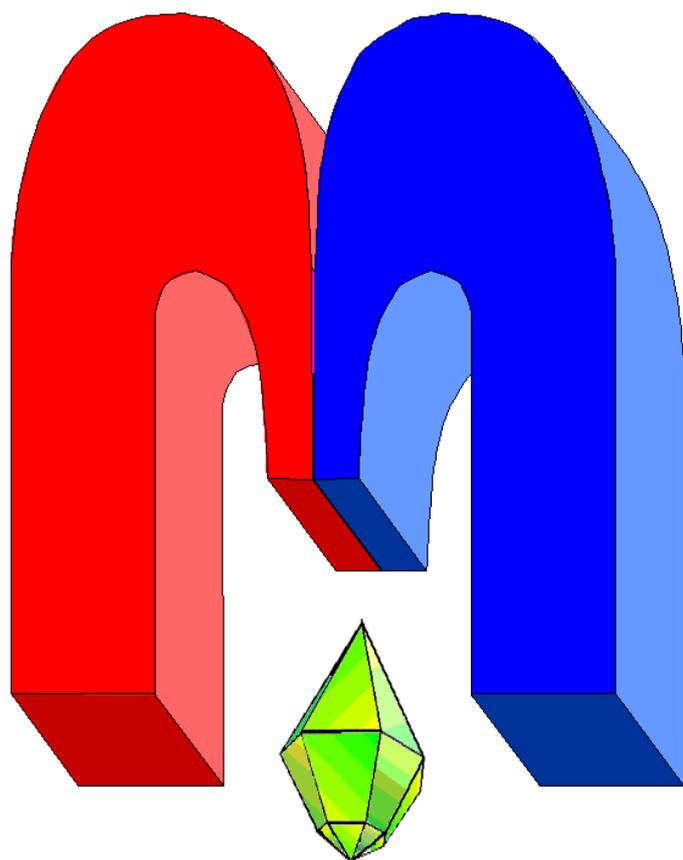


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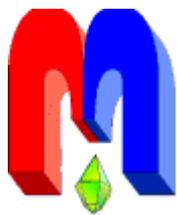
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# High-entropy oxide $\text{Mg}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2}\text{O}$ : synthesis, X-ray diffraction and Mössbauer studies<sup>†</sup>

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High-entropy oxide  $\text{Mg}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2}\text{O}$  was successfully synthesized. Using X-ray diffraction analysis, it was found that the sample has a single-phase composition with the NaCl-type face-centered cubic structure and the lattice constant of 4.22 Å. The sample was studied using Mössbauer spectroscopy at temperatures from 80 K to 295 K. It was determined that the relative content of divalent and trivalent iron ions in the sample is 67% and 33%, respectively. Based on the temperature dependence of the hyperfine magnetic field on  $^{57}\text{Fe}$  nuclei, the magnetic transition temperature was determined to be 201 K.

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**Keywords:** high-entropy oxide, X-ray diffraction analysis, Mössbauer spectroscopy

## 1. Introduction

High-entropy oxides (HEOs) are solid solutions consisting of five or more ions of different chemical elements in the cation sublattice in proportions close to equiatomic [1]. Due to the mixing of a large number of chemical elements in the HEO, the value of the configurational entropy prevails over the enthalpy of mixing, which leads to the formation of a single-phase structure. In this case, each of the ions occupies any sublattice site with equal probability, thereby forming a solid solution. As a result, the material exhibits unusual properties.

The development of high-entropy oxides began in 2015 with the pioneering study by C. Rost of a complex five-component material based on the oxides CoO, CuO, MgO, NiO, and ZnO [2]. Later, high-entropy nitrides [3], sulfides [4], carbides [5,6], borides [7,8] and silicides [9] were synthesized. However, HEOs remain the most actively studied kind of high-entropy ceramics. It was found that HEOs have improved mechanical properties, amorphous-like thermal conductivity, colossal permittivity, catalytic activity and superionic conductivity [10,11]. Nevertheless, this is only part of the functional properties of HEOs and many of their characteristics are relatively poorly studied. Such characteristics include the magnetism of HEOs.

One of the first studies in this area was presented in the work [12], where the role of composition and disorder in the exchange anisotropy of entropy-stabilized oxide heterostructures was investigated. The magnetism of high-entropy perovskites with the general structural formula  $\text{ABO}_3$ , where A is any element of the rare earth ions and B is any element of the transition metal ions, has been studied [13]. The results of magnetometry and Mössbauer spectroscopy indicated a complex magnetic state, in which antiferromagnetic interactions mainly dominate. A nanocrystalline powder of the spinel type  $(\text{CoCrFeMnNi})_3\text{O}_4$  was synthesized, and the ferromagnetic behavior of the samples was found at room temperature [14]. It was also found that crystallinity, crystal size, lattice constant and lattice distortion strongly affect the magnetic

<sup>†</sup>This paper was selected at the International Conference devoted to the 80th anniversary of the discovery of Electron Paramagnetic Resonance “Magnetic Resonance – Current State and Future Perspectives” (EPR-80), September 23-27, 2024, Kazan, Russia. The guest Editor, Prof. M.R. Gafurov, was responsible for the publication, which was reviewed according to the standard MRSej procedure.

properties of the nanopowder. However, they can be easily changed by controlling the synthesis temperature. The transition from the paramagnetic to the long-range antiferromagnetic state was discovered in  $(\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$  HEO with a rock salt structure [15, 16]. Also local deviations from the antiferromagnetic order were observed, which is expected for such a disordered system. In addition, the authors note the very low values of the coercive force  $H_c$  and residual magnetization  $M_r$  of the material, which makes it promising for applications in spintronics and random access memory applications [16]. Several  $(\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$  HEOs with a rock salt structure, doped with additional impurity elements, were studied. It was found that all of the studied materials, depending on the number of magnetic ions, exhibit long-range antiferromagnetic ordering under cooling or are in a spin glass state [17]. At the same time, the authors point out that, there is the possibility of controlling the dielectric properties through magnetodielectric coupling, because these materials show colossal dielectric properties as well.

Here, we present the results of the synthesis and characterization of  $\text{Mg}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2}\text{O}$  HEO with the NaCl-type crystal structure. The crystal structure of the obtained material was investigated. The Mössbauer hyperfine parameters as well as the critical temperature of magnetic transition were determined.

## 2. Experimental details

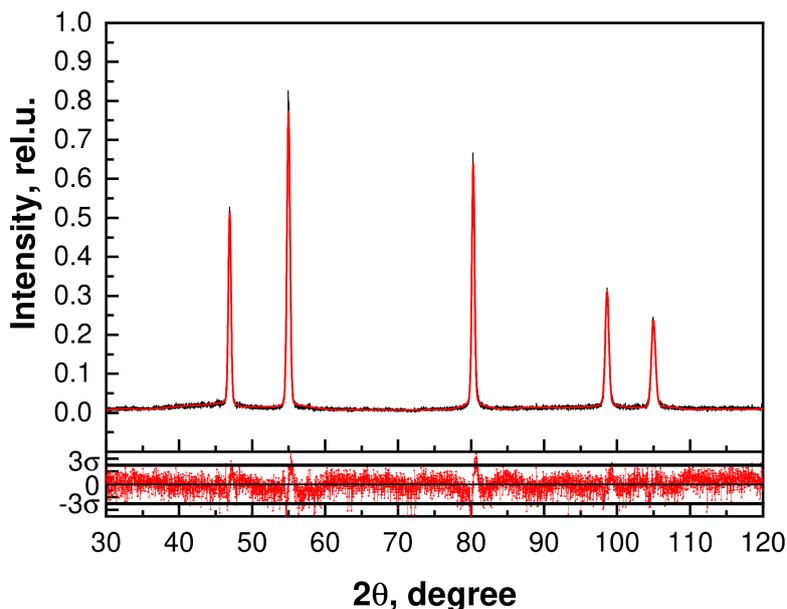
The oxides MgO (purity 97%), CoO (99%), NiO (99%), ZnO (99%) and  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  (99%) in powder form were used for the synthesis. These powders were weighed in stoichiometric proportions relative to the cations. The resulting mixture was thoroughly ground in an agate mortar for 2.5 hours. The obtained powder was then pressed into pellets weighing  $\sim 500$  mg under uniaxial pressure of  $\sim 1400$  atm for 15 minutes. The pellet was annealed in a horizontal tube furnace for 1 hour at temperature of  $1070^\circ\text{C}$  in a nitrogen flow. Then, the sample was cooled down to room temperature for  $\sim 5$  minutes by moving it out of the heating zone. The annealed pellet was then thoroughly ground in an agate mortar to a fine powder for subsequent study.

The phase composition and crystal structure of the synthesized samples were studied by powder X-ray diffraction (XRD), using MD-10 diffractometer (Radikon) operating in the Debye-Scherrer scheme with Fe- $K_\alpha$  radiation tube ( $\lambda = 1.93728 \text{ \AA}$ ). The study was carried out at  $2\theta$  angle range from  $20^\circ$  to  $130^\circ$ . Qualitative phase analysis of the diffraction patterns was performed using the QualX2.0 program [18].

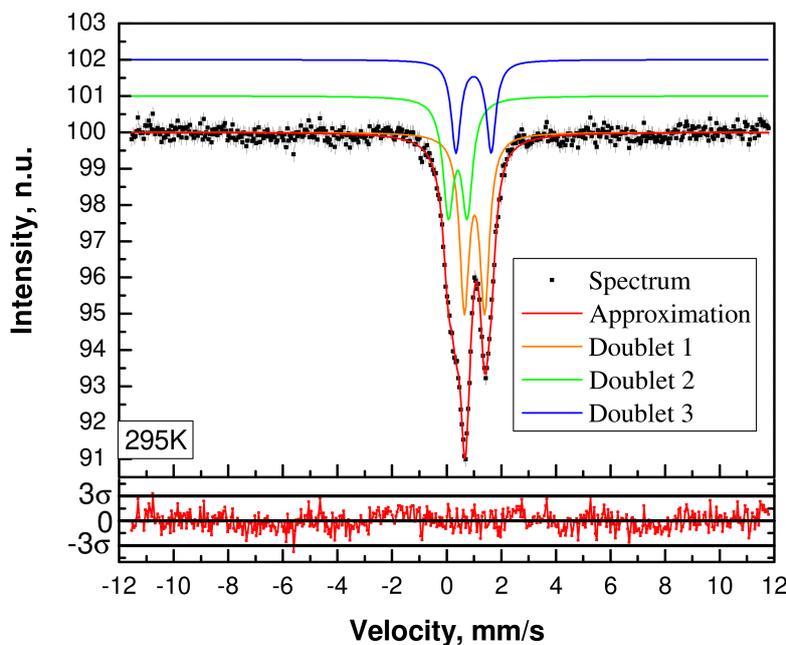
Mössbauer studies were conducted to investigate the hyperfine interactions on  $^{57}\text{Fe}$  nuclei in the sample. The measurements were carried out on the conventional spectrometer from WissEl (Germany), operating in the constant acceleration mode. The nuclide  $^{57}\text{Co}$ (Rh) with an activity of 50 mCi was used as a source of resonance photons. The spectrometer velocity scale was calibrated using the spectrum of thin  $\alpha$ -Fe foil. The isomer shift values were determined relative to the  $\alpha$ -Fe spectrum at room temperature. Low-temperature measurements were carried out in the helium flow cryostat (CFICEV, ICEOxford) at temperatures of 80 K, 160 K, 200 K, 235 K, 270 K, and 295 K. Temperature stabilization was performed using a temperature controller (Model 32B, Cryo-Con) with an accuracy of  $\pm 1$  K. Experimental spectra were processed using the SpectrRelax 2.0 software [19].

## 3. Results and Discussion

The X-ray diffraction pattern of the synthesized sample is shown in Figure 1. The diffraction pattern of the sample shows only reflections related to the NaCl-type face-centered cubic (FCC)



**Figure 1.** The XRD pattern of the synthesized sample



**Figure 2.** Mössbauer spectrum of the synthesized HEO sample at room temperature

crystal structure (space group  $Fm-3m$ ) with a lattice parameter of  $4.22 \pm 0.01 \text{ \AA}$ . The reflections of the starting materials as well as other impurity phases were not observed.

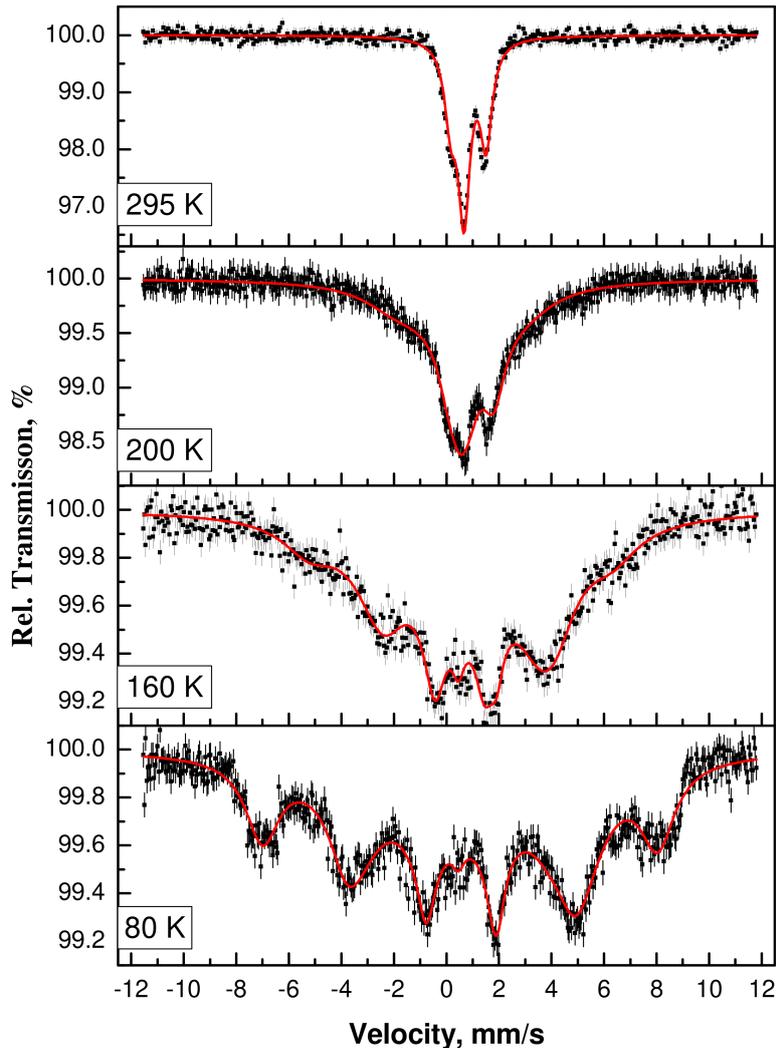
Figure 2 shows the Mössbauer spectrum of the sample, recorded at room temperature. The spectrum was processed by three doublets. The Mössbauer hyperfine parameters of these components, obtained by fitting the experimental spectra, are listed in Table 1. The hyperfine parameters of the first doublet correspond to high-spin trivalent iron ions in an octahedral oxygen environment, whereas the parameters of the second and third doublets allow us to relate these components with high-spin divalent iron ions in the same environment. The relative areas of the divalent and trivalent components of the spectrum are 67% and 33%, respectively. The Mössbauer hyperfine parameters in our study were compared with the values

**Table 1.** Parameters of the model components of the Mössbauer spectrum of the sample.

	Doublet 1	Doublet 2	Doublet 3
Isomer shift, mm/s	$0.41 \pm 0.01$	$0.99 \pm 0.01$	$1.02 \pm 0.01$
Quadrupole splitting, mm/s	$0.69 \pm 0.01$	$1.29 \pm 0.01$	$0.74 \pm 0.01$
Relative area, %	$33 \pm 1$	$23 \pm 1$	$44 \pm 1$
Local environment	$[Fe^{3+}O_6]$	$[Fe^{2+}O_6]$	$[Fe^{2+}O_6]$

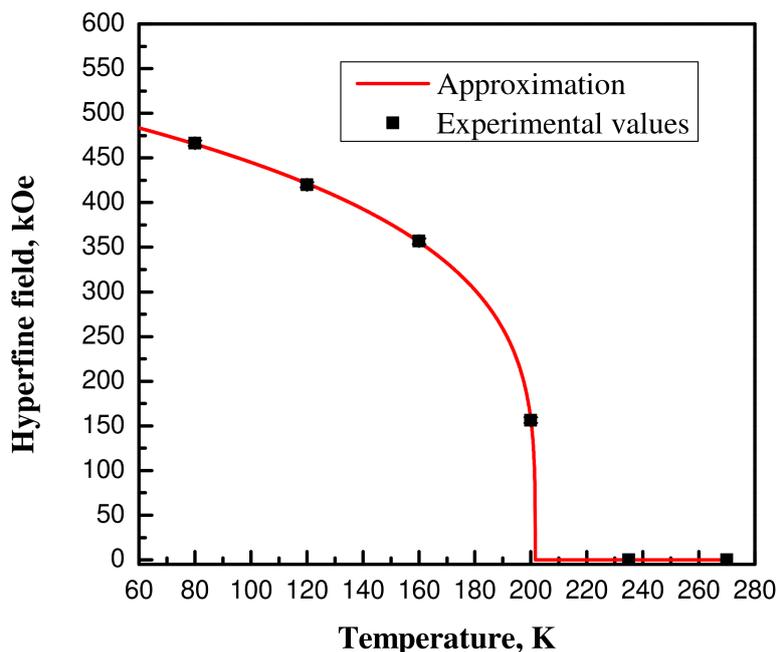
for the  $Mg_{0.2}Co_{0.2}Ni_{0.2}Fe_{0.2}Mn_{0.2}O$  HEO sample [20]. These HEOs have a very similar chemical composition and the same crystal structure, so it is expected that the hyperfine parameters of the Mössbauer spectra components will have close values. Indeed, the spectral parameters are quite close, which indicates the effectiveness of the method we used for synthesizing the high entropy oxide  $Mg_{0.2}Co_{0.2}Fe_{0.2}Ni_{0.2}Zn_{0.2}O$  with a rock salt structure.

Figure 3 shows the spectra obtained at temperatures of 295 K, 200 K, 160 K and 80 K. It is seen that with the temperature decrease magnetically ordered component onset in the spectrum. The appearance of the magnetic component of the spectrum, and the further growth of its



**Figure 3.** Selected Mössbauer spectra of the synthesized sample measured at different temperatures

relative area indicate the transition of Fe ions from a paramagnetic to the magnetically ordered state.



**Figure 4.** The temperature dependence of the hyperfine magnetic field on  $^{57}\text{Fe}$  nuclei

The temperature dependence of the hyperfine magnetic field on iron nuclei is shown in Figure 4. This dependence was approximated using the expression  $H = H_0 \cdot (1 - T/T_c)^\beta$ , where  $H_0$  is the hyperfine field at 0 K,  $T_c$  is the temperature of the magnetic ordering, and  $\beta$  is the critical exponent. The following values were obtained:  $H_0 = 528 \pm 3$  kOe,  $T_c = 201 \pm 1$  K and  $\beta = 0.25 \pm 0.01$ . It should be noted that, according to the Ising model, the “bulk” value of the critical exponent  $\beta$  is 0.325 [21]. The difference between the value obtained in this work and the Ising model value is presumably due to the peculiarities of magnetic interactions of the transition elements included in the material, the wide diversity of their local environment leading to different types of indirect exchange interaction, and structural disorder.

#### 4. Summary

The high-entropy oxide of the composition  $(\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$  with NaCl-type face-centered cubic crystal structure (space group  $Fm\bar{3}m$ ) and the lattice parameter of  $4.22 \pm 0.01$  Å was successfully synthesized by the solid state reaction route in the nitrogen flow. The room temperature Mössbauer spectrum is a set of three doublets, the parameters of which correspond to high-spin divalent and trivalent iron ions in an octahedral oxygen environment. Their relative content is 67% and 33%, respectively. The appearance of doublets shows the paramagnetic state of iron ions at room temperature. With the decrease of temperature magnetically split component onset in the spectrum. This indicate the magnetic transition, the critical temperature of which was determined as  $201 \pm 1$  K.

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