

Research Article

Morphology and Photoluminescence of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{MoO}_4$ Powders by a Molten Salt Method

Ling Wei, Yunfei Liu, Yinong Lu, and Tao Wu

College of Materials Science and Engineering, Nanjing University of Technology, Jiangsu, Nanjing 210009, China

Correspondence should be addressed to Yinong Lu, yinonglu@njut.edu.cn

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$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{MoO}_4$ powders with scheelite-type tetragonal structure were successfully synthesized by a molten salt method. The structure, morphology, and luminescent property of the as-prepared powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and photoluminescence (PL), respectively. The results show that the tetragonal $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{MoO}_4$ powders were synthesized at 650°C for 6 h by the molten salt method. The calcining temperature, the soaking time, and the molar ratio of the salt to Na_2MoO_4 have great influence on the phase, size, morphology, and PL properties. The better crystallinity and smaller particle size, the higher PL emission peak is.

1. Introduction

The fabrication of nano- to microscale inorganic materials with special size and morphology is of great interest for the study of material chemistry because of the importance in basic scientific research and potential technology applications of such materials [1, 2]. In recent years, molybdates and tungstates have attracted the interest of many technological fields and scientific areas owing to their wide potential application, including solid-state lasers [3], optic fiber [4], stimulated Raman scatters [5], catalysts [6], and microwave applications [7].

The molybdates with scheelite-type tetragonal structure are characterized by the general formula ABO_4 ($A = \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}$; $B = \text{Mo}$), space group $I4_1/a$, and symmetry C_{4h}^6 [8, 9]. These materials have been prepared in both powder and film forms by means of several technologies, such as electrochemical method [10], hydrothermal [11], solid-state reaction [12], and sol-gel method [13]. However, these approaches still have some limitations, for example, the as-prepared samples are not only irregular in morphology and large in particle size, but also of small production and high cost.

Recently, researchers mostly pay attention to unit material systems and binary or multivariate molybdate thin films.

Pôrto et al. [14] investigated the structure and photoluminescence of $\text{Ca}_x\text{Sr}_{1-x}\text{WO}_4$ system at room temperature by a soft chemical method and heat treated between 400°C and 700°C . Rangappa et al. [15] studied fabrication of Ba-rich crystalline $\text{Ba}_{1-x}\text{Sr}_x\text{WO}_4$ and $\text{Ba}_{1-x}\text{Ca}_x\text{WO}_4$ films at room temperature by mechanically assisted solution reaction. Shi et al. [16] synthesized $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{MoO}_4:\text{Eu}^{3+}$ powder using a sol-gel method. Fewer researchers on improving the luminescent property of solid-solution powders were reported. In order to fully research their properties, the study of alkaline earth molybdate materials is necessary.

Molten salts are widely used as an effective chemical reaction medium to produce a high-temperature liquid environment for crystal growth. The ionic fluxes molten salts possess high reactivity toward different inorganic species and relatively low melting points which makes them convenient for preparation of inorganic materials. Molten salt method has advantages of simple instrumentation and easy manipulation. And it is environmentally friendly and available to a large-scale production. In this paper, we report on the synthesis of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{MoO}_4$ with perfect crystalline morphology and homogeneous chemical composition by a molten salt method. Different synthesis parameters were discussed, and a possible crystallization was proposed. Finally, the luminescent properties of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{MoO}_4$ under different soaking times were investigated.

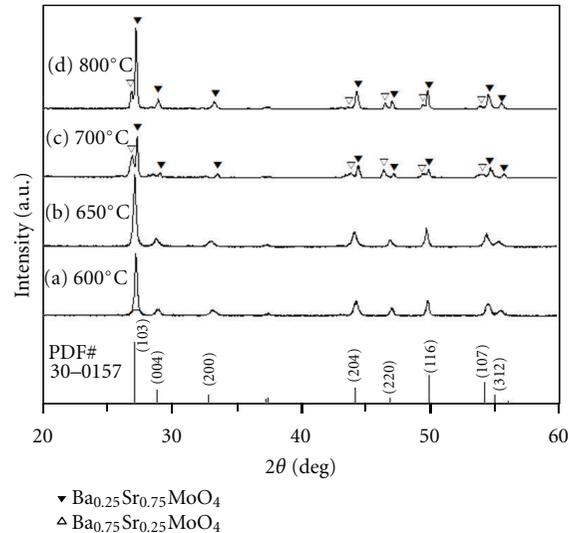


FIGURE 1: XRD patterns of the products obtained at different synthesis temperatures for 6 h, with 3 : 1 molar ratio of the salt to Na_2MoO_4 .

2. Experimental

2.1. Materials. Na_2MoO_4 , BaCl_2 , and SrCl_2 of analytic reagent grade were used as the raw materials. The molar ratio of Na_2MoO_4 , BaCl_2 , and SrCl_2 was 2 : 1 : 1, While the molar ratio of the KCl salt to Na_2MoO_4 was selected as 1 : 1, 3 : 1 and 6 : 1, respectively. Then, the mixture was ground well with absolute ethanol for 6 h. After drying at 80°C for 24 h in air, the mixture was calcined at $600^\circ\text{C} \sim 800^\circ\text{C}$ for 1 h \sim 8 h. Finally, the products were thoroughly washed with distilled water for several times and then dried at 80°C .

2.2. Characterizations. The crystallographic characterization of the products was investigated by X-ray diffractometer with $\text{Cu K}\alpha$ radiation at a scan speed of $5^\circ/\text{min}$ in the 2θ range from 20° to 60° . The morphologies of the products were observed by a scanning electron microscope. Room temperature PL spectrum was recorded on FL3-221 fluorescence spectrometer excited with a Xe lamp as excited source.

3. Results and Discussion

The XRD patterns of the as-prepared products obtained at different calcining temperatures for 6 h with 3 : 1 molar ratio of the KCl salt to Na_2MoO_4 as shown in Figure 1. The XRD results reveal that the calcining temperature plays an important role in controlling the phase purity. It is obviously observed that the product obtained at 600°C is pure scheelite-type tetragonal phase $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{MoO}_4$ (JCPDS 30-0157), and no impurities could be detected. Increasing the calcining temperature to 650°C , the diffraction peaks become stronger and sharper, which suggests that elevating heating temperature would favor the crystallization. But with further increasing calcined temperature above 700°C (Figures 1(c) and 1(d)), the strength of the peaks decreases, and the diffraction peaks split. The split is ascribed to phase separation. According to the comparison of the interplanar

distance, the separation phase is $\text{Ba}_{0.25}\text{Sr}_{0.75}\text{MoO}_4$ (JCPDS 28-1207) and $\text{Ba}_{0.75}\text{Sr}_{0.25}\text{MoO}_4$ because of the high temperature.

Figure 2 shows SEM images of the as-prepared products at different calcining temperatures for 6 h, with 3 : 1 molar ratio of the salt to Na_2MoO_4 . It can be noted that when the reaction temperature keeps at 600°C , $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{MoO}_4$ powders have octahedron shape with inhomogeneous size. The size distribution of the particle is board. When the temperature increases to 650°C , the size distribution of the octahedrons narrows, and the mean size is $4.68 \mu\text{m}$. With the increasing of temperature, abnormal particle growth is observed, and the mean size of the products increases to $6.50 \mu\text{m}$. When the temperature further increases to 800°C , flake-like particles substitute the octahedrons gradually.

Figure 3 shows XRD patterns of the as-prepared products synthesized by the molten salt method at 650°C for 6 h, varying the molar ratio of the salt to Na_2MoO_4 . It is obvious that the three XRD patterns are similar when the molar ratio is 1 : 1, 3 : 1 and 6 : 1, and all the patterns can be indexed to a pure tetragonal phase of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{MoO}_4$. Further increasing the ratio of the molar ratio of the salt to the Na_2MoO_4 from 1 : 1 to 6 : 1 does not lead to obvious changes in the intensity and the width of the peaks.

During the molten salt synthesis process, the mass transfer process is related to the liquids formed by salt melting, so the size and morphology of the particles can be influenced by the content of the salts directly. The effect of the mole ratio of the salt to Na_2MoO_4 on $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{MoO}_4$ crystallizing morphology is shown in Figure 4. When the molar ratio is 1 : 1, the surface of the powders is irregular, and the size of the particles is board. When the molar ratio increased to 3 : 1 in Figure 2(b), homogeneous octahedrons with well-defined faces are obtained. When the molar ratio increases to 6 : 1, the dimension distribution of the particles broadens, and the edges of octahedrons turn vague. The reason is that with the increasing of salts, the content of the

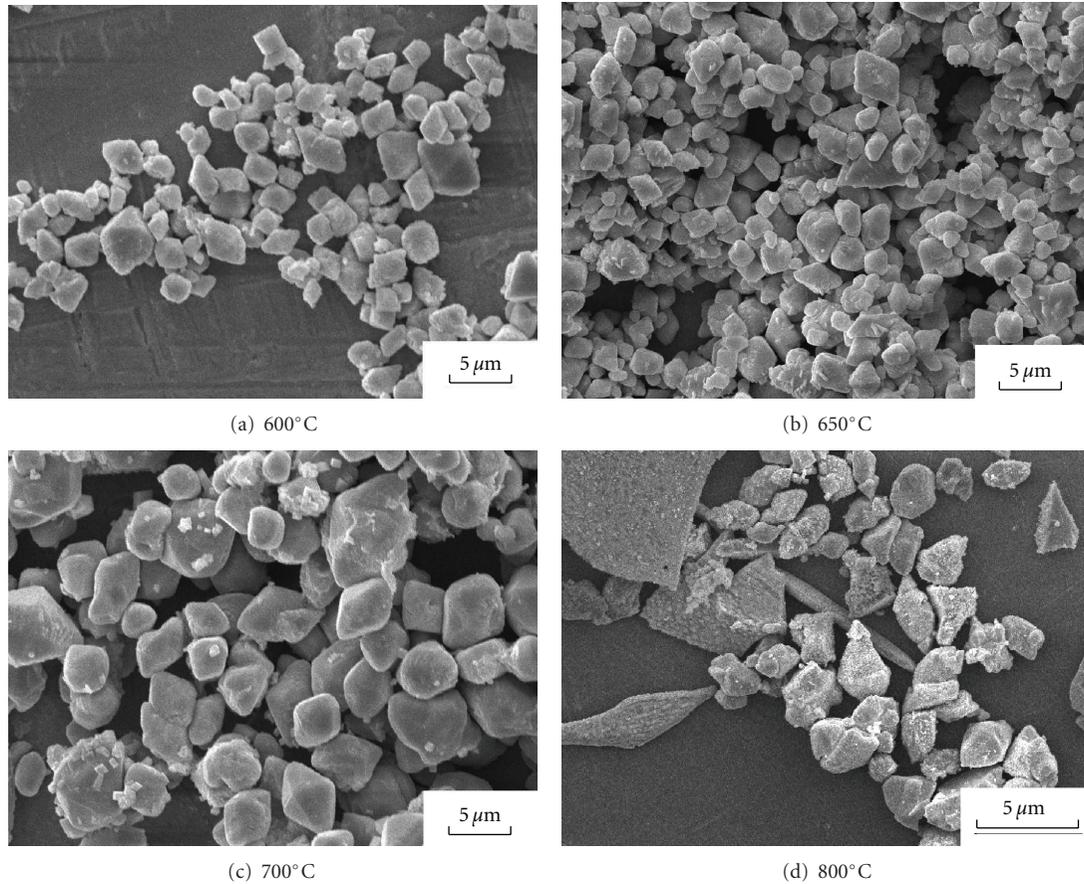


FIGURE 2: SEM images of the products obtained at different synthesis temperatures for 6 h, with 3 : 1 molar ratio of the salt Na_2MoO_4 .

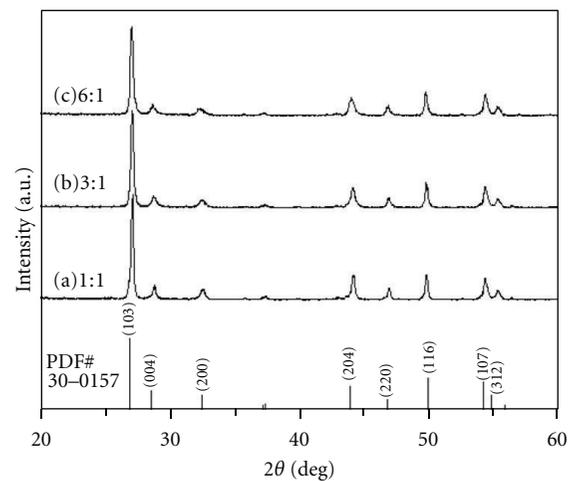


FIGURE 3: XRD patterns of the products obtained at 650°C for 6 h, with different molar ratio of the salt to Na_2MoO_4 .

liquid phase increases gradually at high-temperature reaction system. The reaction changes from solid-state reaction to liquid phase reaction. At last, the liquid-phase reaction plays a dominant role. Thus, the size of particles decreases. When the content of salts is too much, redundant liquid phase is obtained, which depresses particle growth.

Figure 5 shows XRD patterns of the products obtained at 650°C for different soaking time, with 3:1 molar ratio of the salt to Na_2MoO_4 . The XRD results reveal that the soaking time plays an important role in controlling the phase structures. When the soaking time is 1 h, only BaMoO_4 peaks (JCPDS 08-0455) and other impurity $\text{Sr}_{0.8}\text{Ba}_{0.2}\text{CO}_3$ phase

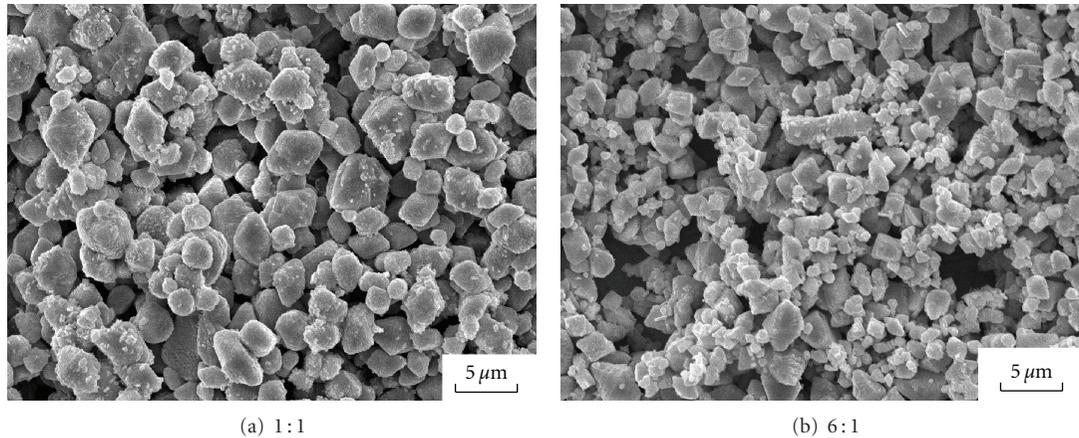


FIGURE 4: SEM images of the products obtained at 650°C for 6 h, with different molar ratio of the salt to Na_2MoO_4 .

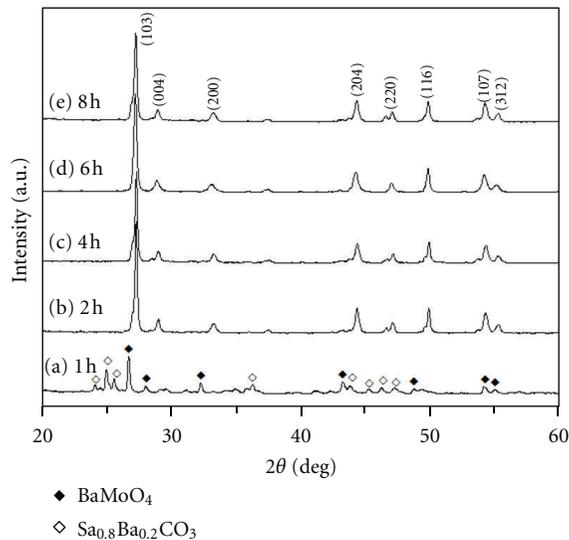


FIGURE 5: XRD patterns of the products obtained at 650°C for different soaking times, with 3:1 molar ratio of the salt to Na_2MoO_4 .

peaks appear (Figure 5(a)). As the soaking time is prolonged to 2 h, no impurity phase peaks are detected and all of the diffraction peaks can be indexed to the scheelite-type tetragonal structure. The tetragonal phase of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{MoO}_4$ remained when the soaking time is controlled in the range from 4 h to 8 h (Figures 5(c)–5(e)). In addition, the strong and sharp diffraction peaks indicate a good crystallinity of the products.

According to Donnay-Harker rules [17], as to tetragonal structure, the surface of $\{001\}$ faces is higher than that of $\{101\}$ faces. The high-energy faces have higher reactivity and growth rate, which makes $\{001\}$ faces shrink to disappear completely, so as to form octahedrons [18]. It is reported that anions play a key role in morphology [19]. In the growth process of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{MoO}_4$, Chloride could preferentially and selectively adsorb on the $\{101\}$ and $\{001\}$ faces of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{MoO}_4$. The faster growing rate along the $[001]$

directions than that along the $[101]$ directions facilitates the formation of octahedron morphology with exposed $\{101\}$ faces.

Figure 6 shows SEM images of the as-prepared products obtained at 650°C for different soaking times with 3:1 molar ratio of the salt to Na_2MoO_4 . Figure 6(a) shows that micro-octahedrons are observed, and some micro-octahedrons self-assemble to big octahedrons along $\{111\}$ faces at 2 h. Figure 6(b) shows that when the soaking time is 4 h, inhomogeneous octahedrons are identified, and the mean size is $5.69\ \mu\text{m}$ (Figure 7). When the soaking time is 6 h, the morphology of octahedrons is more uniform and well defined. The distribution of the particles also narrows. Eventually, when the soaking time is prolonged to 8 h, the distribution broadens.

Figure 8 shows the PL spectra of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{MoO}_4$ powders obtained at 650°C for the holding time of 2 h~8 h, with 3:1 molar ratio of the salt to Na_2MoO_4 . All $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{MoO}_4$ powders with different morphologies exhibited the same blue peaks around 460 nm using a 398 nm excitation line. Wu et al. [20] verified the blue emissions of molybdates, which were attributed to the ${}^1\text{T}_2 \rightarrow {}^1\text{T}_1$ electronic transitions into the $[\text{MoO}_4]$ tetrahedron groups, which can be treated as excitons. Our results also indicate that with the increase of the soaking time from 2 h to 8 h, the intensity of the diffraction peaks increases gradually (Figure 5). And the mean particle size is $3.18\ \mu\text{m}$, $5.69\ \mu\text{m}$, $4.68\ \mu\text{m}$, and $6.20\ \mu\text{m}$, respectively (Figure 7). According to Figure 8, when the soaking time is 6 h, the luminescence of the particles is the best. Therefore, the better crystallinity and smaller particle size, the higher PL emission. The same conclusion has been reported before [21].

4. Conclusions

In this paper, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{MoO}_4$ powders with octahedrons can be synthesized by a molten salt method at 650°C for 6 h. The particle size, morphology, and crystallinity of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{MoO}_4$ crystallites depend on the reaction temperature, the holding time, and the molar ratio of KCl to the Na_2MoO_4 . The PL

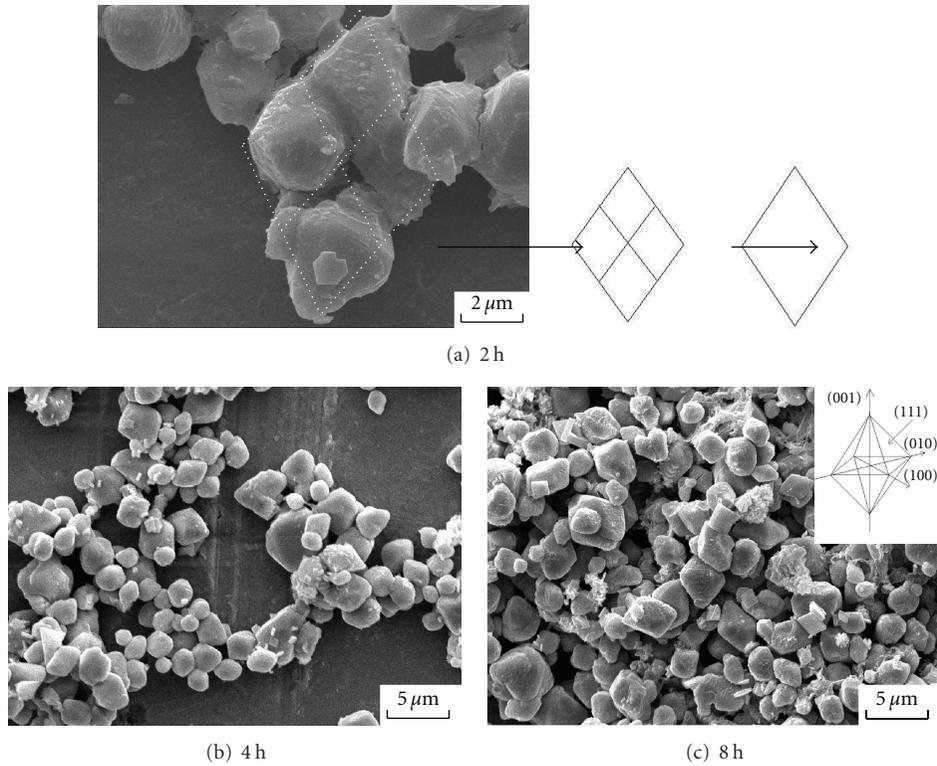


FIGURE 6: SEM images of the products obtained at 650°C for different soaking times, with 3 : 1 molar ratio of the salt to Na_2MoO_4 .

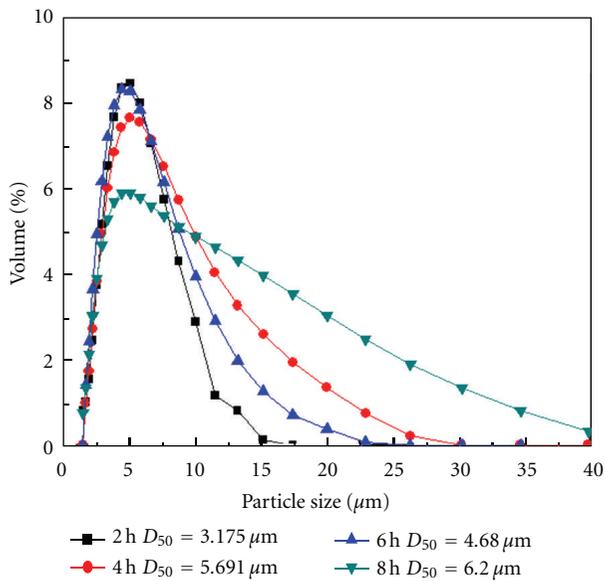


FIGURE 7: Particle size distribution of the products obtained at 650°C for different soaking times, with 3 : 1 molar ratio of the salt to Na_2MoO_4 .

properties are strongly dependent on their particle size and crystallinity. The better crystallinity and smaller particle size, the higher PL emission peak.

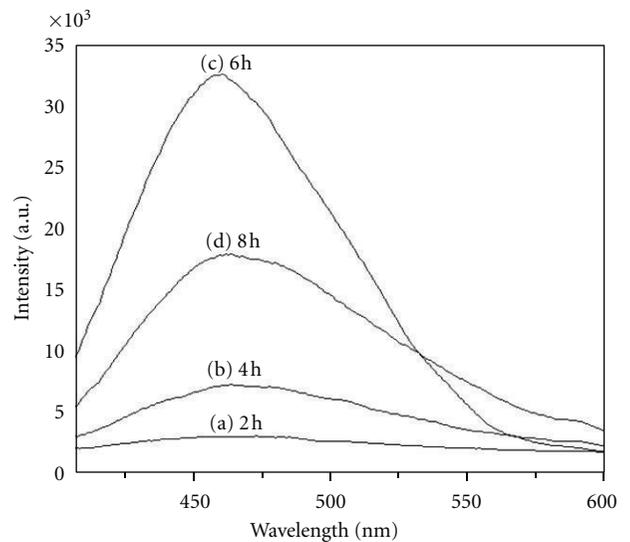


FIGURE 8: PL spectra of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{MoO}_4$ powders obtained at 650°C for different soaking times, with 3 : 1 molar ratio of the salt to Na_2MoO_4 .

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