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BRIEF COMMUNICATIONS

Structural Change in $Li_{1-x}VO_2$ ($x \approx 0.2$) Single Crystals

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The phase transition around 500 K of $Li_{0.8}VO_2$ has been studied using single-crystal specimens grown by the flux method. Single-crystal X-ray diffraction reveals that the marked superstructure streaks elongated in the $\langle 00 \cdot l \rangle^*$ direction at room temperature disappear on heating above 500 K, and that the structure becomes an ideal "ordered rock salt" type of α-$NaFeO_2$. The phase change occurs reversibly during heating and cooling cycles. Partial decomposition into a spinel phase is also observed.

1. Introduction

$LiVO_2$ is a typical ABO_2 compound with an α-$NaFeO_2$-like "ordered rock salt" (ORS) structure having two-dimensionally oriented V^{3+} ions, and its electrical and magnetic properties have been watched with keen interest (*1–11*). Bongers (*1*) found the first-order phase transition in $LiVO_2$ at temperature T_t between 450 and 550 K. Goodenough (*7*) and Goodenough *et al.* (*8*) have suggested that the transition is a result of the V^{3+}–V^{3+} interaction which makes a triangular trimer of three V^{3+} ions within the two-dimensional $(00 \cdot l)$ plane.

Recently, our group has successfully grown centimeter-sized single crystals of Li-deficient $Li_{1-x}VO_2$ ($x \approx 0.2$) in the form of hexagonal plates by a flux method, and details of the growth as well as the characterization of the obtained crystals at and below room temperature have been reported (*12*). The crystals showed significant superstructure diffractions of $\sqrt{3}a_0$ and $2c_0$ with respect to the hexagonal parameters of the α-$NaFeO_2$-type structure, suggesting a formation of V-trimmers within the $(00 \cdot l)$ plane.

The present paper describes the structure change of $Li_{1-x}VO_2$ ($x \approx 0.2$) single crystals at T_t. The results are discussed in terms of the cluster model proposed by Goodenough (*7*).

2. Experimental

Specimens of Li-deficient single crystals $Li_{1-x}VO_2$ ($x \approx 0.2$), which typically appear as shown in Fig. 1, prepared by the Li BO_2–Li_2O flux method (*12*) were used in this experiment. High-temperature X-ray powder diffraction and DTA-TG were also carried out in N_2 on pulverized single crystals using a MXP18 diffractometer and a Mac Science Co. 001 thermal analyzer, respectively. High-temperature X-ray single-crystal analyses were performed using a Buerger precession camera from Rigaku Co. with a heating attachment and Mo$K\alpha$ radiation

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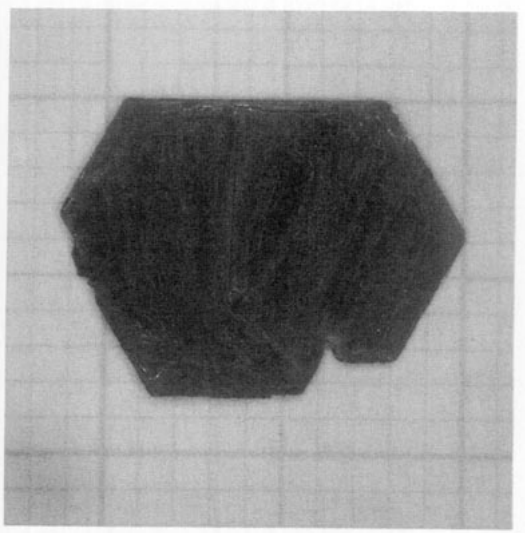

FIG. 1. A typical single-crystal plate of $Li_{0.8}VO_2$ grown from the high-temperature solution Li_2O–$LiBO_2$. (Scale: 1 grid = 1 mm.)

filtered by Zr. To avoid oxidation, crystal specimens vacuum-sealed in a glass tube were used.

3. Results and Discussion

To determine the phase transition temperature T_t precisely, DTA-TG and high-temperature X-ray powder diffraction were first performed on pulverized single-crystal specimens. Endothermic and exothermic peaks were observed at 500 and 450 K during the heating and subsequent cooling processes on DTA, respectively, whereas no remarkable change was detected on TG. The peak temperatures of the DTA curves, which correspond to the phase change with remarkable thermal hysteresis, were reproducibly observed within ±6 K on several heating–cooling cycles. The values of T_t nearly agree with those observed on the

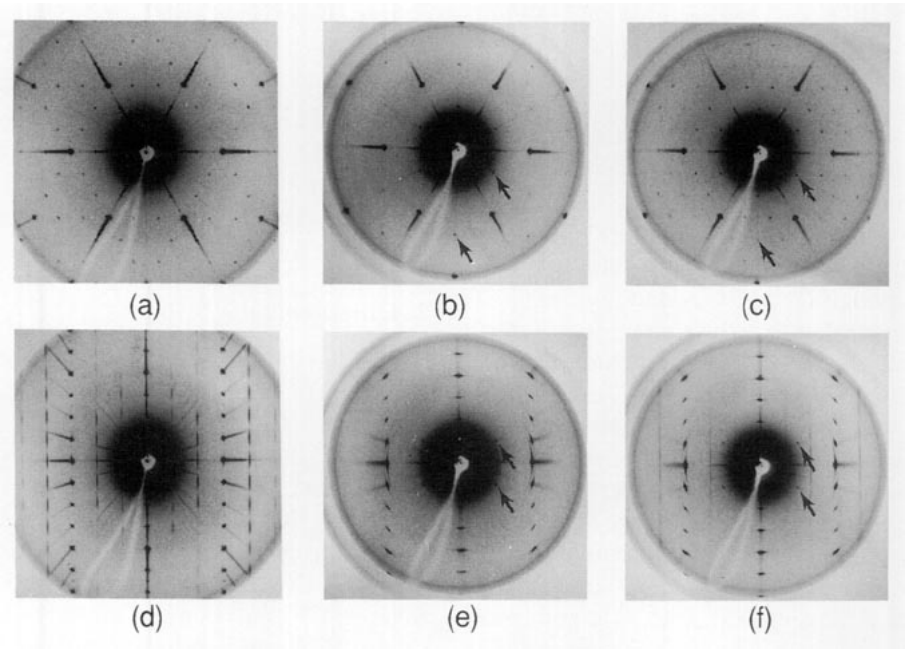

FIG. 2. Precession photographs of single-crystal $Li_{0.8}VO_2$ on the $h\,k0$ (*a*, *b*, and *c*) and $h0 \cdot l$ (*d*, *e*, and *f*) planes. They were taken at room temperature (*a* and *d*), at 573 K (*b* and *e*), and at room temperature after cooling (c and f). The arrows in photographs (b), (c), (e), and (f) indicate the origination of the spinel phase (see text). The radiation was Mo$K\alpha$ filtered by Zr.

X-ray measurements, where an abrupt increase in a_0 and a simultaneous decrease in c_0 were observed upon heating at 530 K, and reverse changes occurred at 420 K upon cooling. Similar hysteresis, characteristic of the first-order phase transition, was reported by Cardoso *et al.* in the nonstoichiometric powders $Li_{0.7}VO_2$ (*13*).

Figure 2 shows the precession photographs of $Li_{1-x}VO_2$ ($x \approx 0.2$) single crystals taken perpendicular to and along the developed hexagonal plane ($00 \cdot l$) at room temperature and above the highest T_t of 530 K. At room temperature, significant commensurate superstructure spots in the $hk0$ photograph (Fig. 2a) and broken streaks in the $h0 \cdot l$ photograph (Fig. 2d) were observed in addition to the fundamental, strong diffraction spots of the trigonal (pseudo-hexagonal) cell with the ORS $R\bar{3}m$ structure.

As previously reported (*12*), the superstructure spots in Fig. 2a are sections of the streak-like diffractions in Fig. 2d with a spacing of $(1/\sqrt{3})a^*$ along the c^*-direction. They indicate a characteristic extinction rule of $-h + k \neq 3n$ on the hkl plane. These figures give the following structural data: the space group is $P3_112$ or $P3_212$ and the hexagonal lattice parameters a_0' and c_0' are 4.92 Å $\approx \sqrt{3}a_0$ and 29.65 Å $\approx 2c_0$, respectively. The commensurate superstructure spots in Fig. 2a can be explained by considering the new two-dimensional cell, where three V^{3+} ions in the hexagonal ($00 \cdot l$) plane form a triangular trimer, and random stackings of each ($00 \cdot l$) plane along the c-direction result in the streak lines in Fig. 2d. An example of the stacking feature of the V^{3+} layers of the ($00 \cdot l$) plane along the c-axis is schematically illustrated in Fig. 3. The formation of V^{3+}-trimers in $LiVO_2$ has already been supposed by Goodenough and co-workers (*7*, *8*).

The high-temperature precession photographs taken at 573 K show a complete disappearance of the superstructure patterns, whereas the simple spots related to the ORS

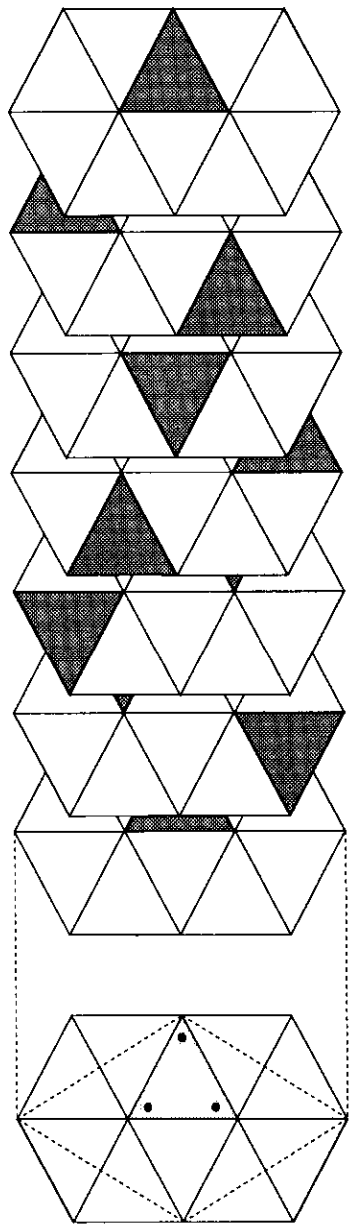

FIG. 3. A schematic representation of the stacking feature of the ($00 \cdot l$) planes in $LiVO_2$. The shaded triangles indicate cells where three V^{3+} ions make a trimer. The unit cell is shown by the dotted lines at the bottom of the figure.

structure remained unchanged, as shown in Figs. 2b and 2e. The superstructure reappeared when the heated specimen was cooled to room temperature, as shown in Figs. 2c and 2f. These changes took place reversibly in several heating and cooling runs.

In addition to the structural change related to the dissolution or formation of V^{3+}-trimers around 500 K, an obvious difference in the streak patterns was observed: the reappearing streaks of the specimen in Fig. 2f are more continuous than those of the as-grown specimen shown in Fig. 2d. Simultaneously, the diffraction spots from the subcell became somewhat diffuse. This suggests an increase in the randomness of stackings of the V^{3+} layers by the phase change from the ORS to the trimerized structure.

The precession photographs at 573 K of the *h0l* plane also present extra weak spots in the ORS, as shown in Figs. 2b and 2e, where the spots are indicated by the arrows. No considerable change in the spot intensities was observed after the specimen was cooled to room temperature, as shown in Figs. 2c and 2f. By comparing the data with those reported previously (*14, 15*), the spots were reasonably explained by the diffractions of the cubic spinel phase LiV_2O_4 with $a_0 = 8.25$ Å, which was possibly formed by the following disproportionation reaction upon heating above 530 K (*3, 8, 11*):

$$Li_{0.8}VO_2 \rightarrow 0.6LiVO_2 + 0.2LiV_2O_4.$$

The lattice relation between the ORS and the spinel was determined from Fig. 2 to be $[11 \cdot 0]_{ORS}//[100]_{spinel}$ and $(00 \cdot 1)_{ORS}//(111)_{spinel}$. Electron diffraction analyses also revealed that the heated specimens were made of a mosaic structure of $LiVO_2$ and spinel with a domain size of submicrometers.

Acknowledgments

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