

Crystal Data and Phase Transitions of KLiWO_4 and KLiMoO_4

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Crystal data and phase transitions of KLiWO_4 and KLiMoO_4 were investigated using a high-temperature X-ray powder diffractometer. Phase transitions were observed at 350°C for KLiWO_4 and at 360°C for KLiMoO_4 . It was found that the room temperature phases were isostructural with stuffed derivatives of tridymite and the high-temperature phases were isostructural with stuffed derivatives of cristobalite.

Introduction

It had been reported by many workers (1) that the structures of ABCO_4 compounds are almost always stuffed derivatives of silica structures when *A* is large in size and both *B* and *C* are small. In the case of ALiWO_4 and ALiMoO_4 , Okada and Osaka (2) reported that the crystal structures (*A*: Rb and Cs) were isostructural with the stuffed derivative of cristobalite¹. However, the crystal structures of KLiWO_4 and KLiMoO_4 have yet to be reported. It is of interest to elucidate the crystal chemistry of the stuffed derivative of the silica structure. The crystal chemical investigations of those compounds were, therefore, undertaken using a high-temperature X-ray powder diffractometer.

Experimental

Crystals of KLiWO_4 and KLiMoO_4 were synthesized by heating an intimate mixture

¹ After this we abbreviate the stuffed derivative of tridymite and that of cristobalite as ST and SC, respectively.

of K_2CO_3 , Li_2CO_3 , and WO_3 or $\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ in the molar ratio of 1:1:2 at 800°C for 5 hr. They were fairly hygroscopic and gradually transformed to hydrated compounds in air.

The X-ray measurements at room temperature and at high temperatures were performed on a high-temperature X-ray diffractometer using $\text{CuK}\alpha$ radiation. Heating and cooling rates were about $10\text{--}20^\circ\text{C}/\text{min}$. Data were corrected using Si powder as the standard. Lattice parameters were calculated from 7 to 13 reflections using a least-squares program, RSLC-3 (3). Computations were carried out at the computer center of the Tokyo Institute of Technology. The temperature of phase transition was determined by the DTA method. Heating and cooling rates were $10^\circ\text{C}/\text{min}$. The temperature of phase transition was considered to be the starting temperature of the signal.

Results and Discussion

KLiWO_4

Lattice parameters and volumes per mol-

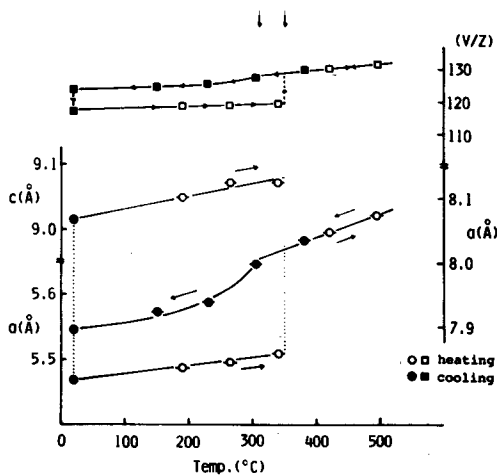


FIG. 1. Lattice parameters and volumes per molecule of KLiWO_4 . Estimated standard deviations of the lattice parameters and temperature variations in the measurements are represented by the error bars.

ecule (V/Z) are plotted vs temperature in Fig. 1. The X-ray powder pattern of the room temperature phase could be indexed in the hexagonal system by comparison with KAlSiO_4 (4); lattice parameters were $a = 5.468(2)$ and $c = 9.014(6)$ Å at 20°C. As the systematic absences were hhl for l odd and $00l$ for l odd, the possible space groups were $P\bar{6}c2$, $P6_3mc$ or $P6_3/mmc$. It is, of course, impossible to determine the crystal structures of trigonal and hexagonal systems by powder data; the space groups $P31c$ or $P\bar{3}1c$ are also possible structures. The structure of this phase was then regarded to be isostructural with the ST type. The thermal expansion coefficients of α_a and α_c between 20 and 350°C were 24 and $23 \times 10^{-6}/^\circ\text{C}$, respectively. A phase transition was observed at 350°C during heating and 310°C in cooling; although Belyaev (5) reported a phase transition temperature of 360°C. The X-ray powder pattern of the high-temperature phase could be indexed in the cubic system by comparison with that of CsLiWO_4 (2); the lattice parameter was $a = 8.047(2)$ Å at 420°C. As the hkl reflections were systematically missing for

$h + k$, $k + l$, and $l + h$ odd, the possible space groups were $F\bar{4}3m$, $F432$, or $Fm\bar{3}m$, as reported for CsLiWO_4 (2). The structure type of this phase was regarded to be isostructural with the SC type. The volume change in the phase transition at 350°C was estimated to be 8.3%. During the cooling process, the lattice parameter of the SC-type phase changed discontinuously at 310°C but this phase remained until room temperature under the present experimental conditions. It was observed that the SC-type phase transformed to the ST-type phase after several hours at room temperature. The volume change in the phase transition at room temperature was 5.4%. It was found that the $\text{ST} \rightleftharpoons \text{SC}$ phase transition in KLiWO_4 showed large hysteresis.

KLiMoO_4

Lattice parameters and volumes per molecule are plotted vs temperature in Fig. 2. The X-ray powder pattern of the room temperature phase could be indexed in the hexagonal system as in the case of KLiWO_4 ; lattice parameters were $a = 5.456(2)$ and $c = 9.000(8)$ Å at 20°C. Thus, the structure of this phase was regarded to

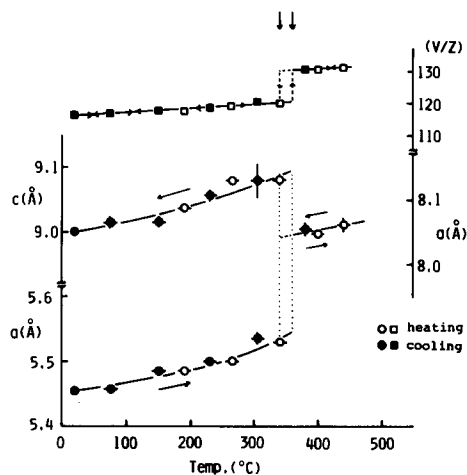


FIG. 2. Lattice parameters and volumes per molecule of KLiMoO_4 . Notations are as in Fig. 1.

be isostructural with the ST type. The thermal expansion coefficients of α_a and α_c between 20 and 340°C were 42 and $29 \times 10^{-6}/^\circ\text{C}$ respectively. A phase transition was observed at 360°C during heating and at 340°C during cooling. This result was somewhat different from that reported by Belyaev (5), who reported phase transitions at 390 and 440°C. The X-ray powder pattern of the high-temperature phase could be indexed with cubic system as with KLiWO_4 ; the lattice parameter was $a = 8.048(3) \text{ \AA}$ at 400°C. The structure type of this phase was regarded to be isostructural with the SC type. The volume changes in the phase transitions were 8.2% in heating and 7.6% in cooling.

In this way, it was found that both structures of the room temperature phases of KLiWO_4 and KLiMoO_4 were isostructural with ST and those of the high-temperature phases of the two compounds were isostructural with SC and that the SC \rightarrow ST phase transition in KLiWO_4 was fairly sluggish compared with that in KLiMoO_4 .

Construction of a structure field map for ABCO_4 compounds with stuffed derivatives of silica structures and related structures was tried utilizing all available data. It was

found that these structures could be classified by the ionic radii of the A cation located in the large cavity existing in these structures. Most of the compounds are isostructural with CaAl_2O_4 (6) when A is Ca or Na. Most of the compounds are isostructural with ST when A is Sr, Pb, Ba, or K. Most of the compounds are isostructural with NH_4LiSO_4 (7) when A is Tl, Rb, NH_4 , or Cs, but are isostructural with SC when A is Rb or Cs, B is Li, and C is W or Mo (2).

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