An Improved Method for Obtaining Single-Phase Sr₂MoO₄ under Controlled Ultralow Oxygen Partial Pressure

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We investigated a method for obtaining a sintered bulk sample of single-phase Sr₂MoO₄, which has recently increased in importance due to its similarities to superconducting Sr₂RuO₄. We discovered that with the aid of Ti₂O₃ as a p(O₂) buffer, high-purity Sr₂MoO₄ is successfully synthesized in a sealed tube. We confirmed the space group and determined the exact elemental composition of the compound in order to establish its stoichiometry. The guideline for the rational choice of a p(O₂)-buffer material is discussed.

KEYWORDS: Sr₂MoO₄, layered molybdate, Sr₂RuO₄, synthesis, K₂NiF₄ structure, p(O₂) buffer, Ti₂O₃

For many years there had been debates over the existence of the compound Sr₂MoO₄₁⁻³ until Lindblom and Rosén described their method for synthesizing it and reported that it crystallizes in a K₂NiF₄-type structure.⁴,⁵ What they actually obtained, however, was the mixture of Sr₂MoO₄ and SrO, and the latter had to be washed away with methanol. Recently, renewed interest in Sr₂MoO₄ has emerged in solid-state physics with the discovery of unconventional superconductivity in Sr₂RuO₄.⁶,⁷ The need for a bulk sintered sample rather than a powder sample in many physical measurements urged the development of sintered Sr₂MoO₄ bulk, which is single-phased as-prepared. Moreover, the paper of Lindblom and Rosén does not provide the detailed information necessary for a cross-examination. Recently, Steiner and Reichelt attempted to reproduce their result,⁸ but were only able to obtain samples containing relatively large amounts of Mo metal and other phases. We will consider the reason later. This large amount of Mo metal makes it difficult to look into the possibility of superconductivity in Sr₂MoO₄ below 0.9 K, the Tc of Mo metal.

Here we describe our new method that solves all of these problems and enables us to obtain a single-phase sintered bulk of Sr₂MoO₄ with ease and perfect reproducibility. In addition, this procedure gives new life to the conventional sealed-tube method and has the potential for creating many new materials in the future.

As illustrated in Fig. 1, we placed a pellet of the 2 : 1 molar mixture of Sr₃MoO₆ and Mo metal powder (99.9%) on top of an open inner quartz tube holding Ti₂O₃ powder inside. An outer quartz tube with the above contents was first evacuated and then charged with Ar gas at a pressure that was going to be 1 atm at the firing temperature. Finally, the outer tube was sealed by fusion. The optimal molar amount of Ti₂O₃ turned out to be 0.75 per mole of Sr₂MoO₄ after several trials. The sealed tube was kept at 1150°C for one week. Prior to this, Sr₃MoO₆ had been prepared according to the reaction 3SrCO₃ + MoO₃ → Sr₃MoO₆ + 3CO₂ ↑. The mixture of SrCO₃ (99.99%) and MoO₃ (99.99%) was heated in flowing Ar atmosphere at 1000°C for 24 h with two intermittent grindings.

Samples were examined for phase purity by powder X-ray diffraction (PXRD) at room temperature with Cu-Kα radiation. Electron diffraction (ED) was performed to determine the space group. The lattice constants were calculated from the peak positions in the PXRD pattern and the Miller indices that had been assigned based on ED results. The ratio of metal elements (Sr to Mo) was measured by a thermogravimetric analysis (TGA). The TGA was performed in an atmosphere of 1-volume mixture of argon and oxygen.

We show a PXRD pattern of a typical Sr₂MoO₄ sample, obtained according to the above procedure, in Fig. 2. The only impurity phase visible in this figure is a tiny peak at 40.5°, which we attribute to Mo metal. Basic physical properties, such as electrical resistivity, magnetic susceptibility, and specific heat, of our samples have been reported elsewhere.⁹,¹⁰ No superconductivity has been observed as yet even down to a temperature of 30 mK.

Figure 3 shows three patterns of convergent-beam electron diffraction (CBED) on our sample of Sr₂MoO₄. They are all consistent with the space group I4/mmm, ensuring that its crystal structure is actually tetragonal K₂NiF₄-type, as first suggested by Balz and Plüth.¹¹ We indexed the peaks in the PXRD pattern and calculated the lattice parameters. Our results, a = 3.9168(4) Å and c = 12.859(2) Å, are more consistent with the lattice parameters of Steiner and Reichelt⁸ than those of Lindblom and Rosén.¹²

We determined the ratio of Sr : Mo to be 2.02 ± 0.01 by an ICP-AES. The result of TGA is shown in Fig. 4. Assuming that all the Mo⁶⁺ ions had become Mo⁵⁺ species by heating to 840°C, where a plateau was achieved, the oxygen content x in Sr₂O₂.0₂±0.01MoO₃ turned out to be 4.001 ± 0.003. We may safely say that the composition of what has been called Sr₂MoO₄ is actually 2 : 1 : 4. We also note that no appreciable oxygen nonstoichiometry exists in this system, at least

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Fig. 1. Schematic of the sealed tube for reaction.
on the reduction side of Mo$^{4+}$, by comparing the peak positions in the PXRD patterns with various amounts of Mo metal precipitation.

Lindblom and Rosén have measured the oxidation potential for the equilibrium $2\text{SrO}(s) + \text{Mo}(s) + O_2(g) \rightleftharpoons \text{Sr}_2\text{MoO}_4(s)$ and concluded that the equilibrium oxygen partial pressure $p(O_2)$ is $10^{-21}$ atm at 1200 K. To maintain this extremely low $p(O_2)$, they used the mixture of SrO and Mo metal as the $p(O_2)$ buffer, which was placed on top of the starting materials in a sealed Al$_2$O$_3$ tube. However, they did not report the ratio of the amount of the buffer to that of the starting materials. Apart from this, their starting materials were the 3:1 molar mixture of Sr(OH)$_2$ and MoO$_2$, which necessitated the separation of SrO from the resultant mixture.

Steiner and Reichelt started from the stoichiometric (2:1) mixture of SrO and MoO$_2$, which was sealed in a quartz tube along with a $p(O_2)$ buffer of SrO and Mo. It resulted in a mixed-phase sample containing Sr$_2$MoO$_4$ (the main phase), Mo, SrMoO$_3$, and so forth. We can understand this in the following way: The starting materials (2SrO + MoO$_2$) and the $p(O_2)$ buffer (SrO + Mo) can exchange O$_2$ mutually. As a consequence of thermal equilibrium, metallic Mo or an oxide containing Mo$^{5+}$ should emerge on the starting material’s side. In other words there is no reason for all of the Mo ions in the starting materials to remain 4+ in valence, while there is metallic Mo on the buffer’s side and oxygen can be exchanged between both sides.

In Lindblom and Rosén’s case, another equilibrium, $2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + O_2$, was also involved thanks to the usage of Sr(OH)$_2$. This may have helped maintain $p(O_2)$ at the level suitable for Sr$_2$MoO$_4$ formation. The condition seems, however, so subtle that we could not obtain any Sr$_2$MoO$_4$ according to their procedure.

We began investigating an alternative method for obtaining the target compound with more ease and reliability. Another goal was to produce phase-pure Sr$_2$MoO$_4$ samples that need no postproduction treatment for removing other phases. Thus, we fixed the starting mixture at 2Sr$_3$MoO$_6$ + Mo, which was to yield 3Sr$_2$MoO$_4$ only. We concentrated on finding the right $p(O_2)$-buffer material using a logical and rational approach. We emphasize that sealing the starting mixture under high vacuum of $\sim 10^{-3}$ Torr and firing it produced no Sr$_2$MoO$_4$, as had already been observed by McCarthy and Gooden. Lower $p(O_2)$ than can be achieved by usual pumping was required, as mentioned by Lindblom and Rosén.

To simply reduce $p(O_2)$, the use of an oxygen-getter element is effective. We tried putting Ta foil in the sealed tube along with the starting mixture. It resulted in a large amount of Mo metal, seemingly due to the too low $p(O_2)$ in the tube. Since Ta has a stronger ionization tendency than Mo does, Ta foil may have absorbed not only residual oxygen in the tube, but also oxygen in the starting materials and made Sr$_2$MoO$_4$ unstable. Our objective then was to highly stabilize Mo$^{4+}$ ions in order to promote the formation of Sr$_2$MoO$_4$, which contains Mo as Mo$^{4+}$ ions.

This is where the concept of ionization tendency of ions comes in. It is an extended version of ionization tendency of metallic elements. Let us present an example. A Mo$^{5+}$ ion cannot be ionized further by any chemical means. On the other hand, elemental Mo is ionized more easily than all the other Mo ions. A Mo$^{5+}$ ion falls between these two extremes. Consequently, we can draw an ionization tendency of ions.
stating $\text{Mo}^{6+} < \text{Mo}^{4+} < \text{Mo}^{0}$.

When choosing the buffer material to stabilize $\text{Mo}^{4+}$, the following two points must be taken into consideration. 1) The buffer should be weaker than $\text{Mo}^{0}$ in the ionization tendency. This ensures that the buffer does not reduce $\text{Mo}^{4+}$ to Mo metal. 2) The buffer should be stronger than $\text{Mo}^{4+}$ in the ionization tendency. If this condition is met, the buffer will act as a weak reducing agent on the compound containing $\text{Mo}^{4+}$, thereby suppressing the absorption of oxygen into the target compound and its decomposition due to oxidation.

What kind of buffer material can satisfy these requirements? We expanded the range of candidates from metallic elements to oxides and chose $\text{Ti}_2\text{O}_3$, containing $\text{Ti}^{3+}$. Judging from the tables for oxidation potentials of various ions, the condition $\text{Mo}^{4+} < \text{Ti}^{3+} < \text{Mo}^{0}$ was apparently met. We decided to use $\text{Ti}_2\text{O}_3$ as the buffer material. This was the main part of our technique that supplied a high-purity bulk of $\text{Sr}_2\text{MoO}_4$, as manifested in Fig. 2.

The role of Ar gas sealed in the quartz tube is not yet understood. However, without Ar gas, the sample did not become as pure as in Fig. 2 under the same firing condition. We speculate that Ar works as a carrier gas for oxygen molecules. Since $p(\text{O}_2)$ in the tube is extremely low, an oxygen molecule is rarely scattered by other oxygen molecules. If the total pressure in the tube is also low, oxygen molecules travel linearly over a long distance and collide infrequently with both the starting mixture and the buffer. In this situation it will take very long for the whole system to reach equilibrium. Argon gas may contribute to increasing the efficiency of the exchange of oxygen between the starting materials and the buffer.

Actually we are not the first to use a transition-metal oxide in order to make a complex oxide of another transition metal. Nozaki et al. used TiO as a “reducing agent” for making $\text{Sr}_2\text{VO}_4$. They switched the agent to $\text{Ti}_2\text{O}_3$ for preparing $\text{Sr}_3\text{V}_2\text{O}_7$. This paper of ours, however, explains how and why their method worked and gives the guidelines for rationally choosing a $p(\text{O}_2)$-buffer material for synthesizing other difficult-to-obtain oxides.

In conclusion, we have succeeded in synthesizing truly phase-pure $\text{Sr}_2\text{MoO}_4$, which is useful for physical-properties measurements. It was necessary to control $p(\text{O}_2)$ in the sealed tube at an extremely low level that stabilized $\text{Sr}_2\text{MoO}_4$ and we solved this problem by using $\text{Ti}_2\text{O}_3$ as the $p(\text{O}_2)$ buffer. We described how to choose a buffer material rationally, which was based on the concept of the ionization tendency of ions. The oxidation potential data of various ions have been useful.

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