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Low-temperature phase formation in the ZrO_2–In_2O_3 system

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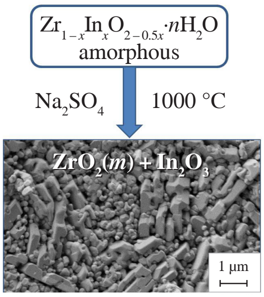
This study provides insights into the phase transformations of In_2O_3–ZrO_2 system under varying thermal and chemical conditions and the crystallization behavior of amorphous precursors containing 10–30 mol% In_2O_3, synthesized *via* the coprecipitation of oxides from chloride solutions. When subjected to molten sodium nitrate at 500 °C, a cubic solid solution of $Zr_{1-x}In_xO_{2-0.5x}$ is obtained. Conversely, exposure to molten sodium sulfate at 1000 °C results in the formation of the mixture consisting of In_2O_3 and monoclinic ZrO_2, with no evidence of intermediate phases including any ordered fluorite-like structures.



Keywords: zirconia, zirconium dioxide, indium oxide, phase diagram, solid solution, fluorite, molten salt, coprecipitation.

Zirconia-based materials are of considerable interest as ceramics, thermal barrier coatings, jewelry materials, media for storage of radioactive waste and solid electrolytes.[1–9] Among the materials for electrochemical devices, a solid solution of scandium oxide in a high-temperature cubic modification of ZrO_2 attracts special attention, inasmuch as it is characterized by the highest oxygen conductivity.[10–12] The problem is the ordering of this solid solution with the formation of fluorite-like phases, which results in the decrease in ionic conductivity and degradation of the solid electrolyte.[13–22]

The low-temperature ordering of cubic solid solutions in ZrO_2–M_2O_3 (M is the rare-earth element) systems has not been sufficiently studied owing to the very low values of the cation diffusivity. As it was emphasized by Thornber *et al.*,[23] the actual structure and compositions of the ordered phases are unknown, because the cationic lattice in the studied samples shows no signs of ordering. Whereas the anionic sublattice is ordered, the cationic one is not, owing to the extremely slow cationic diffusion. Notably, in the Ce_2O_3–CeO_2 system, where the ordering is determined only by anionic diffusion, a whole homological series of ordered phases has been revealed.[24] Presumably, the similar phenomena might be observed in ZrO_2–M_2O_3 systems.

The ZrO_2–In_2O_3 system sparks the interest in terms of finding ordered phases, inasmuch as indium oxide is a crystallochemical low-melting analogue of scandium oxide. The materials formed in this system are of particular interest, including as ion-electronic conductors.[25,26]

Phase diagram of the ZrO_2–In_2O_3 system was studied by Morozova *et al.*[25,26] and Sasaki *et al.*[27] The overall picture of the phase equilibria is presented in Online Supplementary Materials, Figure S1. Solid solutions based on the components are formed in the system. It should be noted that in these works, the temperatures of phase in the high temperature region transformations do not differ much, and for individual compounds they are close to the IVTANTHERMO DB data,[28] although there are significant differences in the data[25–27] when determining the boundaries of solid solutions of coexisting F and C phases. The solid solution based on a cubic modification of ZrO_2 (F-phase) decomposes *via* eutectoid reaction at ~1250 °C. However, in the low-temperature region Sasaki *et al.*[27] have estimated the temperature of the eutectoid decomposition of the tetragonal T-phase to be about 300 °C higher than that determined by Morozova *et al.*[25,26]

Attempts to learn more about the phase states in the low-temperature region of this system were made[29,30] by studying the phase states in the system after hydrothermal treatment of coprecipitated hydroxides at 350 and 400 °C. The results did not allow us to obtain reliable data on the nature of the equilibrium state of phases in the low-temperature region. Thus, the formation of intermediate phases in this system was not detected.[25–27,29,30]

The purpose of this work has been to study the low-temperature phase formation in this system using salt fluxes, which help to accelerate the achievement of equilibrium.[31–33] Amorphous precursors of the samples were synthesized *via* co-precipitation from aqueous chloride solutions of zirconium and indium using an aqueous solution of ammonia.[29,30]

Heating of precursors resulted in their dehydration and crystallization (exoeffect on thermograms at 450–500 °C (Figure S2), with the formation of a cubic solid solution of $Zr_{1-x}In_xO_{2-0.5x}$ (see Figure S1, phase F).

After heat treatment in a sodium nitrate melt, the formation of a cubic solid solution of a fluorite structure was observed for samples with a content of 10–30 mol% In_2O_3. The powder was obtained after rinsing the samples with double-distilled water to remove

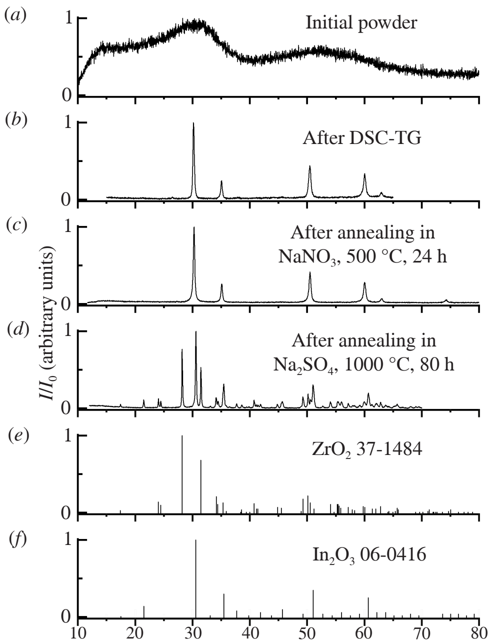


Figure 1 X-ray patterns of samples of composition 80 mol% ZrO_2–20 mol% In_2O_3: (*a*) initial after precipitation, (*b*) after differential scanning calorimetry (DSC) and thermogravimetry (TG), (*c*) exposure in $NaNO_3$ melt, (*d*) exposure in Na_2SO_4 melt. Reference X-ray patterns of (*e*) monoclinic ZrO_2 and (*f*) cubic In_2O_3.

sodium nitrate. The changes in the lattice parameters depending on the solid solution concentration are very small (Figure 2).

The results of the chemical analysis are presented in Tables S1–S3, Online Supplementary Materials. The main impurities in the samples are Hf (0.74–1.07 mass%), Na (0.13–0.30 mass%), Al (0.25–0.35 mass%) and Si (0.04–0.18 mass%).

A completely different picture was observed after the heat treatment of precursors in the molten sodium sulfate. A mixture of two phases was detected by the X-ray diffraction: cubic indium oxide and monoclinic modification of ZrO_2 (Figure 1). The formation of these two phases was confirmed by scanning electron microscopy (Figure 3).

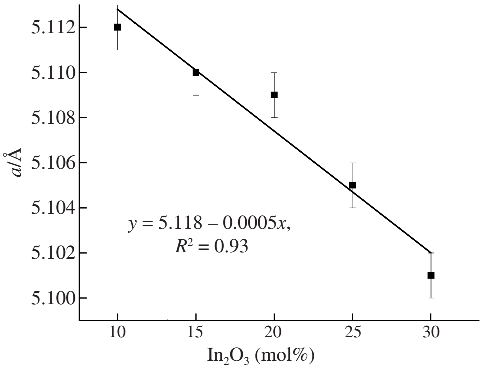


Figure 2 The dependence of the crystal lattice parameters on the composition of a solid solution of $Zr_{1-x}In_xO_{2-0.5x}$ type fluorite obtained by heat treatment of an amorphous precursor in molten sodium nitrate.

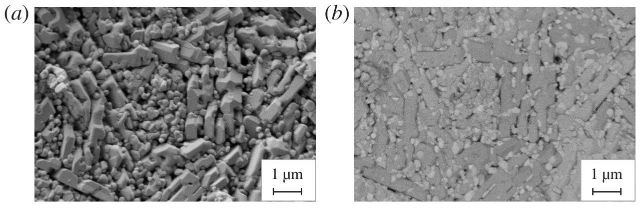


Figure 3 Micrographs of the sample of composition 80 mol% ZrO_2–20 mol% In_2O_3 after exposure to sulfate flux: (*a*) the topographic contrast and (*b*) the phase contrast.

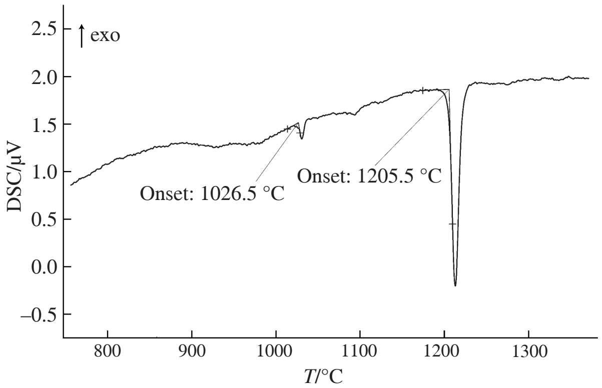


Figure 4 Thermogram of the sample of composition 80 mol% ZrO_2–20 mol% In_2O_3 after exposure in a sulfate flux.

The thermogram of this sample is shown in Figure 4. The presented thermal effects can be interpreted in accordance with the phase diagram of the ZrO_2–In_2O_3 system in Figure S1: the temperature of 1205 °C at which the effect is observed is close to the data[25–27] showing the formation of a cubic solid solution $Zr_{1-x}In_xO_{2-0.5x}$ and the effect at 1027 °C apparently corresponds to the transformation of the monoclinic modification of ZrO_2 into a tetragonal one, that also correlates with earlier data.[27]

Thus, our results qualitatively confirmed the nature of the phase diagram of the ZrO_2–In_2O_3 system constructed earlier.[25–27] At the same time, the data obtained at 1000 °C are close to the previously reported interpretation.[27] Accordingly, at this temperature, phase equilibrium M + In_2O_3 occurs. In the low-temperature region of the ZrO_2–In_2O_3 phase diagram at 500 °C, our results are close to the previously reported data.[29,30] Apparently, the use of salts with low-melting point or hydrothermal fluids as reaction media in the low-temperature region results in the formation of metastable phases with similar structures in this system (see Figure S1).

Noteworthy, ordered fluorite-like phases similar to those formed in the ZrO_2–Sc_2O_3 system were not detected. Though, the heat treatment of amorphous precursors in a sodium nitrate melt makes it possible to obtain a solid solution of the fluorite structure in the concentration range of 10–30 mol% In_2O_3. This solid solution is in a metastable state, but it can apparently serve as a basis for obtaining the functional materials.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7642.

References

1 A. K. Chitoria, A. Mir and M. A. Shah, *Ceramics Int.*, 2023, **49**, 32343; https://doi.org/10.1016/j.ceramint.2023.06.296.

2 P. P. Fedorov and E. G. Yarotskaya, *Condens. Matter Interphases*, 2021, **23**, 169; https://doi.org/10.17308/kcmf.2021.23/3427.

3 J. R. Kelly and I. Denry, *Dent. Mater.*, 2008, **24**, 289; https://doi.org/10.1016/j.dental.2007.05.005.

4 V. V. Osiko, M. A. Borik and E. E. Lomonova, in *Springer Handbook of Crystal Growth*, eds. G. Dhanaraj, K. Byrappa, V. Prasad and M. Dudley, Springer, Berlin, Heidelberg, 2010, pp. 433–477; https://link.springer.com/chapter/10.1007/978-3-540-74761-1_14.

5 J. F. Fergus, *J. Power Sources*, 2006, **162**, 30; https://doi.org/10.1016/j.jpowsour.2006.06.062.

6 N. Mahato, A. Banerjee, A. Gupta, S. Omar and K. Balani, *Prog. Mater. Sci.*, 2015, **72**, 141; https://doi.org/10.1016/j.pmatsci.2015.01.001.

7 E. R. Andrievskaya, *J. Eur. Ceram. Soc.*, 2008, **28**, 2363; https://doi.org/10.1016/j.jeurceramsoc.2008.01.009.

8 C. Pascual and P. Durán, *J. Am. Ceram. Soc.*, 1983, **66**, 23; https://doi.org/10.1111/j.1151-2916.1983.tb09961.x.

9 V. S. Stubican, G. S. Corman, J. R. Hellmann and G. Senft, in *Advances in Ceramics*, eds. N. Claussen, M. Ruehle and A. H. Heuer, American Ceramic Society, Columbus, OH, 1984, vol. 12, pp. 96–106; https://pure.psu.edu/en/publications/phase-relationships-in-some-zro2-systems.

10 F. M. Spiridonov, L. N. Popova and R. Ya. Popil'skii, *J. Solid State Chem.*, 1970, **2**, 430; https://doi.org/10.1016/0022-4596(70)90102-7.

11 T. Sekiya, T. Yamada, H. Hayashi and T. Noguchi, *J. Chem. Soc. Jpn.*, 1974, **9**, 1629; https://doi.org/10.1246/nikkashi.1974.1629.

12 R. Ruh, H. J. Garrrett, R. F. Domagala and V. A. Patel, *J. Am. Ceram. Soc.*, 1977, **60**, 399; https://doi.org/10.1111/j.1151-2916.1977.tb15521.x.

13 A. V. Zyrin, V. P. Red'ko, L. M. Lopato, A. V. Shevchenko, I. M. Maister and Z. A. Zaitseva, *Izv. Akad. Nauk SSSR. Neorg. Mater.*, 1987, **23**, 1325 (in Russian); https://elibrary.ru/contents.asp?titleid=26220.

14 T.-S. Sheu, J. Xu and T.-Y. Tien, *J. Am. Ceram. Soc.*, 1993, **76**, 2027; https://doi.org/10.1111/j.1151-2916.1993.tb08328.x.

15 H. Fujimori, M. Yashima, M. Kakihana and M. Yoshimura, *J. Am. Ceram. Soc.*, 1998, **81**, 2885; https://doi.org/10.1111/j.1151-2916.1998.tb02710.x.

16 H. Fujimori, M. Yashima, M. Kakihana and M. Yoshimura, *J. Appl. Phys.*, 2002, **91**, 6493; https://doi.org/10.1063/1.1471576.

17 H. J. Rossell, *J. Solid State Chem.*, 1976, **19**, 103; https://doi.org/10.1016/0022-4596(76)90156-0.

18 K. Wurst, E. Schweda, D. J. M. Bevan, J. Mohyla, K. S. Wallwork and M. Hofmann, *Solid State Sci.*, 2003, **5**, 1491; https://doi.org/10.1016/j.solidstatesciences.2003.09.008.

19 S. Meyer, E. Schweda, N. J. M. Meta, H. Boysen, M. Hoelzel and T. Bredow, *Z. Kristallog.*, 2009, **224**, 539; https://doi.org/10.1524/zkri.2009.1218.

20 M. A. Borik, S. I. Bredikhin, A. V. Kulebyakin, I. E. Kuritsyna, E. E. Lomonova, F. O. Milovich, V. A. Myzina, V. V. Osiko, V. A. Panov, P. A. Ryabochkina, S. V. Seryakov and N. Yu. Tabachkova, *J. Cryst. Growth*, 2016, **443**, 54; https://doi.org/10.1016/j.jcrysgro.2016.03.004.

21 P. P. Fedorov and E. V. Chernova, *Condens. Matter Interphases,* 2023, **25**, 257; https://doi.org/10.17308/kcmf.2023.25/11106.

22 O. I. Gyrdasova, R. F. Samigullina, E. V. Vladimirova, I. S. Medyankina, L. Yu. Buldakova, M. Yu. Yanchenko and L. A. Pasechnik, *Mendeleev Commun.*, 2024, **34**, 640; https://doi.org/10.1016/j.mencom.2024.09.005.

23 M. R. Thornber, D. J. M. Bevan and E. Summerville, *J. Solid State Chem.*, 1970, **1**, 545; https://doi.org/10.1016/0022-4596(70)90140-4.

24 M. Zinkevich, D. Djurovic and F. Aldinger, *Solid State Ionics*, 2006, **177**, 989; https://doi.org/10.1016/j.ssi.2006.02.044.

25 L. V. Morozova, P. A. Tikhonov and V. B. Glushkova, *Dokl. Akad. Nauk SSSR*, 1983, **273**, 140 (in Russian); https://elibrary.ru/title_about_new.asp?id=7781.

26 L. V. Morozova, P. A. Tikhonov, A. V. Komarov, V. P. Popov, V. B. Glushkova and Yu. P. Zarichnyak, *Zh. Fiz. Khim.*, 1986, **60**, 1430 (in Russian); https://elibrary.ru/item.asp?id=21779464.

27 K. Sasaki, P. Bohac and L. J. Gauckler, *J. Am. Ceram. Soc.*, 1993, **76**, 689; https://doi.org/10.1111/j.1151-2916.1993.tb03661.x.

28 G. V. Belov, V. S. Iorish and V. S. Yungman, *High Temp.*, 2000, **38**, 191; https://doi.org/10.1007/BF02755944.

29 O. V. Artamonova, O. V. Almjasheva, V. V. Gusarov and I. Ya. Mittova, *Inorg. Mater.*, 2006, **42**, 1072; https://doi.org/10.1134/S0020168506100049.

30 O. V. Artamonova, O. V. Almjasheva, I. Ya. Mittova and V. V. Gusarov, *Perspektivnye Materialy*, 2009, **1**, 91 (in Russian); https://elibrary.ru/download/elibrary_11779849_45210854.pdf.

31 P. P. Fedorov, *J. Phase Equilib. Diffus.*, 2024, **45**, 475; https://doi.org/10.1007/s11669-024-01099-7.

32 P. Fedorov, M. Mayakova, A. Alexandrov, V. Voronov, S. Kuznetsov, A. Baranchikov and V. Ivanov, *Inorganics*, 2018, **6**, 38; https://doi.org/10.3390/inorganics6020038.

33 P. P. Fedorov and A. A. Alexandrov, *J. Fluorine Chem.*, 2019, **227**, 109374; https://doi.org/10.1016/j.jfluchem.2019.109374.

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