High Entropy Spinel Oxides prepared *via* mechanosynthesis

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ABSTRACT

In the present work, for the first time a novel class of spinel type high entropy oxides as well as lithiated high entropy oxyfluorides and oxychlorides are introduced. The nanostructured samples were prepared *via* high-energy ball milling of the oxide precursors and LiF or LiCl as a lithium source for particular oxyfluorides and oxychlorides. Their structure is investigated by XRD, HR-TEM and EDS. It is revealed, that incorporation of lithium into the structure together with anionic exchange has significant influence on the short-range structural features, size and morphology of crystallites within the structure of AB_2O_4 spinels.

METHODS AND MATERIALS

$(Zn_{0.25}Cu_{0.25}Mg_{0.25}Co_{0.25})Al_2O_4$ (HEOAl) was synthesized *via* one-step mechanochemical method. The oxides precursors were weighed in an equimolar ratio and milled at 600 rpm in an air atmosphere with a milling time of 390 minutes in the planetary ball mill (Pulverisette 7, Fritsch). In the case of Li-doped HEOAls, i.e. $Li_{0.5}(Zn_{0.25}Cu_{0.25}Mg_{0.25}Co_{0.25})_{0.5}Al_2O_{3.5}F_{0.5}$ (LiHEOAlF) and $Li_{0.5}(Zn_{0.25}Cu_{0.25}Mg_{0.25}Co_{0.25})_{0.5}Al_2O_{3.5}Cl_{0.5}$ (LiHEOAlCl), lithium fluoride or lithium chloride precursors were added in an equimolar ratio to the reaction mixture described above. The preparation conditions were similar to HEOAl followed by calcination in the presence of air at 600°C with a calcination time of 4 h.

RESULTS AND DISCUSSIONS

In Fig.1 the XRD diffraction peaks of mechanosynthesized compounds containing lithium and fluorine/chlorine are shifted towards higher 2 Theta angels. It clearly demonstrates that the mechanochemically synthesized Li containing high-entropy spinels have modified value of lattice parameter, *i.e.* observed lattice contraction as a consequence of lithium incorporation into the spinel structure with different Shannon radii of ions and formation of oxygen defects for electroneutrality compensation. A representative TEM micrographs reveal nanoscale character of mechanosynthesized samples (Fig.2). It is shown, that as-prepared nanoparticles are in agglomerated state with average crystallite size ~ 17 nm for LiHEOAlF. As it is further shown, the selected area electron diffraction (SAED) patterns are characterized by broad rings and most intensive are attributed to (*111*), (*202*), (*311*), (*400*), (*404*), (*422*), (*511*) and (*602*) crystallographic planes of the spinel structure. The result is in good agreement with XRD analysis, *i.e.* smaller size of crystallites and partial amorphous character of the sample. In addition, the HR-TEM image reveal lattice fringes corresponding to the crystallographic plane with the average interplanar distances: $d_{(110)}$ = 5.6 Å for LiHEOAlF. In order to further assess of the uniformity of elemental distribution of synthesized samples, Fig. 3 displays the EDS mapping of Al, Co, Cu, Zn, Mg, O, F elements. All analyses reveal elemental homogeneity.

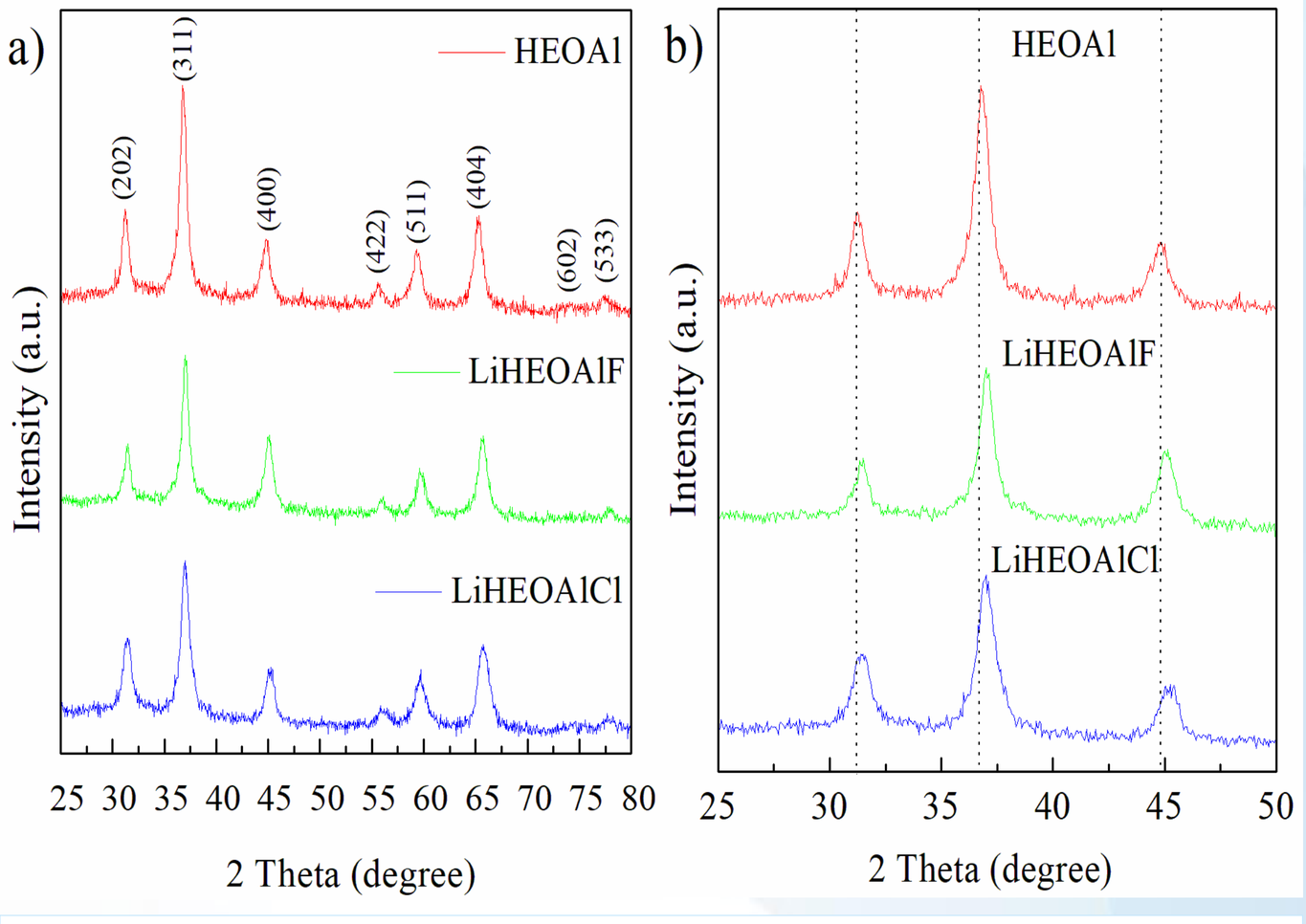

Fig.1 a) XRD patterns of the mechanosynthesized HEOAl, LiHEOAlF and LiHEOAlCl; b) detail on variation in lattice parameter as a consequence of elemental composition.

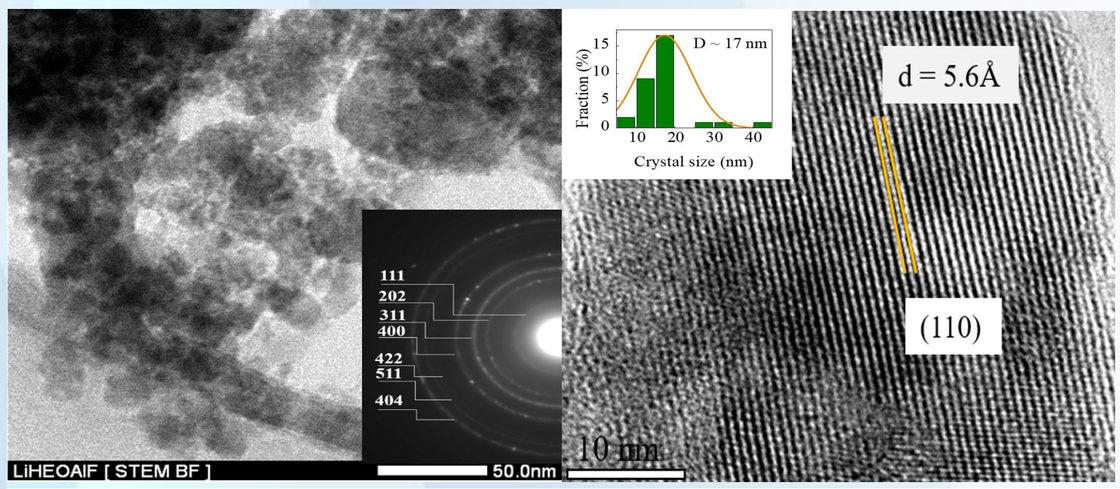

Fig. 2 STEM (inset: SAED) and HR-TEM micrographs (inset: crystallite size distribution) of LiHEOAlF.

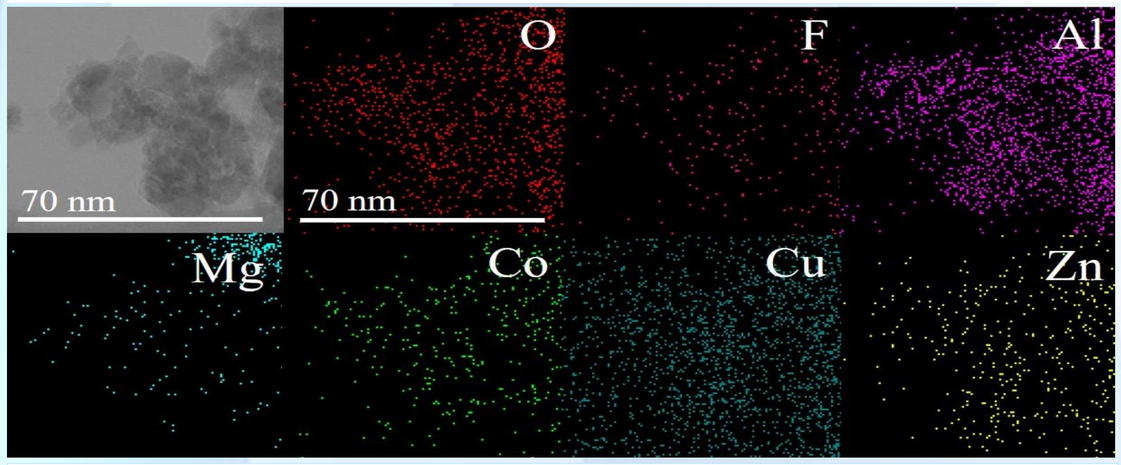

Fig. 3 The EDX mapping of LiHEOAlF.

CONCLUSIONS

- High Entropy Oxide $(Zn_{0.25}Cu_{0.25}Mg_{0.25}Co_{0.25})Al_2O_4$ was synthesized with spinel structure;
- $(Zn_{0.25}Cu_{0.25}Mg_{0.25}Co_{0.25})Al_2O_4$ was successfully doped with Li and F/Cl for the first time with final composition: $Li_{0.5}(Zn_{0.25}Cu_{0.25}Mg_{0.25}Co_{0.25})_{0.5}Al_2O_{3.5}F_{0.5}$ and $Li_{0.5}(Zn_{0.25}Cu_{0.25}Mg_{0.25}Co_{0.25})_{0.5}Al_2O_{3.5}Cl_{0.5}$;
- X-ray powder diffraction showed that the diffraction peaks are shifted toward higher angles as a result of reducing the lattice parameter;
- TEM studies have demonstrated the nanocrystalline nature of the synthesized samples as well as variation in d-spacing according composition of the samples;
- The EDS elemental mapping revealed homogeneous distribution of all elements confirming production of single-phase compounds.

ACKNOWLEDGEMENTS

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