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Structural stabilization and strengthening of Li_2ZrO_3-based ceramics by doping with Y_2O_3 and CeO_2

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The study investigates the effect of modifying lithium metazirconate with yttrium and cerium oxides on the phase composition, structural parameters, and mechanical properties of lithium-containing ceramics. The samples were obtained by mechanochemical mixing followed by sintering at a temperature of 1000 °C . It was found that when adding Y_2O_3 and CeO_2 (0.01–0.15 M), substitution phases and dispersed secondary inclusions are formed without significant disruption of the structural ordering of the main phase Li_2ZrO_3 . It has been shown that modification is accompanied by an increase in the stability of the obtained materials to single compression due to the effects of solid-solution and dispersion strengthening, and growth in the density of interphase boundaries. The most pronounced strengthening effect is achieved by using yttrium oxide, which provides higher values of critical failure load compared to cerium oxide. The obtained results can be used in the development of lithium-containing ceramics designed for operation under increased mechanical stress and high temperatures.

Keywords: lithium metazirconate; lithium-containing ceramics; stabilizing dopants; cerium oxide; yttrium oxide; phase composition; interphase strengthening; crack resistance

Introduction

Lithium metazirconate is considered a promising functional and structural material due to its high thermal and phase stability, chemical inertness and resistance to aggressive factors, which determines the interest in Li_2ZrO_3 for use in energy

systems operating in harsh conditions, at high temperatures and mechanical loads. However, the limiting factor for the exploitation of lithium metazirconate is its brittleness and limited crack resistance [1–4].

To improve the performance properties of ceramic materials, their structure is modified by introducing stabilizing oxide dopants capable of initiating processes of cationic substitution, defect formation, and phase transformations [5, 6]. Among the stabilizing additives, yttrium (Y_2O_3) and cerium (CeO_2) oxides are of particular interest, widely used to modify zirconium-containing ceramics [7, 8].

As reported in several studies, Y^{3+} ions substituting for Zr^{4+} promote the formation of oxygen vacancies and induce elastic distortions in the crystal lattice. The formation of vacancies in the oxygen sublattice leads to a decrease in local repulsion between O^{2-} ions, partial removal of internal stresses and stabilization of high-temperature tetragonal or cubic modifications, which in some cases has a positive effect on the mechanical stability of the material [9, 10]. At the same time, the isovalent nature of substitution upon introduction of CeO_2 containing Ce^{4+} ions allows us to consider this dopant as an effective tool for fine structural modification of Li_2ZrO_3 , ensuring a balance between the stability of the crystal lattice and a controlled level of defects without a significant increase in the concentration of point defects [11, 12].

The main objective of the work is to determine the patterns of influence of yttrium and cerium oxide dopants on the phase composition, crystal structure parameters and mechanical properties of Li_2ZrO_3 -based ceramics in a wide range of concentrations. It is expected that modification of Li_2ZrO_3 with oxide additives Y_2O_3 and CeO_2 will lead to the formation of substitution phases and dispersed inclusions, an increase in the density of interphase boundaries, which in turn can lead to the manifestation of solid-solution and dispersion strengthening effects and an increase in fracture resistance.

Materials and methods

Ceramics based on lithium metazirconate were obtained by introducing yttrium and cerium oxides into the initial Li_2ZrO_3 powder, while the dopant concentration ranged from 0.01 to 0.15 M. The choice of dopant concentrations in the composition was carried out on the basis of a priori experimental work, including detailing the processes of phase transformations in zirconium-containing ceramics with the addition of stabilizing dopants, which intensifies polymorphic transformations, as well as the associated structural changes, leading to strengthening and increased stability of the crystal structure [13]. The addition of stabilizing dopants to the lithium metazirconate composition was carried out at the stage of mechanical mixing, the use of which made it possible to equally distribute the stabilizing dopant within the ceramics, which, upon subsequent thermal annealing, made it possible to initiate phase transformation processes throughout the entire volume of the ceramics. Samples were ground in a PULVERISETTE 6 planetary mill (Fritsch, Berlin, Germany) at 200 rpm (30 minutes). Subsequent

heat treatment was performed in a Nabertherm LE 4/11/R6 muffle furnace (Nabertherm, Lilienthal, Germany). The sintering temperature was 1000 °C, the heat treatment time was 5 hours, after which the furnace and samples were cooled for 24 hours until completely cooled.

The phase composition of the resulting ceramics before and after modification was analyzed using X-ray diffraction analysis on a D8 ADVANCE ECO diffractometer (Bruker, Karlsruhe, Germany). To evaluate the phase composition, the DiffraEVA v.4.2 software was used; the phase composition and structural parameters were refined using the PDF-2 database. For the initial sample of Li_2ZrO_3 ceramics, the PDF-00-033-0843 card was used, which describes the structural features of Li_2ZrO_3 with a monoclinic type of crystal lattice. The weight fractions of each phase were determined by refining the areas of all diffraction reflections characteristic of that phase, followed by calculating their contribution to the overall diffractogram while accounting for the corundum numbers for each phase.

Tests of ceramic samples for resistance to cracking under compression were carried out on a LFM-L 10kH testing machine (Walter + Bai AG, Loningen, Switzerland) by placing ceramic samples in a special holder, followed by increasing the pressure on the sample and recording the formation of microcracks in the sample under compression, followed by determining the value of the maximum critical pressure at which the sample fails. Loading was applied at a constant rate of 0.05 mm/s. The dependence of applied load on deformation was recorded during the experiment. The critical failure load was determined when the pressure decreased by at least 75% of the maximum value. At least four samples were tested for each composition. The resulting critical load values were averaged, and the average values were used as the final values. Tests were conducted on cylindrical specimens (tablets) with a diameter of $\sim$12 mm. All specimens had identical geometry and similar linear dimensions, ensuring a reliable comparative analysis of mechanical test results based on load magnitude.

Results and Discussion

Figures 1–2 show the diffraction patterns of the studied samples of Li_2ZrO_3 ceramics modified by adding yttrium (Y_2O_3) and cerium (CeO_2) oxides at different dopant concentrations. The data on the structural parameter estimates are presented in Tables 1–2. Doping of lithium-containing Li_2ZrO_3 ceramics with Y_2O_3 leads to the formation of $(YZr)O_2$ grains at low dopant concentrations (0.01–0.05 M), and at high concentrations, as a result of polymorphic transformations, yttrium zirconate grains ($Y_2Zr_2O_7$) are formed.

The formation of $(YZr)O_2$ grains at low concentrations of the Y_2O_3 dopant occurs due to cationic substitution of the $Zr^{4+} \rightarrow Y^{3+}$ type, which ultimately displaces inclusions of the cubic phase $(YZr)O_2$ from the Li_2ZrO_3 phase and leads to the formation of oxygen vacancies in the structure of the studied ceramic samples. Thus, the proportion of inclusions in the composition of the obtained materials increases with increasing variation in the concentration of the dopant,

while cationic substitution is caused by an increase in the proportion of oxygen vacancies in the structure of the ceramics, which, when the structure is saturated, leads to phase transformations of the type $(YZr)O_2 \rightarrow Y_2Zr_2O_7$. The fixation of polymorphic transformations occurs at a dopant concentration of 0.1 M, and with an increase in the concentration of yttrium oxide from 0.10 M to 0.15 M, the content of $Y_2Zr_2O_7$ increases from 7 wt.% to 11 wt.%.

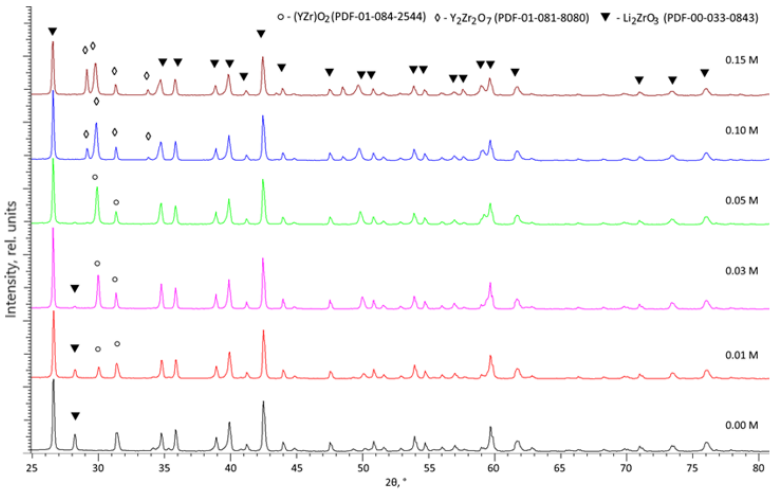


Figure 1. Results of X-ray diffraction of the studied Li_2ZrO_3 ceramic samples modified with a dopant in the form of Y_2O_3.

With the growth of inclusions in the composition of the obtained ceramics, the degree of structural ordering remains 2–3%, which indicates that the processes of phase transformations on the crystal structure of the main phase in the structure of Li_2ZrO_3 ceramics associated with the polymorphism of ZrO_2 have an insignificant effect.

Table 1.
Data on the structural parameters of the studied Li_2ZrO_3 ceramics when modified with Y_2O_3 dopant.

Phase	Concentration of dopant Y_2O_3, M					
	0	0.01	0.03	0.05	0.10	0.15
Li_2ZrO_3	$a = 5.4201$ Å $b = 9.0046$ Å $c = 5.4089$ Å $\beta = 112.740°$ $V = 243.47$ Å^3	$a = 5.4149$ Å $b = 9.0116$ Å $c = 5.4110$ Å $\beta = 113.052°$ $V = 242.96$ Å^3	$a = 5.4085$ Å $b = 9.0115$ Å $c = 5.4344$ Å $\beta = 112.654°$ $V = 244.43$ Å^3	$a = 5.4106$ Å $b = 9.0576$ Å $c = 5.4153$ Å $\beta = 112.256°$ $V = 245.62$ Å^3	$a = 5.4106$ Å $b = 9.0611$ Å $c = 5.4174$ Å $\beta = 112.786°$ $V = 244.87$ Å^3	$a = 5.4213$ Å $b = 9.0222$ Å $c = 5.4110$ Å $\beta = 112.875°$ $V = 243.85$ Å^3
$(ZrY)O_2$	–	$a = 5.1451$ Å $V = 136.20$ Å^3	$a = 5.1552$ Å $V = 137.00$ Å^3	$a = 5.1532$ Å $V = 136.84$ Å^3	–	–
$Y_2Zr_2O_7$	–	–	–	–	$a = 5.1844$ Å $V = 139.35$ Å^3	$a = 5.1905$ Å $V = 139.84$ Å^3

When adding a stabilizing dopant CeO_2 to lithium metazirconate at a dopant concentration of 0.03 M, $(CeZr)O_2$ grain inclusions with a cubic crystal lattice are formed. Moreover, an increase in the dopant in the ceramics does not lead to any other phase transformations in the ceramics, and the analysis of the weight contributions in the obtained ceramics showed an increase in the $(CeZr)O_2$ phase from 1 wt.% to 7–8 wt.% at a maximum concentration of 0.15 M.

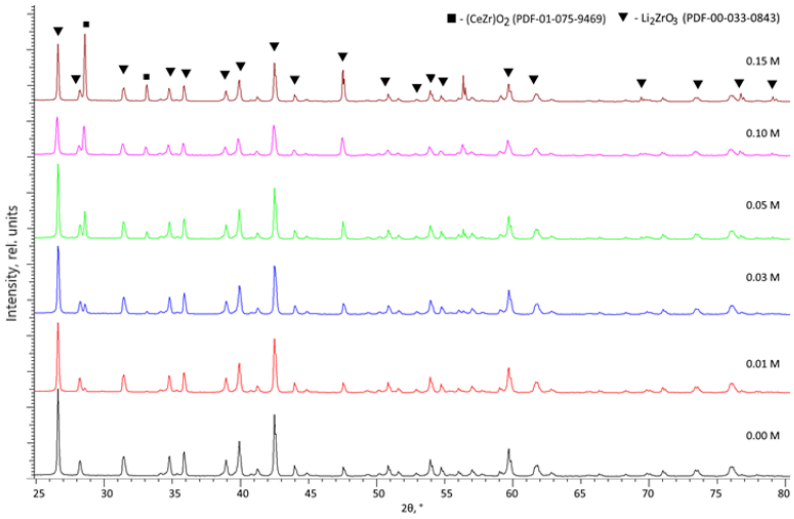


Figure 2. Results of X-ray diffraction of the studied Li_2ZrO_3 ceramic samples modified with a dopant in the form of CeO_2.

The absence of other types of phase transformations in lithium metazirconate ceramics with an increase in the proportion of CeO_2 is caused by the peculiarities in the mechanisms of cation substitution for different types of dopants. In the case of using CeO_2 dopant, the process of cationic substitution is not accompanied by the formation of oxygen vacancies, the presence of which is observed during cationic substitution $Zr^{4+} \rightarrow Y^{3+}$, in which the formation of oxygen vacancies occurs due to the need to maintain charge electroneutrality [14, 15].

Table 2.
Data on the structural parameters of the studied Li_2ZrO_3 ceramics when modified with CeO_2 dopant

Phase	Concentration of dopant CeO_2, M					
	0	0.01	0.03	0.05	0.10	0.15
Li_2ZrO_3	$a = 5.4085$ Å $b = 8.9761$ Å $c = 5.4153$ Å $\beta = 112.474°$ $V = 242.93$ Å^3	$a = 5.4255$ Å $b = 9.0222$ Å $c = 5.4089$ Å $\beta = 112.521°$ $V = 244.57$ Å^3	$a = 5.4192$ Å $b = 9.0186$ Å $c = 5.4065$ Å $\beta = 112.609°$ $V = 243.94$ Å^3	$a = 5.4043$ Å $b = 9.0222$ Å $c = 5.4068$ Å $\beta = 112.388°$ $V = 243.75$ Å^3	$a = 5.4447$ Å $b = 9.0505$ Å $c = 5.4089$ Å $\beta = 112.477°$ $V = 246.29$ Å^3	$a = 5.4383$ Å $b = 9.0044$ Å $c = 5.4174$ Å $\beta = 113.184°$ $V = 243.86$ Å^3
$(CeZr)O_2$	–	–	$a = 5.4015$ Å $V = 157.60$ Å^3	$a = 5.4047$ Å $V = 157.88$ Å^3	$a = 5.4121$ Å $V = 158.52$ Å^3	$a = 5.4058$ Å $V = 157.97$ Å^3

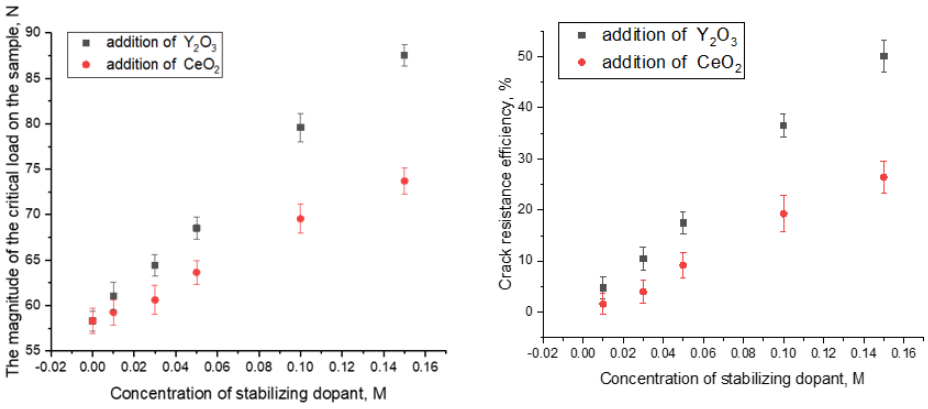
Changes in crystal lattice parameters with varying dopant concentrations of Li_2ZrO_3 ceramics is due to deformation processes accompanied by processes of cation substitution and subsequent polymorphic phase transformations.

In the course of the studies, it was established that the addition of stabilizing dopants leads to the initialization of polymorphic transformation processes associated with the formation of grains of $(YZr)O_2$, $Y_2Zr_2O_7$, $(CeZr)O_2$ in the composition of ceramics. Moreover, the presence of such inclusions in the composition of ceramics ensures strengthening of Li_2ZrO_3 ceramics due to interphase strengthening.

Figure 3 shows the results of assessing the change in the critical load value at which cracking of ceramic samples occurs when the external pressure on the sample changes.

From the presented data, the introduction of stabilizing oxides Y_2O_3 and CeO_2 into the structure of lithium metazirconate, which promotes the formation of substitution phases in the crystal lattice and the appearance of dispersed inclusions, significantly affects the mechanical strength of the material. Analysis of the results showed that with an increase in the concentration of dopants, an increase in the critical failure load is observed, but the dynamics of this change varies depending on the nature of the additives introduced.

The addition of Y_2O_3 provides the most pronounced strengthening: starting from moderate concentrations (about 0.05 M and above), the strength increases nonlinearly and reaches maximum values of about 75–82 N. This is due to the fact that the Y^{3+} ion, replacing Zr^{4+}, causes the appearance of compensating oxygen vacancies and forms significant elastic distortions of the lattice due to the formation of substitution phases of the $(YZr)O_2$ type. Such distortions increase the density of internal barriers to dislocation movement and reduce the mobility of grain boundaries, which contributes to the stabilization of the fine-grained structure. In addition, the formation of a solid solution based on Li_2ZrO_3 – $Y_2Zr_2O_7$ is accompanied by the appearance of small secondary inclusions that provide dispersion strengthening and effectively prevent the propagation of cracks.



a) b)

Figure 3. Results of changes in the strength properties of the studied ceramics modified with stabilizing dopants: a) results of the assessment of the critical load under compression;b) results of the assessment of the effectiveness of resistance to compression cracking depending on the structure and type of dopants.

In the case of adding CeO_2, the observed increase in critical load is less pronounced and develops more smoothly. The Ce^{4+} ion is close in radius and charge state to Zr^{4+}, so its inclusion in the lattice causes smaller elastic distortions and leads to a less pronounced rearrangement of the defect structure. Secondary inclusions based on cerium oxide also form, but they have a lesser effect of pinning grain boundaries and inhibit crystallite growth less effectively. As a result, the material exhibits moderate strengthening, limited to the region of 65–70 N, without the sharp jumps characteristic of the Y_2O_3 modification.

A common mechanism for both systems is the enhancement of resistance to local mechanical loading due to the combination of solid solution effects,

dispersion strengthening and structure stabilization. However, differences in the nature of the substituent ions determine a qualitative difference in the behavior of the materials: Y_2O_3 acts as a stronger structural modifier due to the generation of oxygen vacancies, significant deformation of the crystal lattice, and an increase in the number of phase boundaries that effectively dissipate energy under loading. This behavior is explained by the fact that in the case of the $Zr^{4+} \rightarrow Y^{3+}$ substitution, as a mechanism of sequential charge imbalance to maintain the electroneutrality of the structure, oxygen vacancies are formed as point defects of compensating charges. CeO_2 , on the contrary, changes the structure more gently, which leads to a lower degree of hardening. This is confirmed in [4], where, according to atomistic modeling, if divalent and trivalent cations (Y) are used as dopants in Zr, an oxygen-deficient structure is formed. However, when doped with tetravalent cations (Ce), binding to oxygen vacancies will already be with lower binding energies, and the substitution is isovalent.

Conclusion

It has been established that modification of Li_2ZrO_3 with stabilizing oxide additives is accompanied by the formation of secondary phases and dispersed inclusions, as well as the development of a system of interphase and intergranular boundaries, while the crystal structure of the main phase retains a high degree of order. This indicates that the observed phase and microstructural transformations are local in nature and do not lead to destabilization of the Li_2ZrO_3 crystal lattice, which is an important factor in the development of structural and functional ceramic materials.

It has been established that stabilization of ceramics with dopants leads to an increase in the resistance of ceramics to fracture under compression, which indicates the implementation of a complex strengthening mechanism, including the contribution of solid-solution effects, dispersion strengthening and interphase interaction. The development of interphase boundaries and the formation of secondary inclusions create additional energy barriers for the initiation and propagation of cracks, which helps to increase the mechanical stability of the material under the influence of external forces. For the yttrium oxide modified system, the most pronounced strengthening effect was observed at a critical failure load of about 75–82 N, while for the cerium oxide modified system it was about 65–70 N.

It has been established that the nature and efficiency of strengthening are largely determined by the chemical nature of the dopant and the mechanism of its inclusion in the Li_2ZrO_3 structure. Yttrium oxide exhibits itself as a more active structural modifier, providing a more pronounced increase in the critical failure load due to aliovalent cationic substitution, the formation of oxygen vacancies and the associated elastic distortions of the crystal lattice. In contrast, the incorporation of CeO_2 exerts a milder effect on the material structure, primarily due to the isovalent nature of substitution, resulting in moderate strengthening while maintaining high structural stability of the ceramics.

The obtained results demonstrate the fundamental possibility of targeted control of the mechanical properties of ceramics based on Li_2ZrO_3 by selecting the type and concentration of the stabilizing oxide dopant. This opens up prospects for optimizing the composition and microstructure of lithium-containing ceramics for use under elevated thermomechanical loads, including in power and high-temperature applications where a combination of structural stability and enhanced fracture resistance is required.

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