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Low-temperature phase formation in the ZrO_2–In_2O_3 system

Pavel P. Fedorov, Oksana V. Almyasheva, Alexander A. Alexandrov, Vera Yu. Proydakova, Natalia A. Korotkova, Vasilisa B. Baranovskaya and Victor V. Gusarov

Experimental

Zirconium oxychloride $ZrOCl_2 \cdot 8H_2O$, (Chemically pure, Technical certificate 6-09-3677-74), indium chloride $InCl_3 \cdot 3H_2O$ (Chemically pure, Technical certificate 6-09-4758-79), sodium nitrate $NaNO_3$ (Chemically pure, 'Chimmed Group'), sodium sulphate Na_2SO_4 (Chemically pure, 'Chimmed Group'), aqueous solution of ammonia NH_4OH, (Pure, Russian State Standart 3760-79, 'Chimmed Group') and double distilled water were used as the starting materials.

The prepared amorphous precipitates were kept in melts of sodium nitrate at 500 °C for 24 hours and sodium sulfate at 1000 °C for 80 hours. Heating was carried out at a rate of 10 °C/min. After cooling, the samples were washed with double distilled water. Glazed porcelain and platinum-rhodium crucibles were used, respectively.

X-ray powder diffraction was performed on a Bruker D8 Advance diffractometer (Germany) with CuK_α radiation in the angle range 2Θ = 10-80 with a signal set time of 0.4 s per point. Data processing was performed in TOPAS software. Thermoanalytical studies were carried out on a Netzsch STA 449 F3 Jupiter differential scanning calorimeter, in the temperature range of 20 °C to 1100 °C with heating rate 20 °C/ min. The sample weight was 20 mg, placed in a platinum - ruthenium crucible.

The particle size and morphology of the samples were studied by scanning electron microscopy (SEM) on a Carl Zeiss NVision 40 electron scanning microscope (Germany) with an Oxford Instruments XMAX microprobe analyzer (UK) (80 mm^2) for X-ray spectral microanalysis in high vacuum mode, at an accelerating voltage of 20 kV (cathode LaB_6). The images were generated using a backscattered electron detector (BSE) and a secondary electron detector (SE).

Chemical analysis of the samples aimed to the elemental composition determination was carried out by inductively coupled plasma atomic emission spectrometer (ICP-AES) iCAP XP.

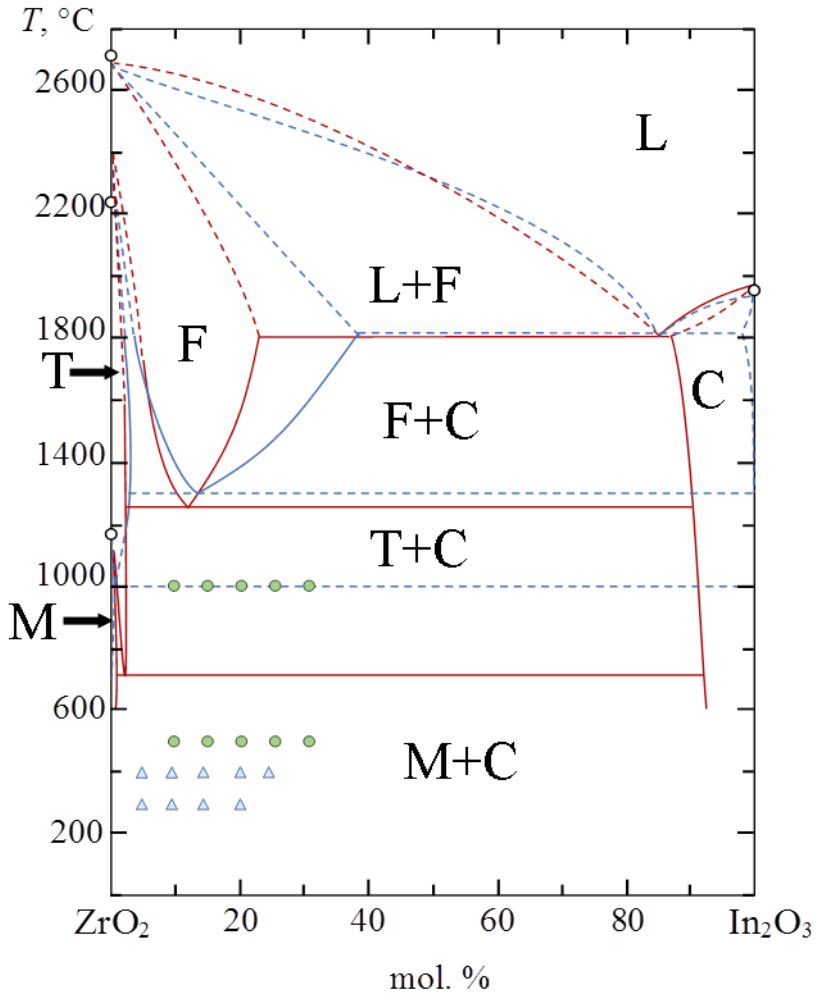
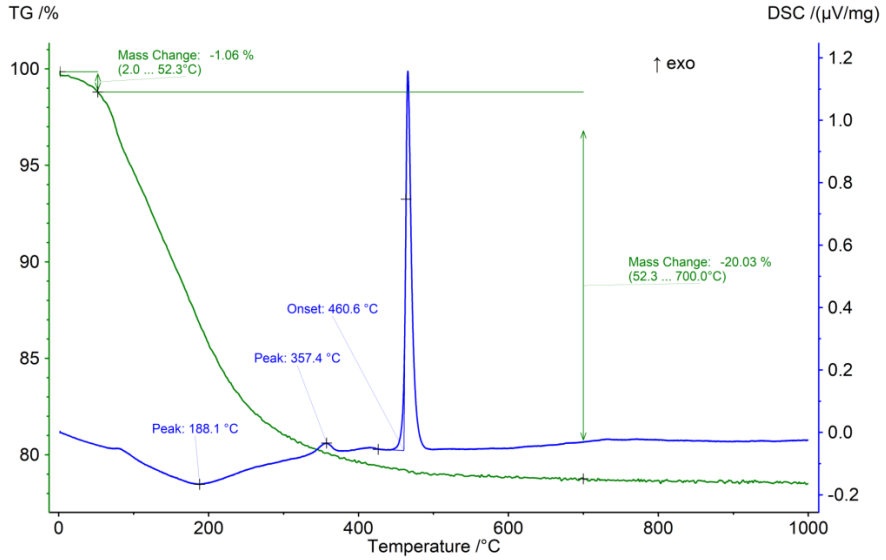


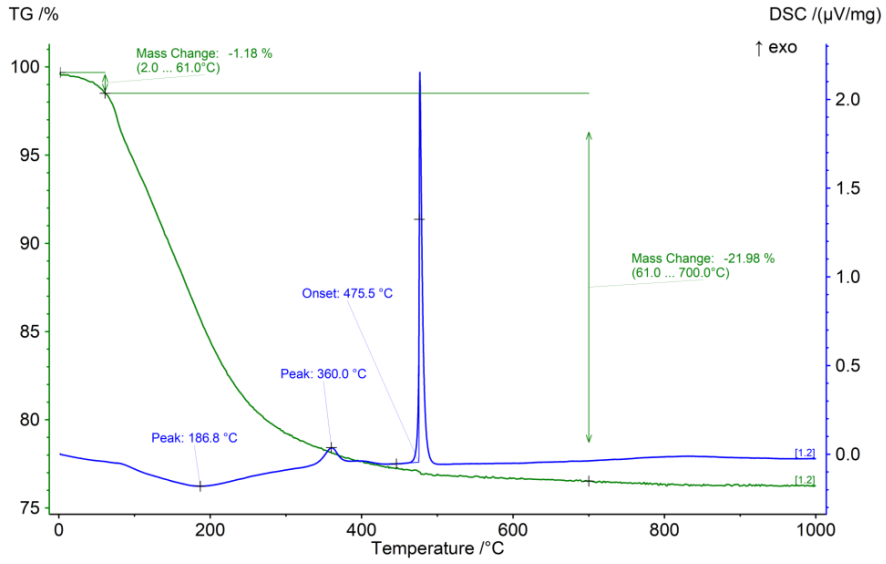
Figure S1 Phase diagrams of ZrO_2-In_2O_3

- Blue lines are the results of work[S1];
- Red lines – results of work[S2];
- White dots – phase transition temperatures from the IVTANTHERMO thermodynamic database
- Blue triangles – data from works[S3,S4]. Samples were prepared under hydrothermal treatment conditions at temperatures of 350 and 400 °C (pressure ~ 700 atm), the duration of isothermal exposure ranged from 0.25 to 3 hours. Nanocrystals based on a cubic solid solution are recorded $Zr_{1-x}In_xO_{2-0.5x}$. and monoclinic ZrO_2. For a sample with composition 25 mol% In_2O_3, nanocrystals based on a cubic solid solution of $Zr_{1-x}In_xO_{2-0.5x}$. and InOOH are observed;
- Green dots – designations related to the samples studied in this work:

1. The compositions were processed at a temperature of 1000 °C in a Na_2SO_4 melt with an isothermal exposure of 80 hours, resulting in the detection of cubic In_2O_3 and monoclinic ZrO_2;
2. The compositions were processed at a temperature of 500 °C in a $NaNO_3$ melt with an isothermal exposure for 24 hours, resulting in the formation of a cubic solid solution of $Zr_{1-x}In_xO_{2-0.5x}$.



a



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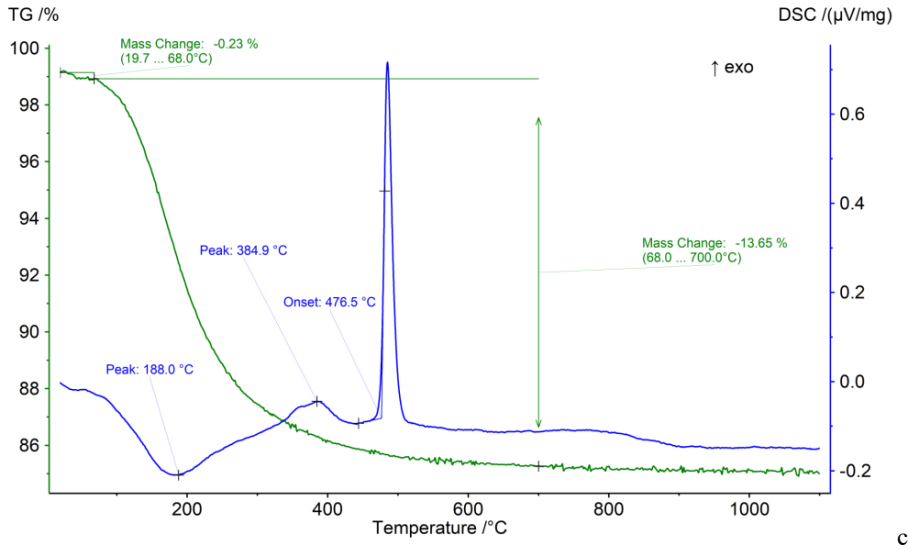

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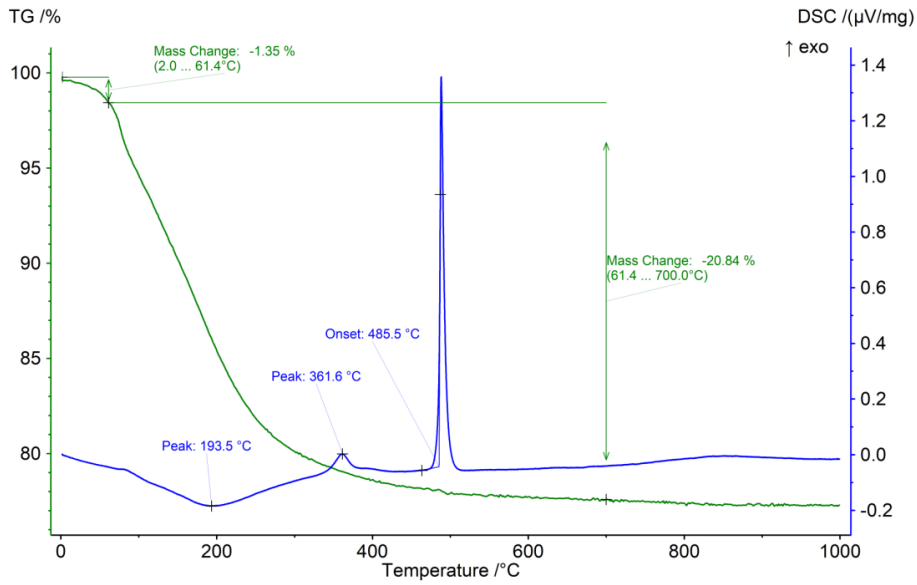

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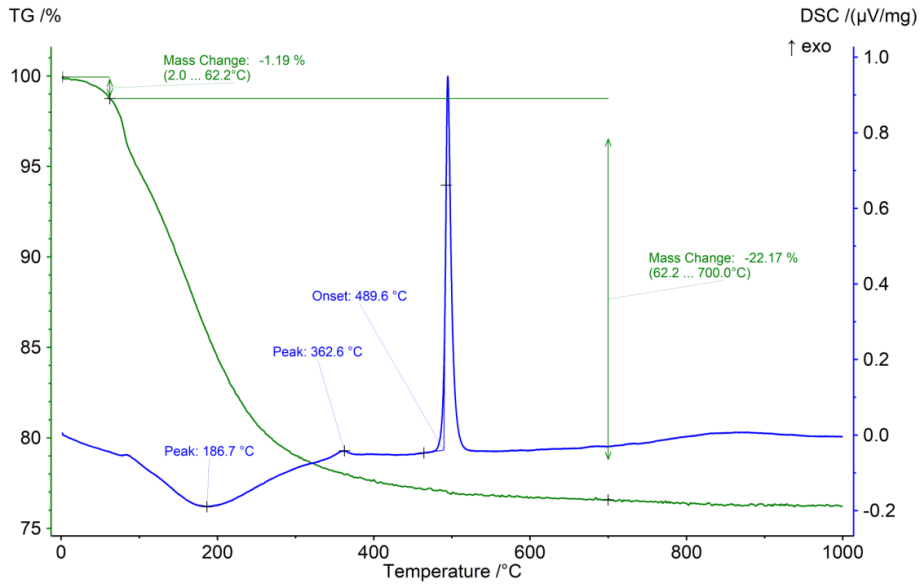

e

Figure S2 Thermograms of the precursors. Compositions of the samples: a - 90 mol% ZrO_2 - 10 mol % In_2O_3, b - 85 mol% ZrO_2 - 15 mol% In_2O_3, c - 80 mol% ZrO_2 - 20 mol % In_2O_3, d - 75 mol% ZrO_2 - 25 mol% In_2O_3, e - 70 mol% ZrO_2 - 30 mol% In_2O_3.

Results of elemental analysis

Table S1 ZrO_2-In_2O_3 (10 mol% In_2O_3), exposure in the melt with a tenfold molar excess of $NaNO_3$, T=500°C, t=24 h.

Element	Content, Content,	Element	Content, Content,	Element	Content, Content,	Element	Content, Content,	Element	Content, Content,
Li	0.001	Cr	<0.0002	Y	<0.0002	Ba	<0.0002	Lu	<0.0002
Be	<0.0002	Mn	<0.0003	Zr	53.80	La	<0.0002	Hf	1.07
B	0.002	Fe	0.012	Nb	<0.0004	Ce	<0.0002	Ta	<0.0005
Na	0.30	Co	<0.0002	Mo	<0.0003	Pr	<0.0002	W	<0.0002
Mg	<0.0003	Ni	<0.0002	Ru	<0.0004	Nd	<0.0002	Re	<0.0004
Al	0.35	Cu	0.001	Rh	<0.0002	Sm	<0.0002	Ir	<0.0002
Si	0.05	Zn	<0.0002	Pd	<0.0002	Eu	<0.0002	Pt	<0.0002
P	<0.0004	Ga	<0.0003	Ag	<0.0005	Gd	<0.0002	Au	<0.0002
S	<0.0002	Ge	<0.0004	Cd	<0.0003	Tb	<0.0002	Hg	<0.0005
K	0.002	As	<0.0006	In	15.80	Dy	<0.0002	Tl	<0.0002
Ca	<0.0002	Se	<0.001	Sn	<0.0002	Ho	<0.0002	Pb	<0.0002
Sc	<0.0002	Br	Не опр.	Sb	<0.0002	Er	<0.0002	Bi	<0.0003
Ti	<0.0002	Rb	<0.0005	Te	<0.001	Tm	<0.0002	Th	<0.001
V	<0.0002	Sr	<0.0002	Cs	–	Yb	<0.0002	U	<0.001

Table S2 ZrO_2-In_2O_3 (20 mol% In_2O_3), exposure in the melt with a tenfold molar excess of $NaNO_3$, T=500°C, t=96 h.

Element	Content, Content,	Element	Content, Content,	Element	Content, Content,	Element	Content, Content,	Element	Content, Content,
Li	0.0015	Cr	<0.0002	Y	<0.0002	Ba	<0.0002	Lu	<0.0002
Be	<0.0002	Mn	<0.0003	Zr	43.70	La	<0.0002	Hf	0.87
B	0.002	Fe	0.008	Nb	<0.0004	Ce	<0.0002	Ta	<0.0005
Na	0.22	Co	<0.0002	Mo	<0.0003	Pr	<0.0002	W	<0.0002
Mg	<0.0003	Ni	<0.0002	Ru	<0.0004	Nd	<0.0002	Re	<0.0004
Al	0.30	Cu	0.001	Rh	<0.0002	Sm	<0.0002	Ir	<0.0002
Si	0.18	Zn	<0.0002	Pd	<0.0002	Eu	<0.0002	Pt	<0.0002
P	<0.0004	Ga	<0.0003	Ag	<0.0005	Gd	<0.0002	Au	<0.0002
S	<0.0002	Ge	<0.0004	Cd	<0.0003	Tb	<0.0002	Hg	<0.0005
K	0.001	As	<0.0006	In	28.35	Dy	<0.0002	Tl	<0.0002
Ca	<0.0002	Se	<0.001	Sn	<0.0002	Ho	<0.0002	Pb	<0.0002
Sc	<0.0002	Br	Не опр.	Sb	<0.0002	Er	<0.0002	Bi	<0.0003
Ti	<0.0002	Rb	<0.0005	Te	<0.001	Tm	<0.0002	Th	<0.001
V	<0.0002	Sr	<0.0002	Cs	–	Yb	<0.0002	U	<0.001

Table S3 ZrO_2-In_2O_3 (30 mol% In_2O_3), exposure in the melt with a tenfold molar excess of $NaNO_3$, T=500°C, t=24 h.

Element	Content, Content,	Element	Content, Content,	Element	Content, Content,	Element	Content, Content,	Element	Content, Content,
Li	0.002	Cr	<0.0002	Y	<0.0002	Ba	<0.0002	Lu	<0.0002
Be	<0.0002	Mn	<0.0003	Zr	36.52	La	<0.0002	Hf	0.74
B	0.003	Fe	0.006	Nb	<0.0004	Ce	<0.0002	Ta	<0.0005
Na	0.13	Co	<0.0002	Mo	<0.0003	Pr	<0.0002	W	<0.0002
Mg	<0.0003	Ni	<0.0002	Ru	<0.0004	Nd	<0.0002	Re	<0.0004
Al	0.25	Cu	0.001	Rh	<0.0002	Sm	<0.0002	Ir	<0.0002

Si	0.04	Zn	<0.0002	Pd	<0.0002	Eu	<0.0002	Pt	<0.0002
P	<0.0004	Ga	<0.0003	Ag	<0.0005	Gd	<0.0002	Au	<0.0002
S	<0.0002	Ge	<0.0004	Cd	<0.0003	Tb	<0.0002	Hg	<0.0005
K	0.001	As	<0.0006	In	37.08	Dy	<0.0002	Tl	<0.0002
Ca	<0.0002	Se	<0.001	Sn	<0.0002	Ho	<0.0002	Pb	<0.0002
Sc	<0.0002	Br	Не опр.	Sb	<0.0002	Er	<0.0002	Bi	<0.0003
Ti	<0.0002	Rb	<0.0005	Te	<0.001	Tm	<0.0002	Th	<0.001
V	<0.0002	Sr	<0.0002	Cs	–	Yb	<0.0002	U	<0.001

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