New high-entropy oxide phases with the perovskite structure

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Abstract. Results of studying the structure and chemical composition of perovskite phases synthesized by solid-state sintering in multicomponent oxide systems: (Ba,Sr,Ca,Mg,Pb)(Ti,Zr)O₃, (Ba,Sr,Ca,Mg,Pb)(Ti,Zr,Hf)O₃, (Ba,Sr,Ca,Mg,Pb)(Ti,Zr,Hf,Sn)O₃, and (Ba,Sr,Ca,Mg,Pb)(Ti,Zr,Hf,Sn,Mn)O₃ are presented. The chemical composition of the obtained samples was investigated using a JEOL JSM7001F scanning electron microscope equipped with an Oxford INCA X-max 80 energy-dispersive X-ray fluorescence spectrometer. The structure was studied with a Rigaku Ultima IV powder X-ray diffractometer. It was demonstrated the possibility of obtaining a high-entropy perovskite phase. Elements (Ba, Sr, Ca, Ti, Zr, Hf, Sn), which can form the high-entropy perovskites have been determined, as well as the elements (Pb, Mg, Mn), which, for various reasons, are hardly incorporated in the high-entropy perovskites.

1. Introduction
The main goal of this research was to obtain new high-entropy oxides with a perovskite structure by solid-state sintering in systems that were not explored before as high-entropy phases [1–6], and to study the composition and structure of them. Such materials are of potential interest for further physical studies. It is known that a number of perovskites have pronounced magnetic properties, others can participate in the processes of energy conversion and storage, some exhibit superconductivity or ferroelectric properties. In contrast to the known works on partially substituted perovskites, in the course of present work there were studied systems in the concentration area where the entropy of mixing reaches its maximum, i.e. in the region where the concentrations of the main components of one type (A or B for the formula ABO₃) are close to be equimolar.

The results presented include the preparation of high-entropy perovskites in the 10 metals oxide system (Ba,Sr,Ca,Mg,Pb)(Ti,Zr,Hf,Sn,Mn)O₃, as well as in more simple systems – (Ba,Sr,Ca,Mg,Pb)(Ti,Zr)O₃, (Ba,Sr,Ca,Mg,Pb)(Ti,Zr,Hf)O₃ and (Ba,Sr,Ca,Mg,Pb)(Ti,Zr,Hf,Sn)O₃.

2. Experiment
The analytical grade BaCO₃, SrCO₃, CaCO₃, MgCO₃, PbO, TiO₂, ZrO₂, HfO₂, SnO₂ and MnO₂ were used as precursors. In preliminary experiments the optimum temperature for solid-state sintering was determined. In these experiments, samples of a given composition were heat-treated in air for 5 hours at temperatures from 1000 to 1400 °C with an interval of 50 °C. Then the samples were examined with an electron microscope. The criterion for the optimal synthesis temperature was the large size and well-formed shape of the crystals of high-entropy perovskite phases.
The found optimum temperature (1400 °C) was used for heat treatment of four multi-component compositions. The batch compositions for solid-state sintering were calculated based on the following hypothetical formulas:

\[
\begin{align*}
&(\text{Ba}_{0.2}\text{Sr}_{0.2}\text{Ca}_{0.2}\text{Mg}_{0.2}\text{Pb}_{0.2})(\text{Ti}_{0.5}\text{Zr}_{0.5})\text{O}_3 \\
&(\text{Ba}_{0.2}\text{Sr}_{0.2}\text{Ca}_{0.2}\text{Mg}_{0.2}\text{Pb}_{0.2})(\text{Ti}_{0.33}\text{Zr}_{0.33}\text{Hf}_{0.33})\text{O}_3 \\
&(\text{Ba}_{0.2}\text{Sr}_{0.2}\text{Ca}_{0.2}\text{Mg}_{0.2}\text{Pb}_{0.2})(\text{Ti}_{0.25}\text{Zr}_{0.25}\text{Hf}_{0.25}\text{Sn}_{0.25})\text{O}_3 \\
&(\text{Ba}_{0.2}\text{Sr}_{0.2}\text{Ca}_{0.2}\text{Mg}_{0.2}\text{Pb}_{0.2})(\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Sn}_{0.2}\text{Mn}_{0.2})\text{O}_3.
\end{align*}
\]

These elements were chosen according to the ionic radii of the elements (in the context of the Goldschmidt’s rule), their coordination number in the structures related to the perovskite-type, as well as the literature data on the composition of minerals and artificial multicomponent phases with the perovskite-like structure, which are prone to isomorphism (perovskite, celanite, snaps, loparite, dysanalite, rhinitis, tausonite, macedonite, etc.).

Pellets, pressed from a thoroughly ground batch mixture, were sintered for 5 hours in an air atmosphere at a temperature of 1400 °C on a platinum plate placed in a tubular furnace with silicon carbide heaters.

After heat treatment, the fractured surface of the pellets was investigated using a Jeol JSM7001F scanning electron microscope equipped with an Oxford INCA X-max 80 X-ray spectrometer for elemental analysis of samples. In order to study the structure, the obtained samples were ground and investigated by X-ray phase analysis using a Rigaku Ultima IV X-ray powder diffractometer with Cu Ka radiation.

3. Results and discussions

The powder X-ray diffraction study showed that in all four samples the perovskite phase was formed in significant quantities. The other oxide phases were also found in noticeable quantities. The study of the morphology of the sample by electron microscopy made it possible to detect uniform equiaxial or rectangular microcrystals (figures 1-4).

![Figure 1. Morphology of the (Ba,Sr,Ca,Mg,Pb)(Ti,Zr)O₃ sample.](image)

The electron microscopy study of the fracture of the samples, combined with micro X-ray spectral analysis, made it possible to determine the compositions of the microcrystals. Data on the composition of equiaxial or rectangular microcrystals, that dominate in the sample, are presented in table 1. Here, the content of elements A and B is normalized to 100 atomic % for each group of elements separately. Since several measurements were made for each sample, the table shows average, maximum and minimum results (to demonstrate the range of possible values).
Figure 2. Morphology of the (Ba,Sr,Ca,Mg,Pb)(Ti,Zr,Hf)O$_3$ sample.

Figure 3. Morphology of the (Ba,Sr,Ca,Mg,Pb)(Ti,Zr,Hf,Sn)O$_3$ sample.

Figure 4. Morphology of the (Ba,Sr,Ca,Mg,Pb)(Ti,Zr,Hf,Sn,Mn)O$_3$ sample.
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Table 1. Composition of equiaxial or rectangular microcrystals.

| Sample                  | Composition level | [A], at.% of elements of type “A” | [B], at.% of elements of type “B” |
|-------------------------|-------------------|----------------------------------|----------------------------------|
| (Ba,Sr,Ca,Mg,Pb)        | min               | Ba 24 Sr 16 Ca 10 Mg 3 Pb 4      | Ti 33 Zr 27 Hf 28 Pb 5 Sn 21 Mn 3 |
| (Ti,Zr)O₃              | max               | Ba 45 Sr 31 Ca 30 Mg 11 Pb 23    | Ti 73 Zr 67 Hf 30 Pb 44 Sn 57 Mn 2 |
| (Ba,Sr,Ca,Mg,Pb)        | aver              | Ba 37 Sr 23 Ca 18 Mg 6 Pb 16     | Ti 56 Zr 44 Hf 42 Pb 48 Sn 41 Mn 2 |
| (Ti,Zr,Hf)O₃           | min               | Ba 47 Sr 18 Ca 12 Mg 3 Pb 1      | Ti 25 Zr 14 Hf 30 Pb 44 Sn 57 Mn 2 |
| (Ba,Sr,Ca,Mg,Pb)        | max               | Ba 57 Sr 27 Ca 12 Mg 21 Pb 2     | Ti 30 Zr 26 Hf 30 Pb 44 Sn 57 Mn 2 |
| (Ti,Zr,Hf,Sn)O₃        | aver              | Ba 52 Sr 22 Ca 12 Mg 12 Pb 2     | Ti 28 Zr 20 Hf 31 Pb 42 Sn 52 Mn 2 |
| (Ba,Sr,Ca,Mg,Pb)        | min               | Ba 25 Sr 27 Ca 19 Mg 1 Pb 0     | Ti 33 Zr 15 Hf 30 Pb 44 Sn 57 Mn 2 |
| (Ti,Zr,Hf,Sn,Mn)O₃     | max               | Ba 43 Sr 49 Ca 24 Mg 8 Pb 3     | Ti 36 Zr 25 Hf 31 Pb 44 Sn 57 Mn 2 |
| (Ba,Sr,Ca,Mg,Pb)        | aver              | Ba 39 Sr 23 Ca 20 Mg 0 Pb 2     | Ti 18 Zr 20 Hf 22 Pb 44 Sn 57 Mn 2 |

An analysis of the composition shows that in the ABO₃ perovskite formula, Ca, Sr, and Ba can certainly act as element "A". Mg in the equiaxial or rectangular microcrystals was found in quantities noticeably smaller than expected from the batch composition. On the other hand, Mg is a component of other phases formed, primarily of phases with octahedral crystals. Pb in the studied samples either is not found or is present in quantities significantly less than expected. This is probably due to the evaporation of Pb oxide during heat treatment.

From table 1 follows that in the perovskite formula, Ti, Zr, Hf, and Sn can certainly act as "B" elements. Mn in the samples is found in quantities noticeably smaller than expected, so, as well as Mg, it may be a component of the formed side phases.

4. Conclusion

Investigation of the structure and chemical composition of the samples belonging to the oxide system (Ba,Sr,Ca,Mg,Pb)(Ti,Zr,Hf,Sn,Mn)O₃, showed the possibility of obtaining high-entropy perovskite phases. The elements that easily form the high-entropy phase are Ca, Sr, Ba, Ti, Zr, Hf and Sn. Pb, Mg, Mn for various reasons practically do not enter the high-entropy phase. Further studies in this direction will make it possible to obtain phase pure samples suitable for studying its electromagnetic characteristics.

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