日本化学会 第105春季年会 (2025)

Optimization of synthesis conditions for metastable tetragonal zirconium dioxide

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Keywords: Zirconium dioxide; Structural phase transition; Zirconia

Introduction Zirconium dioxide (ZrO_2) is an interesting material due to its use in solid oxide fuel cells and other applications. ZrO_2 is a monoclinic phase at room temperature, but undergoes a phase transition to a tetragonal phase between 1170 °C and 2370 °C. In addition, to stabilize tetragonal ZrO_2 at room temperature, rare earth such as Y_2O_3 must be doped. Our research group reported that tetragonal ZrO_2 can be obtained at room temperature by sintering a precursor obtained by dropping an NH_3 aqueous solution into an aqueous $ZrCl_4$ solution, and cooling rapidly. In this study, we changed the stirring time and stirring temperature during precursor synthesis as parameters and researched the effect on the appearing fraction of tetragonal ZrO_2.

Synthesis 38.4 mL of 25% NH_3 aqueous solution was dropped to the $ZrCl_4$ aqueous solution, and the solution was stirred at 50 °C for a certain period (sample **1**: 20 hours, sample **2**: 22 hours, sample **3**: 24 hours, sample **4**: 26 hours, sample **5**: 28 hours). After that, the precipitate was washed with ethanol by centrifuging and dried at 60 °C for 24 hours to obtain the precursor. The precursor was sintered at 850 °C for 5 minutes and quenched to obtain a sample. The powder X-ray diffraction (XRD) measurements were performed to study the crystal structure of the samples.

Result and Discussion Rietveld analysis of the XRD patterns measured for samples **1**-**5** showed that all samples were composed of two phases, tetragonal and monoclinic. From Rietveld analysis, about the fraction of tetragonal phase, 52.40 % ($a = b = 3.595$ Å, $c = 5.184$ Å) for **1**, 51.95 %($a = b = 3.596$ Å, $c = 5.185$ Å) for **2**, 53.66 %($a = b = 3.596$ Å, $c = 5.185$ Å) for **3**, 54.11%($a = b = 3.596$ Å, $c = 5.185$ Å) for **4**, 54.12%($a = b = 3.596$ Å, $c = 5.185$ Å) for **5**. Also, about the crystallite size of tetragonal phase, 12.4 nm for **1**, 12.3 nm for **2**, 12.0 nm for **3**, 11.8 nm for **4**, 11.6 nm for **5**. These results suggested that the crystallite size of tetragonal ZrO_2 is smaller when the stirring time during precursor synthesis is increased. Also, when the stirring time during precursor synthesis is 24 hours or more, the fraction of tetragonal phase is increased. On the poster, we will also report the fraction of tetragonal phase dependence on changing of the stirring temperature.

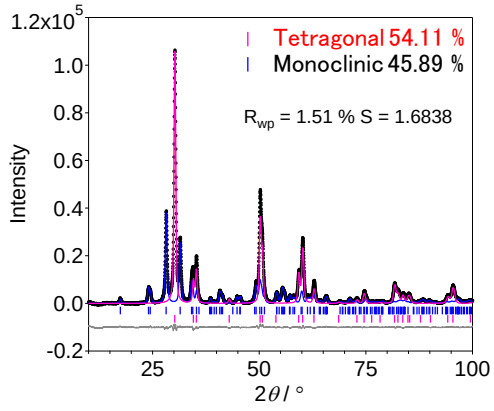

Fig 1. XRD pattern and Rietveld analysis of **4**.

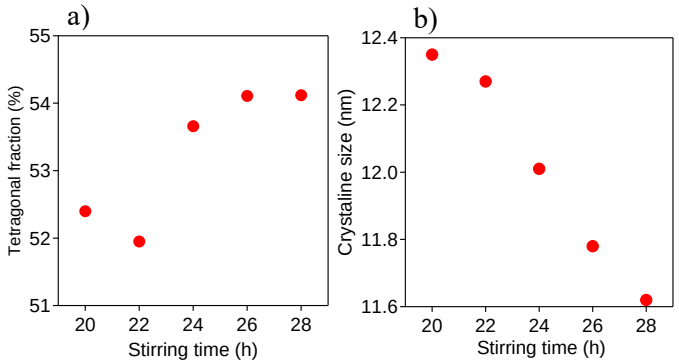

Fig 2. a) Fraction of tetragonal phase dependence on stirring time. b) Crystallite size of tetragonal phase dependence on stirring time.