SUBSTITUTION EFFECTS IN $ZR_2(WO_4)(PO_4)_2$ BY TI ON THE NEGATIVE THERMAL EXPANSION BEHAVIORS

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ABSTRACT: In-situ X-ray diffractometry and dilatometry were applied to evaluate substitution effects in $Zr_{2-x}Ti_x(WO_4)(PO_4)_2$ on negative thermal expansion behavior. The substitution induced a reduction of all the lattice parameter a, b and c and suppressed the coefficient of negative thermal expansion ($\alpha = -2.54\times10^{-6}$ K^{-1} for x=0 and $\alpha = -1.52\times10^{-6}$ K^{-1} for x=0.20). However, the coefficients obtained by the dilatometry were larger than those obtained by X-ray diffractometry, maybe due to preferred orientation of grains in the tested bar.

KEYWORDS: *Negative Thermal Expansion, Dilatometry, In-situ High-Temperature X-ray Diffractometry*

1.0 INTRODUCTION

Most materials show expansion upon heating but a few are known to contract, that is, exhibit a negative thermal expansion (abbreviated as NTE). $Zr(WO_4)_2$ is one of the materials which show NTE [1, 2]. $Zr(WO_4)_2$ is characterized by strong W-O bonds in the corner-shared tetrahedra. In the potential curve against the distance between atoms, the curve generally gets steeper in the shorter interatomic distance and gentler in the longer distance around the equilibrium position of the bond [3]. Because of this asymmetry of the potential curve, excursion to longer interatomic distances are easier than shorter distances and consequently the average interatomic distance increases with an increase of temperature. However, as bonds between atoms strengthen, the curve becomes symmetric and the vibration between the atoms becomes harmonic. That means there might be no detectable thermal expansion in the very strong W-O bond. Net negative thermal expansion appears when dynamical deformation consumes open spaces in the crystal lattice under the condition that the thermal expansion of rigid unit like WO_4 is suppressed. When a vibrational mode consuming a space in a lattice is thermally excited, which yields thermal contraction. That means structural allowance is needed for NTE.

$Zr(WO_4)_2$ has an average linear coefficient of negative thermal expansion of $\alpha_1 = - 9\times10^{-6}\ K^{-1}$ over the temperature range of T = 0–400 K [2, 4]. The linear thermal expansion coefficient can be defined as following equation; $\alpha l = \Delta_l/l0\Delta T$, using the change in length $\Delta 1$, the initial length l0 and the change in temperature ΔT, respectively. However, $Zr(WO_4)_2$ has been reported to possess two cubic phases, α-phase below 423K and β-phase above 423K, and therefore the thermal expansion behavior is sometimes complicated.

$Zr_2(WO_4)(PO_4)_2$ is a derivative of $Zr(WO_4)_2$ where 2/3 of WO_4 tetrahedra were substituted by PO_4 tetrahedra [5,6]. Difference in negative charges between divalent WO_4 and trivalent PO_4 is supposed to induce changes in crystal structure from cubic to orthorhombic. $Zr_2(WO_4)(PO_4)_2$ has been also reported that it exhibits NTE but no phase transition occurs between an operating temperature around 400°C and room temperature.

In this study, dopant-free and Ti-substituted $Zr_2(WO_4)(PO_4)_2$ were synthesized by using a conventional solid-state reaction technique. Ti is smaller than Zr in tetravalent ionic radius and is supposed to be effective in reducing the structural allowance in the lattice so that the negative thermal expansion coefficient may be reduced to converge to zero. Control of thermal expansion is a key technology for providing high performance to device and facilities in many fields of highly advanced modern industries. Trials for preparation of many composite materials with low or zero thermal expansion have been reported [5, 7], but there were few reports on controlling thermal expansion by cation substitution of an NTE material. Dilatometry and in-situ X-ray diffractometry were applied to confirm the substitution effects in $Zr_2(WO_4)(PO_4)_2$ by Ti on NTE behavior.

2.0 METHODOLOGY

ZrO_2, WO_3, $NH_4H_2PO_4$ and TiO_2 powders were used as starting materials. They were properly weighed so as to have a composition of x=0 (Ti-free), 0.05, 0.10 or 0.20 in $Zr_{2-x}Ti_x(WO_4)(PO_4)_2$ after firing. The powders were mixed in an aluminum crucible with an aluminum pestle for 45 minutes, heated at 900°C for 4 hours and then successively heated at 1250°C for 4 hours. The calcined powders were ground and well-mixed again for 15 minutes with the crucible and pestle, pressed into pellet and finally fired at 1350°C for 2 hours. For dilatometry, the fired pellets were filed into bar with a dimension of $5\times5\times10mm^3$.

In-situ high-temperature X-ray measurements were conducted for the powder samples of x=0 and 0.20, which were mounted in a diffractometer Rigaku SmartLab with a Pt-heater in an air. Ni-filtered CuKα radiation generated by applied voltage of 40kV and current of 200mA was used for an incident X-ray and the intensity was monitored by a one-dimensional silicon strip detector D/tex Ultra 250 [8]. X-ray intensity measurements were performed at temperatures of room temperature, 200°C, 300°C, 400°C and 500°C, respectively. The temperature was raised at a rate of 5K/min., and 1 minute's interval was imposed before starting the intensity measurement.

Thermal expansion of the sintered bars of x=0, 0.05 and 0.10 was measured using a thermal mechanical analyzer, MAC Science Dilatometer model TD5000s, with a heating rate of 2K/min over a temperature range of room temperature up to 500°C. The coefficient was calculated from the slope of the plot between the thermal expansion and the temperature.

3.0 RESULTS AND DISCUSSION

All the samples after the firing possessed a single phase $Zr_{2-x}Ti_x(WO_4)(PO_4)_2$. Figure 1 and Table 1 show variation of lattice parameters a, b and c in orthorhombic $Zr_{2-x}Ti_x(WO_4)(PO_4)_2$ as a function of x. At x=0, the lattice parameters were calculated to be a=9.362(3)Å, b=12.333(3) Å and c=9.181(2)Å which are in a good agreement with a=9.35451(9) Å, b=12.31831(9)Å and c=9.16711(8)Å [9] but all are a little larger than the reported ones. All the lattice parameters had a decreasing trend with an increasing substitution amount of Ti, which is due to the difference in ionic radius between Zr^{4+} and Ti^{4+}. As having mentioned in Introduction, contraction in cell volume of $Zr_{2-x}Ti_x(WO_4)(PO_4)_2$ may be able to lead to reduction of coefficient of thermal expansion by means of the Ti-substitution.

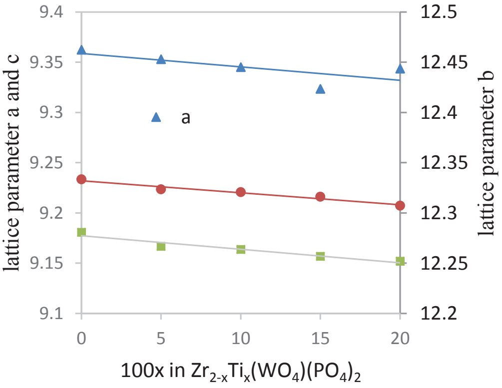

Figure 1: Variation of lattice parameters for $Zr_{2-x}Ti_x(WO_4)(PO_4)_2$ as a function of x.

Table 1: Lattice parameters a, b, c and volume V for Zr_2-x$Ti_x(WO_4)(PO_4)_2$ at room temperature as a function of x.

	x=0	x=0.05	x=0.10	x=0.15	x=0.20
a/Å	9.362(2)	9.353(2)	9.345(2)	9.323(10)	9.343(5)
b/Å	12.333(2)	12.323(2)	12.321(3)	12.316(12)	12.307(6)
c/Å	9.181(2)	9.167(2)	9.164(2)	9.157(10)	9.152(4)
V/Å^3	1060.1(4)	1056.5(3)	1055.1(4)	1051.4(19)	1052.4(8)

Figure 2 shows in-situ X-ray diffraction patterns of sample for x=0 in $Zr_{2-x}Ti_x(WO_4)(PO_4)_2$ at the given temperatures between 200°C and 500°C. Relative density of all the bars prepared by filing the sintered pellets was more than 90%. The strongest diffraction peak in the figure around 40° in 2θ was due to Pt sample holder. Above 200°C, neither phase transition nor decomposition was observed.

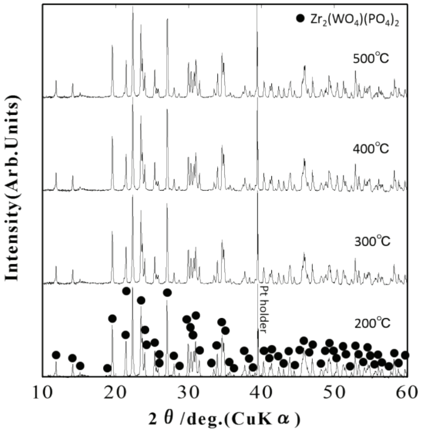

Figure 2: Variation of in-situ XRD patterns for $Zr_2(WO_4)(PO_4)_2$ (Ti-free) at the given temperatures.

Table 2: Lattice parameters a, b, c and volume V for $Zr_{2-x}Ti_x(WO_4)(PO_4)_2$ at the given temperatures as a function of x.

		200°C	300°C	400°C	500°C
x=0	a/Å	9.373(9)	9.367(9)	9.364(8)	9.360(8)
	b/Å	12.425(17)	12.429(17)	12.432(15)	12.433(15)
	c/Å	9.203(2)	9.198(9)	9.194(8)	9.189(8)
	V/Å^3	1071.8(20)	1070.9(20)	1070.3(18)	1069.4(18)
x=0.20	a/Å	9.322(3)	9.323(3)	9.305(3)	9.301(3)
	b/Å	12.313(6)	12.330(5)	12.335(5)	12.346(5)
	c/Å	9.142(3)	9.135(3)	9.132(3)	9.125(3)
	V/Å^3	1049.3(7)	1050.1(6)	1048.1(5)	1047.9(6)

The NTE behavior of $Zr_{2-x}Ti_x(WO_4)(PO_4)_2$ are listed in Table 2. An approximately linear decrease in the lattice parameters a, c and the cell volume and a moderate linear increase in the parameter b were seen in both the samples over the temperature range between 200°C and 500°C. The variation of cell volume as a function temperature clearly demonstrated that addition of Ti in place of Zr suppressed the NTE, resulting from the enhanced thermal expansion behavior in the parameter b. From the diffraction data we calculated an overall coefficient of thermal expansion (defined as $(V_{T2}^{1/3}-V_{T1}^{1/3})/V_{RT}^{1/3}(T_2-T_1)$ where T_2=500°C and T_1=200°C were applied) of $\alpha = -2.54\times10^{-6}\ K^{-1}$ for x=0 and $\alpha = -1.52\times10^{-6}\ K^{-1}$ for x=0.20, respectively. Over 473-673K, the coefficient of thermal expansion of $Zr_2(WO_4)(PO_4)_2$ was reported to $-2.4\times10^{-6}\ K^{-1}$ [5], which is in a good agreement with the result for x=0.

Figure 3 shows the result of dilatometry for the Ti-free sample. The length of bar for the measurement was 1.01cm. Heating and cooling behaviors were both measured, but no hysteresis was detected. The coefficients of thermal expansion of samples x=0, 0.05 and 0.10 in $Zr_{2-x}Ti_x(WO_4)(PO_4)_2$ were $\alpha = -10.6\times10^{-6}\ K^{-1}$, $-10.2\times10^{-6}\ K^{-1}$ and $-9.2\times10^{-6}\ K^{-1}$, respectively. The values were significantly larger than the reported ones. One possible reason for the larger negative coefficient would be preferred orientation of grains in the sample. $Zr_2\text{-}xTi_x(WO_4)(PO_4)_2$ belongs to the orthorhombic crystal system. The lattice parameter b is the largest in length and this material showed a normal, positive thermal expansion toward this direction. If the grains are so aligned that the b-axis is preferentially perpendicular to the measured direction of the tested sample, the sample would shrink more strongly than deduced from the overall coefficient of thermal expansion. We may have to consider such grain orientations when we think of NTE materials with such an anisotropic thermal expansion behavior obtained by dilatometry.

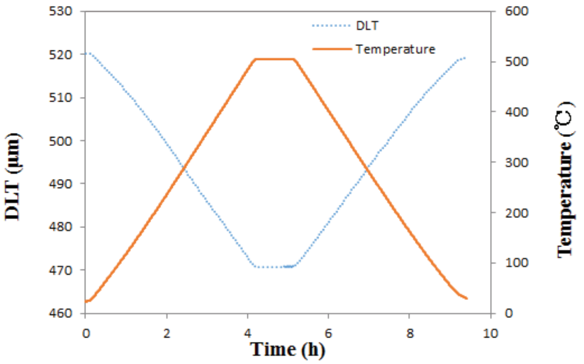

Figure 3: Diagram for dilatometry of $Zr_2(WO_4)(PO_4)_2$.

4.0 CONCLUSION

Effects in $Zr_2(WO_4)(PO_4)_2$ by Ti on NTE behavior were evaluated by means of In-situ X-ray diffractometry and dilatometry. The coefficient of thermal expansion obtained by the diffractometry was -2.54×10^{-6} K^{-1} for Ti-free sample, which agrees well with the reported value whereas that obtained by the dilatometry (-10.6×10^{-6} K^{-1}) seemed larger. This difference would be considered to be due to preferred orientation of grains in the tested bar.

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