
THERMAL
PROPERTIES

Thermal Conductivity of Cubic ZrO₂ Single Crystals Stabilized with Yttrium Oxide

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Abstract—The temperature dependence of the thermal conductivity of cubic ZrO₂ single crystals stabilized with yttrium oxide from 8 to 40 mol % has been studied in the temperature range 50–300 K. The dependence is analyzed taking into account the phase compositions, the features of the local structures and the electro-physical characteristics of these single crystals.

Keywords: zirconium dioxide, thermal conductivity, defect ordering

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1. INTRODUCTION

For technical application of zirconia-based materials, information on their thermophysical properties, in particular, thermal conductivity, the available data on which are limited, is very important. The values of the thermal conductivity of these materials are widely varied in the dependence on the type and the concentration of stabilizing oxides and additionally introduced doping additives. Moreover, the material characteristics are also dependent on the method and conditions of their preparation. First, this is true for ceramic materials, in which the grain size, their boundary extent, the distribution of solid solution components between the grains and the boundaries, etc., are changed in the dependence on the synthesis method. According to this, studies of single-crystal zirconia-based solid solutions enables one to obtain more unambiguous information on the dependence of the thermal–physical characteristics on the structural features of the crystal lattice.

In [1], we studied the thermal conductivity of single-crystal ZrO₂–Y₂O₃ solid solutions with a tetragonal structure, in which the yttrium oxide concentration was varied from 0.5 to 8 mol % in the temperature range 50–300 K. The values of the thermal conductivity of the single-crystal solid solutions have been shown to be widely changed in the dependence on the

content of the stabilizing yttrium oxide impurity, and they are significantly higher than the corresponding values for ceramic analogs [2–6].

There are some works in which the thermal conductivity of single-crystal ZrO₂–Y₂O₃ samples with high content of the stabilizing Y₂O₃ impurity was studied. However, the results of these studies were contradictory with respect to the observed character of the concentration dependence of the thermal conductivity. According to [7], the transition from 8 mol % Y₂O₃ to 17.6 mol % Y₂O₃ is accompanied by the decrease in the thermal conductivity by 1/10 at $T = 300$ K, and temperature dependences $k(T)$ demonstrate inversion near $T \sim 90$ K. In [8], a monotonic decrease in the high-temperature thermal conductivity as the Y₂O₃ content increased from 4 to 20 mol % was revealed theoretically using the molecular-dynamic simulation. In [9], there is a reference to a private report by Hasselman et al. that the thermal diffusivity of ZrO₂–Y₂O₃ crystals related to the thermal conductivity increases as the Y₂O₃ concentration increases from 16 to 37 wt % (from 9.4 to 24.2 mol %).

It is noted in the above works and also in [10, 11] that, at temperatures higher than room temperature, the temperature dependence of the thermal conductivity $k(T)$ of concentrated ZrO₂–Y₂O₃ solid solutions is weak.

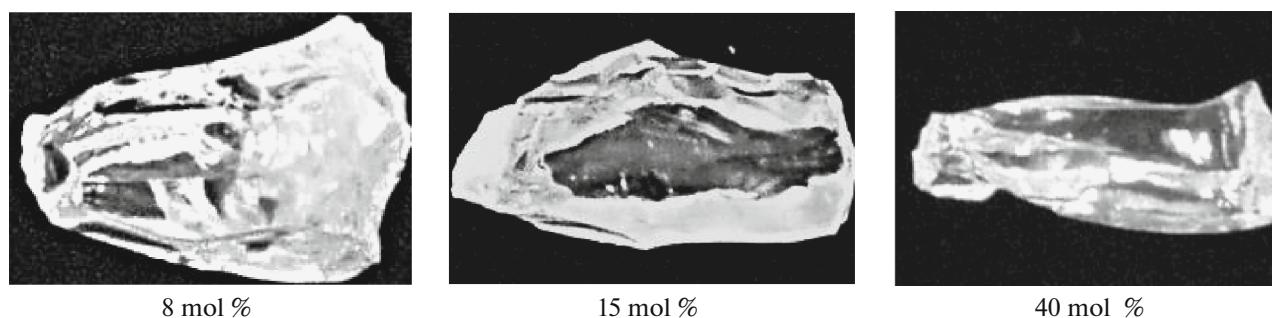


Fig. 1. Appearance of the single crystals.

The results described above demonstrate the advisability of further studies of the thermal conductivity of zirconia-based solid solutions.

The aim of this work is to study the temperature dependence of the thermal conductivity of cubic ZrO_2 single crystals stabilized with yttrium oxide from 8 to 40 mol % in the temperature range 50–300 K.

2. EXPERIMENTAL

The cubic $(\text{ZrO}_2)_{1-x}(\text{Y}_2\text{O}_3)_x$ crystals, where $x = 0.08$ – 0.40 , were grown by directional melt crystallization in a cold container [12–14]. We used a water-cooled cold container 130 mm in diameter; the frequency of the high-frequency generator for direct heating of an insulator in the cold container was 5.28 MHz; and the rate of lowering down the container with a melt with respect to the inductor during crystallization was 10 mm/h. In the text, $(\text{ZrO}_2)_{1-x}(\text{Y}_2\text{O}_3)_x$ crystals are denoted using traditional abbreviation YSZ (yttrium-stabilized zirconia), a head of which numerals show the yttrium oxide content in mol %.

The thermal conductivity was measured on the samples cut with arbitrary crystallographic orientations parallel to the growth axis.

The experimental determination of the thermal conductivity in the temperature range 50–300 K was performed by the absolute steady-state method of longitudinal heat flow. The measurement device and technique are described in [15]. The error of determination of the absolute value of the thermal conductivity was no higher than $\pm 6\%$. At temperatures higher than room temperature, the thermal conductivity was measured by the dynamic method using an IT λ -400 thermal-conductivity meter with an error of $\pm 10\%$.

3. RESULTS AND DISCUSSION

The grown YSZ single crystals were transparent and homogeneous with the cross-section sizes from 5 to 20 mm and heights from 30 to 40 mm. At the growth rate 10 mm/h, the cross-section sizes of the

single crystals decreased as the yttrium oxide concentration increased more than 20 mol % (Fig. 1).

The temperature dependence of the thermal conductivity $k(T)$ of $(\text{ZrO}_2)_{1-x}(\text{Y}_2\text{O}_3)_x$ single crystals with $x = 0.08, 0.10, 0.12, 0.14, 0.15, 0.20, 0.35$, and 0.40 are shown in Fig. 2 and the values of the thermal conductivity are given in Table 1.

It is seen that the crystals with yttrium-oxide contents $x = 0.08$ – 0.15 have close values of the thermal conductivity, and the thermal conductivity increases insignificantly with temperature. The thermal conductivities of these crystals have the lowest values in the entire concentration range. The thermal conductivity is changed from ~ 1.2 – 1.4 to ~ 2.4 W/(m K) as temperature is changed from 50 to 300 K. The difference of the thermal conductivities of these compositions is only noticeable at a temperature of 50 K at

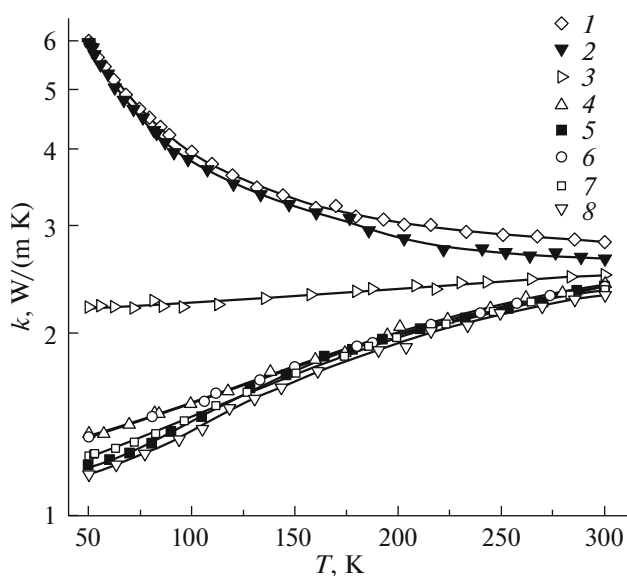


Fig. 2. Temperature dependence of the thermal conductivity $k(T)$ of the $(\text{ZrO}_2)_{1-x}(\text{Y}_2\text{O}_3)_x$ single crystals with $x =$ (1) 0.40, (2) 0.35, (3) 0.20, (4) 0.15, (5) 0.08, (6) 0.12, (7) 0.14, and (8) 0.10.

Table 1. Thermal conductivity of (ZrO₂)_{1-x}(Y₂O₃)_x single crystals with $x = 0.08-0.40$

T, K	$k, W/(m K)$							
	$x = 0.08$	$x = 0.10$	$x = 0.12$	$x = 0.14$	$x = 0.15$	$x = 0.20$	$x = 0.35$	$x = 0.40$
50	1.20	1.17	1.35	1.25	1.36	2.20	5.97	6.00
100	1.43	1.39	1.54	1.46	1.53	2.21	3.84	3.95
200	1.98	1.89	1.98	1.96	2.04	2.37	2.85	3.00
300	2.38	2.30	2.38	2.34	2.40	2.48	2.64	2.81

which the thermal conductivities of 12YSZ and 15YSZ are slightly higher than those of the 8YSZ, 10YSZ, and 14YSZ crystals. The thermal conductivity of the 20YSZ is higher than that of the crystals with the yttrium oxide contents from $x = 0.08$ to 0.15, and it only slightly changed in the temperature range from 50 to 300 K. The further increase in the yttrium oxide concentration substantially changes the values and the character of the temperature dependence of the thermal conductivity. In the 35YSZ and 40YSZ crystals, the thermal conductivity at 50 K increases by a factor of ~six, and decreases as temperature increases, approaching the thermal conductivity of the crystals with other composition at 300 K.

The principally different temperature dependences of the thermal conductivity for the (ZrO₂)_{1-x}(Y₂O₃)_x solid solutions with $x = 0.08-0.15$ and $x = 0.35-0.40$ can be explained as follows. On the one hand, the increase in the phonon concentration with temperature must lead to an increase in the thermal conductivity. On the other hand, the increase in the phonon concentration will favor the enhancement of the phonon-phonon scattering and lead to a decrease in their mean free path. A decrease in the mean free path will determine a decrease in the thermal conductivity. They are exactly two competing factors which will determine the temperature dependence of the thermal conductivity. The first factor will dominate at low phonon concentrations, and the thermal conductivity will increase with temperature. As the phonon concentration will attain a certain value, the second factor will dominate. According to these factors, as temperature increases, the thermal conductivity attains a maximum and then starts to decrease.

If an insulator with disordered structure contains structurally ordered regions with a short-range order, the sizes of which are commensurate with atomic sizes, the phonon scattering at the boundary of these regions will dominate at various temperatures. In this case, the phonon mean free path must not be dependent on temperature. According to this, the thermal conductivity coefficient of these insulators will be proportional to T^3 at low temperatures and will not be dependent on T at high temperatures.

The temperature dependences of the thermal conductivity of the (ZrO₂)_{1-x}(Y₂O₃)_x crystals with $x =$

0.08–0.15 (Fig. 2) show that the first factor is dominant for them.

In the (ZrO₂)_{1-x}(Y₂O₃)_x crystals with $x = 0.35-0.40$, the number of anion vacancies increases. In [16], it was shown that, in these solid solutions, the relative fraction of Y³⁺ ions, which have a vacancy in the first coordination sphere, increases, and there are also Y³⁺ positions which contain two oxygen vacancies in the nearest coordination sphere disposed along the diagonal on a face of a cubic oxygen cell. In addition, in these crystals, Y³⁺ positions having vacancies in both the first and the nearest coordination spheres were observed. Thus, the number of defect complexes formed with participation of oxygen vacancies in (ZrO₂)_{1-x}(Y₂O₃)_x crystals with $x = 0.35-0.40$ is significantly larger than that in the crystals with $x = 0.08-0.15$. This fact must lead to significant phonon scattering on these defect complexes.

The decrease in the thermal conductivity revealed in this work in the temperature range from 50 to 200 K for (ZrO₂)_{1-x}(Y₂O₃)_x solid solutions with $x = 0.35-0.40$ is likely due to the fact that the increase in the number of phonons will lead to significant increase in the intensity of the phonon-phonon scattering on the abovementioned defect complexes and to a decrease in the phonon mean free path. In the temperature range 200–300 K, the phonon scattering by the structural defects will be dominant, which determines the independence of the phonon mean free path on temperature. This fact is well seen on the temperature dependence of the thermal conductivity $k(T)$ of the (ZrO₂)_{1-x}(Y₂O₃)_x single crystals with $x = 0.35-0.40$ in the temperature range 200–300 K.

The temperature dependence of the thermal conductivity of the 20YSZ crystal has an intermediate character between dependences $k(T)$ of the crystals with the yttrium oxide contents from 8 to 15 mol % and with its contents from 35 to 40 mol %. This result is due to the fact that defect complexes consisted of a cation with vacancies in the first and the nearest coordination spheres and also complexes with two oxygen vacancies in the nearest coordination sphere begin to form at these concentrations. But the intermediate character of the thermal conductivity shows that their relative fractions are still low.

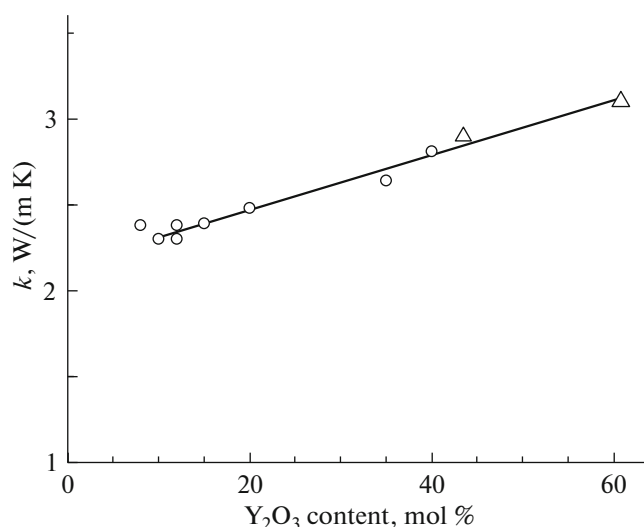


Fig. 3. Concentration dependence of the thermal conductivity of the $(\text{ZrO}_2)_{1-x}(\text{Y}_2\text{O}_3)_x$ solid solutions at $T = 300$ K.

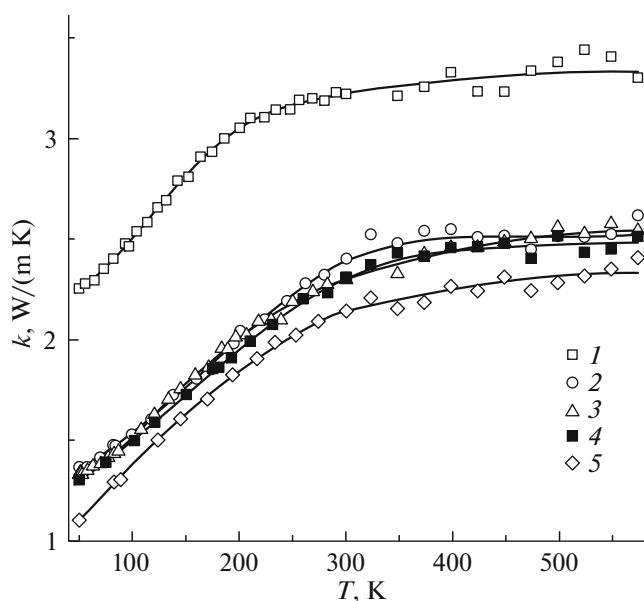


Fig. 4. Temperature dependences of the thermal conductivity of the ZrO_2 crystals with different stabilizing compositions in the temperature range 50–573 K: (1) 1.7Sc2YSZ, (2) 15YSZ, (3) 9Sc1CeSZ, (4) 12YSZ, and (5) 9Y1CeSZ.

Figure 3 shows the concentration dependence of the thermal conductivity $k(x)$ of the $(\text{ZrO}_2)_{1-x}(\text{Y}_2\text{O}_3)_x$ solid solutions. For completeness, we added two points for the compositions with 43.5 mol % Y_2O_3 and 60.8 mol % Y_2O_3 taken from [7]. This dependence demonstrates the ordering of defects in these solid solutions.

As for the character of the dependence, it is adequately described by linear function $k(x) = 0.016x + 2.148$ W/(m K) (x is given in mol %) beginning from 10 mol %.

The regularities of the temperature dependences of the thermal conductivity on the concentration of stabilizing yttrium oxide observed in this work correlate to the results of the studies of the influence of the local structure on the electric conductivity of the $\text{ZrO}_2\text{—Y}_2\text{O}_3$ solid solutions in the concentration range under study [16]. So, as the oxygen vacancy concentration and, correspondingly the number of various defect complexes, increases. The conductivity of the solid solutions decreases, since the complexes are “traps” of oxygen vacancies decreasing their mobility.

Figure 4 shows the results of measurements of the thermal conductivity of zirconia samples with various composition of stabilizing oxides in a wide temperature range. The results obtained on two different installations are quite compatible in the region of conjugating the temperature ranges. However, at temperatures higher than room temperature, the thermal conductivity is almost constant in all the cases, which corresponds to the above literature data.

4. CONCLUSIONS

The temperature dependences of the thermal conductivity of cubic zirconia crystals stabilized with yttrium oxide in the concentration range from 8 to 40 mol % are different for different concentration ranges of the stabilizing oxide, which reflects structural changes in the solid solutions as the concentration of oxygen vacancies caused by the heterovalence substitution of the stabilizing oxide cations for zirconium cations increases. The changes in the thermal conductivity of cubic crystals of zirconia stabilized with yttrium oxide in the dependence of the composition correlate to the changes in the electrical conductivity that are also related to the structural changes in the solid solutions.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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