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Microwave-Assisted Solid-State Synthesis of $NaRE(MO_4)_2$ Phosphors (RE = La, Pr, Eu, Dy; M = Mo, W)

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ABSTRACT

A synthetic method was developed to enable the microwave-assisted solid-state preparation of double molybdate and double tungstate scheelite-type phosphors of formula $NaRE(MO_4)_2$ (RE = La, Pr, Eu, Dy; M = Mo, W). Starting from subgram-scale stoichiometric mixtures of metal carbonates and oxides and with the aid of granular activated charcoal as a microwave susceptor, ternary ($NaEu(MO_4)_2$), quaternary ($NaLa_{0.95}Eu_{0.05}(MO_4)_2$), and quinary phosphors ($NaLa_{0.95}Pr_{0.025}Dy_{0.025}(MO_4)_2$) were obtained upon heating in a countertop microwave oven. The synthesis of crystalline and phase-pure materials required heating times ranging from 18 to 27 min, significantly shorter than those typically encountered in solid-state reactions assisted by conventional heating. Depending on chemical composition, the speed-up factor ranged from 30 to 40. More importantly, photoluminescence studies performed on the compositionally complex quinary molybdate $NaLa_{0.95}Pr_{0.025}Dy_{0.025}(MoO_4)_2$ showed that phosphors synthesized using microwave and conventional heating have nearly identical luminescence responses. The synthetic method described in this contribution is robust, fast, simple, and ideally suited for exploratory synthesis and rapid screening of group VI metalate phosphors, as well as for the preparation of binary precursors to these materials (e.g., Na_2MoO_4 and Na_2WO_4).

INTRODUCTION

Microwave heating is a well-established method for the synthesis of functional materials starting from solution-phase or solid-state precursor mixtures. The physical, chemical, and procedural aspects of this technique have been reviewed in a number of contributions.[1-4] In regard to its application to the solid-state synthesis of rare-earth-activated inorganic phosphors there is an extensive literature describing the microwave-assisted preparation of aluminates,[5-8] silicates,[7, 9-12] germanates,[13, 14] phosphates,[15] oxisulfides,[16] and vanadates.[15, 17] Double molybdate and double tungstate scheelite-type phosphors of formula $NaRE(MO_4)_2$ (RE = rare-earth, Y; M = Mo, W) are a notable absence in this list. These group VI metalates are being extensively investigated as down- and upconverting phosphors,[18, 19] solid-state lasers,[20] optical bioprobes,[21] and luminescent thermometers.[22, 23] Microwave-assisted solution-phase syntheses have been described for double, triple, and quadruple molybdates $Na(La,Gd)(MoO_4)_2$,[24, 25] $Na(Ca,Sr)(La,Gd)(MoO_4)_3$,[26-28] and $(Sr,Pb)(La,Gd,Y)_2(MoO_4)_4$,[29-33] respectively. In all cases, chemical agents (e.g., citric acid, ethylene glycol), postsynthetic conventional heat treatment, and/or specialized ovens had to be used to achieve a crystalline and phase-pure material. These syntheses drew inspiration from those first proposed for the parent alkaline-earth scheelites AMO_4 (A = Ca, Sr, Ba), which had been prepared using sol–gel,[34, 35] hydrothermal,[36] and Pechini[37] methods assisted by microwave heating. By contrast, reports on the microwave-assisted solid-state syntheses of scheelite and scheelite-type materials are scarce. Scheelites $BaMoO_4$ and $CdWO_4$ have been prepared via microwave heating of solid-state precursors in evacuated and sealed quartz tubes.[38, 39] Recently, Zhai and coworkers described the microwave synthesis of Eu^{3+}:Dy^{3+}:$CaMoO_4$ scheelite phosphors by heating a stoichiometric mixture of metal carbonates and oxides in air.[40] To the best of our knowledge, however, the microwave-assisted solid-state synthesis of scheelite-type double molybdates and double tungstates $NaRE(MO_4)_2$ has not been reported. Developing a robust, fast, and simple method to access these phosphors would enable the rapid screening of their luminescence properties (e.g., determination of concentration quenching thresholds) and also speed up exploratory synthesis of novel metalates.

In this article we expand the synthetic toolbox enabling the microwave-assisted solid-state synthesis of inorganic phosphors. We report a procedure to prepare crystalline and phase-pure double molybdates and tungstates of formula $NaRE(MO_4)_2$ (RE = La, Pr, Eu, Dy; M = Mo, W) in less than 30 minutes using a countertop microwave. Emphasis is placed on describing the experimental setup and procedure, assessing the phase-purity of the phosphors, and comparing their room-temperature luminescence response to that of phosphors obtained through conventional heating. The potential of adapting our approach to the rapid synthesis of group V metalates such as niobates and tantalates is discussed.

EXPERIMENTAL

Microwave Synthesis of Na_2MO_4 and $NaRE(MO_4)_2$. Na_2CO_3 (99.5%), La_2O_3 (99.9%), $Pr(C_5H_7O_2)_3$ (99.9%), Eu_2O_3 (99.99%), Dy_2O_3 (99.99%), MoO_3 (99.5%), and WO_3 (99.9%) were used as starting materials. All chemicals were purchased from Sigma-Aldrich and used as received except La_2O_3, which was heated at 1100 °C for 24 h prior to use. In a typical synthesis, stoichiometric amounts of the starting materials were mixed with a small volume of acetone and ground in an agate mortar for ≈30 min. Total masses for unreacted mixtures ranged from ≈0.30 to 0.60 g. The unreacted mixture was transferred to a 5 mL alumina crucible which, as shown in **Figure 1**, was partially immersed in a secondary container filled with ≈18 g of activated charcoal granules (Sigma-Aldrich, 12–20 mesh). Depending on the target reaction temperature and heating time, porcelain or hollow ceramic bricks may be used as secondary containers. Activated charcoal served as the susceptor, absorbing microwaves and heating the reaction mixture in the alumina crucible until reactants coupled directly to microwaves. Next, the reaction system was placed at the center of the cavity of a microwave oven allowing control over power levels and delivering a maximum power of 1200 W (Panasonic Corp., model no. NN–H765BF, cavity dimensions 228 (h) × 418 (w) × 470 (d) mm^3). A 2 cm thick ceramic brick was placed between the microwave glass tray and the secondary container. Heating profiles (i.e., power level and number of heating cycles) were optimized to ensure the phase purity of the target products. Power levels were estimated by multiplying the power setting times the maximum output power (e.g., power

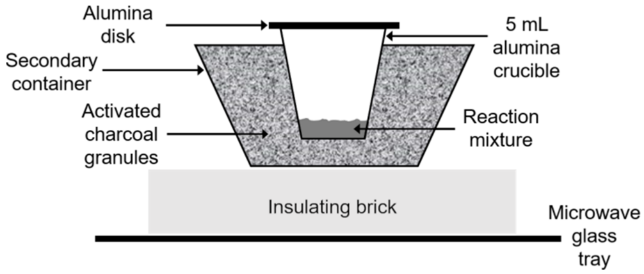

Figure 1. Schematic view of the microwave cavity containing the reaction system and mixture.

Table 1. Heating Profiles for Microwave Synthesis of Molybdate and Tungstate Phosphors

Composition	Sample Mass (g)	Power (W)[a]	Heating Profile	Total Time (min)
Na_2MoO_4	0.60	840	9 cycles of 3 min each	27
Na_2WO_4	0.30	1080	3 cycles of 2 min each	6
$NaEu(MoO_4)_2$	0.31	960	6 cycles of 3 min each	18
$NaEu(WO_4)_2$	0.30	1080	6 cycles of 3 min each	18
$NaLa_{0.95}Eu_{0.05}(MoO_4)_2$	0.31	960	9 cycles of 3 min each	27
$NaLa_{0.95}Eu_{0.05}(WO_4)_2$	0.30	1080	9 cycles of 3 min each	27
$NaLa_{0.95}Pr_{0.025}Dy_{0.025}(MoO_4)_2$	0.43	960	6 cycles of 3 min each	18
$NaLa_{0.95}Pr_{0.025}Dy_{0.025}(WO_4)_2$	0.31	1080	9 cycles of 3 min each	27

[a] Estimated as (power setting) × (maximum output power).

delivered at power setting #8 = 0.8 × 1200 = 960 W). A typical heating cycling included continuous heating for 2 to 3 min followed by a cooling step. Intermediate grindings were performed between heating cycles to improve the homogeneity of the samples. Heating profiles for each of the compounds synthesized in this work are summarized in **Table 1**. We note that the preparation of phase-pure tungstates invariably required higher power levels than that of molybdates. This finding is line with previous studies of metalate phosphors synthesized using conventional heating, which showed that tungstates are obtained at higher temperatures than their molybdate counterparts.[19, 22]

Powder X-ray Diffraction (PXRD). PXRD patterns were collected using a Bruker D2 Phaser diffractometer operated at 30 kV and 10 mA. Cu Kα radiation (λ = 1.5418 Å) was employed. A nickel filter was used to remove Cu Kβ radiation. Diffractograms were collected in the 10−80° 2θ range using a step size of 0.025° and a step time of 1.0 s. Diffraction patterns were recorded at room temperature.

Rietveld Analysis. Rietveld analysis[41, 42] of PXRD patterns was performed using the General Structure Analysis System (GSAS) with the graphical user interphase (EXPGUI) software.[43, 44] Crystal structures of Na_2MO_4 and $NaRE(MO_4)_2$ were refined using cubic ($Fd\bar{3}m$) and tetragonal ($I4_1/a$) space groups, respectively. The following parameters were refined: (1) scale factor, (2) background, which was modeled using a shifted Chebyshev polynomial function, (3) peak shape, which was modeled using a modified Thompson−Cox−Hasting pseudo-Voight function,[45] (4) lattice constants, and (5) isotropic displacement parameters for metal and oxygen atoms ($U_{iso}^{Na/RE}$, U_{iso}^{M}, and U_{iso}^{O}). For $NaRE_{1-x}RE'_x(MO_4)_2$ ($NaRE_{1-x-y}RE'_xRE''_y(MO_4)_2$) phosphors, the occupancy of the rare-earth-containing site was fixed according to the nominal Na:RE:RE′ (Na:RE:RE′:RE″)

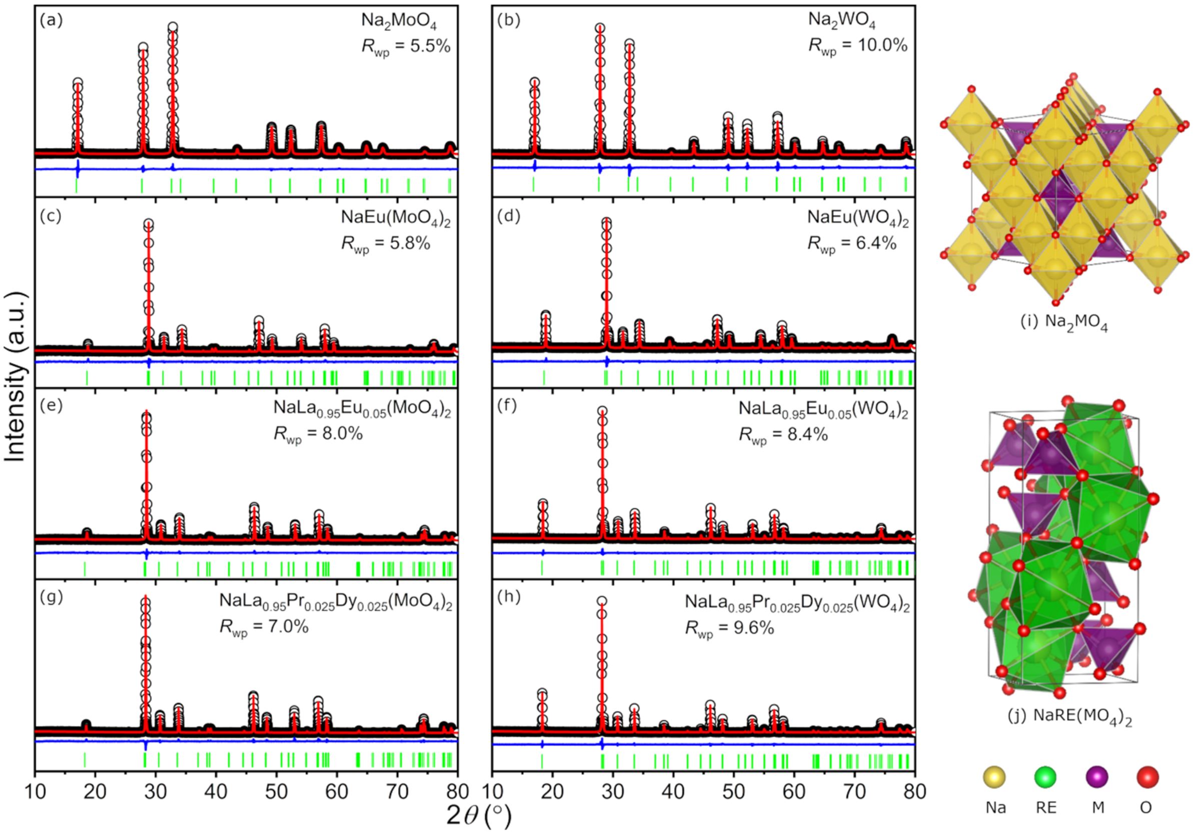

Figure 2. (a–h) Rietveld analyses of the PXRD patterns of Na_2MO_4 and $NaRE(MO_4)_2$. Experimental data (○), calculated patterns (—), and difference curves (—, offset for clarity) are shown. Tick marks (|) corresponding to the calculated position of the diffraction maxima are included. Polyhedral view of the crystal structures of Na_2MO_4 (i) and $NaRE(MO_4)_2$ (j).

molar ratio of $0.5:[0.5 \times (1 - x)]:[0.5 \times x]$ ($0.5:[0.5 \times (1 - x - y)]:[0.5 \times x]:[0.5 \times y]$). Residual R_{wp} values and visual inspection of the difference curves of the Rietveld fits were employed to assess the phase-purity of the samples. Crystal structures were visualized using VESTA.[46]

Spectrofluorometry. Steady-state luminescence spectra were collected using a Fluorolog 3–222 fluorometer (Horiba Scientific) featuring a continuous wave Xe lamp (450 W). Excitation spectra were collected between 250 and 450 nm using a slit width of 1.5 nm, while emission spectra were acquired between 400 and 750 nm using a slit width of 2.0 nm. All spectra were recorded at room temperature.

RESULTS AND DISCUSSION

Rietveld fits to the PXRD patterns of Na_2MO_4 and $NaRE(MO_4)_2$ are shown in **Figure 2**; the corresponding structural parameters are provided in the ESI (**Table S1**). Inspection of difference curves demonstrates the phase purity of all the metalates synthesized using microwave heating. All diffraction maxima are indexed to the corresponding metalate; no maxima arising from crystalline impurities are observed. Microwave heating therefore provides access to crystalline and phase-pure metalates of varying compositional complexity, including binary (Na_2MoO_4, Na_2WO_4), ternary ($NaEu(MoO_4)_2$, $NaEu(WO_4)_2$), quaternary ($NaLa_{0.95}Eu_{0.05}(MoO_4)_2$, $NaLa_{0.95}Eu_{0.05}(WO_4)_2$), and quinary solids ($NaLa_{0.95}Pr_{0.025}Dy_{0.025}(MoO_4)_2$, $NaLa_{0.95}Pr_{0.025}Dy_{0.025}(WO_4)_2$). More importantly, phase-pure metalates are obtained in quantitative yield in a short period of time compared to solid-state reactions in which conventional heating is used. In our experience, the synthesis of phase-pure $NaRE(MO_4)_2$ phosphors using conventional heating requires 12 h at temperatures ranging from 800 to 850 °C.[19, 22] The same result is achieved in less than 30 min if microwaves are used to heat a comparable amount of reactants ($\approx$0.3 g); this represents a 30- to 40-fold reduction of the synthesis time. Thus, microwave-assisted synthesis of solid-state phosphors provides an efficient way to perform rapid screening of the luminescent response of a series of isostructural materials once heating profiles are well-established. This is particularly useful when it comes to establishing the dependence of the emission intensity on the concentration of the activator ion (e.g., determination of concentration quenching thresholds). Additionally, our results show that microwave heating may also be used to prepare binary metalates Na_2MoO_4 and Na_2WO_4, which are commonly employed as precursors in the synthesis of complex metalate phosphors such as quadruple molybdates and tungstates (i.e., $Na_5RE(MoO_4)_4$, $Na_5RE(WO_4)_4$).[22] Noteworthy is the observation that microwave-assisted synthesis also provides access to these quadruple metalates (see ESI, **Figure S1** and **Table S2**).

Once in hand, the luminescence response of metalate phosphors synthesized using microwave heating was probed. Specifically, we sought to investigate whether their response differed from that of the phosphors prepared using conventional heating. Owing to its compositional complexity, the quinary molybdate $NaLa_{0.95}Pr_{0.025}Dy_{0.025}(MoO_4)_2$ was employed as a test material. Results from luminescence studies are summarized in **Figure 3**. Firstly, it should be noticed that phosphors synthesized conventional and microwave heating have identical PXRD patterns (**Figure 3a**). More importantly, their excitation (**Figure 3b**) and emission spectra (**Figure 3c**) show nearly perfect overlap. For both types of phosphors, the metalate host's metal-to-oxygen charge-transfer band and the *f*–*f* intraconfigurational transitions of the Pr^{3+} and Dy^{3+} activators exhibit nearly identical positions and intensities. The overall luminescence response of the

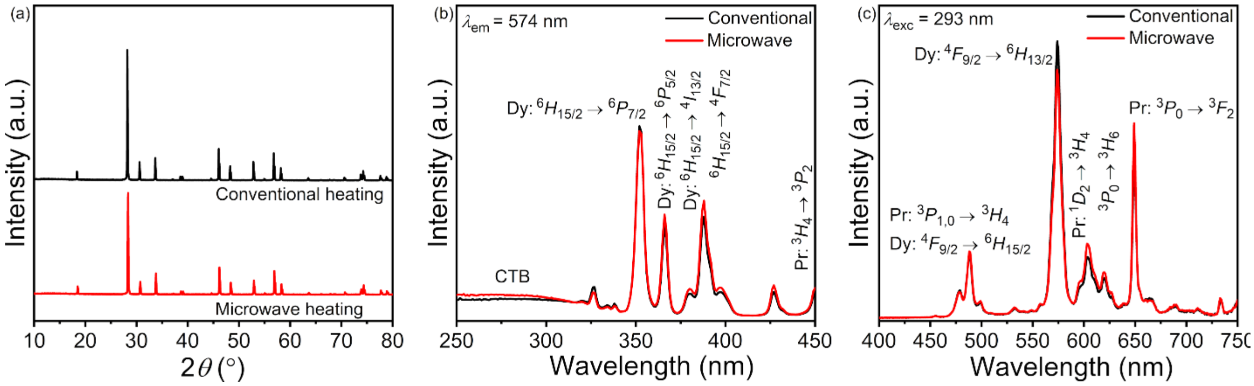

Figure 3. (a) PXRD patterns, (b) excitation spectra, and (c) emission spectra of quinary molybdate phosphors $NaLa_{0.95}Pr_{0.025}Dy_{0.025}(MoO_4)_2$ synthesized using conventional and microwave heating. Metal-to-oxygen charge-transfer band (CTB) and selected intraconfigurational *f*–*f* transitions of Pr^{3+} and Dy^{3+} are indicated in (b) and (c). Excitation spectra were monitored at 574 nm ($^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition of Dy^{3+}). Emission spectra were obtained upon excitation at 293 nm (charge-transfer band of the metalate host).

phosphor is therefore practically independent of the heating method. A major implication of this finding is that metalate phosphors may be synthesized much faster using microwave heating without compromising the figures-of-merit that describe their luminescence response. This conclusion is valid not only for the most compositionally complex of the metalates studied in this work, but also for the simpler ternary and quaternary phosphors activated by Eu^{3+} (see ESI, **Figure S2**). As a final note, it is worth mentioning that double metalate phosphors of formula $NaRE(MO_4)_2$ are well-known to exhibit local clustering of the rare-earth activators;[19, 47] the occupational disorder of the Na/RE site provides the structural basis for this phenomenon. The nearly identical luminescence responses of phosphors synthesized using microwave and conventional heating demonstrate that the distribution of the rare-earth emitters in the oxide host is practically independent of the heating method, even in the most compositionally complex materials.

CONCLUSIONS

In conclusion, we reported a procedure enabling the microwave-assisted solid-state synthesis of metalate phosphors of formula $NaRE(MO_4)_2$ and varying compositional complexity. Robustness, speed, simplicity, and the ability to yield phosphors with nearly identical luminescence response to that of those obtained using conventional heating are among the advantages of our synthetic approach. Whether for exploratory synthesis, production of highquality materials, or rapid screening of luminescence properties, this method should be applicable to the preparation of a broad range of molybdate and tungstate phosphors. Further, appropriate optimization of reaction conditions such as nature and mass of the susceptor, maximum output power of the microwave, and power level should enable the microwave-assisted synthesis of niobate and tantalate phosphors starting from Nb_2O_5 and Ta_2O_5 oxides, respectively. We expect that decreasing the mass of susceptor will allow higher temperatures to be reached within the reaction mixture (i.e., more microwave power available to couple to the reactants), thereby facilitating interdiffusion of the refractory Nb_2O_5 and Ta_2O_5 precursors.

ELECTRONIC SUPPLEMENTARY INFORMATION

The following ESI is provided: (1) structural parameters of Na_2MO_4, $NaRE(MO_4)_2$, and $Na_5La(MoO_4)_4$, and (2) excitation and emission spectra of Eu^{3+}-containing phosphors.

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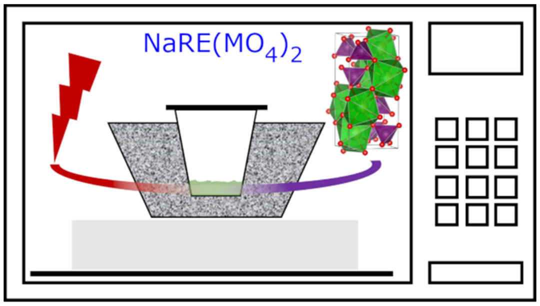

Microwave heating provides rapid access to crystalline and phase pure double molybdate and double tungstate phosphors activated by rare-earth metal ions.