Mechanochemical Synthesis of (Co,Cu,Mg,Ni,Zn)O High-Entropy Oxide and Its Physicochemical Properties

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The study describes the physicochemical properties of transition metal (Co,Cu,Mg,Ni,Zn)O high-entropy oxide prepared using mechanochemical synthesis (MS) followed by thermal treatment, as well as the structural evolutions in the powder with milling time. The microstructure and electrical properties of the materials were studied using x-ray diffraction, scanning electron microscopy—energy dispersive spectroscopy and electrochemical impedance spectroscopy. The powders obtained after 30 h and 100 h of MS contained a mixture of two phases with a rock salt structure and, in addition, about 11 wt.% of Co₃O₄. Sintering these materials for 10 h in air at 1273 K led to the formation of a single-phase, solid solution with a rock salt structure. The developed sinters exhibited a fine-crystalline structure of grains and a uniform distribution of elements. The highest electrical conductivity was measured at 1148 K, and it was equal to $8.03 \times 10^{-2} \text{ S cm}^{-1}$.

Key words: Milling, electrical conductivity, transition metal oxides, high-entropy oxides

INTRODUCTION

Materials stabilized via a high-configuration entropy of the system are a very interesting example of a materials engineering concept that originated with high-entropy alloys (HEAs), also known as multi-principal element alloys. Such materials exhibit very desirable strength properties at low densities^{1,2} as well as advantageous magnetic,³ electrical⁴ and chemical^{5,6} properties. Because of the increased interest in the use of energy from renewable sources and hydrogen as an energy carrier, alloys such as CoFeMnTi_xV_yZr_z may become a new generation of hydrogen storage materials.⁷

With the development of this concept, which involves the stabilization of a solid solution via a

high-configuration entropy maintained by at least five constituents randomly distributed across the crystalline structure at an equimolar ratio, three new systems of this type were designed, namely high-entropy alloy nitrides (HEANs),⁸ high-entropy metal diborides (HEBs),⁹ and high-entropy carbides as a novel class of multicomponent ceramics.¹⁰

Since the successful synthesis of an equimolar, *Fm*–*3m* single-phase (Co,Cu,Mg,Ni,Zn)O solid solution by Rost et al.¹¹ in 2015, the scientific community has taken a growing interest in the new group of ceramic materials referred to as high-entropy oxides (HEOx). The stabilization of ceramics via a high-configuration entropy may yield a number of unique properties as a result of the synergistic interactions between various pairs of ions. This is the main difference in relation to conventional materials, in which properties are determined entirely by one or two main components.

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Bérardan et al.^{12,13} combined such stabilization with doping by means of different alkali ions (Li, Na) and obtained modified HEOx materials that exhibited enormous dielectric constants. Moreover, the $(\text{Co,Cu,Mg,Ni,Zn})_{0.7}\text{Li}_{0.3}\text{O}$ oxide they synthesized was characterized by high ionic conductivity at room temperature, making it a promising material for the development of LiPON cells to be applied in mobile devices. The results of this investigation and the subsequent studies conducted by Rak et al.,¹⁴ Djenadic et al.,¹⁵ Bérardan et al.¹⁶ and Rost et al.¹⁷ in order to better understand the structural and physicochemical properties of such materials provided the inspiration for the development of new classes of HEOx ceramics—one with a perovskite structure, which was synthesized by a team led by Luo,¹⁸ and another with a $(\text{Co,Cr,Fe,Mn,Ni})_3\text{O}_4$ spinel structure, synthesized by Danielewski's group.¹⁹

Current research on transition metal high-entropy oxides (TM-HEOs) indicates that it is possible to synthesize these materials by means of techniques other than the solid-state reaction.^{11,12,18,19} For example, numerous studies conducted for different ceramic systems have determined that wet chemistry methods, which include the sol-gel method, the citrate process, and co-precipitation, among others, are far superior to solid-state reaction methods, since they allow the degree of powder granularity and the purity of the system to be controlled, ensure a narrow particle size distribution, and—in the case of multi-component systems—their high homogeneity. Furthermore, they enable lower sintering temperatures and shorter thermal treatment times.

Sarkar et al.²⁰ applied nebulized spray pyrolysis (NSP), flame spray pyrolysis (FSP) and reverse co-precipitation (RCP) techniques to synthesize $(\text{Co,Mg,Ni,Zn})\text{O}$ and $(\text{Co,Cu,Mg,Ni,Zn})\text{O}$, successfully obtaining nanomaterials stabilized via high-configuration entropy. According to these authors, the application of the NSP method allows the single-phase, rock salt $(\text{Co,Cu,Mg,Ni,Zn})\text{O}$ to be directly stabilized at a lower temperature, without the thermal treatment stage that is required in the case of FSP and RCP.

In view of the above-mentioned results, it seemed worth undertaking the preparation of a TM-HEOs material with the composition of $(\text{Co,Cu,Mg,Ni,Zn})\text{O}$ via mechanochemical synthesis (MS). This type of processing is a special method that involves the mechanical activation of solid-state chemical reactions via displacement during ball milling; it has been extensively studied in recent years and was used to synthesize metallic, oxide and sulfide nanoparticles.^{21–24} The main advantage of this method is that the process is carried out in the solid state and makes it is easier to control the overall particle size distribution. If suitable conditions, such as milling parameters, ball-to-powder ratio (BPR) and the stoichiometric ratio of the

starting materials, are selected, mechanochemical processing can be used to synthesize nanocrystalline powders with a precise chemical composition and homogeneous microstructure. An attempt to apply the mechanochemical method for the preparation of the $(\text{Co,Cu,Mg,Ni,Zn})\text{O}$ sample was made, since this would have allowed the Co_3O_4 starting material to be used as a precursor of Co. Co_3O_4 is inexpensive and more readily available than CoO in the rock salt form, i.e. the material usually used for this purpose.

The primary goal of this study was to synthesize a fine, single-phase $(\text{Co,Cu,Mg,Ni,Zn})\text{O}$ solid solution bulk sample using MS technique by optimizing the milling process and the thermal treatment conditions. The structure and morphology of the powders and the bulk sample were studied by means of x-ray diffraction (XRD), scanning electron microscopy (SEM), whereas the electrical conductivity of the bulk sample was investigated via electrochemical impedance spectroscopy (EIS). The structural evolutions of the powder with milling time were also evaluated.

EXPERIMENTAL PROCEDURE

Chemicals

The following commercial binary oxide powders were used as starting materials: magnesium oxide (Sigma-Aldrich, 99.99%, – 325 mesh), cobalt(II,III) oxide (Fluka Chemie, > 71.0 wt.% of Co, < 10 μm), nickel(II) oxide (Sigma-Aldrich, 99%, – 325 mesh), copper(II) oxide (Sigma-Aldrich, 99.99%, – 200 mesh) and zinc oxide (Sigma-Aldrich, $\geq 99\%$, -200 mesh).

As per the criteria for the choice of the cations for the synthesis of the TM-HEOs material, suggested by Rost et al.,¹¹ Table I gives an overview of the crystal structure, space group, oxidation state, coordination number and corresponding cationic radius of each of the individual binary oxides used as starting materials in the present study.^{25,26}

Preparation of Materials

The starting oxide powders were weighed in equimolar proportions and mixed by means of the MS technique. A shaker-type ball mill (SPEX 8000 Mixer/Mill) was used. The ball-to-powder weight ratio (BPR) was 6:1 during the first 30 h of synthesis and 11:1 during the subsequent 70 h of synthesis. The rationale for modifying the BPR during synthesis is given in a later section of this work. The applied balls and mixing vial were both made of stainless steel. The entire MS process lasted 100 h and was carried out in air. Two types of samples were studied—powders synthesized for 30 h, and powders synthesized for 100 h. The first synthesis stage was briefly interrupted at certain time intervals (5 min, 1 h, 4 h, 8 h, 15 h, 30 h and 100 h) in

Table I. Crystal structure, space group, oxidation state, co-ordination number (CN) and corresponding cationic radius (r_c) of binary oxides used as starting materials

Oxide	Structure	r_c (Å) ²⁵	Space group (number) ²⁶	Oxidation state	CN
Co ₃ O ₄	Spinel	0.58	<i>Fd</i> $\bar{3}m$ (227)	2 + (high-spin state)	IV
		0.55		3 + (low-spin state)	VI
CuO	Tenorite	0.73	<i>C12/c1</i> (15)	2+	VI
MgO	Rock salt	0.72	<i>Fm</i> $\bar{3}m$ (225)	2+	VI
NiO	Rock salt	0.69	<i>Fm</i> $\bar{3}m$ (225)	2+	VI
ZnO	Wurtzite	0.60	<i>P6₃mc</i> (186)	2+	IV
ZnO	Rock salt	0.74	<i>Fm</i> $\bar{3}m$ (225)	2+	VI

Source of data indicated in column heading, where appropriate.

order to study the structural evolutions occurring in the powders.

To prepare bulk samples with a diameter of 8 mm and a height of about 2 mm, the powders were pressed under 200 MPa, and the obtained green bodies were then free-sintered for 10 h in static air at 1273 K, with a heating rate of 5 K min⁻¹. After heat treatment, the samples were promptly removed and air-quenched. The obtained sinters are subsequently referred to as HEOX-30 h MS and HEOX-100 h MS.

Methodology

A PANalytical Empyrean powder diffractometer (Cu K α_1 radiation, $\lambda = 1.5405952$ Å) was used to investigate the structure of the investigated powders. XRD measurements were performed at room temperature. The voltage and anode current were 45 kV and 40 mA, respectively. The XRD profiles were refined with the Rietveld method using the Maud software.

Another diffractometer, namely the PANalytical X'Pert, was used for the phase analysis of the sintered pellets, which involved heating them to 1273 K, and then cooling them to room temperature. An MRI temperature camera (MRI TC) with a Pt strip heater was used for this purpose. Measurements were performed in a standard configuration (step: 0.008°, time per step: 80 s, X'Celerator strip detector). Qualitative phase analyses were conducted using the HighScore Plus software (PANalytical) coupled with the X'Pert diffractometer and the PCPDFWIN v.2.3 standard data set.

The morphology of agglomerates and chemical composition of the obtained MS powders were determined via SEM and energy dispersive spectroscopy (EDS) performed by means of the Tescan VEGA TS5135 digital imaging microscope. A field-emission scanning electron microscope (JEOL JSM-7000F) coupled with EDAX's Octane Silicon Drift Detector (SDD) for EDS was used to examine the morphology and chemical composition of the sinters.

The relative density of the investigated bulk samples was determined by dividing the apparent density obtained experimentally (via the

hydrostatic weighing of sinters in distilled water) by the theoretical density calculated based on crystallographic data. The total porosities were computed from the following equation:

$$P_c = \left(1 - \frac{d_a}{d_{XRD}}\right) \times 100\% \quad (1)$$

where: P_c —total porosity (%), d_a —apparent density (g cm⁻³), d_{XRD} —theoretical density (g cm⁻³).

The electrical resistance of the studied samples was measured using a Hioki LCR meter in the AC mode, an amplitude of 0.2 V, and with a frequency ranging from 0.1 Hz to 1 Hz. The obtained values were assumed as the DC resistance values (no imaginary impedance component at this frequency). Electrodes were prepared by covering sinter samples with Pt paste (Heraeus) and heated to 1273 K at a rate of 5 K min⁻¹ in laboratory air. Samples were then placed in-between spring loaded Pt meshes. The temperature dependence of electrical resistance was measured between 478 K and 1148 K at 25 K intervals during cooling; at each measurement temperature, data was collected after the temperature had been stable for 30 min.

The electrical conductivity of the sinters was determined based on the obtained electrical resistance values, their dimensions, and the following dependence:

$$\sigma = \frac{L}{S \cdot R} \quad (2)$$

where R represents electrical resistance (Ω), S represents the cross-sectional surface area (cm²), L represents sample thickness (cm). The sample preparation and the apparatus and methods used to measure electrical resistance are described in Ref. 27.

RESULTS AND DISCUSSION

Physicochemical Characteristics of the Studied Powders

The objective of the synthesis was to obtain a single-phase solid solution with a rock salt

structure, which crystallizes in the $Fm\bar{3}m$ space group. This space group is also observed in the case of MgO and NiO (Table I).

Figure 1 presents XRD patterns recorded for a mixture of MgO, Co_3O_4 , NiO, CuO and ZnO powders mechanochemically synthesized in air over 5 min and 1 h, 4 h, 8 h, 15 h, 30 h or 100 h. It is evident that the ZnO and CuO diffraction peaks, which were initially relatively sharp, became broader and less pronounced for longer milling times. After 15 h of MS, the peaks originating from these phases were no longer visible. In this case, they co-formed the NiO- and MgO-based NaCl-type solid solutions or the Co_3O_4 -based solid solution (structure crystallized in an $Fd\bar{3}m$ space group, Table I). Moreover, a reflection attributed to the NaCl structure was visible after 30 h of MS. Due to the MS process, both solid solutions (NiO- and MgO-based) became homogenized. Unfortunately, Co_3O_4 peaks were still visible after 30 h of MS. The Co oxide did not react with the remaining oxides, perhaps due to the insufficient energy of the synthesis. To verify this,

Fig. 1. XRD patterns of a mixture of MgO, Co_3O_4 , NiO, CuO and ZnO powders mechanochemically synthesized over different times.

the BPR was increased from 6:1 to 11:1 and the material underwent another 70 h of MS. Despite this, Co_3O_4 failed to dissolve in the solid solution with the rocksalt structure; the reason for this was the high stability of this phase in air at ambient temperature, as indicated by the phase diagram for the $\text{Co}_3\text{O}_4\text{--CoO}$ system.²⁸

The results of qualitative phase analyses performed based on the Rietveld profile refinement method indicate that the mechanochemical synthesis of the powders obtained after 30 h or 100 h of milling yielded a mixture of two phases with a rock salt structure and a phase of Co_3O_4 -based solid solution. This can be seen by examining the XRD pattern recorded for the powder obtained after 30 h of MS, shown in Fig. 2; in addition to the experimental curve, this figure also includes a curve plotted based on the performed Rietveld analysis and its constituents related to the two afore-mentioned phases.

Table II lists the relative mass contribution of phases formed in the studied powders after milling for either 30 h or 100 h; the actual compositions of the NaCl-type solid solution, calculated based on the corresponding data, are also listed. These data show that the main phase with a rock salt structure in either of the afore-mentioned powders is a four-component compound with the composition of $\text{Cu}_{0.25}\text{Mg}_{0.25}\text{Ni}_{0.25}\text{Zn}_{0.25}\text{O}$ and a mass contribution of ca. 68 wt.%. This is because a significant fraction of the Co_3O_4 spinel (11% of the total powder mass) had not incorporated into the NaCl-type solid solution structure. In fact, only a small amount of the spinel formed the $\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2}\text{O}$ compound with four other components; the mass contribution of this compound was estimated to be ca. 32%. It should be noted that prolonging the milling time by 70 h did not result in a significant increase in the contribution of cobalt in the five-component phase with a rock salt structure

Fig. 2. XRD pattern recorded for a powder obtained after 30 h of MS and the corresponding curve plotted based on Rietveld analysis.

Table II. Relative mass contribution of phases identified in powders after 30 h and 100 h of MS and the corresponding actual NaCl-type solid solution compositions

Powder	Mass contribution (%)		Actual composition of NaCl-type solid solution (mass fraction of individual oxides)
	NaCl-type solid solution	Co ₃ O ₄	
30 h MS	89.0	11.0	Co _{0.2} Cu _{0.2} Mg _{0.2} Ni _{0.2} Zn _{0.2} O (31.5%) Cu _{0.25} Mg _{0.25} Ni _{0.25} Zn _{0.25} O (68.5%)
100 h MS	89.4	10.6	Co _{0.2} Cu _{0.2} Mg _{0.2} Ni _{0.2} Zn _{0.2} O (31.7%) Cu _{0.25} Mg _{0.25} Ni _{0.25} Zn _{0.25} O (68.3%)

Fig. 3. SEM micrographs of the powders obtained after 30 h and 100 h of MS and corresponding EDS element maps of Co K α_1 , Cu K α_1 , Fe K α_1 , Mg K α_1 , Ni K α_1 , O K α_1 and Zn K α_1 .

(Table II), but it merely made the spinel phase finer, as indicated by the broadening of reflections such as the one originating from the (511) family of planes for the Co₃O₄ phase.

Figure 3 shows the SEM micrographs of the obtained powders after 30 h and 100 h of MS and the EDS element maps corresponding to the areas shown in the micrographs. Regardless of the time of synthesis, Mg, Cu, Ni, Co, Zn and O elements were uniformly distributed across virtually the entire area of the material. In addition to the elements present in the starting materials, Fe atoms were found during EDS measurements. The mass fraction of this element ranged from 1.5 wt.% to 1.9 wt.%. This iron contamination originated from

the stainless steel of the mixing vial and the milling balls.

SEM micrographs of the powders obtained after 30 h and 100 h of MS are shown in Fig. 4. The morphology of the two materials was similar—small grains forming agglomerates with a size of 0.1–5 μ m.

Physicochemical Properties of the Obtained Sinters

XRD phase analyses were performed in situ at room temperature and over the temperature range of 373–1273 K during heating and cooling for HEOX-30 h MS and HEOX-100 h MS sinters obtained by thermally treating (10 h, air, 1273 K)

Fig. 4. SEM micrographs of the powders obtained after 30 h and 100 h of MS.

green bodies prepared from powders after 30 h and 100 h of MS. These analyses showed that the structure of the NaCl-type solid solution in the studied sinters did not change with temperature; instead, they retained their $Fm\bar{3}m$ rock salt form, indicating (Co,Cu,Mg,Ni,Zn)O stoichiometry. Moreover, reflections originating from the Co_3O_4 phase were no longer visible. The lattice parameters of the HEOX-30 h MS and HEOX-100 h MS sinters at room temperature were determined to be $4.23842 (\pm 0.0005)$ and $4.23624 (\pm 0.0012)$ Å, respectively. These results are consistent with those reported by other authors.^{11,20}

Figure 5 shows a number of XRD patterns that were recorded for the HEOX-30 h MS sinter while it was being heated in the temperature range of RT–1273 K. In addition to the reflections attributed to the rock salt phase, some low-intensity reflections can also be seen; the latter originated from the alundum plate on which the sample had been placed during high-temperature x-ray measurements.

Figure 6 presents the temperature dependence of lattice parameter a of the HEOX-30 h MS sinter observed while this material was being heated and cooled over the range of RT–1273 K. This dependence is linear for the cooling process. On the other

Fig. 5. RT and high-temperature x-ray diffraction patterns recorded for the HEOX-30 h MS sinter while this material was being heated from room temperature and up to 1273 K.

Fig. 6. Lattice parameter a as a function of temperature in the HEOX-30 h MS sinter while this material was being heated and cooled over the range of RT–1273 K.

hand, when heating the sample, an anomaly in the plot representing the values of this lattice parameter can be observed in the temperature range between 773 K and 1073 K. This is associated with the phase reversal temperature, a phenomenon first observed by the authors of paper.¹¹ The thermal expansion coefficient of the HEOX-30 h MS sinter, determined based on the linear plot representing parameter a (corresponding only to cooling for the above-mentioned reasons), is equal to $13.4 \times 10^{-6} (\text{K}^{-1})$.

As an example, Fig. 7 shows the SEM micrograph of a fracture cross-section of the HEOX-30 h MS sinter. The presented sample was compact and featured a certain number of pores between the grains. The micrograph indicates that its grains had a fine-crystalline structure. The size of these grains ranged from 1 μm to 5 μm .

To further confirm the uniformity of the HEOX-30 h MS sinter, EDS mapping was performed. As can be seen from Fig. 8, no tendencies to segregate or form other phases were found.

There is a certain feature that is worth noting. Due to the presence of pores with varying size in the sample, the quantities of Co, Cu, Ni, Zn, Mg and O

seen in their distribution maps (Fig. 8) differ significantly, even though these elements were present in equimolar fractions. This stemmed from the differences in the energy of K-alpha emission lines observed for these elements.²⁹ The energy of Mg and O ($K_{\alpha}(\text{Mg}) = 1.254$ keV; $K_{\alpha}(\text{O}) = 0.523$ keV) is much lower than the energy of the remaining elements ($K_{\alpha}(\text{Co}) = 6.929$ keV; $K_{\alpha}(\text{Cu}) = 8.046$ keV; $K_{\alpha}(\text{Ni}) = 7.477$ keV; $K_{\alpha}(\text{Zn}) = 8.637$ keV), which is why the K-alpha emission of the former is unable to travel outside the majority of the pores. In the case, of Co, Cu, Ni and Zn, the situation is different. Their K-alpha emission escapes most pores in the sample—it can only be contained in the pores with the largest size.

Table III lists the values of total porosity as well as the apparent density measured for the HEOX-30 h MS and HEOX-100 h MS sinters after 10 h of sintering in air at 1273 K and the corresponding values of relative densities calculated using theoretical density established based on crystallographic data.

The presented data demonstrate that the HEOX-100 h MS sinter exhibits slightly higher density than the sample prepared from the powder that had undergone only 30 h of milling (HEOX-30 h MS). The porosity does not exceed 12% for either type of sample.

Since the porosities and phase compositions of the two investigated types of sinter samples were very similar, only the HEOX-30 h MS sinter obtained in the presented study was evaluated in terms of its electrical conductivity.

Figure 9 shows the temperature dependence of electrical conductivity (σ_m) for this sinter in an Arrhenius plot. The plot clearly shows that the electrical conductivity of the sample increases together with temperature, which is typical of a thermally activated process.

Fig. 7. SEM-COMPO and SEM-SEI micrographs of fracture cross-sections of HEOX-30 h MS sinter after 10 h of sintering in air at 1273 K.

Fig. 8. SEM micrograph of HEOX-30 h MS sinter after 10 h of sintering in air at 1273 K and EDS element maps of Co $K_{\alpha 1}$, Cu $K_{\alpha 1}$, Mg $K_{\alpha 1}$, Ni $K_{\alpha 1}$, O $K_{\alpha 1}$ and Zn $K_{\alpha 1}$.

Table III. Determined porosity and theoretical and relative density of the studied sinters after 10 h of sintering in air at 1273 K

Sinter	Theoretical density (g cm ⁻³)	Apparent density (g cm ⁻³)	Relative density (%)	Total porosity (%)
HEOX-30 h MS	6.002	5.29 ± 0.13	88.1	11.9
HEOX-100 h MS	6.037	5.41 ± 0.08	89.6	10.4

Fig. 9. Temperature dependence of electrical conductivity of the HEOX-30 h MS sinter after 10 h of sintering in air at 1273 K in an Arrhenius plot.

The conductivity of the HEOX-30 h MS sinter at 1148 K was equal to 8.03×10^{-2} S cm⁻¹. Moreover, a three-step course visible in the slope of the curves representing the dependence in the question can be noticed in the studied range; this effect is related to phase transformation rather than a change in the mechanism that determines electrical conductivity. This is confirmed by the high-temperature x-ray investigations shown in Fig. 6.

Another possibility that might be taken into account is that heating the material during electrical conductivity measurements causes phase separation due to the low compatibility of Zn²⁺ and Cu²⁺ with other elements. The Zn²⁺ and Cu²⁺ are more prone to form non-rock salt phases—Zn²⁺ in the tetrahedral coordination (the most stable co-ordination state for Zn in the oxide form, see Table I) has an ionic radius that differs significantly from those of the remaining elements, while Cu²⁺ is affected by Jahn–Teller distortion.^{16,20} After electrical conductivity measurements had been completed and the sample was cooled to room temperature, a single-phase rock salt structure was observed; this phase had a lattice parameter of $4.23515 (\pm 0.00011)$ Å.

The course of the conductivity vs. temperature dependence, which is linear in three temperature ranges, i.e. 478–641 K, 730–885 K and 990–1148 K,

Table IV. Activation energy of electrical conduction (E_a) for the HEOX-30 h MS sinter

Temperature range (K)	E_a (eV)
478–641	1.01 ± 0.01
730–885	0.91 ± 0.03
990–1148	0.62 ± 0.03

suggests the activated character of electrical conductivity in the investigated sinter, in accordance with the following equation:

$$\sigma_m = \frac{\sigma_o}{T} \exp\left(\frac{-E_a}{k \cdot T}\right) \quad (3)$$

where σ_m is specific conductivity (S cm⁻¹), σ_o is the pre-exponential factor, i.e. the material constant containing the carrier concentration term (S cm⁻¹ K), E_a is the activation energy of small polaron hopping (eV), k is the Boltzmann constant (eV K⁻¹), and T is absolute temperature (K).

Based on the linear dependencies presented in Fig. 7, the activation energy of electrical conductivity of the investigated sinter was calculated using Eq. 3. The results obtained for the three specified temperature ranges are shown in Table IV.

The available literature data^{30–32} suggests that the small polaron mechanism which involves pairs of Co²⁺/Co^{III} or Cu⁺/Cu²⁺ ions in the octahedral coordination may be responsible for conduction in the investigated sinter.

The contribution of iron contamination to electrical conductivity was ignored due to the negligibly low concentration of this element in studied sinter.

CONCLUSIONS

The mechanochemical synthesis (MS) technique was combined with the appropriate thermal treatment to obtain a fine, single-phase (Co,Cu,Mg,Ni,Zn)O solid solution samples with the desired chemical and phase compositions. XRD examinations of the powders prepared via either 30 h or 100 h of MS indicated the presence of a mixture of two phases of rock salt structure and a phase of a Co₃O₄-based solid solution; the latter was found even after the MS time and BPR had been

increased. After sintering the green bodies prepared from these powders for 10 h in air at 1273 K, the (Co,Cu,Mg,Ni,Zn)O high-entropy oxide in the form of a single-phase, solid solution with rock salt structure was obtained. SEM–EDS studies of the powders and sinters indicated the fine-crystalline structure of grains, with a uniform distribution of all elements. The porosity of the studied sinters did not exceed 12%. The electrical conductivity of the studied sinter based on the powder obtained after 30 h of MS was measured by means of EIS, in the temperature range of 478–1148 K in air. The three-step course of the temperature dependence of electrical conductivity suggests that the studied sample exhibits behavior typical of a thermally activated process, and it is related to the phase reversal temperature. The highest activation energy, which was equal to 1.01 eV, was observed for the lowest temperature range (478–641 K), whereas the lowest value of 0.62 eV was determined for the temperature range of 990–1148 K. The electrical conductivity of the (Co,Cu,Mg,Ni,Zn)O high-entropy oxide at the highest temperature at which measurements were performed (1148 K) was equal to $8.03 \times 10^{-2} \text{ S cm}^{-1}$.

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