Superconductivity of Alkali Metal Intercalated Niobate with a Layered Perovskite Structure

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Alkali metal intercalated compounds of a layer structured perovskite, $KCa_2Nb_3O_{10}$, have been prepared by the reaction with n-butyllithium or alkali metal azides, AN_3 (A = Li and Na). The magnetic susceptibility measurements showed that the compounds became superconductors with transition temperatures ranging from 3 - 6 K.

Since the discovery of high-Tc cuprate superconductors with layered perovskite structures, much attention has been attracted to non-cuprate layered analogues in an effort to understand the mechanism of high-Tc superconductivity. There have been reported two series of layered perovskites; one is the Ruddlesden-Popper series of the general formula of $A'_2[A_{n-1}B_nO_{3n+1}]$, and the other is the Dion-Jacobson series of the general formula of $A'[A_{n-1}B_nO_{3n+1}]$, where n denotes the thickness of the corresponding perovskite layers.[1-3] Some typical examples are $KLaNb_2O_7$ and $KCa_2Nb_3O_{10}$ for $n = 2$ and 3 members of the latter series,[4,5] the idealized structure for the $n = 3$ member is shown in Figure 1. All of the cuprate superconductors have interstratified layer structures, and the superconductivity occurs within two-dimensional CuO_2 planes of the perovskite layers separated by charge reservoir oxide layers. Charge carriers or holes are doped to the CuO_2 layers.[6] Although most of non-cuprate layered perovskites are insulators, we found that some niobate layered perovskites showed metallic conductivity on the reductive intercalation by lithium; a color change from white to black was also accompanied.[7] In this study, we have examined low temperature magnetic susceptibilities of the alkali metal intercalated $KCa_2Nb_3O_{10}$, and found that some samples show superconductivity at temperatures below 3 - 6 K.

The layered perovskite $KCa_2Nb_3O_{10}$ was prepared from K_2CO_3, $CaCO_3$, and Nb_2O_5 according to the method reported by Jacobson *et al.*.[8] The alkali metal intercalation was carried out by using two different kinds of reducing agents: n-butyllithium (BuLi) in hexane (15%) at room temperature, and lithium and sodium azides in evacuated glass tubes at elevated temperatures. Sodium azide was used as received (Katayama Chemical) and lithium azide was prepared by an ion-exchange method from sodium azide.[9,10] Magnetic susceptibility was measured using a SQUID magnetometer (Quantum Design MPMS-5S) under a field of 50 Oe on zero-field-cooled (ZFC) samples. X-ray powder diffraction (XRD) patterns of the intercalated compounds were measured in an Ar atmosphere using a cover with polyethylene windows and graphite monochromated Cu-$K\alpha$ radiation. Alkali contents of the intercalated samples were determined by using an inductively coupled plasma (ICP) spectrometer after dissolving them into a sulfuric acid solution.

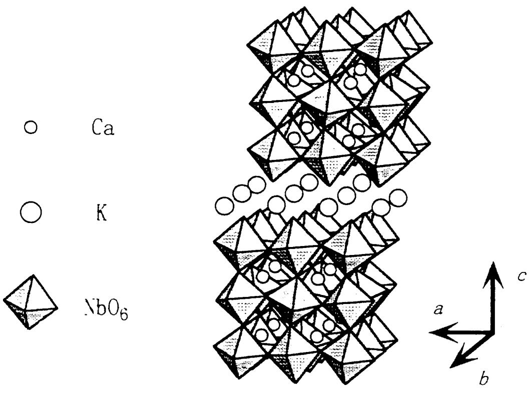

Figure 1. A schematic structural model of $KCa_2Nb_3O_{10}$.

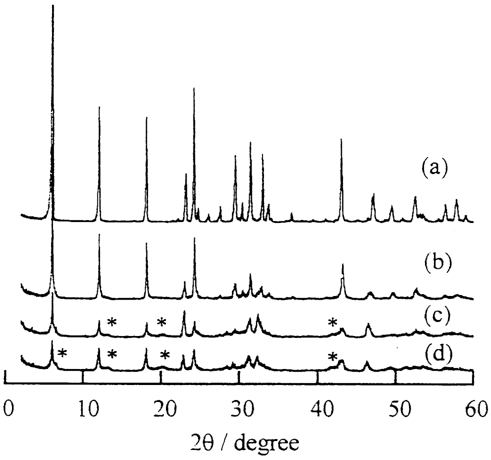

Figure 2. X-ray diffraction patterns of the starting $KCa_2Nb_3O_{10}$ (a) and its reaction products with BuLi for different reaction times, 10 (b), 22 (c) and 40 (d) days. The diffraction peaks due to the additional phase are marked by *.

By continuous stirring in the BuLi solution in hexane at room temperature, the white powder sample of $KCa_2Nb_3O_{10}$ was changed to dark blue-black in color. Figure 2 shows the XRD patterns of products treated in the BuLi solution for various reaction times. The lattice parameters of $KCa_2Nb_3O_{10}$ were essentially unchanged by the intercalation of lithium: $a = b = 0.7755(4)$ and $c = 2.933(1)$ nm for the product treated with BuLi for 10 days in comparison with $a = b = 0.7727(5)$ and $c = 2.940(1)$ nm for the starting $KCa_2Nb_3O_{10}$. No additional peaks were observed for 5 and 10 days products, whereas for the samples obtained after longer reaction times (22 and 40 days), intensities of the diffraction peaks became weak, and new peaks due to an unknown phase were observed as shown in the figure. The lithium contents were determined, and are shown in Figure 3 as a function of the reaction time. The amount of intercalated lithium increases gradually to $x = 1.3$ for $Li_xKCa_2Nb_3O_{10}$ with the reaction time. However it appears that the amount of lithium exceeding $x = 1.0$ might be used for the formation of the additional phase in the samples of 22 and 40 days . Figure 4

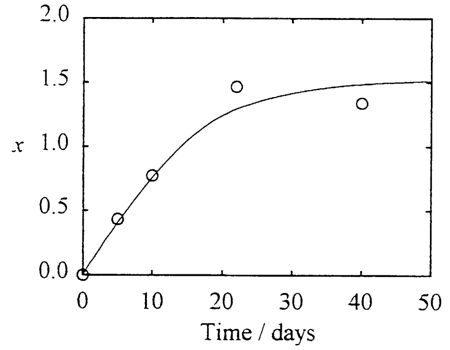

Figure 3. The amount of Li uptake (x) by $KCa_2Nb_3O_{10}$ as a function of reaction time.

shows the magnetic susceptibilities measured on the samples shown in Figure 3. A sharp drop in the susceptibility due to superconducting diamagnetism was observed at 6.0 K (onset). Although the fraction of diamagnetic susceptibility was only 1 - 2% of the perfect diamagnetism, the fraction increased with the increase of the amount of intercalated lithium until $x = 0.78$. The formation of the additional phase with excess lithium uptake resulted in a decrease of the superconducting fraction.

The reaction of an equimolar mixture of $KCa_2Nb_3O_{10}$ and LiN_3 was performed in an evacuated glass tube at 250 °C for 20 min. At this temperature the azide decomposed into lithium metal and nitrogen, and acted as an intercalation reagent. The XRD study of the resulting product showed that the lattice parameters were $a = 0.7741(4)$ nm and $c = 2.944(1)$ nm, which were almost unchanged from those of $KCa_2Nb_3O_{10}$. The product also showed a superconducting transition in the magnetic susceptibility measurement at 4.0 K, which was lower than that of the product obtained by the reaction with BuLi. A similar reaction was carried out by using NaN_3 at 390 °C, which also gave a superconductor with a transition temperature (Tc) of 3.5 K. The reactions with excess azides also resulted in the formation of unknown phases, and the superconducting fraction decreased with the increase of these phases.

The reason for the lower Tcs of the samples prepared by using azides is not clear. It was reported that alkali metal azides were useful reagents for the preparation of alkali metal fullerides such as Li_xC_{60} and Na_xC_{60}.[10] The use of azides has an advantage in the point that the reaction can be carried out at elevated temperatures and much faster compared with the reaction in a BuLi solution. However, it is not under a condition of soft chemistry; some additional reactions other than intercalation may take place. In case of the reactions with oxides such as layered perovskites, a fear of too much reduction should be considered. More detailed studies on the comparison of the two kinds of intercalation compounds prepared by the reactions with BuLi and azides should be made for further discussion.

We have prepared a new non-cuprate superconductor with a layered perovskite structure. In contrast to the hole superconductivity for most of cuprate perovskites, the alkali metal intercalated niobate perovskite is an electron doped superconductor. There are a variety of series of layered perovskites other than niobates, and each series include a variety of members with different thickness of layers. In an effort to elucidate the superconducting mechanism, it is important to investigate the possibility of the superconductivity of the alkali metal intercalated compounds of these non-cuprate perovskites more systematically.

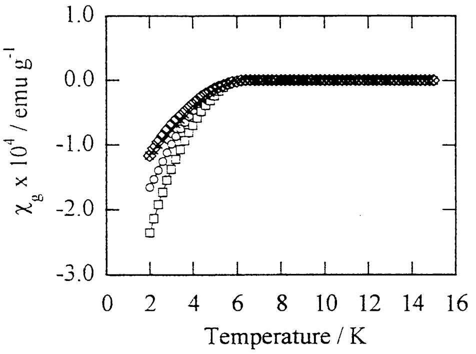

Figure 4. The magnetic susceptibilities of the lithium intercalated samples obtained by the reaction with BuLi for different reaction times: (○), 5; (□), 10; (◇),22; (×), 40 days.

This paper was presented in the 72th Annual Meeting of the Chemical Society of Japan.[11] During the course of the preparation of this paper, we have received a preprint of the communication on superconductivity of the same intercalated system $Li_xKCa_2Nb_3O_{10}$ by Takano et al..[12] Although they have not showed the XRD data and the amount of lithium intercalated, they could manage to confirm the superconductivity by electrical resistivity below 1 K.

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