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INTRODUCTION

This study presents optimization of the hydrothermal synthesis of novel triple perovskites $Sr_3Mn_2WO_9$ and $Sr_3Mn_2TeO_9$, from aqueous solution of metal salt precursors. It is important for the design of perovskite materials to stabilize metal cations in desired oxidation states. For that purpose, electrochemical measurements were carried out to determine oxidation state of manganese cation under the given reaction conditions. Manganese is often connected to iron triad elements (Fe, Co, Ni) because it sometimes has similar chemical properties. Interesting fact is that Mn^{3+} (coordination number 6, high spin state) has ionic radius of 0.645 Å which corresponds to the ionic radius of Fe³⁺ (also coordination number 6, high spin state). Hence, isostructurality to $Sr_3Fe_2WO_9$ and $Sr_3Fe_2TeO_9$, is expected.

IDEA			
SITE	ION	COORDINATION	ION
		NUMBER	
Α	Sr ²⁺	12	
B'	Fe ³⁺ (HS)	6	
	Mn ³⁺ (HS)	6	
B''	Te ⁶⁺	6	
	W ⁶⁺	6	
0	O ²⁻	2	

Isostructurality of previously synthesized Sr₃Fe₂V (*CrysEngComm* 21, 2019) and Sr₃Fe₂TeO₉ (*Cryst. Growth* 2016) with **novel** Sr₃Mn₂WO₉ and Sr₃Mn₂TeO





CONCLUSIONS

Cyclic voltammetry has shown that manganese is the only electrochemically active specie in given experimental procedure and that it is stabilized in +3 oxidation state in 1:3 ration in NaOH solution. Powder X-ray diffraction has shown successful synthesis of Sr₃Mn₂TeO₉, but still with some impurities. Sr₃Mn₂WO₉ was present in small amounts in given samples along with SrMnO₄ as a dominant phase in the sample.

Hydrothermal synthesis and structural investigation of perovskite-like mixed oxides of manganese with tungsten or tellurium

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THERMOGRAVIMETRIC ANALYSIS



NIC RADIUS



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Cyclic voltammograms of reactants in the starting solution before the hydrothermal synthesis. Electrode polarization rate, 100 mV/s.

A. Blank (••••), $(NH_4)_{10}H_2(W_2O_7)_6$ (---), $Sr(NO_3)_2$ (--), $(NH_4)_2TeO_4$ (--) and $Mn(NO_3)_2$ (----) (c = 1x10⁻³ mol dm⁻³, I_c = $0,1 \text{ M KNO}_{3}$).

B. Blank (—), $Mn(NO_3)_2$ (—) ($c = 5x10^{-4}$ mol dm⁻³, $I_c = 0,1$ M KNO₃) and manganese(II) nitrate and NaOH solution in ratios 3:1 (---), 1.5:1(---), 1:1 (----), 1:1.3 (—), 1:1.6 (—) and 1:2. (—).

C. Blank (••••), $Mn(NO_3)_2$ (---) ($c = 5x10^{-4}$ mol dm⁻³, $I_c = 0,1$ M KNO₃) and manganese(II) nitrate and NaOH solution in 1:3 (—) ratio.

DTG curves of uncalcined samples after the hydrothermal synthesis. The biggest mass loss is around 850 °C, after which samples appear to be thermally stable. Therefore, calcination temperature was set to 900 °C after the hydrothermal synthesis.









HYDROTHERMAL SYNTHESIS

Powder XRD patterns of calcined samples containing tellurium synthesized at 150 °C (up) and 200 °C (down) with A. 3 M NaOH and B. 6 M NaOH. Red vertical tics correspond to Sr₃Fe₂TeO₉ (*Cryst. Growth* Des. 16(5), 2016), isostructural to $Sr_3Mn_2TeO_9$.

Powder XRD patterns of calcined samples containing tungsten synthesized at 150 °C (up) and 200 °C (down) with A. 3 M NaOH and B. 6 M NaOH. Red vertical tics correspond to Sr₃Fe₂WO₉ (*CrysEngComm* 21, 2019), isostructural to $Sr_3Mn_2WO_9$.