## *X-ray characterization of $Sr_3Zr_2O_7$ hydrate**

The investigation of the phase equilibrium diagram $SrO-ZrO_2$ is of great interest on account of the refractory properties of these materials. Previous work on this binary system was reported by Cocco and Chiacigh [1], Noguchi, Okubo and Yonemochi [2], Traverse and Foex [3] and Tilloca and Perez Y Jorba [4]. Further research on the structural properties of binary compounds belonging to the $SrO-ZrO_2$ system was reported by the present authors [5–7], who, among other things, stated the existence of a high-temperature phase transition in the compound $Sr_3Zr_2O_7$ [6, 7]. Since this compound shows a strong tendency to hydrate [1, 6, 7], the present investigation was undertaken to shed light on its behaviour under water absorption conditions and to determine crystal data and the thermal stability of a new hydrated phase, $Sr_3Zr_2O_7 \cdot 2H_2O$.

Mixtures of reagent-grade purity $SrCO_3$ and $ZrO_2$ in a 3:2 molecular ratio were mixed in agate mortar, pressed into pellets and air-fired in an electric furnace at 1600° C for 12 hours. The sintered material was then subjected to X-ray diffraction and reflected-light microscopic analyses to check the attainment of equilibrium conditions (equilibrium was considered to have been attained when no change could be detected in single-phase samples).

The compound $Sr_3Zr_2O_7$ was then introduced into a 25° C thermostated room with 70% relative humidity, and its weight changes were checked at long time intervals. Gradual hydration of the compound was observed; equilibrium was practically reached after 40 days. Thermogravimetric analysis of hydrated specimens yielded a water content of two moles per mole of $Sr_3Zr_2O_7$. Hence, the stoichiometric formula of this new phase is assumed to be $Sr_3Zr_2O_7 \cdot 2H_2O$. The thermogravimetric analysis also revealed that the hydrated phase is stable up to 300 ± 20° C; its

TABLE I Crystal data for $Sr_3Zr_2O_7 \cdot 2H_2O$

| Parameter | Value |
|---|---|
| $a$ | 4.107 ± 0.002 Å |
| $b$ | 4.094 ± 0.003 Å |
| $c$ | 24.896 ± 0.020 Å |
| $V$ | 418.6 Å$^3$ |
| $MW$ | 593.33 |
| $Z$ | 2 |
| $\delta_{calc}$ | 4.70 g cm$^{-3}$ |
| $\delta_{obs}$ | 4.63 g cm$^{-3}$ |

TABLE II X-ray powder diffraction data of $Sr_3Zr_2O_7 \cdot 2H_2O$

| $hkl$ | $d_{obs}$ | $d_{calc}$ | $I^*_{obs}$ |
|---|---|---|---|
| 0 0 2 | 12.45 | 12.45 | m |
| 0 0 4 | 6.25 | 6.22 | w |
| 1 0 2 | 3.900 | 3.901 | mw |
| 1 0 4 | 3.431 | 3.428 | mw |
| 1 0 5 | 3.170 | 3.169 | vvw |
| 0 1 5 | | 3.162 | |
| 0 0 8 | 3.112 | 3.112 | w |
| 1 0 6 | 2.926 | 2.919 | vs |
| 0 1 6 | 2.912 | 2.914 | s |
| 1 1 0 | 2.901 | 2.900 | vvs |
| 1 1 2 | 2.830 | 2.824 | w |
| 0 0 9 | 2.757 | 2.766 | vvw |
| 1 1 5 | 2.500 | 2.506 | w |
| 0 0 10 | 2.481 | 2.490 | mw |
| 1 0 8 | | 2.480 | |
| 0 1 8 | | 2.478 | |
| 1 1 6 | 2.382 | 2.377 | mw |
| 0 1 10 | 2.123 | 2.127 | w |
| 1 1 8 | | 2.121 | |
| 0 0 12 | 2.079 | 2.075 | m |
| 2 0 0 | 2.054 | 2.054 | ms |
| 0 2 0 | 2.048 | 2.047 | m |
| 2 0 1 | | 2.046(7) | |
| 2 0 2 | 2.026 | 2.026 | w |
| 0 2 2 | | 2.020 | |
| 1 1 9 | 2.000 | 2.002 | vvw |
| 2 0 3 | 1.993 | 1.994 | vw |
| 0 2 3 | | 1.989 | |
| 0 2 5 | 1.888 | 1.893 | vw |
| 1 1 10 | | 1.889 | |
| 2 0 6 | 1.841 | 1.841 | vw |
| 2 1 2 | 1.815 | 1.816 | vw |
| 1 2 2 | | 1.813 | |
| 2 1 3 | 1.798 | 1.792 | w |
| 2 0 7 | 1.778 | 1.779 | vvw |
| 0 0 14 | | 1.778 | |
| 0 2 7 | | 1.774 | |
| 2 1 4 | 1.756 | 1.761 | w |
| 1 2 4 | | 1.758 | |
| 2 1 5 | 1.725 | 1.722 | m |
| 1 1 12 | 1.689 | 1.687 | ms |
| 2 1 6 | 1.680 | 1.679 | w |
| 1 2 6 | 1.678 | 1.676 | ms |
| 1 0 14 | 1.634 | 1.632 | vvw |
| 2 1 7 | | 1.631(2) | |
| 0 1 14 | | 1.631 | |

*Intensities: vvs = very very strong, vs = very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, vw = very weak, vvw = very very weak.

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*Work supported by the Consiglio Nazionale delle Ricerche, Roma, Italy.

decomposition starts at this temperature and is completed at 360 ± 20° C.

Powdered specimens of the hydrated phase were inspected by the X-ray powder diffraction technique. A Guinier–de Wolff camera and a Siemens horizontal goniometer, using CuK$\alpha$ radiation, permitted us to collect diffraction patterns in the $2\theta$ range 20° to 100°.

The X-ray diffraction pattern of $Sr_3Zr_2O_7 \cdot 2H_2O$ was indexed on the basis of an orthorhombic unit cell, with $a = 4.107$, $b = 4.094$, $c = 24.896$ Å at room temperature. The lattice parameters were least-squares refined [8] by choosing 21 reflections of the Guinier pattern, calibrated against $Pb(NO_3)_2$ as the internal standard. Crystal data of the phase are summarized in Table I; spacing values are reported in TableII.

In a previous paper [6] it was reported that the compound $Sr_3Zr_2O_7$ undergoes an $\alpha \leftrightarrow \beta$ phase transition at 680 ± 20° C. The $\alpha$-phase, stable at temperatures above 680° C, is tetragonal with lattice parameters $a = b = 4.113$, $c = 21.065$ Å. The $\beta$-phase, stable at room temperature, is orthorhombic with $a = 4.113$, $b = 4.102$, $c = 20.941$ Å. Both phases show $Sr_3Ti_2O_7$-type structures, [9] with double perovskite layers interleaved with SrO layers.

$Sr_3Zr_2O_7$ tends to hydrate, and the formula of the hydrated compounds was found to be $Sr_3Zr_2O_7 \cdot 2H_2O$. This hydrated compound exhibits a well-defined crystal habit and chemical composition; its structure is pseudo-tetragonal, with axis ratio $c/a$ of 6.07. The elongation of the model along the $c$-axis suggests the presence of water molecules near the SrO layers of the lattice, probably due to the open sizes existing in such positions. Contrary to the anhydrous phase, $Sr_3Zr_2O_7 \cdot 2H_2O$ is stable at room temperature and does not decompose after prolonged heating up to about 300° C.

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*Received 9 January*
*and accepted 17 February 1978*

DINO MINICHELLI
*ARCO SMALTI S.p.A.*
*Sassuolo (Modena),*
*Italy*
VITTORIO LONGO
*Istituto di Chimica Applicata e Industriale,*
*Università degli Studi,*
*Trieste,*
*Italy*