High-Entropy Perovskites as Multifunctional Metal Oxide Semiconductors: Synthesis and Characterization of (Gd$_{0.2}$Nd$_{0.2}$La$_{0.2}$Sm$_{0.2}$Y$_{0.2}$)CoO$_3$

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ABSTRACT: Single-phase multicomponent perovskite-type cobalt oxide containing five cations in equiatomic amounts on the A-site, namely, (Gd$_{0.2}$Nd$_{0.2}$La$_{0.2}$Sm$_{0.2}$Y$_{0.2}$)CoO$_3$, has been synthesized via the modified coprecipitation hydrothermal method. Using an original approach for heat treatment, which comprises quenching utilizing liquid nitrogen as a cooling medium, a single-phase ceramic with high configuration entropy, crystallizing in an orthorhombic distorted structure was obtained. It reveals the anomalous temperature dependence of the lattice expansion with two weak transitions at approx. 80 and 240 K that are assigned to gradual crossover from the low- via intermediate- to high-spin state of Co$^{3+}$. The compound exhibits weak ferromagnetism at $T \leq 10$ K and signatures of antiferromagnetic correlations in the paramagnetic phase. Ab initio calculations predict a band gap $\Delta = 1.18$ eV in the ground-state electronic structure with the dominant contribution of O$_p$ and Co$_d$ orbitals in the valence and conduction bands, respectively. Electronic transport measurements confirm the negative temperature coefficient of resistivity characteristic to a semiconducting material and reveal a sudden drop in activation energy at $T \sim 240$ K from $E_a \sim 1$ eV in the low-temperature phase to $E_a \sim 0.3$ eV at room temperature. The possibility of fine tuning of the semiconducting band gap via a subtle change in A-site stoichiometry is discussed.

KEYWORDS: high-entropy oxides, hydrothermal synthesis, multicomponent equiatomic perovskites, quenching, antiferromagnetic semiconductor

1. INTRODUCTION

Development of new classes of materials with enhanced functional properties is the prerequisite for advances of many technologies, including chemical engineering, energy storage and conversion, data storage, and sensing technologies. The unprecedented progress in designing new classes of multicomponent alloys, that is, high-entropy alloys, stimulated original trends in the development of other classes of materials with high configuration entropy, especially oxides and fluorides. The first report on the successful synthesis of high-entropy oxides (HEOs) with a rocksalt structure formed from equimolar amounts of five transition metals was published in 2015 by Rost et al. In the following years, the concept was developed further by Djenadic et al., Bérandan et al., and Dąbrowa et al., who synthesized five rare-earth CaF$_2$-type oxides, five transition metals and lithium oxides, and transition metal spinel oxide, respectively. Recent studies reveal that a variety of multicomponent oxides systems with high configuration entropy can be produced, which possess remarkable electrical thermal catalytic or magnetic properties. This is why HEOs are considered as attractive functional materials for various fields, such as microelectronics, catalytic converters, and energy and data storage.

HEOs have drawn great attention as promising materials for the next generation of solid-state batteries. The high lithium and sodium ion mobility has been observed in HEOs composed of (MgCoNiCuZn)$_{1-x-y}$Ga$_x$A$_y$O (where A = Li and Na) because of high density of oxygen vacancies, which increases the number of percolation channels for easy cation diffusion. Li-containing high-entropy oxyfluoride (Li$_x$(Co$_{0.3}$Cu$_{0.2}$Mg$_{0.3}$Ni$_{0.2}$Zn$_{0.2}$)OF$_y$) is considered to act as a...
cathode material with superior cycling performance. The possible mechanism involves a reaction synergic effect from entropy-driven stabilization and the matrix Li-intercalation process. On the other hand, perovskite oxides with cobalt (cobaltites) exhibit relatively high oxygen ion conductivity. Cobaltites are considered as one of the most promising multicomponent conductive materials. They exhibit relatively high ionic and electron conductivity at medium and high temperature. Thus, there is high potential for the development of new types of electronic composite-type materials based on HEOs. It yields additional degrees of freedom for the design of advanced devices based on multifunctional (magnetic, ionic, and electronic) properties of perovskite oxides stabilized by high entropy.

Successful synthesis of perovskite-type HEOS was reported for the first time in 2018 by Sarkar et al.28 They obtained a series of multicomponent oxides of rare earth and transition metals with high configuration entropy, namely, multicomponent equiatomic perovskite oxides (ME-POs), employing the nebulized spray pyrolysis technique. ME-POs should be considered as a key idea for controlling electronic and magnetic properties of transition metal perovskite oxides, providing a means for subtle control of the B-site charge and orbital ordering by formation of electronic states. Cobalt exhibits di

2.2. Methods

2.2.1. Scanning Electron Microscopy—Energy Dispersive X-ray Spectrometer. The microstructure and elemental composition were studied using a FEI Versa 3D FEG scanning electron microscope equipped with a energy dispersive X-ray spectrometer (EDS) made by Amptek Corp.

2.2.2. X-ray diffraction. X-ray diffraction (XRD) studies were performed using a Empyrean PANalytical diffractometer equipped with a Cu Kα anode. Powdered samples were measured in Bragg–Brentano geometry. Low-temperature studies (15–300 K) were performed using an Oxford Instruments Phoenix closed-cycle helium refrigerator. The position of the sample stage was corrected against thermal displacement using a motorized stage, which was calibrated using a LaB6 standard sample.

2.2.3. Magnetic Properties. DC magnetic susceptibility was measured in the temperature range from 3 up to 300 K at a magnetic field of 100 mT using the vibrating sample magnetometer option of the quantum design physical property measurement system (PPMS-9). The isothermal magnetization profiles were acquired in an external magnetic field of up to 9 T.

2.2.4. Electronic Transport. The electric properties were measured using the magnetoresistance option of the LakeShore model 7407 magnetometry platform using the four-point (pin) constant-current method. Measurements were performed in a cryostat made by Janis Research in the temperature range from 225 up to 450 K.

2.2.5. Electronic Structure Calculations. The ab initio calculations were carried out based on density functional theory as implemented in the Vienna Ab initio Simulation Package (VASP). The electron-ion interaction was described by the projector-augmented wave method. The generalized gradient approximation with the Perdew–Burke–Ernzerhof functional was used to calculate the exchange–correlation energy. The valence electron configuration for O, Co, Y, La, Nd, Sm, and Gd atom was $2s^22p^4$, $3p^64s^24d^6$, $4s^24p^65s^24d^4$, $5s^25p^66s^25d^1$, $5s^25p^54f^46s^25d^1$, and $5s^25p^44f^65s^25d^1$, and the part played by strong electronic correlations, hybridization, and also charge and orbital interaction between electrons in occupied 3d orbitals. Thus, the physical properties of perovskite cobalt oxides are intimately connected with the existence of low-, high-, and intermediate-spin states. ReMeO$_2$ perovskites (Re = rare earth, Me = transition metals) have regained great interest since the discovery of the giant magnetoresistive effect and high-temperature superconductivity. Contrary to commonly described superconductors, the rare earth transition metal perovskites exhibit robust oxygen stoichiometry in a wide range of temperatures. Most of the known compounds of the ReMeO$_2$ family reveal temperature-induced metal-to-insulator transition accompanied by the vanishing long-range magnetic order.

In this paper, we describe an original and efficient method for the synthesis of the high-entropy multicomponent perovskite-type oxide of (Gd$_{0.2}$Nd$_{0.2}$La$_{0.2}$Sm$_{0.2}$Y$_{0.2}$)CoO$_3$ composition and report on its structural, magnetic, and electronic transport properties. Based on the previous explanation, we focus on electrical and magnetic properties of the obtained multicomponent perovskite oxide and its possible application in electronic devices.

2. MATERIALS AND METHODS

2.1. Synthesis. The ceramics were synthesized using a modified coprecipitation hydrothermal method. The nitrate salts of yttrium Y(NO$_3$)$_3$$\cdot$6H$_2$O (99.9%), lanthanum La(NO$_3$)$_3$$\cdot$6H$_2$O (99.9%), neodymium Nd(NO$_3$)$_3$$\cdot$6H$_2$O (99.9%), samarium Sm(NO$_3$)$_3$$\cdot$6H$_2$O (99.9%), gadolinium Gd(NO$_3$)$_3$$\cdot$6H$_2$O (99.9%), and cobalt Co(NO$_3$)$_2$$\cdot$9H$_2$O (99.9%) were used to prepare two aqueous solutions of the Y:La:Nd:Sm:Gd:Co cation system in 0.2:0.2:0.2:0.2:0.2:1 M ratio. Two different routes of hydrothermal synthesis were adopted. The first labeled RCO$_3$ (R = Gd$_{0.2}$Nd$_{0.2}$La$_{0.2}$Sm$_{0.2}$Y$_{0.2}$Y$_{0.2}$; (C = Co, O = O$_3$, S = NaOH pptm.) was precipitated with sodium hydroxide solution. The second labeled RCO$_4$ (R = Gd$_{0.2}$Nd$_{0.2}$La$_{0.2}$Sm$_{0.2}$Y$_{0.2}$Y$_{0.2}$; (C = Co, O = O$_3$, A = NH$_4$OH pptm.) was obtained using ammonia solution as a precipitate agent. Both samples of substrates have been mixed in 30 mL of deionized water, using a magnetic stirrer for 30 min at 50°C. A total of 10 mL of 3.5 M NaOH was added to RCO$_3$ during continuous mixing, leading to precipitation of sapphire-color suspension, whereas the RCO$_4$ was precipitated with 15 mL of 25% ammonia solution. The gelatinous coprecipitates were transferred to Teflon vessels with addition of 10 mL of deionized water, then sealed, and placed in separate stainless-steel pressure vessels for hydrothermal treatment. The hydrothermal synthesis was carried out for 72 h at 150°C under autogenous pressure in order to allow complete substrate recrystallization and homogenization. After that, the RCO$_3$ precursor was filtered, diluted in 150 mL of deionized water, and repeatedly centrifuged for 10 min at 1500 rpm. The RCO$_4$ precursor has not been subjected to any unit operations aimed at removing ammonia cations. Finally, both precursors were dried for 48 h at 50°C in an oven.

Subsequently, synthesized powders were prepared for high-temperature calcination. The powders were pressed into a form of thin pellets (less than 1 mm thickness). Based on previous experiments, the conditions for heat treatment were optimized, that is, the pellets were heated up to 1200°C and kept at this temperature for 2 h in an air atmosphere. Afterward, pellets were quenched in liquid nitrogen, that is, they were rapidly moved to a vessel filled with liquid nitrogen in order to prevent possible crystallizing of spurious phases during slow cooling. For the sake of comparison, we have also prepared a RCO$_3$ sample labeled as RCO$_3$, which was cooled in air under ambient conditions.

2.1.1. X-ray diffraction (XRD). X-ray diffraction (XRD) studies were performed using a Rigaku SmartLab X-ray diffractometer equipped with a Cu Kα anode. Powdered samples were measured in Bragg–Brentano geometry. Low-temperature studies (15–300 K) were performed using an Oxford Instruments Phoenix closed-cycle helium refrigerator. The position of the sample stage was corrected against thermal displacement using a motorized stage, which was calibrated using a LaB6 standard sample.

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5s^25p^64f^56s^25d^1, respectively. Based on the Pnma symmetry, the 1 x 5 x 1 supercell, containing 60 atoms of oxygen and 20 atoms of cobalt, was constructed. The four atoms of yttrium, neodymium, samarium, lanthanum, and gadolinium were randomly distributed in nodes (A-sites). The Γ-centered 3 x 1 x 3 mesh of k-points was used for sampling the Brillouin zone. The energy cut-off was set to 500 eV. The structure relaxation was carried out until the forces acting on each atom reached 0.04 eVÅ⁻¹. The density of state (DOS) computations were performed with the Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional.41–43

3. RESULTS AND DISCUSSION

3.1. Structural Characterization. Considering the general perovskite formula ABO₃, we have selected yttrium and four rare earth cations in equiatomic amounts, which are intended to fill the A-site (A = Y, La, Nd, Sm, and Gd), while the B-site is intended to be filled uniquely with cobalt to form the (Gd₀.₂Nd₀.₂La₀.₂Sm₀.₂Y₀.₂)CoO₃ phase. One of the main factors for stabilization of the single-phase structure in multicomponent systems is maximization of configuration entropy. Yeh¹ attributed values of configuration or mixing entropy to random solid solution containing several, different elements. In the Gibbs free energy equation, \( \Delta G = \Delta H - T \Delta S \), increasing entropy (\( \Delta S \)) introduces a contribution, which decreases \( \Delta G \) and stabilizes the single-phase structure in the multicomponent oxides or metallic system. It leads to a general equation for determining mixing entropy (eq 1).

\[
\Delta S_{\text{mix}} = -R \sum_{i=1}^{N} c_i \ln c_i
\]  

(1)

where \( R \) is the ideal gas constant, \( N \) is the number of elements or components, and \( c_i \) is the atomic fraction of the component \( i \). It is noticeable that there are several definitions describing entropy-stabilized materials; the term “high entropy” is used further to emphasize a high value (specifically over 1.5R per mole, where \( R \) is the universal gas constant) of configuration entropy in a multicomponent solid solution.35 For the 6-cationic system reported here, the configuration entropy calculated using eq 1 is equal to 1.61R (0.0134 K·mol⁻¹·K⁻¹).¹⁹

Morphology and uniformity of the elemental distribution in the two types of (Gd₀.₂Nd₀.₂La₀.₂Sm₀.₂Y₀.₂)CoO₃ ceramics studied, namely, RCO₃ and RCO₄, as derived by scanning electron microscopy (SEM)-EDS are illustrated in Figure 1. SEM imaging shows a homogenous distribution of few-micrometer-diameter grains, without any visible traces of foreign phases on a large area of ceramics. EDS data were collected from 20 randomly distributed points for each of the samples. The average composition obtained from such analysis is given in Table 1. It supports the expected chemical composition in both RCO₃ and RCO₄ samples. The deviation from the nominal formula is within the accuracy of the technique, which is of the order of a few percent for such a complex chemical composition.

XRD patterns of the as-synthesized powders obtained by different chemical and thermal treatments are presented in Figure 2. All the peaks for both samples quenched in liquid nitrogen (RCO₃ and RCO₄) correspond to the perovskite structure and no significant difference between XRD patterns for samples precipitated with sodium hydroxide and ammonia solution has been observed. However, closer inspection of XRD patterns reveals some contribution to the background, originating likely from the nanostructural Re₂O₃ phase(s) precipitated at grain boundaries. The most intense 222 reflection of Re₂O₃ phases is expected at 28.9–29.1° of 2θ. The Rietveld refinement unveils some minor changes in lattice parameters, as gathered in Table 2.

On the other hand, the XRD pattern of the RCO₃ sample (quenched in air) reveals rich multiphase composition with large background, indicating structural disorder. The RECoO₃ and RE₂O₃ precipitations were recognized. For this sample, only La Bail refinement was successful, revealing significant decrease in lattice parameters in comparison to the above discussed cases. This is likely a sign of the nonstoichiometry of the specimen and confirms that the modification of the final cooling rate introduced to the synthesis procedure is crucial for obtaining single-phase ME-PO ceramics of the (Gd₀.₂Nd₀.₂La₀.₂Sm₀.₂Y₀.₂)CoO₃ system via coprecipitation using ammonia solution. The reason for the presence of more than one phase in the sample quenched in air (RCO₄) is likely related to a low cooling rate (estimated as 20 °C·min⁻¹). Hence, thermodynamically favorable phases, stable at room temperature, might occur because of free crystallization.

In Figure 3, the Rietveld refinement of the XRD pattern of the RCO₃ sample is presented. The sample exhibits a desired Pnma space group (no. 62) with small (less than 4%) precipitation of the RE₂O₃ (RE = Gd, Nd, La, Sm, and Y) phase crystallizing with the Ia₃ space group (no. 206). Parameters of the lattice and structural positions refined from the pattern collected at T = 300 K are shown in Table 2.

The temperature dependence of the lattice parameters is presented in Figure 4. Remarkably, the unit cell is nearly unchanged from 20 K up to approx. 80 K. Then, the volume is expanding slightly but only in \( a \) and \( c \) directions, which indicates strongly the anisotropic behavior of RCO. Expansion along a direction becomes significant above 200 K. Besides, \( a \) and \( c \) parameters also show a weak anomaly around 150 K (see
dependence of isothermal magnetization process and thus a lack of sudden structural phase transitions, which for good accommodation of such deformation by the lattice can be seen at 125 K. This feature is likely related to the onset of aforementioned changes in other lattice parameters taking place at around 150 K. Such complex but gradual evolution of the unit cell volume (Figure 4d). An additional anomaly for a low value of $H_{C}$ to be preferable for Co3+ and t2g 0 with spin 0 with the spin S = 1/2 to be preferable for Co3+ and t2g 0 with spin 0 with the spin S = 1/2 to be preferable for the Co4+ ion ground state, which is called low magnetic response is observed at $T = 10$ K and below, which is indicated by opening of a weak hysteresis. Coercive field probed at $T = 3$ K is $H_{C} \sim 0.3$ mT (inset in Figure 5). Such a low value of $H_{C}$ along with a small remanence-to-saturation ratio indicates the soft nature of this ferromagnetic phase. Based on the XRD measurements, which reveal the presence of a low amount (<4% at.) of RE2O3 precipitates, we attribute the ferromagnetism emerging below 10 K to nanosized precipitates of Gd2O3.46

Magnetic interactions in RCoO3 systems usually originate in mixed-valence-related double-exchange-like interactions between cobalt ions in the neighboring octahedral through a common nonmagnetic oxygen ion (Co=O−Co), where (Co3+−O2−−Co4+) or (Co3+−O2−−Co3+) pairs exhibit ferromagnetic or antiferromagnetic coupling, respectively. However, at the lowest temperature, the crystal field acting on a single CoO octahedron splits the 3d orbitals into two $e_g$ and three $t_{2g}$ degenerate levels, as shown in the Figure 6. The 3d shell of the ion contains six (five) electrons for Co3+ (Co4+). At high crystal field, Hund’s rule suggests the $t_{2g}$ configuration with spin S = 0 to be preferable for Co3+ and $e_g$ configuration with the spin S = 1/2 to be preferable for the Co4+ ion ground state, which is called low
At decreasing crystal field splitting, increasing Zeeman field (exchange coupling), and lowering of the crystal field symmetry or increasing temperature, it may transform to the configuration \( t_{2g}^5 e_{g}^1 \) with the spin \( S = 1 \) and \( t_{2g}^4 e_{g}^1 \) with \( S = 3/2 \) for the Co\(^{3+}\) and Co\(^{4+}\) ions (intermediate-spin states—IS), respectively.

Ultimately, when crystal field splitting is negligible with respect to Zeeman splitting or thermal energy, the \( t_{2g}^4 e_{g}^2 \) electronic configuration with the spin \( S = 2 \) for Co\(^{3+}\) and \( t_{2g}^3 e_{g}^2 \) with the spin \( S = 5/2 \) for Co\(^{4+}\) (the high-spin state—HS) are observed. Different magnetic states of the cobalt ion give rise to the unique transport and magnetic properties of LaCoO\(_3\) and related compounds. In the case of oxygen deficiency or substitution of divalent cations into the A-site, the appearance of Co\(^{4+}\) ions in the B-site may lead to the weak ferromagnetic coupling.
Figure 7 depicts the temperature dependence of DC magnetic susceptibility $\chi(T)$ and the reciprocal magnetic susceptibility $\chi^{-1}(T)$. Therefore, the modified Curie–Weiss law should be considered to describe the $\chi^{-1}(T)$ curve

$$\chi = \frac{C}{T - \theta_C} + \chi_0$$

where $C$ is the Curie constant, $\theta_C$ is the paramagnetic Curie temperature, and $\chi_0$ is the temperature-independent van Vleck and diamagnetic contributions.

The decreasing value of the reciprocal susceptibility suggests that the Curie constant is variable and is increasing with temperature. Having in mind that the Curie constant is proportional to the effective magnetic moment of the ensemble of magnetic ions, such behavior may be rationalized by the gradual increase in the effective magnetic moment of Co$^{3+}$ expected for the transition from LS (via IS) to HS electronic configuration in analogy to LaCoO$_3$.

Fitting of the modified Curie–Weiss law to experimental data reveals following parameters: $\theta_C = -1.24(1)$ K; $\mu_{\text{eff}} = 3.801(1) \mu_B$ and $\chi_0 = 0.0011(1)$ emu/(Oe·g). The negative value of paramagnetic Curie temperature indicates the dominance of antiferromagnetic correlations between magnetic ions. The obtained small value of $\theta_C$ nicely corresponds to equivalent parameters probed in rare earth cobalt oxides, that is, $\theta_C = -1.25$, $-1.50$, and $-3.1$ K for NdCoO$_3$, SmCoO$_3$, and GdCoO$_3$, respectively. The orthorhombic perovskite YCoO$_3$ shows a nonmagnetic behavior, indicating the low-spin state of the Co$^{3+}$ ion. The observed effective magnetic moment $\mu_{\text{eff}} = 3.801(1) \mu_B$ can be deconvoluted into rare earth and Co contributions. Assuming that all rare earth ions are trivalent, the corresponding magnetic moment yields $2.482 \mu_B$. If one considers that the lanthanides and Co moments are uncoupled, the value of $1.318 \mu_B$ per Co ion is expected. This value is significantly lower than $2.83 \mu_B$ expected for Co$^{3+}$ at IS spin configuration ($S = 1$). This could be explained by the coexistence of Co$^{3+}$ LS and IS spin configurations.

It is thus evident that magnetic properties of (Gd$_{0.2}$Nd$_{0.2}$La$_{0.2}$Sm$_{0.2}$Y$_{0.2}$)CoO$_3$ reveal a mixture of magnetic properties of individual ReCoO$_3$-like phases existing in its composition. Therefore, transport and magnetic properties of such perovskite-type cobalt oxides are dependent upon the competition between local exchange coupling energy and crystal field splitting energy. However, the detailed description of all the possible magnetic phases involved in the formation of a weak ferromagnetic ground state, which likely involves exchange interactions between rare earth cations as well, is beyond the scope of this paper.

When we compare the same composition made using the nebulized spray pyrolysis technique with heat treatment from the Witte group, the magnetic properties are similar to those of our sample. The composition shows a Curie-like paramagnetic behavior at all measurement temperature range. The only difference is in the hysteresis loop because in our case, at 3 K, we have an open loop, which may indicate a small amount of Gd$_2$O$_3$ in our sample.

3.3. Electronic Transport. Four-point resistance was probed at the temperature varied from 225 to 450 K. The results are presented in an Arrhenius-type plot shown in Figure 8. It reveals two regimes in electronic conductivity, which are characterized by significantly different activation energies. The activation energy was calculated using the Arrhenius equation given by

$$\frac{1}{R} = \frac{1}{R_0} \exp \left( \frac{-E_a}{2k_BT} \right)$$

where $R(T)$ is the resistance at different temperatures, $R_0$ is the resistance at 0 K, $E_a$ is the activation energy, and $k$ is the Boltzmann constant.

The resistivity close to 240 K changes the value from 0.5 MΩ to 5 kΩ; it is changed by $10^2$ factor. At 229 K, the resistivity is close to 5 MΩ, while at a temperature of 450 K, we observe it at the level of a few ohms.

The linear fitting, which resulted from the Arrhenius equation, is depicted in Figure 8. The activation energy fit to the high-temperature data (violet line) results in $E_a = 0.336$ eV, while the fit to low-temperature data (red line) provides $E_a = 0.995$ eV. The relatively sharp transition between these two regions corresponds to $T = 240$ K. It is the temperature above which a lattice constant is variable. This is why we expect that the semiconductor-to-semiconductor transition is related to the evolution of the electronic structure related to structural distortion.

The resistivity of LaCoO$_3$-based compounds is strongly dependent on the composition and the magnetic state of A-site cations. For instance, LaCoO$_3$ has a very weak anomaly of resistivity, against the low-temperature anomaly of magnetic susceptibility that is observed around 100 K. The activation energy is approx. 0.2 eV. Also, the value of the activation...
energy near room temperature observed in some other rare earth cobalt oxides nicely corresponds to that derived in our study, for example, $E_a = 0.272$ and $0.039$ eV for GdCoO$_3$ and NdCoO$_3$, respectively. The substitution of La with other rare-earth elements in LnCoO$_3$ causes the mixed-valence Co$^{3+}$/Co$^{4+}$ and consequently dramatically changes the activation energy and causes strong modification of the temperature of metal−insulator transition in a wide temperature range from a few K to 1000 K. Transitions observed in LaCoO$_3$ (385–570 K) and YCoO$_3$ (575–850 K) exhibit a second-order semiconductor-to-metal transition, in contrast to NdCoO$_3$, which exhibits a sharp first-order semiconductor-to-semiconductor transition at 342 K. However, the origin of metal−insulator transition and spin state transition around 500–600 K in LaCoO$_3$ is still a matter of discussion. Most of the studies suggest a fully high-spin state above the metal−insulator transition. We expect that fine tuning of the A-site stoichiometry in the rare earth cobalt MCPO provides a convenient platform for the effective modification of the value of the activation energy and temperature of phase transitions, which is crucial in terms of possible applications. Large change in resistance can be used to define logic 0 (low resistance above 240 K) and logic 1 (high resistance below 240 K).

### 3.4. Electronic Structure Calculations

In order to determine the structural and electronic properties of the (Gd$_{0.2}$Nd$_{0.2}$La$_{0.2}$Sm$_{0.2}$Y$_{0.2}$)CoO$_3$ ground state, the ab initio calculations were carried out. The result of full structural optimization, performed for the elementary cell $(1 \times 5 \times 1)$, indicates the orthorhombic structure, which distorted and tilted the oxygen octahedron (Figure 9a). The obtained lattice constants $a$, $b$, and $c$ are equal to 5.75, 7.37, and 5.01 Å, respectively.

The calculated total DOS (grey area on Figure 9b) proves the semiconducting character of the compound. The value of 1.18 eV of energy gap ($E_g$) between the valence band maximum (VBM) and conduction band minimum is observed. The inset shows magnification of the DOS region around Fermi energy ($E_F$). It is noteworthy that the conduction bands are composed of two distinct regions (labeled I and II), separated by a small gap of 0.17 eV. The summed contributions of particular chemical elements, marked by different colors, demonstrate that the majority of the valence and conduction bands originate from O and Co atoms, whereas in the whole considered energy range, the role of Y and La atoms is on the negligible level. To determine the contribution of valence electrons of particular elements to the DOS structure, the orbital-projected DOS (PDOS) distribution was calculated. The appropriate results, presented in Figure 9c, indicate that the low-energy part of the valence band is composed of O_p and Co_d orbitals with 60 and 30% average contribution, respectively. However, the increase in energy results in a slow decrease of those orbitals contribution and simultaneous growth of the impact of Nd_f, Sm_f, and...
The measurements and ab initio calculations result in nice agreement of the semiconducting band gap at low temperature, which can be approximated close to $\Delta = 1.2$ eV. As shown by theoretical calculation, the electronic structure of the RCO is additionally narrow. In view of low DOS at the bottom of the conductive band, one could expect that electronic transport in such a complex material will be shaped by the Moss Burstein effect occurring in degenerate doping semiconductors. However, this effect rationalizes the increase in the effective band gap upon complete filling of the in-gap states. In the case of $\text{CoO}_3$ we observe the opposite effect—the reduction in the band gap at increasing temperature. As such, the effect must be related either to electronic delocalization (Mott-like transition) or to remodeling of the electronic structure caused by increased spin state degeneracy of Co$^{3+}$ ions. Because our ab initio calculation could only be made at 0 K, the more sophisticated method, which includes electronic correlations, need to be employed in order to understand the origin of the transition observed.

4. CONCLUSIONS

We present a successful synthesis of multicomponent rare earth perovskite cobalt oxide (Gd$_{0.2}$Nd$_{0.2}$La$_{0.2}$Sm$_{0.2}$Y$_{0.2}$)CoO$_3$, via the modified coprecipitation hydrothermal method with quenching in liquid nitrogen. Structural, electronic, and magnetic properties of the obtained ME-PO system have been investigated experimentally and theoretically.

The major conclusions are as follows:

i The method for the synthesis of multicomponent perovskite in the (Gd$_{0.2}$Nd$_{0.2}$La$_{0.2}$Sm$_{0.2}$Y$_{0.2}$)CoO$_3$ system was developed. The method involves fast quenching of ceramic powders in liquid nitrogen medium. XRD analysis confirms that the occurrence of secondary phases and amorphous structures is related to the speed of quenching.

ii XRD and ab initio structural investigations indicate a distorted orthorhombic structure of (Gd$_{0.2}$Nd$_{0.2}$La$_{0.2}$Sm$_{0.2}$Y$_{0.2}$)CoO$_3$ perovskite oxide.

iii Magnetic properties of (Gd$_{0.2}$Nd$_{0.2}$La$_{0.2}$Sm$_{0.2}$Y$_{0.2}$)CoO$_3$ show gradual spin state transition from LS to HS for Co$^{3+}$ ions. The magnetic behavior of the compound shows a mixture of different magnetic properties, characteristic to rare earth perovskite cobalt oxides (paramagnetic, antiferromagnetic, and weak ferromagnetic) at low temperature down to 10 K.

iv Electronic transport measurements indicate phase transition at $T \sim 240$ K, from a medium (1 eV, below 240 K) to narrow (0.33 eV, above 240 K) band gap semiconductor.

v The calculation of the electronic structure and electronic transport indicates a semiconducting character with a low-temperature band gap of approx. 1.2 eV at low temperature and 0.2 eV at higher temperature.

vi Based on these findings, we expect that fine tuning of cationic stoichiometry in high-entropy cobalt oxides may be used to optimize the value of activation energy and temperature of phase transition in a wide range required by the different applications of perovskite cobalt oxides. Substantial change in resistance can be used to de-
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