Superconductivity in the electrochemically Li-intercalated niobates with the layered perovskite structure

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Abstract

Li-intercalated layered perovskites $Li_xAB_2Na_{n-3}Nb_nO_{3n+1}$ (A = K, Rb, Cs; B=Ca, Sr, Ba) with n =3 and 4 have been prepared by an electrochemical technique. For the $Li_xAB_2Nb_3O_{10}$ superconducting materials, the value of T_c has been found to increase up to about 5-6 K as the a-axis length increases. For $Li_xCsBa_2Nb_3O_{10}$ with the largest a-axis length, however, superconductivity does not appear. In addtion, $Li_xKCa_2NaNb_4O_{13}$ shows no superconductivity.

Key words: superconductor; Li-intercalation; niobium oxide; layered perovskite structure

It is reported by Takano et al. [1,2] that superconductivity appears below about 5 K in the layered niobates $Li_xACa_2Nb_3O_{10}$ (A = K, Rb, Cs) with the triple-layered NbO_6 octahedrons, which are prepared by a chemical Li-intercalation technique. The values of $T_c \sim 5$ K in these niobates are much lower than those in high-T_c cuprates, though the crystal structures are similar to those of high-T_c cuprates, as shown in Fig. 1 [3]. Therefore, it is interesting to study how the value of T_c increases in other members of the Dion-Jacobson series, $AB_2Na_{n-3}Nb_nO_{3n+1}$ (A = alkaline metal; B = alkaline earth metal). However, it takes as long as several weeks or months to carry out the Li-intercalation by a chemical technique using a solution of n-buthyllithium. In contrast, an electrochemical technique is a useful method for Li-intercalation as described in our earlier report [4], because it is possible not only to incorporate Li efficiently but also to control the Li content. The main objective of this study is to investigate the value of T_c for selected layered perovskites $Li_xAB_2Na_{n-3}Nb_nO_{3n+1}$ with n = 3 which are prepared by the electrochemical Li-intercalation technique. In addition, the results for n = 4 are reported.

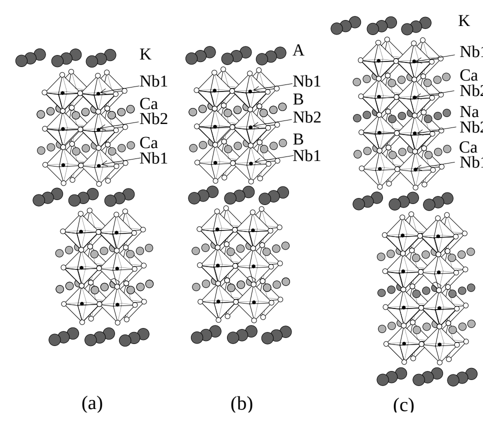

Fig. 1. Schematic representations of the crystal structures of (a) $KCa_2Nb_3O_{10}$, (b) $AB_2Nb_3O_{10}$ (A=Rb, Cs; B=Ca, Sr, Ba) and (c) $KCa_2NaNb_4O_{13}$.

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Polycrystalline host samples were prepared by the solid-state reaction method. Finally, the samples thus obtained were mixed with napfthalene of 25 percent of their weight, pelletized and then sintered again to obtain the porus samples which were suitable for the homogeneous intercalation of Li. The electrochemical Li-intercalation was carried out at R.T. under a constant potential using a potentio-galvanostat. A three-electrode cell was set up as sample|1.0M $LiClO_4$/PC|Pt. A Hg/Hg_2Cl_2 electrode was used as a reference electrode. The potential for the intercalation was determined to be 2.5 V. The amount of Li intercalated into the host sample was estimated according to the simple Faraday law. It took 20 min and 20 h to intercalate Li up to $x = 0.1$ and 0.6 for $Li_xCsSr_2Nb_3O_{10}$, respectively. These times are tiny fractions of the time required in the chemical technique.

Fig. 2 shows the x dependence of T_c and the superconducting volume fraction at 2 K, estimated from the magnetic susceptibility measurements. Notice that T_c is almost independent of x, while the superconducting volume fraction exhibits a maximum at $x \sim 0.1$. These results indicate the superconductivity seems to occur only at $x \sim 0.1$.

Shown in Fig. 3 is a relationship between T_c and a-axis length for $Li_xAB_2Nb_3O_{10}$. T_c tends to increase as the a-axis length increases. However, $Li_xCsBa_2Nb_3O_{10}$ with the largest a-axis length does not show the superconductivity down to 2 K. This behavior may be explained as follows. The increase in a-axis length weakens the interaction between the Nb4d and O2p orbitals, which leads to the decrease in the width of the Nd4d-O2p band. This decrease causes the increase in the density of states at the Fermi energy, resulting in the increase in T_c. With further increasing of a-axis length, the superconductivity may be suppressed due to the transition from metal to insulator. Another possible reason why T_c increases with the increase of x up to $\sim$ 7.8 Åis that the tilt of the NbO_6 octahedrons is relieved with the increase in a-axis length, as reported that the tilt of octahedrons suppresses the value of T_c in $(La, Sr)_2CuO_4$ and $(Ba, K)BiO_3$ [5, 6].

In the case of $Li_xKCa_2NaNb_4O_{13}$ with the four-fold NbO_6 octahedrons, superconductivity does not appear for $x \leq 0.34$. The reason why $Li_xKCa_2NaNb_4O_{13}$ shows no superconductivity may be explained as follows. The oxygen ions in the Nb1-O and Nb2-O planes are likely to be attracted toward Ca^{2+} rather than Na^+ and K^+. This roughness in the Nb1-O and Nb2-O planes leads to the weakness of the interaction between the Nd4d and O2p orbitals, resulting in the suppression of superconductivity. One might expect the similar consideration for $Li_xKLaNb_2O_7$ with the double NbO_6 octahedrons, which shows no superconductivity as reported by Takano et al. [1]. Accordingly, the flatness of the Nb2-O plane is considered to be important for the appearance of superconductivity in $Li_xAB_2Nb_3O_{10}$.

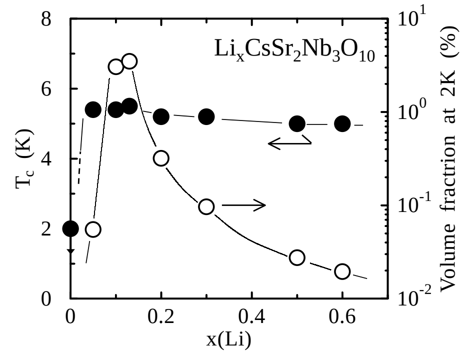

Fig. 2. Variations of T_c and the superconducting volume fraction at 2 K with x for $Li_xCsSr_2Nb_3O_{10}$.

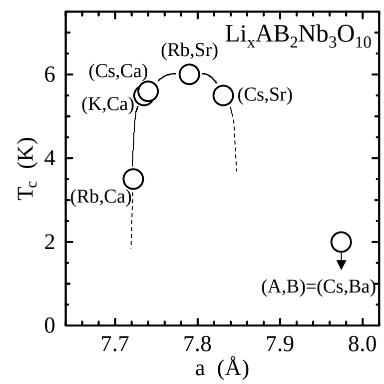

Fig. 3. Relationship between T_c and a-axis length for $Li_xAB_2Nb_3O_{10}$. The maximum value of T_c in each system is shown.

In conclusion, the Li-intercalated layered niobates $Li_xAB_2Na_{n-3}Nb_nO_{3n+1}$ with n =3 and 4 have been prepared by the electrochemical Li-intercalation technique. The maximum T_c for n = 3 seems to be about 6 K, while no superconductivity appears for n = 4.

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