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Phase relation in Li_2MoO_4–Li_2WO_4 system

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Abstract

The compounds Li_2MoO_4 and Li_2WO_4 have the phenacite structures with almost the same lattice constants. It is expected and was actually reported that the Li_2MoO_4–Li_2WO_4 quasi-binary system forms a complete solid solution. In the present study, however, we found by differential thermal analysis (DTA) that the system actually forms a partial solid solution with the peritectic reaction. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

According to Gloeikler et al. [1], the Li_2O–MoO_3–WO_3 system has following features. (1) The compounds MoO_3 and WO_3, which themselves have considerably different structures, form a solid solution in a wide composition range. (2) Neither $Li_2Mo_3O_{10}$ nor $Li_2W_3O_{10}$ exists but nevertheless $Li_2M_3O_{10}$ (M=Mo and W) exists in a wide composition range. (3) The compounds Li_2MoO_4 and Li_2WO_4, which have the same crystal structure (phenacite structure, space group $R\bar{3}$) with very close lattice parameters, form a complete solid solution. Yamaoka and Fukunaga [2] also reported that the Li_2MoO_4–Li_2WO_4 quasi-binary system formed a complete solid solution. Although these features seem quite interesting, they have not been fully confirmed yet. In the present study, we reexamined the phase relation of Li_2MoO_4–Li_2WO_4 system by differential thermal analysis (DTA) and X-ray diffraction (XRD).

2. Experimental

We used Li_2MoO_4 powder (nominally 99.9% pure, CERAC, Wisconsin, USA), Li_2WO_4 powder (nominally 99.9% pure, CERAC) and Li_2CO_3 powder (nominally 99.9% pure, Rare Metallic, Japan) as starting materials. X-ray diffraction revealed that the Li_2WO_4 powder contained trace of $Li_2W_2O_7$ in spite of its nominal purity. We were able to reduce this $Li_2W_2O_7$ below the detection limit of the diffractometer (RINT 2200, Rigaku, Japan) by adding 0.5 wt.% Li_2CO_3 to the Li_2WO_4 and heating it at 650°C for several hours. After then we always added this amount of Li_2CO_3 to Li_2WO_4 while preparing samples.

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In the differential thermal analysis (instrument: DTA 92, SETARAM, France), each sample was loaded in a Pt-10% Rh cell and then melted prior to the measurement in order to make good contact between the sample and the cell. The heating or cooling rate was 2°C/min and the sample atmosphere was an argon flow of 20 cm^3/min.

We also prepared the samples for XRD phase identification in two different ways. One is fusing: the mixture of the starting materials was heated well above the melting point. The other is solid-state reaction: the mixture was heated just below the melting point. If the same phase(s) result via such different processes, it evidences that the phase(s) are true equilibrium one(s).

3. Results and discussion

Some of the obtained DTA curves are shown in Fig. 1, where the DTA signal is plotted as a function of temperature. The curves during heating have endothermic peaks corresponding to the melting of the samples. Among them the peaks for x=0.80 and 0.90 have different features from others. They have almost the same onset temperature as that for x=0.70, whereas the others have the onset temperatures increasing with x (Li_2WO_4 content). In addition, they are broader than others and could be separated into two peaks. These facts imply that the Li_2MoO_4–Li_2WO_4 quasi-binary system does not form a complete series of solid solutions.

Note also that the curves during cooling have exothermic peaks at the temperatures 70–120°C lower than the melting temperatures. These peaks changed in position and profile run by run, but always located at much lower temperatures than the melting temperatures. (The cooling rate was often uncontrollable around these exothermic peaks). Such marked supercooling seems intrinsic to the Li_2MoO_4–Li_2WO_4 system.

As for the solidus temperature, we determined it as the extrapolated onset of the endothermic peak, i.e. as the intersection of the baseline with the steepest tangential line to the peak. It was, however, impossible to determine the liquidus temperature from the DTA curve during *cooling* because of the supercooling. Therefore, to estimate the liquidus temperature, we measured the DTA signal under stepwise heating. Some results are shown in Fig. 2.

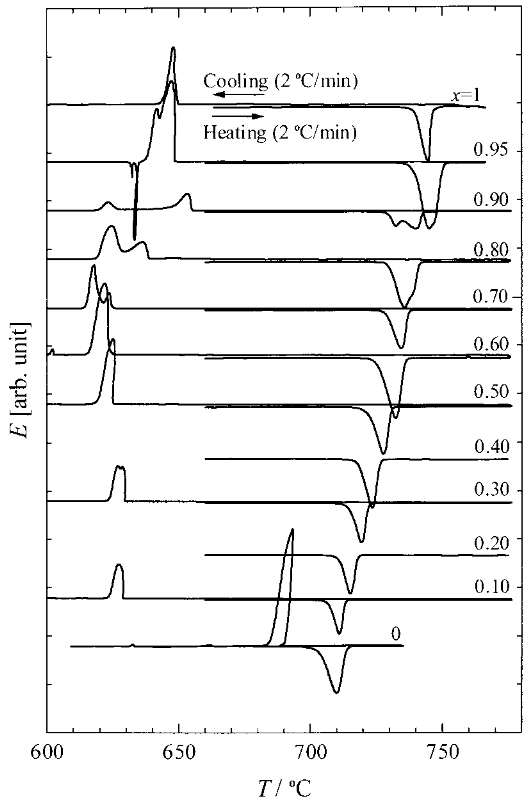

Fig. 1. The DTA curves for (1−x)Li_2MoO_4–$x$$Li_2WO_4$; the DTA signal E is plotted as a function of temperature T. The curves during heating for the samples with x=0.7–0.9 have very close onset temperatures. The curves during cooling show marked supercooling, which makes it impossible to determine the liquidus temperature.

As seen from the figure, we stopped raising the furnace temperature just after the sample started to melt — the DTA signal started to deviate from the baseline — and kept the temperature constant for 5 min; then we repeated the process of increasing the temperature by 1°C with heating rate of 2°C/min followed by keeping it constant for 5 min. Our interpretation of the 'DTA' curve thus obtained is as follows. If the temperature increase causes the DTA signal to deviate the baseline further, it indicates that considerable part of the sample remains in a solid state. If the temperature increase hardly affects the DTA signal, it indicates that (almost) all the part of the sample has already melted. The liquidus temperature

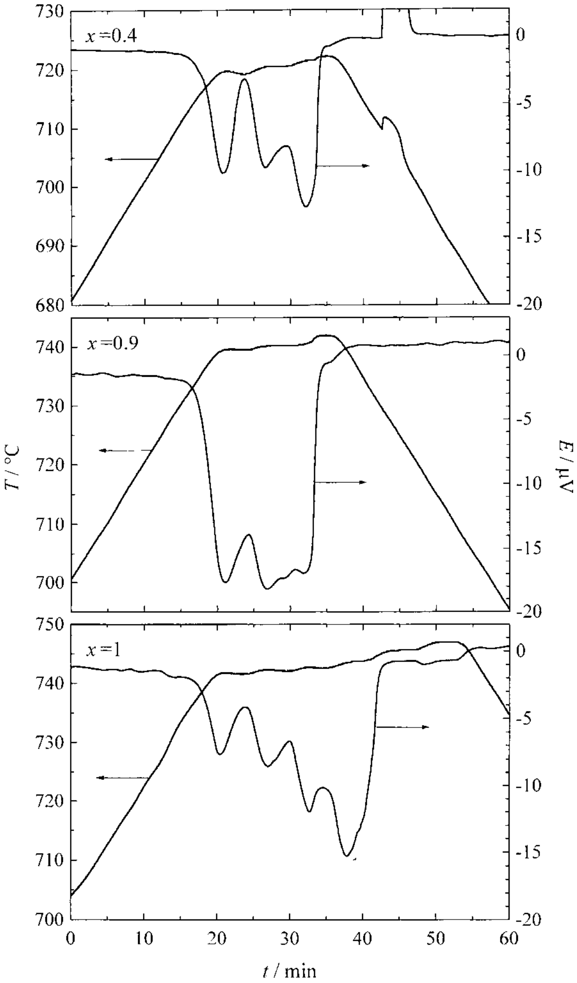

Fig. 2. Some examples of the ‘DTA’ curves for $(1-x)Li_2MoO_4$–xLi_2WO_4 under stepwise heating for estimating the liquidus temperature; the furnace temperature T and the DTA signal E are plotted as a function of time t. The liquidus temperature should be close to the temperature at which no more heat absorption with increasing temperature occurred.

should be close to the temperature at which the latter is the case for the first time.

Actually, the stepwise heating gave rise to more than one peak in the ‘DTA’ curve even for pure Li_2MoO_4 and pure Li_2WO_4 (Fig. 2). As a result, the liquidus temperatures that we estimated from these curves, by the above mentioned method, were 3°C higher than the solidus temperatures. We accordingly corrected all the obtained liquidus temperatures by 3°C. The triangles and circles in Fig. 3 denote the solidus and liquidus temperatures, respectively, of the Li_2MoO_4–Li_2WO_4 quasi-binary system. In the composition range of x=0.7–0.9, the solidus temperatures are virtually constant, suggesting coexistence of two solid phases in this composition range.

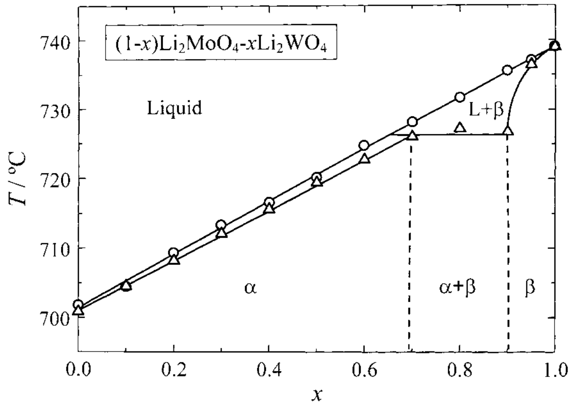

Fig. 3. The phase diagram for Li_2MoO_4–Li_2WO_4 quasi-binary system. The solidus temperatures (triangles) were determined from the onset of the DTA curves during heating; the liquidus temperatures (circles) were estimated by the method described in Fig. 2. Li_2MoO_4 and Li_2WO_4 form a partial solid solution with peritectic reaction in spite of their almost identical crystal structures.

We then tried to confirm the coexistence of the two phases in the fused samples directly by XRD at room temperature. The diffraction patterns observed for the fused samples are shown in Fig. 4, and the widths of their peaks are plotted as a function of the composition in Fig. 5. The diffraction patterns for the samples with x=0.80 and 0.90 showed neither peak separation nor peak broadening; there was no evidence for the coexistence of two phases. One possible explanation for this is that the lattice constants of the coexisting two phases were too close to be distinguished. The lattice constants of Li_2MoO_4 (a_0=1.4338 nm and c_0=0.9588 nm at 25°C [3]) and Li_2WO_4 (a_0=1.4361 nm and c_0=0.9603 nm at 25°C [3]) are very close, and those of the coexisting phases ($x\sim0.7$ and $x\sim0.9$–0.95) are expected to be still closer. Another possible explanation is that the samples really consisted of a single phase. When the fused samples for XRD were prepared, they were furnace-cooled with a higher cooling rate than that in the DTA. Such rapid cooling may prevent phase separation because the melt seems to have so high viscosity as to cause the marked supercooling.

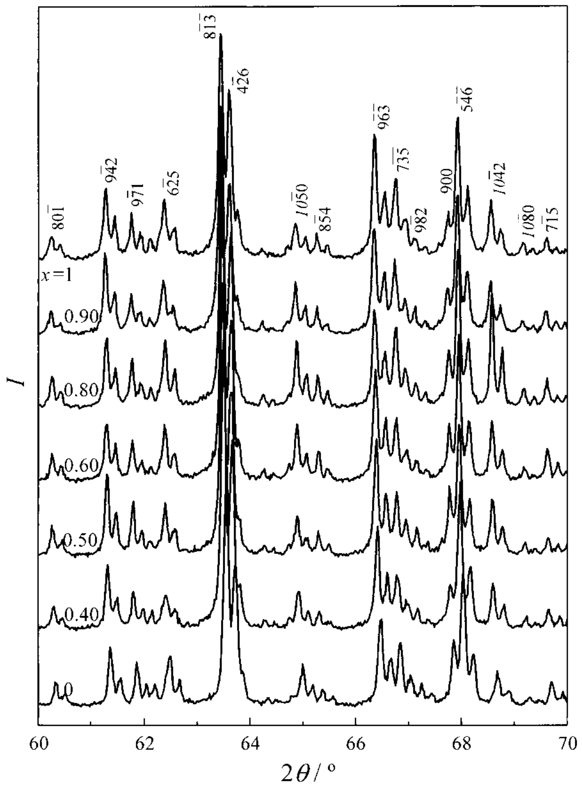

Fig. 4. The XRD patterns for $(1-x)Li_2MoO_4$–xLi_2WO_4. No peak separation is observed for the samples with x=0.8 and 0.9.

These XRD results themselves can be consistent with those of Yamaoka and Fukunaga [2]; they found linear relations between the lattice parameters and the composition. On the basis of that, they concluded that the Li_2MoO_4–Li_2WO_4 system formed a complete solid solution. Because of the above mentioned reasons, however, we do not necessarily think that their XRD results as well as ours contradict our DTA ones.

On the other hand, it seemed very difficult to obtain equilibrium phase(s) through solid-state reaction. When we heated an equimolar mixture of Li_2MoO_4 and Li_2WO_4 at 650°C, its XRD peaks at room temperature decreased in width with total heating time. However, even after heated at 650°C for 30 days, the sample had XRD peaks that were broader than those of the fused sample. This suggests that the reaction to form solid solution is extremely slow. Here, we should point out that WO_4 tetrahedra [4] and probably MoO_4 ones are present even in a liquid state. It is likely that these structural units are so rigid and immobile in a solid state as to prevent the interdiffusion of Mo and W.

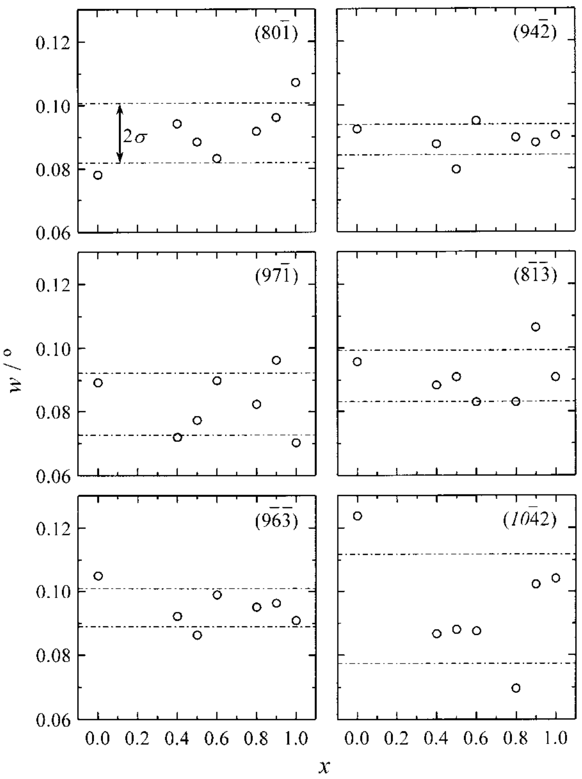

Fig. 5. The change in the width w (half width at half maximum) of the XRD peaks with composition x in $(1-x)Li_2MoO_4$–xLi_2WO_4. The horizontal lines in the figure indicate the values of $m\pm\sigma$, where m is the average and σ standard deviation. The peak width seems to be independent of the composition.

We therefore believe that the equilibrium phase(s) were reflected best in the samples solidified in the DTA. The phase diagram of the Li_2MoO_4–Li_2WO_4 system based on the results of DTA is shown in Fig. 3 by solid and broken lines; Li_2MoO_4 and Li_2WO_4 form a partial solid solution with peritectic reaction in spite of their almost identical crystal structure. Similar behavior has been found in the $PbMoO_4$–$PbWO_4$ system; both of them have scheelite structure yet form a partial solid solution with peritectic reaction [5].

4. Conclusion

We reexamined the phase relation of the Li_2MoO_4–Li_2WO_4 system by DTA and XRD. The

DTA curves indicated the coexistence of two phases in the composition range of 70–90 mol% Li_2WO_4. Although XRD showed no evidence for the coexistence of two phases, it can be attributed to the very close lattice constants of the coexisting two phases or to the rapid cooling in the sample preparation. Thus, we have concluded that Li_2MoO_4 and Li_2WO_4 form a partial solid solution with the peritectic reaction in spite of their almost identical crystal structures.

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