

BRIEF COMMUNICATIONS

Phase Equilibrium Study of the LiV_2O_5 - V_2O_4 - V_2O_5 System at 923 K: A Series of Lithium Vanadium Bronzes, $\text{Li}_x\text{V}_{6n}\text{O}_{15n-m}$

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Received September 17, 1986; in revised form January 28, 1987

Introduction

The lithium vanadium bronzes, $\text{Li}_x\text{V}_2\text{O}_5$ ($0 < x \leq 1$), occur as a series of nonstoichiometric phases, α ($0 < x \leq 0.04$), β ($0.22 \leq x \leq 0.37$), β' ($0.44 \leq x \leq 0.49$), and γ ($0.88 \leq x \leq 1$) (1, 2), and the κ phase, $\text{Li}_{1+x}\text{V}_3\text{O}_8$, in the oxygen-rich region (3). The crystal structures of all these phases are known. The structure of the α phase is based on that of parent oxide V_2O_5 , with lithium ions inserted between V_2O_5 layers (4), whereas in β - and β' - $\text{Li}_x\text{V}_2\text{O}_5$ (1, 2) and γ - $\text{Li}_x\text{V}_2\text{O}_5$ (5), major structural rearrangements of the V_2O_5 framework occur.

Compared to the $\text{Li}_x\text{V}_2\text{O}_5$ system, very little is known about the oxygen-poor region of the Li_2O - V_2O_4 - V_2O_5 system. Although two phases, $\text{Li}_x\text{V}_{30}\text{O}_{71+y}$ ($1.5 \leq x \leq 3$ and $0 \leq y \leq 1.8$) (6) and $\text{Li}_2\text{V}_{12}\text{O}_{29}$ (7), have been reported, they have yet to be confirmed. It has been suggested that the β phase can contain a large amount of oxygen defects (8, 9). This point should be clarified as the β phase has attracted great attention because of its interesting properties as a

electronic and lithium ionic conductor (8-12).

Experiment

Vanadium pentoxide (99.99%) and lithium carbonate (99.99%) were used as starting materials. Prior to use, they were dried by heating at 773 K for 1 day. Lithium metavanadate, LiVO_3 , was prepared by heating an equimolar mixture of Li_2CO_3 and V_2O_5 at 873 K for 5 days with intermediate grinding. In the phase equilibrium experiment, we used VO_2 and LiV_2O_5 rather than V_2O_3 and LiVO_3 to minimize weighing errors and adsorption of water. By reducing V_2O_5 in hydrogen at 1023 K, V_2O_3 was obtained; this was mixed with V_2O_5 in equimolar ratio. The mixture was sealed in evacuated silica tubes and fired at 1123 K for 5 days to get VO_2 . The stoichiometric lithium vanadium bronze LiV_2O_5 was also prepared by the silica tube method according to the reaction, $\text{LiVO}_3 + \text{VO}_2 = \text{LiV}_2\text{O}_5$. The three compounds, V_2O_5 , VO_2 , and LiV_2O_5 , thus obtained were mixed under acetone in the desired ratio in an agate mortar. After drying in nitrogen at 423 K for a

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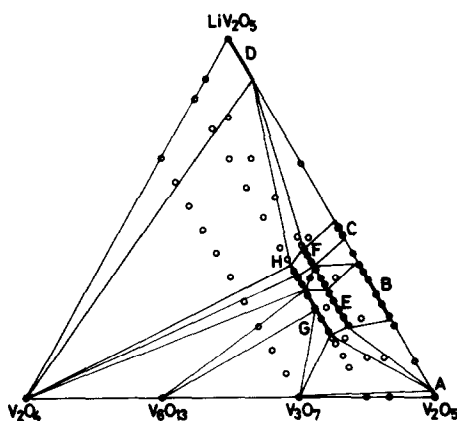


FIG. 1. Phase diagram of the $\text{LiV}_2\text{O}_5\text{-V}_2\text{O}_4\text{-V}_2\text{O}_5$ system at 923 K. A, $\alpha\text{-Li}_x\text{V}_2\text{O}_5$; B, $\beta\text{-Li}_x\text{V}_2\text{O}_5$; C, $\beta'\text{-Li}_x\text{V}_2\text{O}_5$; D, $\gamma\text{-Li}_x\text{V}_2\text{O}_5$; E, $\beta\text{-Li}_x\text{V}_9\text{O}_{22}$; F, $\beta'\text{-Li}_x\text{V}_9\text{O}_{22}$; G, $\beta\text{-Li}_x\text{V}_{12}\text{O}_{29}$; H, $\beta'\text{-Li}_x\text{V}_{12}\text{O}_{29}$. Open circle indicates an experimental point.

few hours, about 3 g of the mixture was sealed in a silica tube. The mix was preheated at 873 K for 1 day in a box-type furnace, then heated at 923 ± 2 K for 48–72 hr, and quenched to room temperature. The product was examined by powder X-ray diffractometry using $\text{CuK}\alpha$ radiation. This procedure was repeated until the powder X-ray pattern of the sample did not change. However, the reaction rate was usually large enough for the sample to reach steady state after the first heating. About 70 mixes of different ratios were examined (see Fig. 1).

Single crystals of compounds found for the first time in the present work were prepared by chemical transport method, using HCl gas as a carrier, and the crystals were characterized by Weissenberg photography.

Results and Discussion

The phase diagram determined in the present study is shown in Fig. 1. Ranges of composition for α -, β -, β' -, and γ - $\text{Li}_x\text{V}_2\text{O}_5$ were taken from earlier works (1, 2). Four

new bronzes were also found in the system. Single crystal structure analysis were done for these phases (13, 14). From the structure analysis and powder X-ray data, the compositions of these compounds were determined to be $\beta\text{-Li}_x\text{V}_9\text{O}_{22}$ ($0.90 \leq x \leq 1.35$), $\beta'\text{-Li}_x\text{V}_9\text{O}_{22}$ ($1.65 \leq x \leq 1.85$), $\beta\text{-Li}_x\text{V}_{12}\text{O}_{29}$ ($1.05 \leq x \leq 1.80$), and $\beta'\text{-Li}_x\text{V}_{12}\text{O}_{29}$ ($2.05 \leq x \leq 2.15$). The prefixes, β and β' are used because of the close relation of these compounds to β - and β' - $\text{Li}_x\text{V}_2\text{O}_5$.

The vanadium bronze, $\beta\text{-Li}_x\text{V}_2\text{O}_5$, is isostructural with $\beta\text{-Na}_x\text{V}_2\text{O}_5$ (15); it has a layered structure (space group $C2/m$) (1, 2). The vanadium-oxygen array (Fig. 2a) consists of V_6O_{15} layers parallel to (100); each layer is translated along Y by $b/2$ relative to the adjacent layers, which are linked to

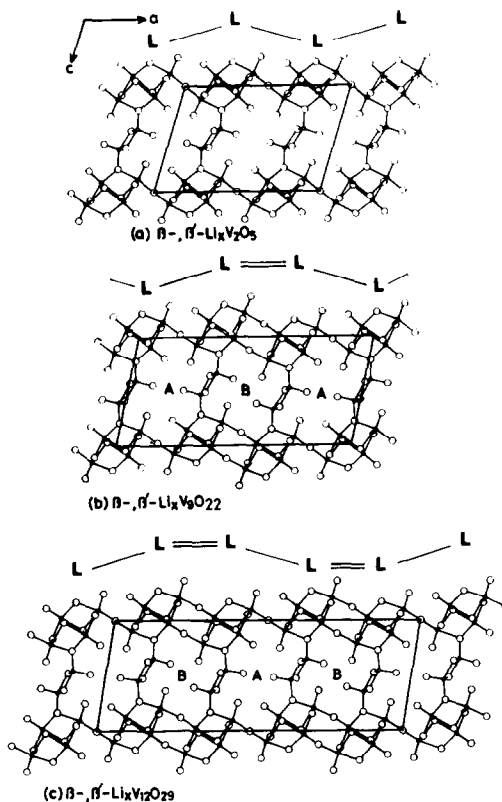


FIG. 2. Projection of the β - and β' - $\text{Li}_x\text{V}_{6n}\text{O}_{15n-m}$ structure onto a (010) plane (1, 2, 13, 14).

each other by one oxygen ion per unit cell. This feature of the structure is schematically shown in upper part of Fig. 2a. Lithium ions occupy 7-fold sites in tunnels between two layers in β - $\text{Li}_x\text{V}_2\text{O}_5$. In β' - $\text{Li}_x\text{V}_2\text{O}_5$, the vanadium–oxygen array is similar to that of β - $\text{Li}_x\text{V}_2\text{O}_5$, except the lithium ions occupy tetrahedral sites within the tunnels (1, 2).

Vanadium–oxygen arrangements and schematic representations of them for $\text{Li}_x\text{V}_9\text{O}_{22}$ and $\text{Li}_x\text{V}_{12}\text{O}_{29}$ are shown in Figs. 2b and 2c. The vanadium–oxygen framework is similar in the β and β' phases for both $\text{Li}_x\text{V}_9\text{O}_{22}$ and $\text{Li}_x\text{V}_{12}\text{O}_{29}$, as well as in β - and β' - $\text{Li}_x\text{V}_2\text{O}_5$. $\text{Li}_x\text{V}_9\text{O}_{22}$ has space group $P2_1/m$, whereas $\text{Li}_x\text{V}_{12}\text{O}_{29}$ has space group $C2/m$ (13). The structure of $\text{Li}_x\text{V}_9\text{O}_{22}$ consists of two kinds of layers parallel to (100). One layer is similar to that of β - and β' - $\text{Li}_x\text{V}_2\text{O}_5$, whereas the other layer has the composition $\text{V}_6\text{O}_{14.5}$ and is linked to an adjacent layer by two oxygen atoms per unit cell. The two layers connected by two oxygen atoms are not glide-related along Y . In Li_x

Compound	a (Å)	b (Å)	c (Å)	β (deg)
β - $\text{Li}_{0.3}\text{V}_2\text{O}_5^a$	15.464(6)	3.599(2)	10.068(6)	110.9(1)
β' - $\text{Li}_{0.48}\text{V}_2\text{O}_5^a$	15.266(6)	3.618(2)	10.100(6)	107.7(1)
β - $\text{Li}_{1.3}\text{V}_9\text{O}_{22}$	21.813(2)	3.6037(4)	10.095(1)	105.31(1)
β' - $\text{Li}_{1.7}\text{V}_9\text{O}_{22}$	21.601(2)	3.6220(7)	10.125(1)	102.57(1)
β - $\text{Li}_{1.5}\text{V}_{12}\text{O}_{29}$	28.204(2)	3.6074(3)	10.114(1)	102.09(1)
β' - $\text{Li}_{2.1}\text{V}_{12}\text{O}_{29}$	28.016(2)	3.6203(4)	10.121(1)	100.02(1)

^a From Ref. (2).

$\text{V}_{12}\text{O}_{29}$, the structure consists of one kind of layers which are similar to the $\text{V}_6\text{O}_{14.5}$ layer of $\text{Li}_x\text{V}_9\text{O}_{22}$.

There are two kinds of tunnels in which lithium atoms are located in both $\text{Li}_x\text{V}_9\text{O}_{22}$ and $\text{Li}_x\text{V}_{12}\text{O}_{29}$, denoted A and B in Figs. 2b and 2c. Tunnel A is very similar to that of β - and β' - $\text{Li}_x\text{V}_2\text{O}_5$. Although we have to wait for final refinement of the structure analysis to determine the position of lithium ions within these tunnels, preliminary analysis shows that the difference between β and β' phase in $\text{Li}_x\text{V}_9\text{O}_{22}$ and $\text{Li}_x\text{V}_{12}\text{O}_{29}$ comes from the difference in position of the lithium ions within tunnel A, as occurs in β - and β' - $\text{Li}_x\text{V}_2\text{O}_5$. The compounds found in the present work, including β - and β' - $\text{Li}_x\text{V}_2\text{O}_5$, may be represented by the general formula, β - or β' - $\text{Li}_x\text{V}_6\text{O}_{15n-m}$ ($n \geq m$). Indeed, $\text{Li}_x\text{V}_2\text{O}_5$, $\text{Li}_x\text{V}_9\text{O}_{22}$, and $\text{Li}_x\text{V}_{12}\text{O}_{29}$ (n , m) correspond to (1/3, 0), (3/2, 1/2), and (2, 1), respectively. However, only these three combinations might be possible at different temperatures.

Figures 3 and 4 indicate variations of lattice parameters with x for the $\text{Li}_x\text{V}_9\text{O}_{22}$ and $\text{Li}_x\text{V}_{12}\text{O}_{29}$ systems, respectively. Table I shows lattice parameters of representative compounds. These systems show abrupt changes in lattice constants across the two-phase region of $\beta + \beta'$; the a cell dimension decreases considerably in the β' phase in both systems. A similar tendency has been observed in β - and β' - $\text{Li}_x\text{V}_2\text{O}_5$ (1, 2).

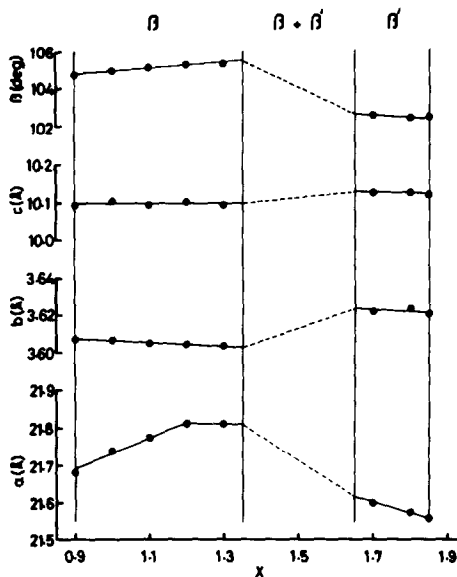


FIG. 3. Lattice parameters versus x for the system $\text{Li}_x\text{V}_9\text{O}_{22}$.

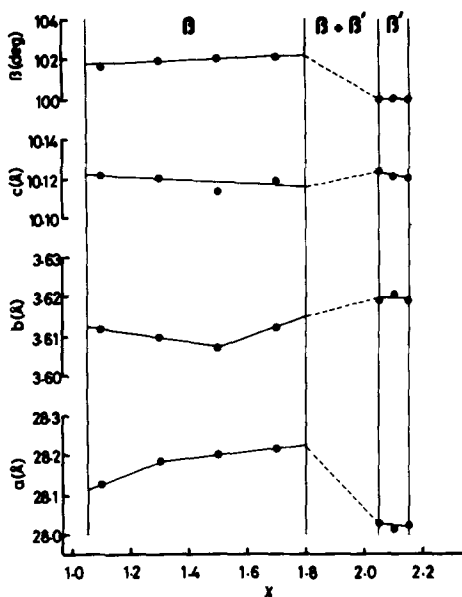


FIG. 4. Lattice parameters versus x for the system $\text{Li}_x\text{V}_{12}\text{O}_{29}$.

Laitinen and Rhodes reported the bronze $\text{Li}_2\text{V}_{12}\text{O}_{29}$, prepared by electrolysis of a melt of V_2O_5 in KCl-LiCl eutectic (7). Except for lithium content, the composition is identical to that of $\text{Li}_x\text{V}_{12}\text{O}_{29}$ found in the present work; however, the powder X-ray patterns are different. Also, we did not find the compound $\text{Li}_x\text{V}_{30}\text{O}_{71+y}$.

Early reports (8, 9) suggested the existence of a homogeneity region with respect to the oxygen in the " $\beta\text{-Li}_x\text{V}_2\text{O}_5$ " phase; thus this phase could contain oxygen defects, as expressed by $\text{Li}_x\text{V}_2\text{O}_{5-y}$ ($0 \leq y \leq 0.2$) (9). We did not find any evidence for such high oxygen deficiency in the present work. It is notable that the composition of $\text{Li}_x\text{V}_{12}\text{O}_{29}$ (convertible to $\text{Li}_x\text{V}_2\text{O}_{4.83}$) is very close to the limit composition of the above

formula. Moreover, when we made $\beta\text{-Li}_x\text{V}_2\text{O}_5$ in an open system under purified nitrogen flow, the sample was sometimes reduced, to give $\text{Li}_x\text{V}_9\text{O}_{22}$ or $\text{Li}_x\text{V}_{12}\text{O}_{29}$ (or a mixture of them) rather than $\beta\text{-Li}_x\text{V}_2\text{O}_5$. As the powder X-ray pattern of β - (or β' -) $\text{Li}_x\text{V}_2\text{O}_5$ resembles that of $\text{Li}_x\text{V}_9\text{O}_{22}$ or $\text{Li}_x\text{V}_{12}\text{O}_{29}$, it is easily to misidentify these phases. At least, it can be concluded that even if $\beta\text{-Li}_x\text{V}_2\text{O}_5$ could contain oxygen defects, the upper limit of y in the above formula is small. We suggest that the results of early experiments on $\beta\text{-Li}_x\text{V}_2\text{O}_5$ prepared in open systems are questionable.

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