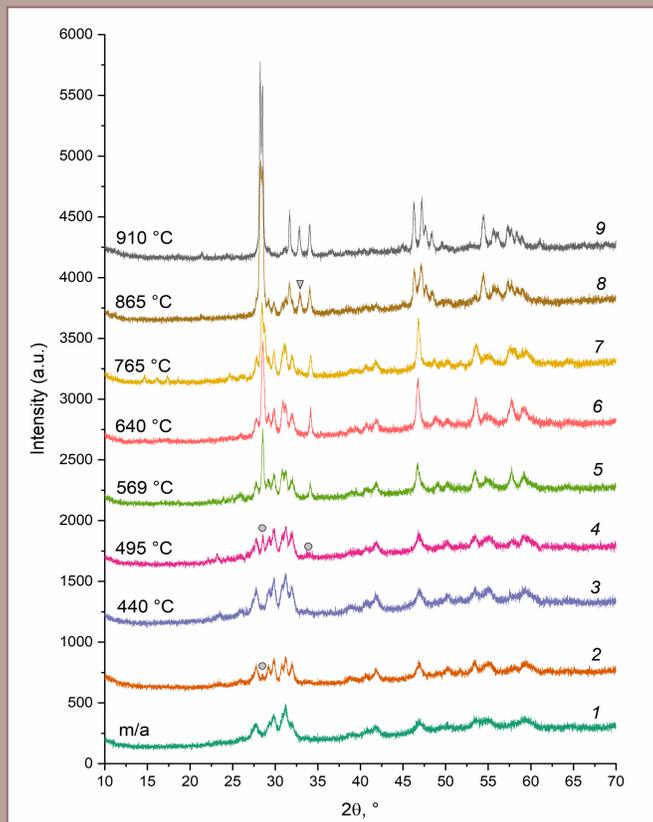
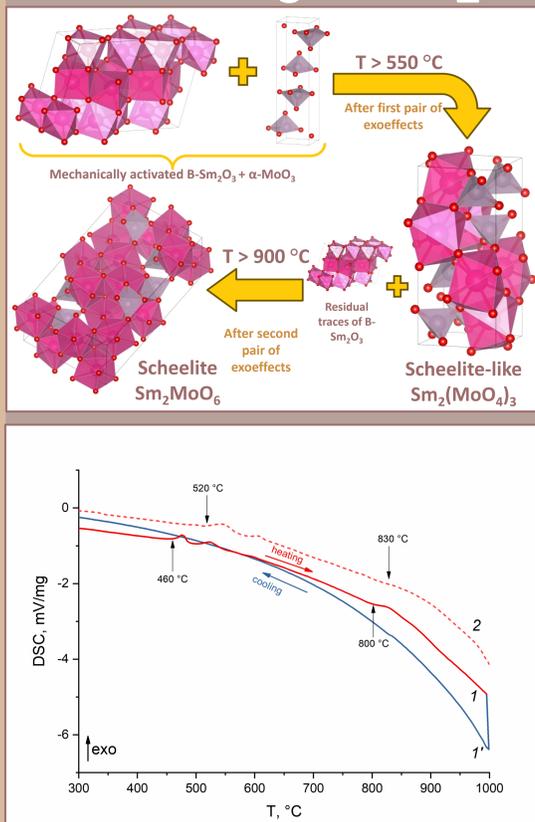
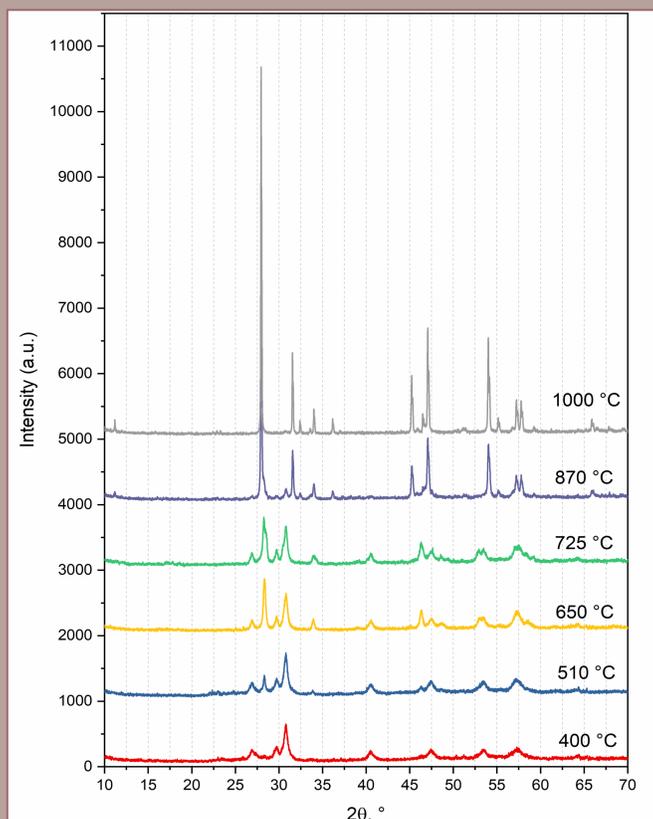
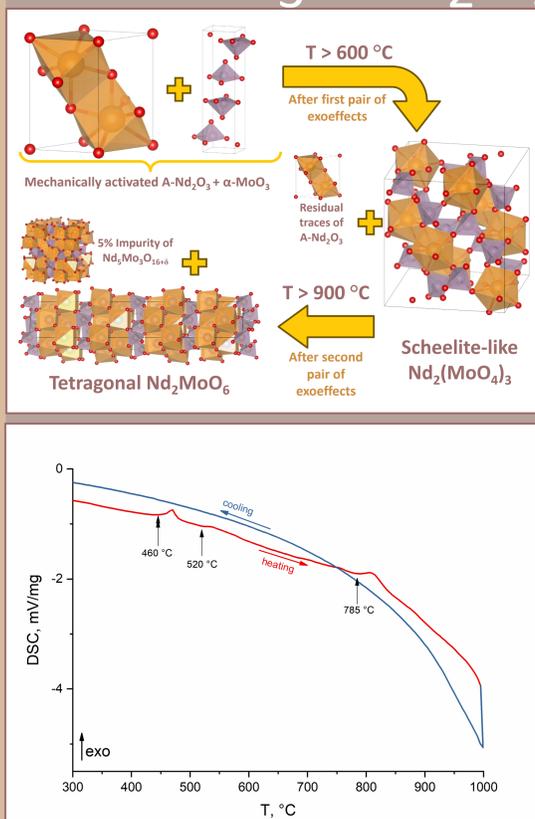


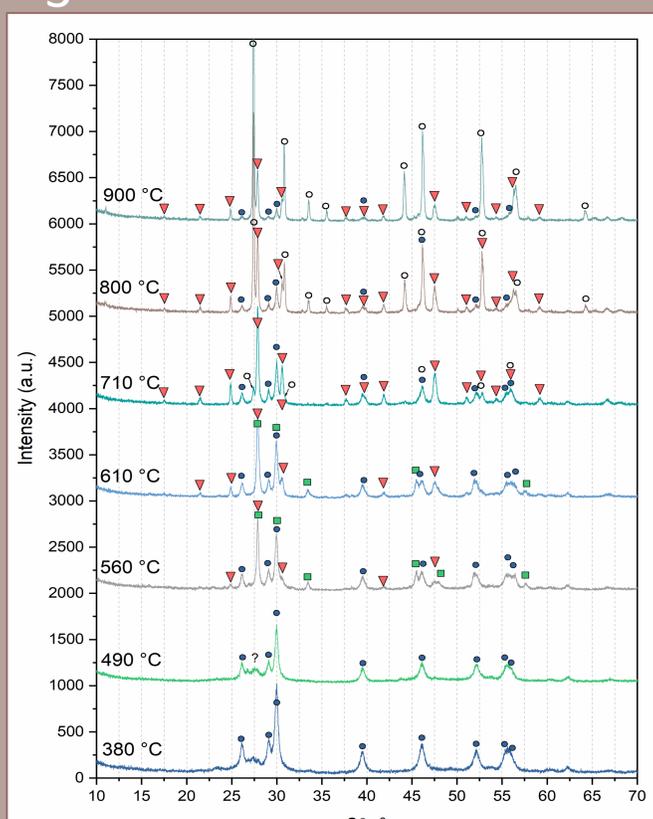
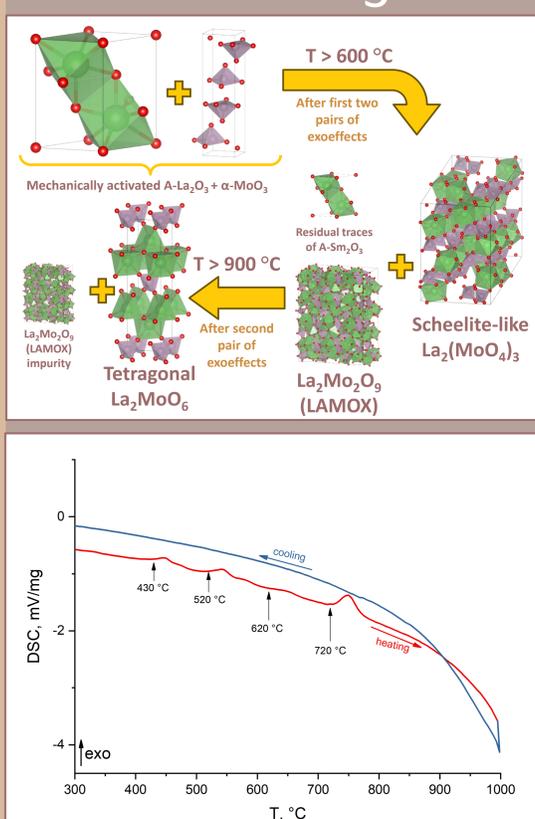
MoO₃+Sm₂O₃ oxide mixture



MoO₃+Nd₂O₃ oxide mixture



10MoO₃+9La₂O₃ oxide mixture



Mechanism of Ln₂MoO₆ (Ln = La, Nd, Sm) Phase Formation from a Mechanically Activated Oxide Mixture

Baldin E. D., Vorobieva G.A., Kolbanev I. V., Shlyakhtina A. V.

N.N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, Moscow, Russia

ABSTRACT

The structure and polymorphism of compounds in the 1:1 molar range of the Ln₂O₃-MoO₃ system, i.e., Ln₂MoO₆, have attracted attention since the middle of the last century and it has been shown that oxymolybdates have a layered tetragonal structure in the case of large rare earth cations La, Pr, Nd, and oxymolybdates of heavy REE crystallise in the scheelite structural type [1]. It is well known that solid state synthesis requires long term high temperature annealing with intermediate grinding in the temperature range of 900-1100 °C. At the same time, the volatility of molybdenum oxide and its rather low melting and sublimation temperatures of 801°C and ~600°C, respectively, must be taken into account. These factors can lead to a change in the composition of the samples. For this reason, it is important to study the synthesis of REE oxymolybdates at temperatures lower than 600 °C. Previously, the possibility of obtaining some molybdates Ln₁₀Mo₂O₂₁ (Ln = La, Y, Er) with a high content of Ln₂O₃ at room temperature has been demonstrated [2]. Mechanoactivation of a mixture of initial oxides is known to result in either mechanochemical synthesis of compounds or formation of nano-sized oxides, affecting the mechanism of compound phase formation during subsequent annealing. The mechanism of phase formation of oxymolybdates Ln₂MoO₆ (Ln = La, Nd, Sm) from nano-sized precursors with increasing temperature has not been investigated.

METHODS

- The starting oxides Ln₂O₃ (Ln = La, Nd, Sm) and MoO₃ were preheated to remove water and carbon dioxide. Then oxide mixture was ground to a nanoscale state in a SPEX8000 ball mill for an 60 min.
- The m/a mixture was then analyzed by differential scanning calorimetry (DSC) using a NETZSCH STA 449C instrument (50-1000°C, heating rate 10°C/min, Al₂O₃ crucible) in an oxygen atmosphere to identify thermal effects associated with phase synthesis.
- The structure of the phases before and after exoeffects was determined by X-ray diffraction. XRD patterns were obtained at room temperature using a Rigaku Smartlab SE diffractometer (Cu Kα radiation, 40 kV, 50 mA) in continuous mode. The range of angles was 2θ = 10–70°, step 0.1°, scanning rate 5°/min.

RESULTS

- When synthesis from m/a precursors, La and Nd oxymolybdates are tetragonal, Sm — monoclinic scheelite.
- Synthesis of oxymolybdates R₂MoO₆ (R = La, Nd, Sm) proceeds with the formation of intermediate phases: In all cases, the formation of the 1Ln₂O₃:3MoO₃ phase was observed. In the 10MoO₃+ 9La₂O₃ system, the formation of LAMOX (1La₂O₃: 2MoO₃) was noticed.
- The annealing time of the powders at high temperatures was significantly reduced and the evaporation of molybdenum oxide was avoided.

References

- Blasse G. Dilanthanide molybdates and tungstates Ln₂MO₆//Journal of Inorganic and Nuclear Chemistry, 1966, Vol. 28, No. 6-7, P. 1488-1489.
- Kolbanev I.V., Shlyakhtina A.V., Degtyarev E.N., Konysheva E.Yu., Lyskov N.V., Stolbov D.N., Streletskii A.N. Room-temperature mechanochemical synthesis of RE molybdates: Impact of structural similarity and basicity of oxides//Journal of the American Ceramic Society, 2021, Vol. 104, No. 11, P. 5698-5710.

Fundings

The work was supported by the subsidy from the Ministry of Education and Science allocated by the FRC CP RAS for the implementation of the state assignment (No.122040500071-0, No. 122040500068-0) and in accordance with the state task for FRC PCP and MC RAS, state registration No. AAAA-A19-119061890019-5.