We have successfully prepared the spinel \( \text{Li}_{1+x}\text{Ti}_2\text{O}_4 \), which is a type II superconductor with \( T_c \sim 12\text{K} \), by solid-state reaction process. Owing to the volatility of lithium, excess lithium precursor up to molar fraction 0.15 was added during the synthesis to result in single phase \( \text{Li}_{1+x}\text{Ti}_2\text{O}_4 \), without any impurity phase in high resolution XRD pattern. The normal state temperature dependence of resistivity shows an initial semiconductor-like behavior, but turn into metallic-like at about 200K. Magnetization measurements show bulk superconductivity in the fresh samples. The sample is unstable to the exposure of air and humidity. It is observed that the resistive transition quickly diminishes with the exposure to air. However, the magnetic transition remains as sharp, only with the decrease in its superconducting volume fraction, even when the resistive transition completely disappears. An anomalous metal-insulator transition in the aged sample is observed at the same temperature as the superconducting transition temperature of the fresh sample.

PACS numbers:74.25.fy, 74.70.Dd
1. INTRODUCTION

The intrigue behavior of Li based spinel oxide attracts many attentions due to its potential use as electrodes in batteries for electronic devices. Among all the spinel oxides, $Li Ti_2 O_4$ is the only one that becomes superconducting with a transition temperature $\sim 13K$. Although it was treated as a d-band BCS superconductor during its discovery of superconductivity, the more recent studies show that it has strong electron-electron interactions and conventional mechanism of superconductivity may fail to explain it. $Li Ti_2 O_4$ has an electron occupation of the titanium band of $3d^{0.5}$, a nearly empty 3d shell. Thus, it becomes an ideal system in the comparison between oxide superconductors involving electrons in nearly empty 3d shells and the cuprate superconductors, which involve electrons and holes in nearly full 3d shell. On the other hand, it has long been known that this compound deteriorates rapidly after exposing to air or moisture. Therefore, it is important to reexamine this intriguing oxide superconductor by carefully studying the doping effect on its superconducting properties. On the other hand, due to the mobile $Li^{+}$ ions at room temperature in $Li Ti_2 O_4$, this compound has the potential become electrodes of Li-based battery. The reaction between mobile $Li^{+}$ ions and oxygen or moisture make the compound not stable in air. Here we report the investigation of R(T) and XRD in both fresh and aged samples in order to get more idea about this compound.

2. EXPERIMENTS

Polycrystalline $Li_{1+x} Ti_2 O_4$ is synthesized by the conventional solid-state reaction method. The usual processes include two-steps reactions. They generally will form two intermediate compounds, $Li_2 TiO_3$ or $Li_2 Ti_2 O_5$. The process employed here is

$$Li_2 CO_3 + 2TiO_2 \rightarrow Li_2 Ti_2 O_5 + CO_2$$ (1)

$$Li_2 Ti_2 O_5 + TiO_2 \rightarrow 2Li Ti_2 O_4$$ (2)

Both $Li_2 CO_3$ (99.99%) and $TiO_2$ (98.5%) were first dried at 150 $^0C$ for 2hr. The excess molar fraction $x$ of $Li_2 CO_3$ is added in step (1) for $Li_{1+x} Ti_2 O_4$. The well mixed powders of $Li_2 CO_3$ and $TiO_2$ were calcined in air at 750 $^0C$ for 8hr. This step was repeated again with intermediate grinding and calcined for 12hr. After this process, the reactants and proper amount of $Ti_2 O_3$ (99.9%) were ground thoroughly and pressed into pellets. The pellet with diameter of 1cm was sintered at 880 $^0C$ for 24hr in quartz tube under dynamic vacuum with pressure less than $10^{-4}$ torr. Because of
The preparation of $Li_{1+x}Ti_2O_4$ and its aging effect

the volatility of $Li$, it was hard to get the exact composition of $Li$. Here we just show the nominal composition of $Li$. The polycrystalline sample is stored in $Ar$ atmosphere in order to avoid the aging reaction with oxygen and moisture.

To investigate the aging effect, the fresh samples were placed in air to allow aging. We even emerged the sample into boiled water to speed up the aging process. The X-ray diffractometer using $Cu$ $Kα$ line ($λ = 1.5406\AA$) was used for first-hand in structure determination. Resistance-v.s.-temperature curve was measured by the standard 4-probe method. The electrical contact is made by $In$ and $Pt$ wire with a calibrated $Si$-diode for accurate temperature measurements.

3. RESULTS AND DISCUSSION

The evolution of XRD pattern of $Li_{1+x}Ti_2O_4$ from $x = 0$ to $x = 0.4$ is shown in figure 1. There exists a $Ti_2O_3$ impurity phase in $x=0$ sample. It is most likely due to the deficiency of $Li$ because of the volatility of this element. We can compensate this deficiency by adding more lithium. We obtained pure $LiTi_2O_4$ phase samples in the range of $0.1 \leq x \leq 0.15$. For $x \geq 0.2$, the $Li_2TiO_3$ impurity phase emerges. Figure 2 shows the temperature dependence of resistance for as grown samples with different $Li$-content. The excess $Li$ may enter the octahedral site 16c of the spinel structure and further push the $Li$ in tetrahedral site 8a on to octahedral site 16c. This leads to the structure of $\{Li_{1+x}\}[Ti_2]O_4$, where the curly bracket encloses cations in 16c, the square bracket for 16d. The structure preserves the space group Fd3m,
Fig. 2. The evolution of R(T) of \( Li_{1+x}Ti_2O_4 \) polycrystalline sample. Inset: the variation of \( T_{\text{max}} \) vs. \( x \) of Li.

the same with the normal spinel \( Li[Ti_2]O_4 \). In consideration of electrical neutrality, the electronic configuration of Ti will increase from \( d^{0.5} \) for \( x \geq 0 \) in \( \{Li_{1+x}\}[Ti_2]O_4 \). It means that there are more electrons in the sample. This is consistent with our results of resistivity, which becomes more metallic with increasing composition of Li. The evolution of electronic configuration of Ti in \( \{Li_{1+x}\}[Ti_2]O_4 \) may give rise to this change. An interesting feature of the aged sample is that the resistance of a fresh sample exhibits a broad maximum, defined as \( T_{\text{max}} \), at around \( \sim 100K \) for \( Li_{1.1}Ti_2O_4 \). And \( T_{\text{max}} \) increases linearly with doping \( x \), as shown in the inset of figure 2. The aging processes were investigated in two different samples of \( Li_{1+x}Ti_2O_4 \) (\( x = 0 \) and 0.05). XRD patterns, shown in figure 3, of \( Li_{1.05}Ti_2O_4 \) powders clearly showed that the gradual appearance of second phase in the aged sample. In addition to the presence of some not yet identified peaks, the original peaks became broaden, suggesting the weakening of crystallinity.

The (533) and (622) peaks essentially become undetectable after aging for 157 days. Figure 4 displays the temperature dependence of resistance of polycrystalline \( LiTi_2O_4 \) after aging for days. The overall resistance increases with aging time. After 4 days, only trace of superconductivity was detected, and no resistive transition above 4.2K was observed after 5 days. Mag-
The preparation of $Li_{1+x}Ti_2O_4$ and its aging effect

Fig. 3. The evolution of XRD of $Li_{1.05}Ti_2O_4$ powder during the aging process.

netization measurements show bulk superconductivity in the fresh samples. However, the magnetic transition remains as sharp, only with the decrease in its superconducting volume fraction, even when the resistive transition completely disappears. A real surprise to us was to observe a metal-insulator transition in the aged (after 5 days) sample at almost the same temperature as the superconducting transition temperature in a fresh sample. Based on the XRD results we expect that after aging 5 days the pure phase responsible for superconductivity remains to be the major phase in the sample. Nevertheless, no resistive transition can be detected. This strongly suggests that there may exist some electronic structural change in the aged sample though the crystal structure remains the same. A preliminary $^7Li$ NMR study indeed indicates that the $T_2$ relaxation is different for fresh and aged sample. More detailed investigation of this characteristic is undergoing.

4. SUMMARY

We have successfully prepared the spinel $Li_{1+x}Ti_2O_4$ by two-step reaction process with reduced atmosphere annealing. To overcome the volatility of lithium, excess lithium precursor up to molar fraction 0.15 was added during the synthesis to result in single phase $Li_{1+x}Ti_2O_4$. The normal state temperature dependence of resistivity shows an initial semiconductor-like behavior, but turn into metallic-like at about 150K, which vary with Li-content. An anomalous metal-insulator transition in the aged sample is observed at the same temperature as the superconducting transition tem-
Fig. 4. The evolution of R(T) of LiTi$_2$O$_4$ polycrystalline sample during the aging process.

perature of the fresh sample. A more detailed study is needed in order to better understand the correlation of superconductivity and the anomalous metal-insulator transition.

**ACKNOWLEDGMENTS**

This research is supported by NSC grants 90-2112-M-007-055.

**REFERENCES**