$\mathrm{B}-3-3$  New Materials for Josephson Junction Devices (Invited)

T. Inamura, T. Murakami, T. Inukai, Y. Enomoto and M. Suzuki Ibaraki Electrical Communication Laboratory, N.T.T.

162 Shirakata-shirane Tokai-mura, Ibaraki-ken 319-11, Japan

Although many elements and compounds are known to be superconducting,

Josephson junctions made of new materials other than lead-alloy do not have so
many varieties. The necessary condition for superconductors to be made into

Josephson junction is:1) Thin films, 2) Appropriate barrier materials whose thickness and barrier height can be finely controlled and reproduced, and 3) Suitable
resist materials and etchants, are available. Niobium and its compounds of B
1 and A-15 structures are being tried in many laboratories in this country including Ibaraki E.C.L., and a little more time will be needed for them to completely
fulfill the item 2).

The authors started the studies of oxide superconductor  $\operatorname{BaPb}_{1-x}\operatorname{Bi}_x\operatorname{O}_3$  of perovskite structure in 1979 on the knowledge of ceramics  $\operatorname{data}^{1/2}$  and a little later the news of thin film fabrication  $^3$ . Transition temperature  $\operatorname{T_c}$  of bulk ceramics specimens reached up to 10K with some substitution trials to surpass the highest  $\operatorname{T_c}$  value 13K. Then thin film fabrication was tried to fulfill the item 1). Grain boundary layers in this film were found to act as Josephson tunneling junctions.  $\operatorname{Li}_{1+x}\operatorname{Ti}_{2-x}\operatorname{O}_4$  is another high  $\operatorname{T_c}$  (13.7K) superconductor of spinel structure  $^4$ . Li and Ti are light elements in contrast to that Ba, Pb and Bi are heavy, and the formers' electrochemical activity was supposed to bring about new type superconductive functional devices. Ceramics specimen with Ti/Li ratio 2.6 prepared by hot-pressing at 900°C was found to become superconducting at 13.4K. Thin films were recently successfully produced.

## Thin Film Fabrication of BaPb<sub>1-v</sub>Bi<sub>v</sub>O<sub>3</sub>

Superconducting thin films were prepared by RF diode sputtering with a relatively high deposition rate of 50-120 Å/min and subsequent heat treatments. Sputtering targets were obtained by mixing G.R. grade  $BaCO_3$ ,  $PbO_2$  and  $Bi_2O_3$ , heating in oxygen flow at 800°C for two hours, pulverizing and pressing into a disk of 60 mm Ø and 3 mm t, and sintering in oxygen flow at 880°C for 8 hours. The films were prepared by sputtering the target material onto a sapphire substrate in an  $Ar-49\%O_2$  atmosphere at  $8\times10^{-2}$  Torr. The substrate was heated to 260°C during the discharge and the anode voltage was kept at 1.4 kV. Since sputtered films tend to lack Pb and Bi, the target was compensated in advance with excess Pb and Bi, forming the composition  $Ba(Pb_0.7Bi_0.3)_{1.5}O_4$ . All as-sputtered films were found to have the perovskite structure but not to exhibit superconductivity.

They were made superconducting at about 9K by annealing at 530-600°C for 12 hours in an oxygen flow with PbO2 powder. Fig.1 gives the temperature dependences of resistivities of specimens annealed at several temperatures. The film is devided into grains by boundary layers and the average grain size is about 2400  ${\rm \ddot{A}}.$ 

## Boundary Layer Josephson Junctions

The I-V characteristics at 4.2K of  $BaPb_{0.7}Bi_{0.3}O_3$  films 0.5  $\mu m$  thick and 500  $\mu m$  wide with a constriction of 10  $\mu m$  wide by 10  $\mu m$  long are shown in Fig.2. When the current exceeds the critical current of the boundary layers with the lowest one, step-wise voltage increments appear. All the voltage increments are about 2.2 mV, and equal to energy gap  $2\Delta/e$  of this film. When the current is decreased, the I-V traces form a hysteresis curve. This behavior is very similar to that of a series connection of discrete Josephson tunneling junctions of uniform area and nominally uniform critical current densities.  $2\Delta(4.2K)/kT_c=$ 3.3, which is close to the B.C.S. value, was obtained.

## 3. $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ Ceramics

The specimens were prepared as follows: the powder mixtures of  $\mathrm{Ti}_2\mathrm{O}_3$  and  ${ t Li}_2{ t Ti}_2{ t O}_5$  were packed in a graphite die and were hot-pressed for 4 hours under 250 kg/cm $^2$  in an Ar-10%H $_2$  atmosphere. Li-Ti-O become superconductive over the  $\mbox{Ti/Li}$  atomic ratio of 1.5-3.1 and  $\mbox{T}_{_{\rm C}}$  depends on the composition , It is noted that at the ratio of 2.6 excess  ${\rm Ti}_2{\rm O}_3$  remains but  ${\rm T}_{\rm C}$  shows the highest value 13.4K. Electrical resistivity and phase composition depend strongly on hot-pressing temperature.

On the occurrence of superconductivity in oxide superconductors, another mechanism than B.C.S. is suggested<sup>5</sup>, but more experimental data will be needed to prove it. The lack of oxygen in  ${\tt BaPb}_{1-x}{\tt Bi}_x{\tt O}_3$  and the excess in  $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$  destroy superconductivity. From these facts, oxygen would be the key element in these materials.

 A.W.Sleight et al. Solid State Comm. 17(1975)27.
 T.D.Thanh, A.Koma and S.Tanaka Appl. Phys. 22(1980)205.
 L.R.Gilbert et al. Thin Solid Films 54(1978)729.
 D.C.Johnston J. Low Temp. Phys. 25(1976)145.
 T.Tani, T.Itoh and S.Tanaka 15th Int. Conf. Phys. Semicond. Kyoto, Sept.1-171202. 5 (1980).



