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Synthesis and microstructure of the $(Co,Cr,Fe,Mn,Ni)_3O_4$ high entropy oxide characterized by spinel structure

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ABSTRACT

A high-entropy $(Co,Cr,Fe,Mn,Ni)_3O_4$ oxide, characterized by the *Fd-3m* single-phase, spinel structure, was synthesized for the first time. The material was based on the combination of Co, Cr, Fe, Mn and Ni elements, well known from the other group of high-entropy materials, namely high-entropy alloys. The microstructure of the material was studied using SEM + EDS and XRD methods, showing single-phase structure. Additional structural characterization was performed with use of Raman spectroscopy, also showing in the process, the usefulness of this method for characterization of high-entropy oxides.

1. Introduction

In 2015 a new group of materials was developed, the entropy-stabilized oxides, known also as high-entropy oxides (HEOx) [1]. The concept of these materials aroused from the analogy to high-entropy alloys (HEAs) [2,3]. The general idea of high-entropy materials is to use multiple components (usually 5 or more), in order to obtain high configurational entropy of the system, which enhances formation of simple, solid solution structures [4]. Such approach to materials design often leads to extraordinary results, resulting from e.g. synergistic effects [2].

The first HEOx was (Co,Cu,Mg,Ni,Zn)O equimolar, single-phase (*Fm-3m*), solid solution, synthesized by Rost *et al.* [1,5]. Further studies on these materials were conducted by Bérardan *et al.* [6,7,8], Djenadic *et al.* [9], Rak *et al.* [10], Sarkar *et al.* [11] and most recently by Rost *et al.* [12]. Especially interesting are studies by Bérardan *et al.* [7,8], who investigated electrical properties of (Co,Cu,Mg,Ni,Zn)O doped with different alkali ions. The materials exhibited colossal dielectric constants, deemed to be a characteristic for the HEOx [7]. What is more, their results indicated that $(Co,Cu,Mg,Ni,Zn)_{0.7}Li_{0.3}O$ exhibits excellent ionic conductivity, outperforming at room temperature current state-of-the-art solid electrolytes, such as LiPON, by considerable margin [8].

The concept of HEAs was a driving force behind development of HEOx materials and experiences from the metallic systems can be partially carried into oxide ones. Analogically to HEAs, oxides with similar crystal structures, ionic radii, equal valence and high solubility in binary subsystems [13], should be the most feasible candidates for synthesis of new HEOx materials. Basing on these criteria, combinations of the following eight elements are worth considering: Co, Cr, Cu, Fe, Mg, Mn, Ni, Zn. However, Cu and Zn exhibit relatively low compatibility with other elements (different crystal structures), limiting the stability of the resulting materials. While it makes them useful to show e.g. stabilizing effect of entropy at high temperatures [1], it should be viewed rather as an obstacle from the point of view of potential applications, similarly as in the case of HEAs, in which systems stable in a wide temperature range (so stabilized not only by entropy, but also by compatible chemical composition) are considered to be the most promising ones [14].

In the present study the authors examined the possibility of synthesis of new, single-phase, HEOx, based on the Co, Cr, Fe, Mn and Ni cations. This combination is very popular in HEAs [15], due to the similar atomic radii and good solubility of these elements in binary and ternary subsystems. The authors' intention was to check, whether such behavior can be duplicated in oxide systems. The (Co,Cu,Mg,Ni,Zn)O was also synthesized, to provide material for comparison.

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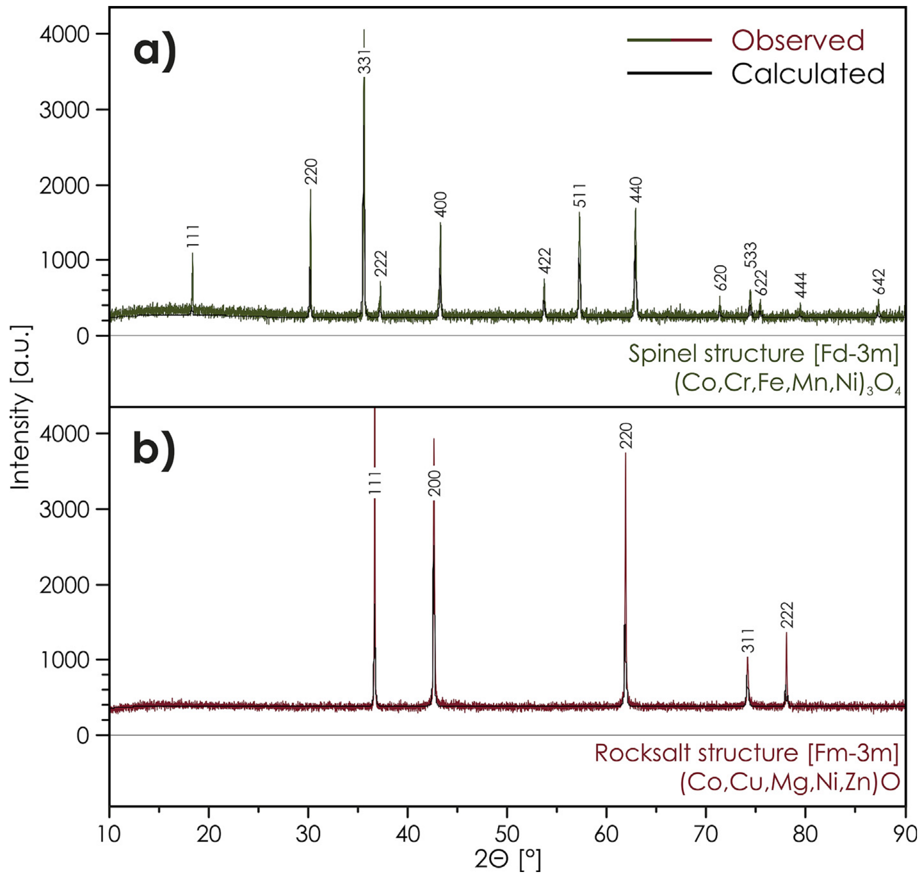

Fig. 1. XRD diffractograms of (a) (Co,Cu,Mg,Ni,Zn)O of Rocksalt (*Fm-3m*) structure; (b) $(Co,Cr,Fe,Mn,Ni)_3O_4$ of spinel (*Fd-3m*) structure.

2. Experimental

Materials were synthesized from the following oxides: MgO, ZnO, CuO, NiO, MnO, Fe_2O_3, Co_3O_4 and Cr_2O_3 of at least 99.7% purity (except for the Cr_2O_3 of 99% purity). The grain sizes for all starting materials (given as sieve "mesh" size), were respectively: −325, −200, −200, −325, −60, −60, 2 ÷ 6 µm and −20. Oxides were weighted in equimolar proportions and mixed using a RETSCH MM 400 vibrational mill for 25 min, with mixing frequency of 20 Hz. Samples were formed into 9 × 1.5 mm pellets, under pressure of 200 MPa. The pellets were free-sintered for 20 hrs at 1050 °C. Finally, the samples were air quenched with use of cooled aluminum sheet for faster heat absorption. The microstructure of the materials was studied by X-ray diffraction (XRD) (PANalytical X'Pert Pro PW 3710 X'Celerator) and SEM + EDS (JEOL JSM-6610LV microscope with EDS detector) techniques. The information on phase composition was supplemented with Raman spectroscopy measurements, performed in Jobin-Yvonne's Labram 800 HR confocal micro-Raman unit based on Czerny-Turner's monochromator. Micro-Raman was working with Nd-YAG laser of 532 nm as an excitation source, 1800 [grooves/mm] grating, long distance optical objective (50×) and Synapse CCD as a detector (1024). The measurements were carried out with 20 s acquisition time, and 2 times accumulation. The mapping was performed using autofocus function on the area of 40 × 40 µm, with 144 point measurements per map. The range of the measurements was 50–1400 cm^{-1}.

3. Results and discussion

The first investigated material was based on Co, Cr, Fe, Mn and Ni cations. All considered cations exhibit similar ionic radii and can exist in the Me^{2+} state, forming Rocksalt-structured (*Fm-3m*) MeO oxides. What is more, practically all of them exhibit high solubility with each other. Therefore, it can be expected that their combination should result in formation of single-phase, *Fm-3m* solid solution. However, in the case of ceramic systems the influence of oxygen partial pressure cannot be ignored, what is visible in pronounced tendency of all considered oxides towards formation of mixed spinel phases e.g. $Fe_{1.7}Ni_{1.43}O_4$, $Cr_{1.5}Mn_{0.5}NiO_4$, $FeCr_2O_4$, $CoFe_2O_4$.

The XRD diffractogram of the sample is presented in the Fig. 1, together with results for (Co,Cu,Mg,Ni,Zn)O. The Co,Cr,Fe,Mn,Ni-based sample exhibited a single-phase, *Fd-3m* spinel structure, imposing a $(Co,Cr,Fe,Mn,Ni)_3O_4$ stoichiometry. The calculated lattice constant was a = 8.35539 (±0.00025) Å. The (Co,Cu,Mg,Ni,Zn) O material exhibited, as expected, the *Fm-3 m* Rocksalt structure. Its lattice constant was determined to be a = 4.23682 (±0.00024) Å. To further confirm the uniformity of the spinel sample, an EDS mapping was performed (Fig. 2). No tendency towards segregation or formation of other phases was visible.

The Raman studies were conducted for both materials. For (Co, Cu,Mg,Ni,Zn)O broad and asymmetric band at 545 cm^{-1} and low-intensity band at 1095 cm^{-1} were observed (Fig. 3a). These values are similar to the ones observed in other Rocksalt-structured materials, such as e.g. $LiMgXO_3$ (X = Ti, Sn, Zr) [16], NiO [17,18] and $Li_{(1-x)/2}Ga_{(1-x)/2}M_xO$ (M = Mg, Zn) [19]. While *Fm-3m* space group has no Raman active modes, the compressed cubic Rocksalt-type structure could be considered as layered-Rocksalt-type structure (space group *R-3m*), thus allowing for two Raman active modes: A_{1g}(LO) and E_g(TO). The A_{1g}(LO) mode implies the movement of oxygen ion in the direction along the hexagonal *c* axis, whereas E_g(TO) - vibration in the perpendicular direction.

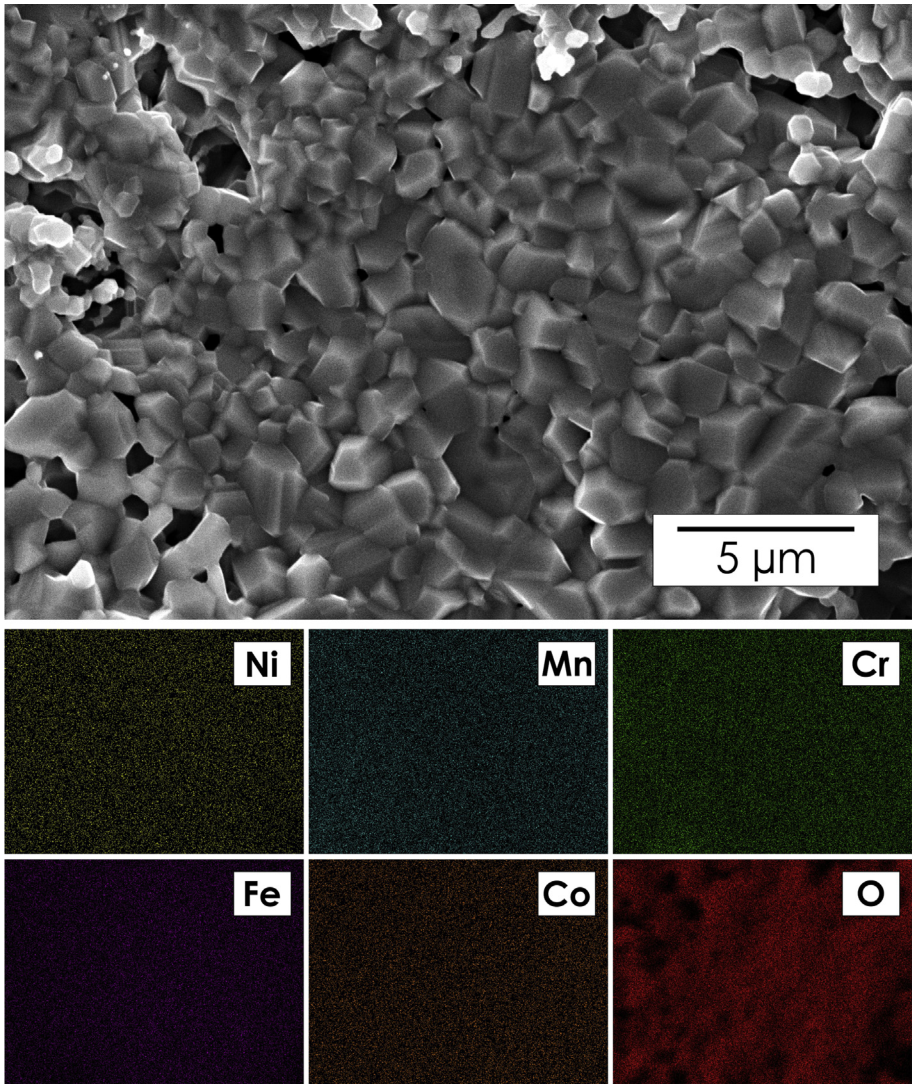

Fig. 2. Results of the EDS mapping of the $(Co,Cr,Fe,Mn,Ni)_3O_4$.

Here, due to cation disorderliness, the softening LO phonon mode occurs and instead of two bands, only one is observed at 545 cm^{-1}. The latter band at 1095 cm^{-1}, due to its position and intensity, could be considered as the overtone band. The material's homogeneity was further confirmed with Raman mapping.

The Raman spectra of $(Co,Cr,Fe,Mn,Ni)_3O_4$ material revealed 6 main bands at 176, 349, 513, 590, 635 and 694 cm^{-1} (Fig. 3b). These results stand in good agreement with the ones reported for analogical structures: Co_3O_4 [20], Fe_3O_4 [21], as well as chromites, ferrites, aluminates and other spinels [22]. From the factor group analysis of *Fd-3m* space group (*Oh* point group), there are five Raman-active modes expected (A_{1g}, F_{1g} and $3F_{2g}$). Based on the aforementioned literature, the 176, 349, 513, 590 and 694 cm^{-1} bands can be attributed to following vibrational modes respectively: $3F_{2g}$, E_g, $3F_{2g}$, $3F_{2g}$ and A_{1g}, whereas extra band at 636 cm^{-1} might suggest existence of distinct octahedral units within the lattice, similarly as in inverse spinels. For the $(Co,Cr,Fe,Mn,Ni)_3O_4$ Raman mapping of the sample's surface also confirmed its phase homogeneity. However, small shifts in the positions of bands and small differences in their internal intensity suggest that small deviations from the average chemical composition may be present. Further studies on the subject of phase homogeneity of $(Co,Cr,Fe,Mn,Ni)_3O_4$ will be pursued, especially in context of the possible segregation of the elements near the grain boundaries. Such phenomena, coupled with the sub-micron grain size, may be of high importance to properties of HEOx materials, similarly as in the case of ZnO doped with other cations [23,24].

4. Conclusions

For the first time a spinel-structured (*Fd-3m*) $(Co,Cr,Fe,Mn,Ni)_3O_4$ high-entropy oxide was synthesized. It should be noted that although multicomponent spinels were reported by Rost [5], none of them was single-phase, while having 5 components or more. The results of XRD, SEM + EDS and Raman spectroscopy studies clearly showed that the material exhibited a single-phase, solid solution structure. The Raman spectroscopy was also successfully used to investigate (Co,Cu,Mg,Ni,Zn)O, further proving usefulness of this method for HEOx characterization. The case of $(Co,Cr,Fe,Mn,Ni)_3O_4$ is a good example that during creation of the new HEOx materials, different structures should be considered, depending on the oxygen partial pressure. Such behavior, drastically different from the one observed in HEAs, opens new ways of synthesis of the high-entropy oxides. Further studies focused on the influence of oxygen partial pressure should be therefore undertaken, in order to maximize the potential of this new group of materials.

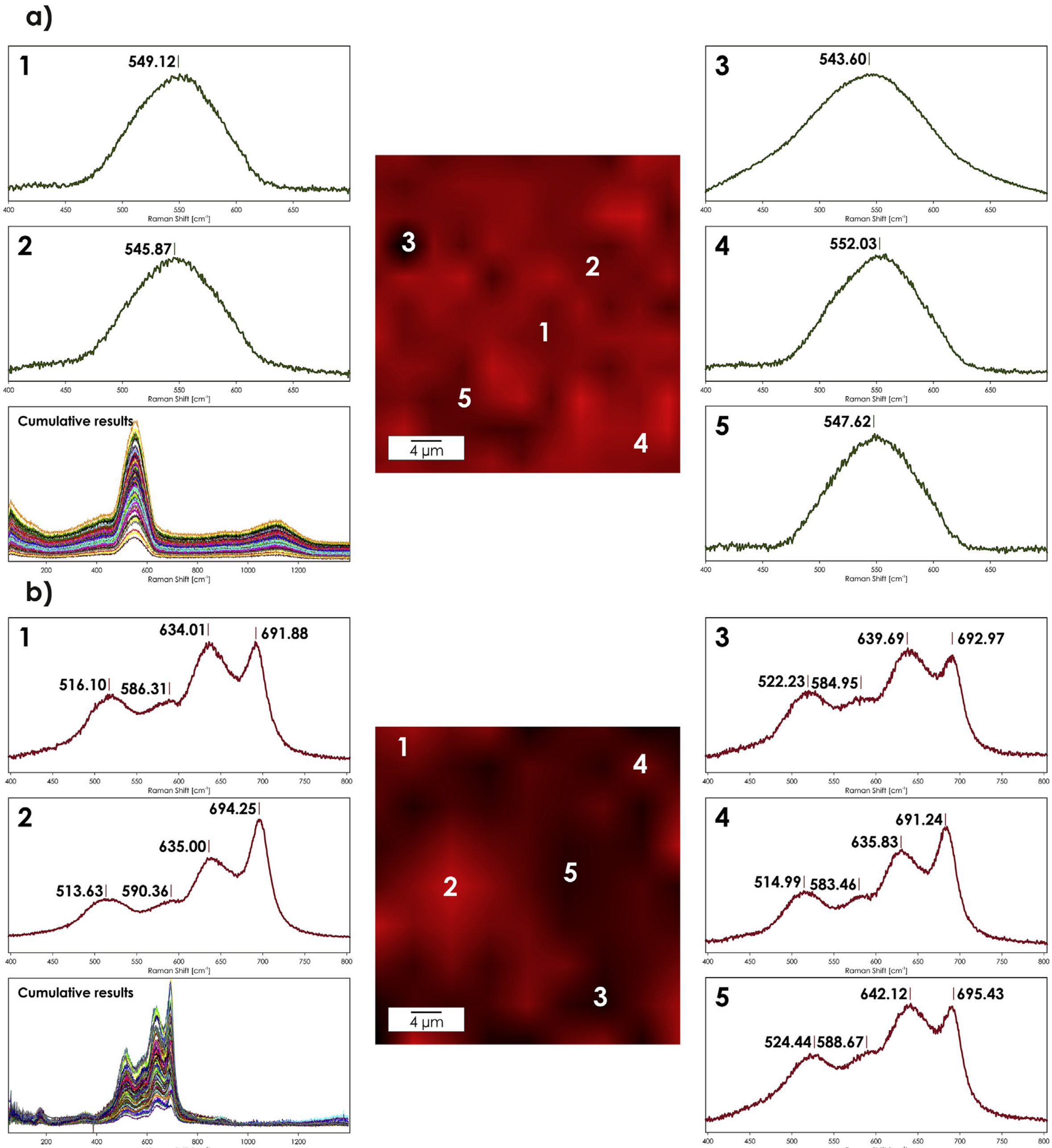

Fig. 3. The results of mapping using Raman spectroscopy of (a) (Co,Cu,Mg,Ni,Zn)O (b) $(Co,Cr,Fe,Mn,Ni)_3O_4$. Exemplary spectra are presented for each material.

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