Aqueous sol-gel synthesis and thermoanalytical study of the alkaline earth molybdate precursors

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Abstract The preparation and characterization of the M'-Mo-O nitrate-tartrate (M' = Mg, Ca, Sr, and Ba) gels, which were produced by the simple aqueous sol-gel method and calcined at 500, 600, 700, 800, 900, and 1,000 °C temperatures are reported. The crystalline alkaline earth metal molybdates (MgMoO₄, CaMoO₄, SrMoO₄, and BaMoO₄) and as-prepared M'-Mo-O nitrate-tartrate gels investigated by thermal analysis (TG/DSC), X-ray diffraction (XRD), and scanning electron microscopy (SEM). TG/DSC analysis showed the possible decomposition mechanism of synthesized gels. XRD studies allowed the identification of main types of crystalline structures in the MgMoO₄, CaMoO₄, SrMoO₄, and BaMoO₄ systems. Moreover, SEM analysis revealed the changes of surface morphology of the final compounds depending on annealing temperatures.

Keywords Alkaline earth metals · Sol–gel processing · Thermal analysis

Introduction

Metal molybdates of the general formula $AMoO_4$ (A = Mg, Ca, Sr, Ba, Cd, Zn, Pb, etc.) have been studied extensively for decades, owing to their technological

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importance in a variety of applications such as phosphors [1–3], scintillation materials [4, 5], microwave devices [6], catalysts [7], or optoelectronic devices [8, 9]. From the structural point, the differences between alkaline earth metal molybdates (AMoO₄, A = Mg, Ca, Sr, and Ba) mainly consist in ionic radius of the A-site. If the ionic radius of the A-site ion is smaller than 1.0 Å as is the case for MgMoO₄ ceramic, the compounds show a wolframite structure with octahedral coordination. Alternatively, if the ionic radius of the A-site is larger than 1.0 Å as is the case for Ca^{2+} , Sr^{2+} , and Ba^{2+} in AMoO₄, the compounds show a scheelite structure with tetrahedral coordination [10, 11]. Moreover, as well as the crystal structure, the surface morphology also significantly affects both the optical and electrical properties of alkaline earth metal molybdates. Thus, according to this the synthesis method that could be chosen for the preparation of these ceramic materials has significant importance.

In the last several decades, many different preparation techniques [12-17] have been used for the preparation of $AMoO_4$ (A = Mg, Ca, Sr, and Ba) ceramics. Nowadays, the results of obtained compounds, depending on the preparation route, are important and have significant influence to the science and technologies. Therefore, the choice of synthesis technique usually depends on variety factors that can shorten, facilitate, and reduce the preparation way. From this point of view, the solution-based synthetic methods play a crucial role in the design and production of fine ceramics and they have been successful in overcoming many of the limitation of the traditional solid-state, high-temperature methods. The use of solution chemistry can eliminate major problems, such as long diffusion paths, impurities, and agglomeration, and result in products with improved homogeneity [18-20]. Moreover, the sintering temperature that usually strong affects

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the properties of final compounds is crucial factor for the preparation of both nano-sized materials and thin films on different substrates.

In this work, the aqueous sol–gel synthesis method was successfully used for the preparation of M'–Mo–O nitrate–tartrate (M' = Mg, Ca, Sr, and Ba) gel precursors, which additional at 500, 600, 700, 800, 900, and 1,000 °C temperatures were calcined.

Experimental

The samples $MMoO_4$ (where M = Mg, Ca, Sr, and Ba) were prepared by an aqueous nitrate-tartrate sol-gel synthesis route taking tartaric acid (TA) as a complexing agent. The magnesium(II) nitrate hexahydrate (Mg(NO₃)₂·6H₂O, 99.97 % AlfaAesar), calcium(II) nitrate tetrahydrate (Ca(NO₃)₂·4H₂O, 99.98 % AlfaAesar), strontium(II) nitrate (Sr(NO₃)₂, 99.97 % AlfaAesar), barium(II) nitrate (Ba(NO₃)₂, 99.95 % AlfaAesar), and molybdenum oxide (MoO₃, 99.95 % Alfa Aesar) were used as starting materials and weighed according to the desired stoichiometric ratio. Nitric acid (HNO₃), distilled water, and ammonia (NH₃·4H₂O) were used as solvents and reagents to regulate the pH of the solutions. TA ($C_4H_6O_6$, 99.5 %) was used as a complexing agent. First, MoO₃ was dissolved in 25 ml of concentrated ammonia solution by stirring at 70-80 °C temperature. Then TA with a molar ratio of Mo/TA = 0.25, dissolved in a small amount of distilled water was added with a continuous stirring at the same temperature to the reaction mixture. Next, after several hours the stoichiometric amount of alkaline earth nitrate was mixed with the previous solution. To prevent precipitation, the excess of ammonia was neutralized with concentrated HNO₃ until the pH reached the value of ~ 1.0 . Finally, the same amount of the aqueous solution of the complexing agent TA was repeatedly added to the reaction mixture to prevent crystallization of metal salts during the gelation process. The beaker with the solution was closed with a watch glass and left for 1 h with continuous stirring. The obtained clear solution was concentrated by slow evaporation at 80 °C in an open beaker. A yellow transparent gel formed after nearly 90 % of the water has been evaporated under continuous stirring. After drying in an oven at 105 °C, fine-grained powders were obtained. The precursor gels were calcined for 5 h at 500 °C in alumina crucibles and reground carefully in an agate mortar. Since the gels are very combustible, slow heating (1 °C min^{-1}) , especially between 150 and 300 °C, was found to be essential. After intermediate grinding, the obtained powders were repeatedly annealed for 5 h at 500, 600, 700, 800, 900, and 1,000 °C. Thermal measurements were performed with TG-DSC, STA 6000 Perkin-Elemer instrument using a sample mass of about 10 mg and a heating rate of 20 °C min⁻¹ in flowing air (20 cm³ min⁻¹) at ambient pressure from room temperature to 1,000 °C. X-ray diffraction (XRD) patterns have been recorded in air at room temperature with a powder X-ray diffractometer Rigaku MiniFlex II using Cu K α_1 radiation. The spectra were recorded at the standard rate of 1.5 2θ min⁻¹. The scanning electron microscope (SEM) Hitachi TM3000 was used to study the surface morphology and microstructure of the obtained ceramic samples.

Results and discussion

Thermal analysis

In order to explain the thermal decomposition behavior and crystallization processes of the synthesized M–Mo–O (M = Mg, Ca, Sr, and Ba) nitrate–tartrate gel precursors, the thermal analysis (TG/DSC) was performed. TG/DSC measurements of the alkaline earth metal molybdate nitrate–tartrate gel precursors carried out up to 1,000 °C at a heating rate of 20 °C min⁻¹ in flowing air (20 cm³ min⁻¹) at ambient pressure with a sample mass of about 5 mg. The curves of analyzed samples are shown in Fig. 1, respectively.

At the initial stage of the explanation of TG curve, shown in Fig. 1a, should be noted that the final mass loss of about 78 % occurred to 580 °C temperature, which gives the conclusion about the decomposition of all volatile organic parts in the gel precursor. In general, the decomposition processes of the Mg-Mo-O nitrate-tartrate system could be roughly divided into eight periods that clearly indicate all mass losses and heat flow transformations occurring during the sample heating in the appropriate range of temperature. The first mass loss of about 1 % in the TG curve goes from 40 to 140 °C temperatures and is related with the removal of surface absorbed water from the gel and/or water from the coordination sphere of the metal complexes. A broad endothermic peak with heat flow of 388 mJ and $\Delta H = 69.7$ J g⁻¹ on the DSC curve corresponds to the first period of mass loss. By further increasing of temperature from 150 to 240 °C, the mass of Mg-Mo-O nitrate-tartrate precursor to 16.5 % has been decreased. A sharp exothermic peak of about 1,280 mJ $(\Delta H = -230 \text{ Jg}^{-1})$ confirmed either by the initial decomposition of excess of TA in the precursor gel or by the decomposition reactions of mixed-metal nitrate and ammonium salts that formed during the sol-gel processing. The third mass loss (4.2 %) of precursor gel in 245-320 °C temperature range has been observed. The endothermic peak of about 510 mJ ($\Delta H = 92 \text{ J g}^{-1}$) shows both the further decomposition of either TA or metal tartrates and



Fig. 1 Combined TG–DSC curves of the Mg–Mo–O (a), Ca–Mo–O (b), Sr–Mo–O (c), and Ba–Mo–O (d) nitrate–tartrate gel precursors in flowing air

the intermolecular rearrangement of organic compounds. Thereafter, on the following increasing of temperature fourth (2.7 %) and fifth (1 %) mass loss stages have started. Both small exothermic peaks of about 195 mJ ($\Delta H = -35 \text{ J g}^{-1}$) and 22 mJ ($\Delta H = -4 \text{ J g}^{-1}$) are

attributed to the beginning of burning processes of residual organic compounds in the precursor gel. Finally, the last sixth mass loss of about 4 % from 470 to 580 °C temperature accords with the burning of elemental carbon in the residual sample. This process by strong exothermic peak of about 4,920 mJ ($\Delta H = -882 \text{ J g}^{-1}$) was confirmed, respectively. By further increasing of temperature, no mass losses in the TG curve have observed. Meanwhile, the results obtained from DSC measurement clearly indicated that at least two broad endothermic peaks 525 mJ $(\Delta H = 94 \text{ J g}^{-1})$ and 6,603 mJ ($\Delta H = 1,185 \text{ J g}^{-1}$) in the 600-1.000 °C range of temperature have been related. Both of them came with the crystallization process of final structural materials. Moreover, according to the stabilized mass at temperatures higher than 800 °C, no impurity phases either crystalline or amorphous have formed.

In conclusion, TG/DSC analysis of Mg–Mo–O nitrate– tartrate gel precursor suggests that single-phase crystalline MgMoO₄ compound at relative low temperature of 550 °C should form.

Slightly different view of TG-DSC curves by thermal treatment of Ca-Mo-O nitrate-tartrate gel precursor, presented in Fig. 1b, is shown. In this case, overall mass loss of about 74 % of analyzed specimen to 775 °C temperature has occurred. The thermal decomposition processes of the Ca-Mo-O nitrate-tartrate system likewise in previous case also into eight periods have divided. The first mass loss of about 2 % in the TG curve takes from 60 to 130 °C temperatures and is related with the removal of surface absorbed water from the gel and/ or water from the coordination sphere of the metal complexes. An endothermic peak of heat flow of 403 mJ and $\Delta H = 40 \text{ J g}^{-1}$ on the DSC curve corresponds to the first period of mass loss. The initial thermal dissociation of TA in the precursor gel or the decomposition reaction of mixed-metal nitrate and ammonium salts that were formed during the sol-gel processing start from 130 to 140 °C temperature, respectively. This mass loss of about 9 % follows the exothermic transformations with a peak width of about 2,247 mJ ($\Delta H = -217 \text{ J g}^{-1}$). The third mass loss of about 14 % from 210 °C temperature, in this case, to the final decomposition of the excess of TA in the sample could be attributed. The exothermic peak of about 2,238 mJ ($\Delta H = -215.9 \text{ J g}^{-1}$) from 240 to 350 °C temperature corresponds with the third period of mass loss. Next to that, the burning of the small amount of elemental carbon of about 1 % that has formed during the partial decomposition and intermolecular rearrangement of TA has been observed. Comparatively to the low mass loss in this stage, a strong exothermic peak of about 1,898 mJ ($\Delta H = -183 \text{ J g}^{-1}$) was measured. The fifth stage on the DCS curve from 520 to 670 °C temperature with no mass changes in the analyzed sample characterized by endothermic effect of about 1,996 mJ $(\Delta H = 192.5 \text{ Jg}^{-1})$ to the crystallization of CaMoO₄ phase is related. Finally, the last mass loss of about 12 % from 700 to 780 °C temperature with the decomposition of carbonates that formed during the partial oxidation of metal tartrates in the Ca-Mo-O gel precursor have occurred. A strong exothermic peak of about 8,225 mJ $(\Delta H = -793 \text{ Jg}^{-1})$ in this period corresponds to the decomposition process of hydrocarbons with the evaporating of CO₂ and H₂O gases. As seen from the DSC curve in the 780-880 °C temperature range, another broad exothermic band of about 2,450 mJ ($\Delta H =$ -236.4 Jg^{-1}) is observed. This negative heat effect is closely related with the earlier exothermic process and the further crystallization of CaMoO₄ phase in the same matter of time. In conclusion, it should be noted that the final decomposition of Ca-Mo-O nitrate-tartrate gel precursor occurs at the temperature of 780 °C. However, the crystallization process, likewise as was mentioned in previous case, also starts at relatively low temperature of 550 °C.

The combined TG-DSC curves of Sr-Mo-O nitratetartrate gel precursor in Fig. 1c are displayed. The decomposition of all volatile parts in Sr-Mo-O sample to 600 °C temperature has occurred. The general behavior of TG-DSC curves of Sr-Mo-O gel in six periods has divided. In the first period, the evaporation of adsorbed water molecules with a mass loss of about 0.5 % and an endothermic peak of about 426 mJ ($\Delta H = 72 \text{ J g}^{-1}$) to 140 °C temperature was occurred. After that in the second period with a mass loss of about 14 % from 150 to 240 °C temperature, the decomposition of TA and either ammonium or nitrate ions was started. The decomposition of abovementioned compounds to CO_2 and NO_x gases by the exothermic peak of about 551 mJ ($\Delta H =$ -94 Jg^{-1}) was confirmed. Next to that in the third and fourth periods from 245 to 500 °C temperatures the further decomposition of metal tartrates with mass loss of about 9 % overlaps with the intermolecular rearrangement of residual products of TA. This conclusion by well-defined exothermic peak of about 166 mJ ($\Delta H =$ -28 Jg^{-1}) from 255 to 270 °C temperatures and by overlapped both exothermic and endothermic processes in the range of 280-450 temperature has suggested. Further increasing of temperature from 450 to 505 °C leads to the start of crystallization of the final SrMoO₄ phase that confirmed a broad endothermic peak of about 175 mJ ($\Delta H = 30 \text{ J g}^{-1}$) in the DSC curve. Finally, the mass loss of about 7 % from 520 to 600 °C temperature with an exothermic peak of about 8,038 mJ ($\Delta H =$ $-1,366.5 \text{ Jg}^{-1}$) by combusting of residual organic compounds and as-formed inorganic carbon has been characterized. In the last six period of thermal investigation of Sr–Mo–O gel precursor, the TG curve has remained constant. However, in the DSC curve a broad endothermic band related with the crystallization process near to the 1,000 °C temperature has been observed. In conclusion, TG/DSC analysis of Sr–Mo–O nitrate–tartrate gel precursor showed that pure singlephase crystalline SrMoO₄ compound at temperature of 600 °C should form. However, the crystallization process of SrMoO₄ starts under 500 °C temperature that clearly the results obtained from DSC curve.

The last combined TG-DSC curves of Ba-Mo-O nitrate-tartrate gel precursor in Fig. 1d are shown. The character of mass loss in the TG curve is similar comparing with previous cases when the mass of Ba-Mo-O nitrate-tartrate gel precursor over 600 °C temperature remains constant. However, the general views of TG-DSC curves of the Ba-Mo-O sample and conclusions that have made from this thermal analysis are significantly different in comparing with the three cases presented before. The TG-DSC analysis of Ba-Mo-O nitrate-tartrate gel precursor was divided into five mass loss periods. The first exothermal peak of about 977 mJ $(\Delta H = -219 \text{ J g}^{-1})$ from 60 to 165 °C temperature indicates that the first mass loss of about 5 % in the sample is closely related with the thermal decomposition of ammonium and nitrate ions to the N₂ and NO_x gaseous products. This exothermal process overcomes the endothermic peak of the evaporation of water molecules from the gel that was not well expressed in the previous cases. By the further increase of temperature from 170 to 300 °C, the typical decomposition process of TA with mass loss of about 60 % has been observed. A strong exothermic behavior of about 8,383 mJ ($\Delta H =$ $-1,878 \text{ Jg}^{-1}$) in the DSC curve was expressed. After that in the range of 300-500 °C temperature further decomposition and the rearrangement of organic parts in the gel precursor with mass loss of about 10 % has occurred. Finally, from the 500 °C temperature the combustion of residual carbon with mass loss of about 10 % in the sample has started. In addition, it is interesting to note that this burning process in at least to mass losses of about 2.5 and 1 % has been divided. In the DSC curve two exothermic peaks of about 2,486 mJ $(\Delta H = -557 \text{ J g}^{-1})$ and 233 mJ $(\Delta H = -52 \text{ J g}^{-1})$ have been shown. By the further increase of temperature, the mass in the TG curve remains constant. The endothermic character of the DSC curve lets us conclude that in this range of temperature the crystallization of BaMoO₄ has dominated.

In conclusion, the thermal decomposition of abovedescribed fourth gel precursors occurred in different ways depending on the alkali earth metal in the starting materials.

X-ray diffraction

The XRD data were collected at room temperature with Cu $K\alpha_1$ radiation and a scan range from 10° to 70° for 2 θ . XRD patterns of Mg-Mo-O nitrate-tartrate gel annealed at different temperatures shown in the top three panels in Fig. 2, are matched with that of standard ICSD card of MgMoO₄ shown in the bottom panel. In addition, XRD results indicated that even at 500 °C crystalline monoclinic MgMoO₄ phase has formed. By increase of temperature to 1,000 °C, the characteristic peaks of investigated samples became sharper and no new crystal phases have appeared. These results are in good agreement with the well-known tendency that at higher annealing temperatures, the crystallinity of mixed-metal oxides increases. These obtained results are consistent with the conclusions made from TG-DSC analysis of Mg-Mo-O nitrate-tartrate gel precursor that showed well-expressed ending temperature of mass loss and suggested possible crystallization point of final material with initial composition of $MgMoO_4$ phase.

Figure 3 exhibits powder XRD patterns of the CaMoO₄ samples obtained by sintering the dried Ca-Mo-O nitratetartrate gel precursor for 5 h at 500, 700, and 1,000 °C temperatures in air atmosphere at ambient pressure. Despite the fact that according to the TG-DSC analysis overall mass loss of about 74 % of analyzed Ca-Mo-O gel precursor to 775 °C temperature has occurred, the crystallization of Powelite-structured CaMoO₄ phase only above 500 °C in XRD pattern (Fig. 3) has been identified. By increasing of temperature from 500 to 700 and 1,000 °C, the characteristic peaks of CaMoO₄ crystal phase became sharper and better indexed that denote the growing of crystallite size in the final material. In addition, according to the XRD and TG-DSC results of investigated Ca-Mo-O precursor and sintered CaMoO₄ compound could be confirmed the conclusion that the mass loss above





Fig. 2 Standard ICSD card of $MgMoO_4$ and XRD patterns of the Mg–Mo–O nitrate–tartrate gel precursor annealed at 500, 700, and 1,000 °C temperatures

Fig. 3 Standard ICSD card of $CaMoO_4$ and XRD patterns of the Ca–Mo–O nitrate–tartrate gel precursor annealed at 500, 700, and 1,000 °C temperatures

700 °C temperature because of the combustion of either hydrocarbons and/or elemental carbon has occurred. Moreover, according to the consistent results of XRD patterns of both investigated systems to explain the marked differences between TG–DSC curves an additional investigation is required.

XRD patterns of Sr–Mo–O nitrate–tartrate gel precursor annealed at 500, 700, and 1,000 °C temperatures in Fig. 4 are shown. In this case, all used annealing temperatures are suitable for preparation of single-phase crystalline SrMoO₄ compound. Moreover, these XRD data of sintered Sr–Mo–O nitrate–tartrate system are in a good agreement with the TG–DSC results presented in Fig. 1c.

Slightly different results compared with previous cases after annealing of Ba–Mo–O nitrate–tartrate gel precursor at 500, 700, and 1,000 °C temperatures have obtained. Corresponding XRD patterns of this system in Fig. 5 are displayed. For Ba–Mo–O nitrate–tartrate sample annealed at 500 °C temperature, an extra XRD peaks at about 18.92°, 24.27°, 26.89°, 28.74°, and 30.94° appeared, which belongs to monoclinic $BaMo_3O_{10}$ crystal phase (ICSD 50274) and compose 13.75 % as side phase in tetragonal crystal structure (ICSD 56109) displayed in a bottom panel (Fig. 5). By further increasing of annealing temperature to 700 °C, the impurity peaks of monoclinic $BaMoO_4$ crystal phase disappeared and only characteristic plane-structured reflections of tetragonal phase have dominated. Finally, the XRD pattern, displayed in next-to-last panel, shows the possible rearrangement of characteristic planes in tetragonal $BaMoO_4$ crystal phase by increasing of temperature to 1,000 °C. This conclusion has confirmed by the strong expressed endothermic signal in the DSC curve above 700 °C, displayed in Fig. 1d.

In summary, the XRD data of all investigated samples have revealed that using aqueous sol–gel processing at relatively low temperature of 500 °C is possible to synthesize pure MgMoO₄, CaMoO₄, and SrMoO₄ crystal phases. Meanwhile, XRD patterns of the Ba–Mo–O





Fig. 4 Standard ICSD card of $SrMoO_4$ and XRD patterns of the Sr-Mo-O nitrate-tartrate gel precursor annealed at 500, 700, and 1,000 °C temperatures

Fig. 5 Standard ICSD cards of $BaMoO_4$ and XRD patterns of the Ba–Mo–O nitrate–tartrate gel precursor annealed at 500, 700, and 1,000 °C temperatures



Fig. 6 SEM micrographs of Mg–Mo–O (a 700 °C, b 1,000 °C), Ca–Mo–O (c 700 °C, d 1,000 °C), Sr–Mo–O (e 700 °C, f 1,000 °C), and Ba–Mo–O (g 700 °C, h 1,000 °C) nitrate–tartrate gel precursors annealed at different temperatures

nitrate–tartrate gel precursor annealed at 500 °C temperature the characteristic peaks that attributed to the monoclinic and tetragonal crystal phases of BaMoO₄ are observed. By increase of the annealing temperature to 700 °C only tetragonal crystal structure of BaMoO₄ has found, as presented in Fig. 5.

SEM micrographs

The surface morphology of MgMoO₄, CaMoO₄, SrMoO₄, and BaMoO₄ compounds prepared by aqueous sol-gel synthesis method and annealed at 700 and 1,000 °C temperatures by scanning electron microscopy (SEM) was investigated. The representative SEM micrographs of MgMoO₄ sample are shown in Fig. 6a, b. The surface of the Mg-Mo-O nitrate-tartrate gel precursor annealed at 700 °C temperature consists of the porous irregular particles of size from 500 nm to 3 µm. With further increasing of annealing temperature to 1,000 °C, the spherical crystalline particles in size of about 1-5 µm have estimated. These obtained results are in a good agreement with the broad endothermic band of about 6,603 mJ in the stage of temperature from 800 to 1,000 C presented in DSC curve that characterizes the crystallization and agglomeration processes of final crystalline material.

Slightly different results from SEM micrographs, presented in Fig. 6c, d, by combustion of Ca–Mo–O nitrate– tartrate gel precursor were obtained. Figure 6c shows SEM image of Ca–Mo–O sample sintered at 700 °C. In this case, the growing of homogenous spherical grains with an average diameter of about 200–300 nm is observed. Thereafter, the annealing temperature of 1,000 C leads to the formation of the crystals with well-expressed spherical shapes and edges that size varies from 1 to 5 μ m.

Interesting results by combustion of Sr–Mo–O nitrate– tartrate gel precursor from SEM micrographs in Fig. 6e, f were observed. The homogeneous spherical grains of SrMoO₄ with an average diameter of about 500 nm have formed when the synthesis at 700 °C was carried out (Fig. 6e). By increasing of annealing temperature to 1,000 °C (Fig. 6f), the surface of SrMoO₄ sample consists of close-packed spherical crystals with well-defined edges of size from 2 to 10 μ m.

The tendency in changing of the surface morphology by combustion of the Ba–Mo–O nitrate–tartrate gel precursor (Fig. 6g, h) followed in the similar manner as was shown in previous cases. With increasing of sintering temperature to 700 °C leads to the agglomeration of close-packed spherical crystals with well-defined edges in size up to 20 μ m that are surrounded by irregular crystals of size less than 5 μ m. Figure 6h shows the formation of crystals that form irregular agglomerates in size from 5 to 50 μ m.

In conclusion, it is clear that the surface morphology of investigated samples has significantly affected by both sintering temperature and nature of alkaline earth element. Summarizing results obtained from TG–DSC, XRD, and SEM measurements can be concluded that aqueous sol–gel synthesis method is a suitable technique for the preparation of single-phase MgMoO₄, CaMoO₄, SrMoO₄, and BaMoO₄ compounds at relatively low temperature of 500 °C. Moreover, according to the SEM results the formation of spherical crystals with well-expressed planes and edges have started up to 700 °C in MgMoO₄, CaMoO₄, and SrMoO₄ cases and below 700 °C in BaMoO₄ case that are closely related with the relative low melting point of barium molybdate crystal phase.

Conclusions

Summarizing results obtained from TG–DSC, XRD, and SEM measurements can be concluded that aqueous sol–gel synthesis method is a suitable technique for the preparation of single-phase MgMoO₄, CaMoO₄, SrMoO₄, and BaMoO₄ compounds at relatively low temperature of 500 °C. Moreover, according to the SEM results the formation of spherical crystals with well-expressed planes and edges have started up to 700 °C in MgMoO₄, CaMoO₄, and SrMoO₄ cases and below 700 °C in BaMoO₄ case that are closely related with the relative low melting point of barium molybdate crystal phase.

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References

- Mikhailik VB, Kraus H, Kapustyanyk V, Panasyuk M, Prots Y, Tsybulskyi V, Vasylechko L. Structure, luminescence and scintillation properties of the MgWO(4)–MgMoO(4) system. J Phys Condens Matter. 2008;20:365219.
- Zakharko Y, Luchechko A, Syvorotka I, Stryganyuk G, Solskii I. Anisotropy of optical absorption and luminescent properties of Ca-MoO₄. Radiat Meas. 2010;45:429–31.
- Li X, Yang ZP, Guan L, Guo QL. A new yellowish green luminescent material SrMoO₄:Tb³⁺. Mater Lett. 2009;63:1096–8.
- Mikhailik VB, Kraus H. Performance of scintillation materials at cryogenic temperatures. Phys Status Solidi B. 2010;247:1583–99.
- Veresnikova AV, Lubsandorzhiev BK, Barabanov IR, Grabmayr P, Greiner D, Jochum J, Knapp M, Oßwald C, Poleshuk RV, Ritter F, Shaibonov BAM, Vyatchin YE, Meierhofer G. Fast scintillation light from CaMoO₄ crystals. Nucl Instrum Methods A. 2009;603:529–31.
- Guo J, Zhou D, Wang H, Chen Y, Zeng Y, Xiang F, Wu Y, Yao X. Microwave and infrared dielectric response of temperature stable (1 - x)BaMoO₄-xTiO₂ composite ceramics. J Am Ceram Soc. 2012;95:232–7.

- Robertson LC, Gaudon M, Jobic S, Deniard P, Demourguess A. Investigation of the first-order phase transition in the Co₁₋ _xMg_xMoO₄ solid solution and discussion of the associated thermochromic behavior. Inorg Chem. 2011;50:2878–84.
- Mi Y, Huang ZY, Hu FL, Li YF, Jiang JY. Room-temperature synthesis and luminescent properties of single-crystalline SrMoO₄ nanoplates. J Phys Chem C. 2009;113:20795–9.
- Spasskii DA, Kolobanov VN, Mikhailin VV, Berezovskaya LY, Ivleva LI, Voronina IS. Luminescence peculiarities and optical properties of MgMoO₄ and MgMoO₄:Yb crystals. Opt Spectrosc. 2009;106:556–63.
- Matar SF, Largeteau A, Demazeau G. AMoO(4) (A = Mg, Ni) molybdates: phase stabilities, electronic structures and chemical bonding properties from first principles. Solid State Sci. 2010;12:1779–85.
- 11. Kim ES, Jeon CJ, Clem PG. Effects of crystal structure on the microwave dielectric properties of ABO(4) (A = Ni, Mg, Zn and B = Mo, W) ceramics. J Am Ceram Soc. 2012;95:2934–8.
- Dutta PS, Khanna A. Eu³⁺ activated molybdate and tungstate based red phosphors with charge transfer band in blue region. ECS J Solid State Sci. 2013;2:R3153–67.
- Mendoza C, de Ligny D, Panczer G, Peuget S, Bardez-Giboire I, Schuller S. Behaviour of the Eu³⁺ D-5(0) → F-7(0) transition in CaMoO₄ powellite type ceramics under Ar and Pb ions implantation. Opt Mater. 2011;34:386–90.

- 14. Yang YL, Li XM, Feng WL, Li WL, Tao CY. Co-precipitation synthesis and photoluminescence properties of $(Ca_{1-x-y}, Ln(y))MoO_4:xEu(3+)$ (Ln = Y, Gd) red phosphors. J Alloys Compd. 2010;505:239–42.
- Sun Y, Ma J, Jiang X, Fang J, Song Z, Gao C, Liu Z. Ethylene glycol-assisted electrochemical synthesis of CaMoO₄ crystallites with different morphology and their luminescent properties. Solid State Sci. 2010;12:1283–6.
- Baldychev I, Javadekar A, Buttrey DJ, Vohs JM, Gorte RJ. A study of the redox properties and methanol oxidation rates for molybdenum-based mixed oxides. Appl Catal A. 2011;394:287–93.
- Liu YF, Xia LL, Lu YN, Dai SH, Takeguchi M, Hong HM, Pan ZG. Surfactant-free microwave-assisted hydrothermal synthesis of BaMoO₄ hierarchical self-assemblies and enhanced photoluminescence properties. J Colloid Interface Sci. 2012;381:24–9.
- Zalga A, Moravec Z, Pinkas J, Kareiva A. On the sol-gel preparation of different tungstates and molybdates. J Therm Anal Calorim. 2011;105:3–11.
- Wu H, Hu Y, Zhang W, Kang F, Li N, Ju G. Sol–gel synthesis of Eu³⁺ incorporated CaMoO₄: the enhanced luminescence performance. J Sol Gel Sci Technol. 2012;62:227–33.
- Perez-Mendoza M, Valles C, Maser WK, Martinez MT, Benito AM. Influence of molybdenum on the chemical vapour deposition production of carbon nanotubes. Nanotechnology. 2005;16:S224–9.