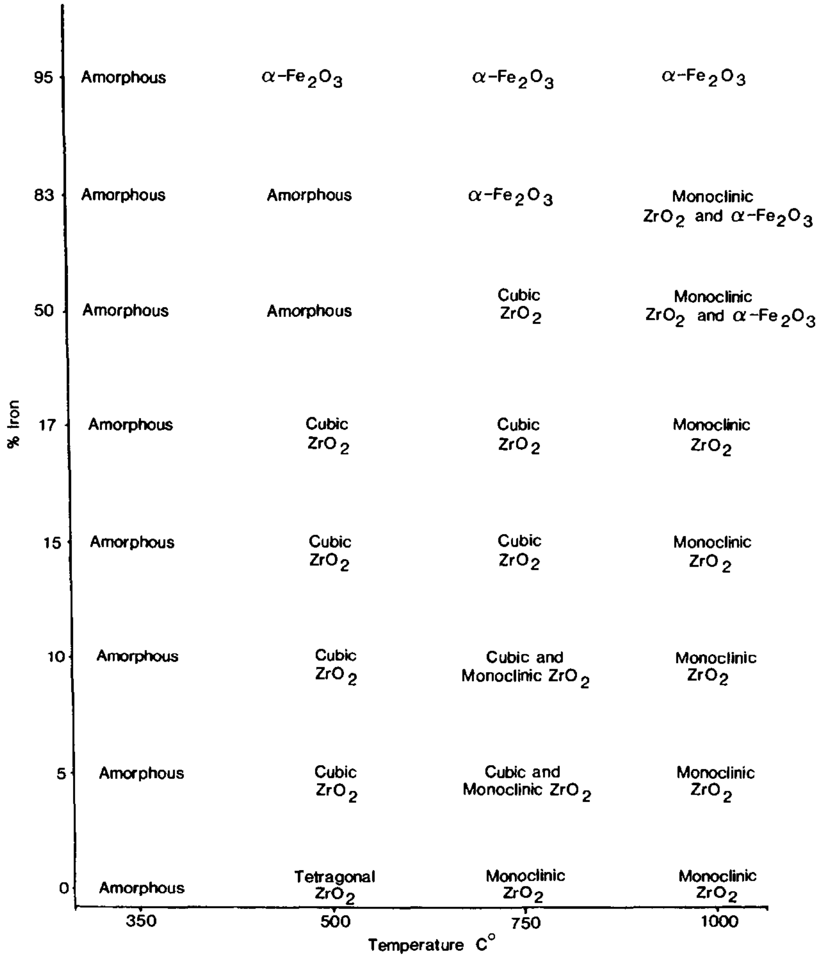

FIG. 1. Phases identified by X-ray powder diffraction in the iron–zirconium–oxygen system formed by the calcination of precipitates.

as homogeneous materials in which hydrated zirconium(IV) species are randomly but intimately mixed with hydrated iron species which were shown by ^{57}Fe Mössbauer spectroscopy to be present as Fe^{3+}. Calcination at 250°C induces the partial dehydration of the precipitates but, at such low temperatures, crystallization is not induced and the materials remain apparently amorphous when examined by X-radiation. At 500°C the pure zirconium-containing precipitate crystallizes as tetragonal zirconium(IV) oxide and the iron–zirconium-containing precipitates with iron concentrations $<$ ca. 17% crystallize with the cubic zirconium dioxide-type structure. Pure tetragonal zirconium dioxide was completely converted to the monoclinic polymorph by further heating at ca. 750°C. In contrast, cubic zirconium dioxides with nominal iron concentrations of 5 and 10% were only partially converted to the monoclinic modification at ca. 750°C and materials with iron concentrations between ca. 15 and 50% did not transform to the monoclinic polymorph until calcined at ca. 1000°C. Given that the X-ray powder diffraction data showed only evidence of thermally induced segregation of discrete iron(III) oxide phases in materials with iron contents exceeding ca. 50%, the results endorse those reported recently from similar materials but prepared by different methods (9) and indicate the amenability of the cubic zirconium dioxide structure to accommodate large concentrations of iron. Furthermore, the incorporated iron appears to stabilize the cubic phase relative to thermal conversion to the monoclinic polymorph. The ^{57}Fe Mössbauer spectra recorded from all monophasic cubic iron-containing zirconium dioxide samples were characterized by quadrupole split absorptions (Fig. 2) with parameters δ ca. 0.35 ± 0.01 mms^{-1}, Δ ca. 0.97 ± 0.04 mms^{-1} characteristic of high-spin Fe^{3+} ions.

The structural properties of the cubic zirconium dioxide-type phase which appears to be stabilized by the incorporation of Fe^{3+} were subjected to further examination. The iron-zirconium oxide formed by the calcination of a precipitate containing 15% iron at 500°C in air was shown by electron microscopy to be composed of irregularly shaped particles which gave microdiffraction patterns consistent with a centered cubic structure. The *a*-lattice parameter of 5.1

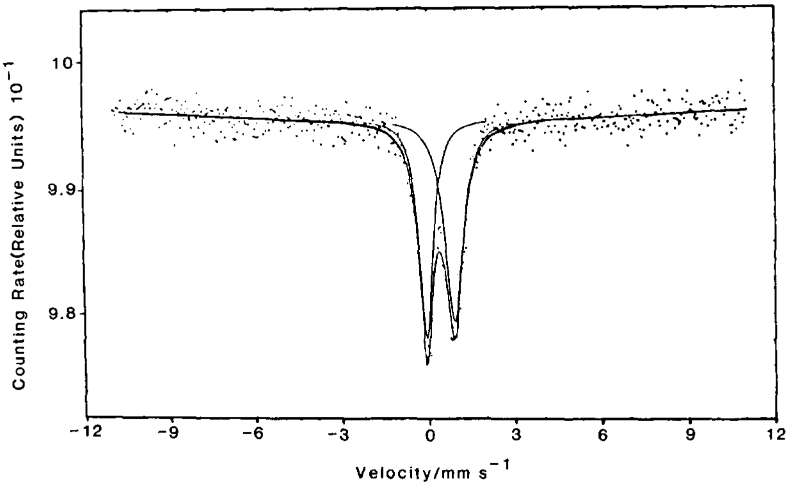

FIG. 2. Iron-57 Mössbauer spectrum recorded from an iron–zirconium oxide formed by the calcination of a precipitate containing 15% iron at 500°C (24 hr) in air.

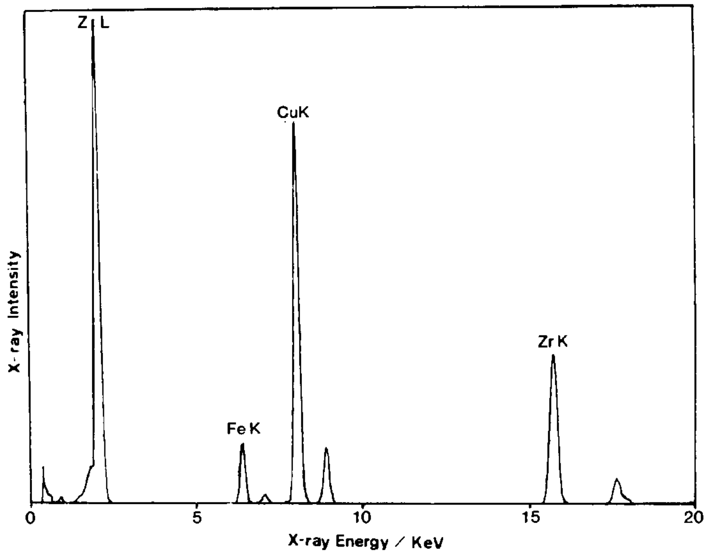

FIG. 3. Energy dispersive X-ray spectrum recorded from an iron–zirconium oxide formed by the calcination of a precipitate containing 15% iron at 500°C (24 hr) in air. (Note that the Cu*K* peak originates from the copper grid.)

Å was not dissimilar to the *a*-lattice parameter reported (*12*) for the face-centered tetragonal phase of zirconium dioxide. Indeed, it should be noted that the possibility of small departures from cubic symmetry cannot be excluded. Energy dispersive X-ray spectra (Fig. 3) recorded from a number of particles using electron probe sizes ranging between 20 and 2000 Å diameter gave consistent iron : zirconium ratios of ca. 15 : 85. Taken together the results suggest that, in materials calcined at 500°C at least, up to 15% and probably more of the Zr^{4+} ions could be substituted by Fe^{3+} in the zirconium dioxide structure. Such a process would result in charge imbalance in the system and, given that nonstoichiometry resulting from oxygen deficiency has been identified in zirconium dioxide (*13*), it is possible that charge neutrality could be maintained by the loss of one O^{2-} ion for every two Fe^{3+} ions substituted into the lattice. Indeed in other cation-stabilized zirconium dioxide phases (*14–16*) defects have been found to order over both short and long ranges and to manifest themselves by diffuse scattering and the appearance of forbidden spots in the selected area diffraction pattern. However, and in distinct contrast to other results (*14–16*), the iron–zirconium oxide containing 15% iron and formed at 500°C which was examined here gave selected area diffraction patterns which showed no evidence for short and/or long range order. Given the reluctance of Fe^{3+} to adopt eightfold oxygen coordination, as would be required if the Fe^{3+} species adopted substitutional sites in the cubic zirconium dioxide lattice, it seems more reasonable to envisage the iron–zirconium oxide containing 15% iron which was formed at 500°C as an interstitial solid solution of Fe^{3+} in cubic zirconium dioxide. Indeed, the ^{57}Fe Mössbauer parameters are similar to those of Fe^{3+} in distorted octahedral oxygen coordination. In this respect it is also interesting to note that the ^{57}Fe Mössbauer spectra recorded from other monophasic iron-containing cubic zirconium dioxide-type phases containing between 15 and 50% iron and heated at 750°C were identical within the margins of errors to those formed at 500°C. Given that pure tetragonal zirconium dioxide transformed to the monoclinic modifications at ca. 750°C, it seems that interstitial Fe^{3+} and oxygen vacancies may stabilize the cubic structure of zirconia at higher temperatures.

The calcination of the Fe^{3+}-stabilized cubic zirconium dioxide phases at 1000°C (24 hr) resulted in products which were shown by X-ray powder diffraction to have been converted to the monoclinic polymorph while the ^{57}Fe Mössbauer spectra (Fig. 4) showed the superposition of the residue of the doublet characteristic of Fe^{3+} on a sextet pattern with parameters δ 0.40 ± 0.01 mms^{-1}, H 531 ± 5 kG which are very similar to those of α-Fe_2O_3. The results suggest that the cubic to monoclinic phase transition is accompanied by a thermally induced partial segregation of the interstitial Fe^{3+} from the zirconium dioxide lattice and the nucleation of a discrete α-Fe_2O_3 phase which probably contains some zirconium. Indeed, energy dispersive X-ray analysis performed in the electron microscope of the iron–zirconium oxide formed by the calcination of a precipitate containing 15% iron at 1000°C showed some regions of the irregular-shaped particles to be iron-rich while others were abundant in zirconium. Microdiffraction patterns recorded in the electron microscope from the zirconium-rich regions were consistent with the presence of monoclinic zirconium dioxide. Analysis of the peak areas in the ^{57}Fe Mössbauer spectrum recorded from the iron–zirconium oxide prepared by calcination of the precipitate containing 15% iron at 1000°C showed that ca. 9% of the total content of the biphasic product remained in the monoclinic zirconium dioxide lattice. The tolerance of the monoclinic zirconium dioxide lattice for the incorporation of iron therefore seems to be less than the 20 mole% previously deduced on the basis of X-ray powder diffraction data (*10*).

It is pertinent to comment further on the stabilization by Fe^{3+} of the cubic modification of zirconium dioxide to conversion to the monoclinic form since, in some respects, it appears to resemble the incorporation of a variety of metallic oxides into zirconium dioxide at temperatures exceed-

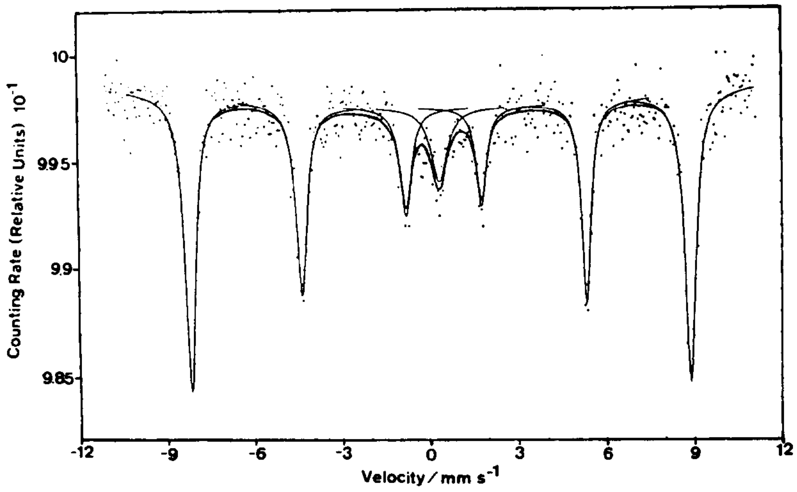

FIG. 4. Iron-57 Mössbauer spectrum recorded from an iron–zirconium oxide formed by the calcination of a precipitate containing 15% iron at 1000°C (24 hr) in air.

ing 1000°C which gives rise to a cubic modification of zirconia which is stable from room temperature to the melting point (*17*). Although the stability of this cubic phase to thermally induced phase transformations has been associated with the incorporated cations and oxygen vacancies, it is important to appreciate that the stabilized cubic zirconia phases (*17*) were prepared by prolonged treatment at elevated temperatures to give materials with ordered defect structures and which had attained thermodynamic equilibrium. In contrast, the stabilized cubic forms of zirconium dioxide examined during this work were treated at lower temperatures for shorter periods of time, gave no evidence in the electron diffraction patterns for ordered defect structures, and are unlikely to be systems which have attained thermodynamic equilibrium.

Finally, we would comment on the unusual behavior observed during examination in the electron microscope of the pure zirconium dioxide formed at 500°C which was shown by X-ray powder diffraction to be tetragonal. Following brief examination in the electron beam the electron diffraction pattern (Fig. 5) showed the presence of fluorite forbidden reflections and, when the specimen was tilted in the microscope to different crystallographic orientations, the resulting diffraction patterns could not be indexed consistently with the low-temperature tetragonal phase but were more appropriately associated with the monoclinic phase of zirconium dioxide. Attempts to monitor the tetragonal to monoclinic transformation in the electron beam were unsuccessful because the transformation occurred quickly compared with the time required to orient and tilt the specimen to defined zone axes.

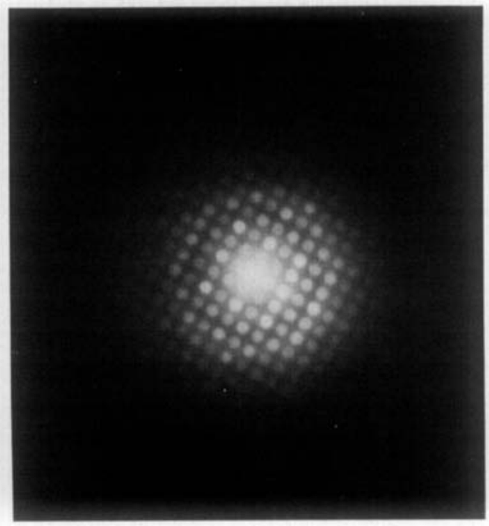

FIG. 5. Electron diffraction pattern (B = [001]) recorded from zirconium dioxide prepared at 500°C and shown by X-ray powder diffraction to be tetragonal.

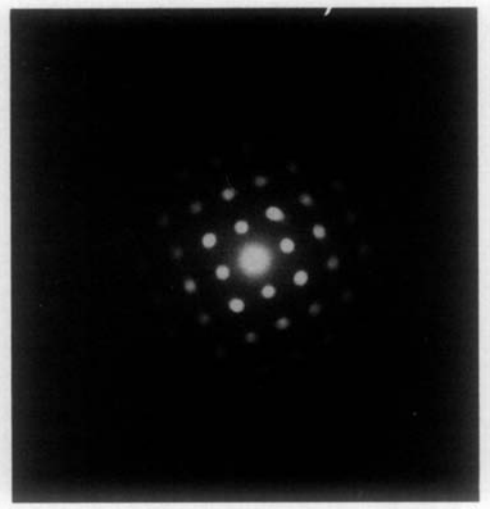

FIG. 6. Electron diffraction pattern (B = [001]) recorded from an iron–zirconium oxide formed by calcination of a precipitate containing 15% iron at 500°C and shown by X-ray powder diffraction to be cubic.

The iron–zirconium oxide formed by the calcination of a precipitate containing 15% iron at 500°C and shown by X-ray powder diffraction to be cubic remained unchanged by exposure to the electron beam and gave electron diffraction patterns characteristic of the cubic polymorph (Figs. 6 and 7).

Hence, the pure tetragonal zirconium dioxide appears to be converted to the mono-

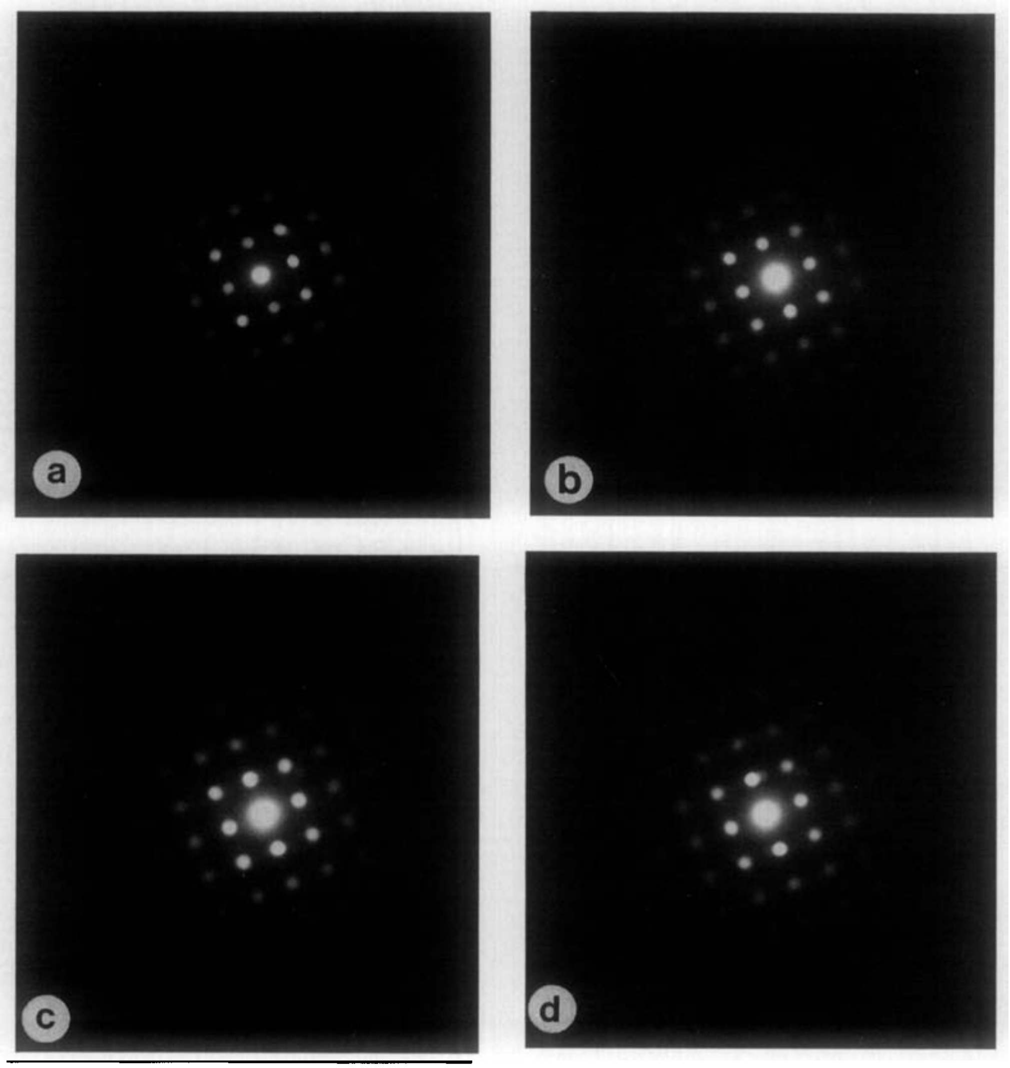

FIG. 7. A series of diffraction patterns ($B = [001]$) recorded from the iron–zirconium oxide shown in Fig. 6 following removal of the second condenser aperture and irradiation in the electron beam for (a) 1 min, (b) 2 min, (c) 3 min, and (d) 4 min.

clinic polymorph by exposure to the electron beam either as a result of heating effects or as a result of ionization damage. The resistance of the iron–zirconium oxides to the cubic-to-monoclinic transformation in the electron microscope may be related to the higher electrical conductivity resulting from an increase in oxide vacancies.

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