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IONIC CONDUCTIVITY AND RAMAN SPECTRA OF Na-Li, K-Li, and K-Sn β-Al_2O_3*

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ABSTRACT

The ionic conductivity and Raman spectra of Na, Na-Li, K, K-Li, and K-Sn β-Al_2O_3 were measured in order to understand the mechanisms of mixed-ion conduction. It was observed that at 300 K, for example, the conductivity of a crystal with composition $Na_{0.82}Li_{0.18}\beta$-Al_2O_3 was about one-fifth that of pure Na crystals, while the conductivity of $K_{0.80}Li_{0.20}\beta$-Al_2O_3 was more than three orders of magnitude lower than that of pure K compounds. The results of a model calculation indicated that the Li^+ ions are the main carrier species in the Na-Li and K-Li mixed compounds. Features observed in the Raman spectra were attributed to paired- and single-ion vibrations. It is concluded that the K^+ ions which contribute to a band at 69 cm^{-1} in K β-Al_2O_3 are the effective carriers for conduction.

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DISCLAIMER

INTRODUCTION

Many studies have been made of ionic conductivity [1-4] and of Raman and infrared spectra [5-14] of the mobile cation motions in beta-alumina. Allen and Remeika [3] associated the frequencies of infrared bands due to motions of the Na^+ and Ag^+ ions with the attempt frequency for ionic diffusion. However, no clear evidence was given for such a relationship. In K β-Al_2O_3 crystals, there are two strong Raman bands which originate from the motions of the K^+ ions. The lower frequency band appears at 69 cm^{-1} and the higher frequency band at 80 cm^{-1}. Klein, Schafer, and Strom [13] measured the change of the intensity of these Raman bands in Na-K mixed compounds as a function of the K concentration. They concluded that both of these bands are caused by the motions of paired K^+ ions. Wang, Gaffari, and Choi [15] have shown from theoretical considerations that the high ionic conductivity and low activation energy of beta-aluminas are primarily due to the motions of such paired cations. The purpose of this paper is to report our measurements of ionic conductivity in Na-Li, K-Li, and K-Sn beta-aluminas and to identify the cation vibration modes in the Raman spectra which are related to ion transport in these materials.

EXPERIMENTAL PROCEDURES

Crystals of Na β-Al_2O_3 measuring about 6 x 2 x 2 mm were cut from a large section of a melt-grown boule (Union Carbide Corporation Crystal Products Department, San Diego). The faces perpendicular to the (001) plane were polished with an ethanol slurry of 0.3 μm alumina. In this study, an orthogonal set of crystal axes is denoted by a, a', and c, where c is the crystallographic c axis. From Laue back reflection patterns, the a axis was found to be about 22° from the [010] crystallographic axis. Polarized Raman spectra were recorded using the spectrometer described previously [12]. The ionic conductivity was measured by applying a fast voltage pulse and measuring the resulting current flow through a resistor [3]. The pulse rate was 1000 Hz and the pulse amplitude was 0.1 to 5 V. Evaporated gold contacts were used as blocking electrodes.

Samples containing K^+ ions were prepared by heating single crystals of Na β-Al_2O_3 in molten KNO_3 at 350°C for 46 h. A chemical analysis showed that the crystals contained 7.11 wt.% K. Assuming a formula unit of

$Na_{2.3}O \cdot 11Al_2O_3$ for the starting materials [3], this value corresponds to 97% substitution of Na^+ by K^+. Na-Li and K-Li mixed compounds were obtained by treating the Na and K crystals in molten $LiNO_3$ for 1 h and 16 h, respectively. By these treatments, 18% of Na^+ and 20% of K^+ were exchanged by Li^+. Other K β-Al_2O_3 were treated in molten $SnCl_2$ at 300°C for a week.

RESULTS AND DISCUSSIONS

The results of the ionic conductivity measurements of Na, $Na_{0.82}Li_{0.18}$, K, K-Sn, and $K_{0.80}Li_{0.20}$ β-Al_2O_3 are shown in Fig. 1. The solid lines are the result of fitting the conductivity values to an Arrhenius expression, and E_a are the activation energies given by the slopes of these lines. The conductivity of Na β-Al_2O_3 at room temperature was 3.1 x 10^{-2} $\Omega^{-1}cm^{-1}$, while the activation energy was 0.15 eV. These values agree well with previously reported results [3]. The conductivity of the Na-Li compound at 300 K was about one-fifth of that the Na crystal, and the activation energy was 0.23 eV. The ionic conductivity of $K_{0.80}Li_{0.20}$ β-Al_2O_3 at 300 K was more than three orders of magnitude less than that of the pure K crystals. The magnitude of the conductivity of the K-Sn crystal was about one half that of the pure K crystals, but the slopes of the respective log σT vs. 1/T curves were the same. Although the Li concentrations in the Na-Li and K-Li mixed crystals were almost equal, the effect of Li^+ on the ionic conductivity of K β-Al_2O_3 was much larger than its effect on that of Na β-Al_2O_3.

We have made model calculations using the methods previously developed for Naβ-Al_2O_3 [15] to aid in understanding the origins of the mixed ion effect on the ionic conductivities in beta-aluminas. The details of these calculations are described in the following report [16]. It is shown that the activation energy for escape of an ion from an interstitial ion pair depends on the types of ions in the pair and on the type of cations occupying nearby BR sites. For the mixed ions considered here, it was found that Na^+-Li^+ pairs are more stable than Na^+-Na^+ pairs in Li-Naβ-Al_2O_3 and that K^+-Li^+ pairs are more stable than K^+-K^+ pairs in Li-Kβ-Al_2O_3. A comparison of the observed activation energies with those calculated for various ion pairs is given in Table I. As seen in these results, the activation energies for escape of a Li^+ ion from a Na^+-Li^+ pair or from a K^+-Li^+ pair is much lower than the energy required for escape of the

Na^+ or K^+ ions. This means that, when Na^+-Li^+ and K^+-Li^+ pairs are formed, the Na^+ and K^+ ions are trapped in the respective pairs because their activation energies are very large. Thus, the Li^+ ions are the primary carriers in both mixed ion beta-aluminas.

The above result agrees with the experimental observation by Roth and Farrington [17] that the main carrier species are the Li^+ ions in Na-Li β-Al_2O_3 crystals having a Li/Na ratio greater than 1. The ionic conductivity is determined by the process with the lowest activation energy. In Na-Li β-Al_2O_3 the apparent activation energy obtained from the conductivity measurements corresponds to the calculated value (Table I) for the escape of the Li^+ ions from the Na^+-Li^+ pairs. In the case of the K-Li mixed crystal, however, the calculated activation energy is lower than that observed. Although the detailed reason for the discrepancy is not yet known, it is noticed that the trend of the calculated values agrees with those observed.

Raman spectra of Na and $Na_{0.82}Li_{0.18}$ β-Al_2O_3 obtained for (a'a) polarization at 12 K are shown in Fig. 2. The bands with centers near 120 and 98 cm^{-1} are due to phonon modes of the spinel block. The intensity and position of these bands depend on the type of mobile cation. At 12 K, Na^+ bands of Na- and $Na_{0.82}Li_{0.18}$β-Al_2O_3 appeared at 63 and 60 cm^{-1}, respectively. The position of the band in the Na crystal did not change with increasing temperature, but the center of the band in the Na-Li compound shifted from 60 to 63 cm^{-1} as the temperature increased from 12 to 300 K. We found in general that the frequency of the Na^+ Raman band in mixed Li-Na beta-aluminas <u>increased</u> as the sample temperature was increased from 12 to 300 K. The origin of this effect is not presently understood, but it may be related to the distribution of single ions and ion pair types at different temperatures.

In the Raman spectrum of pure K β-Al_2O_3 shown in Fig. 3, the bands centered at 69 and 80 cm^{-1} are due to the K^+ ions. When a small amount of Sn^{2+} was exchanged for K^+, the intensity of the 80 cm^{-1} band was essentially unchanged, but that of the 69 cm^1 band was greatly reduced. The effect is apparent in the Raman spectrum of K-Sn β-Al_2O_3 shown in Fig. 3. Charge neutrality requires that the divalent Sn^{2+} replace a K^+-K^+ pair. Hence, the diminution of the 69 cm^{-1} band as a result of Sn^{2+} exchange indicates that this band is due to K^+-K^+ pairs. As mentioned above, Li^+-K^+ pairs are more stable than K^+-K^+ pairs, so that the exchange of a small amount of Li^+ for K^+ in K β-Al_2O_3 is expected to result in a significant reduction in the K^+-K^+ pair concentration. The Raman spectrum of the $K_{0.80}Li_{0.20}$ crystal, in Fig. 3 shows the consequent diminution of the K^+-K^+ band intensity. Comparing the results in Figs. 1 and 3, it is concluded that the K^+ ions which contribute to the band at 69 cm^{-1} are the effective charge carriers. In melt-grown beta-alumina crystals, about 26% of the mobile cations are in pairs [3]. Consequently, the Li^+ ions in $K_{0.80}Li_{0.20}$ β-Al_2O_3 almost completely substitute for the K^+-K^+ pairs. Since the 80 cm^{-1} band remained relatively unaffected as a result of ion exchange by Sn^{2+} or Li^+, it follows that this feature is due to motion of K^+ single ions.

In crystals of K-Sn β-Al_2O_3 a Raman band appeared at 38 cm^{-1}. The intensity of the band increased with Sn^{2+} concentration and is therefore attributed to motion of the Sn^{2+} ions. A very weak band at 50 cm^{-1} in the K crystal was also seen with slightly larger intensity in the K-Sn mixed compound. The origin of this feature is not known at present, but it is noted that a similar band was found in the far infrared spectrum of K beta-alumina [13].

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TABLE I. OBSERVED AND CALCULATED ACTIVATION ENERGIES FOR MIXED ION BETA-ALUMINAS

Beta-Alumina	Activation Energy (eV)		
	Observed	Calculated	(Ion Pair)[a]
Na	0.15	0.20	(Na-Na*)
$Na_{0.82}Li_{0.18}$	0.23	0.24	(Na-Li*)
		0.43	(Li-Li*)
		0.65	(Na*-Li)
K	0.31	0.27	(K-K*)
$K_{0.80}Li_{0.20}$	0.52	0.28	(K-Li*)
		0.54	(Li-Li*)
		0.84	(K*-Li)

(a) The notation (X-Y*) denotes the ion pair for which the activation energy of escape of Y* is calculated.

FIGURE CAPTIONS

Fig. 1 Ionic conductivity of Na, Na-Li, K, K-Sn, and K-Li β-Al_2O_3 as a function of temperature. E_a is the activation energy.

Fig. 2 Raman spectra of Na and Na-Li β-Al_2O_3 showing the change of the Na^+ band caused by substitution of Li^+ for Na^+.

Fig. 3 Raman spectra of K, K-Sn, and K-Li β-Al_2O_3 showing the change of the lower frequency K^+ band by substitution of Sn^{2+} and Li^+ for K^+.

Fig. 1

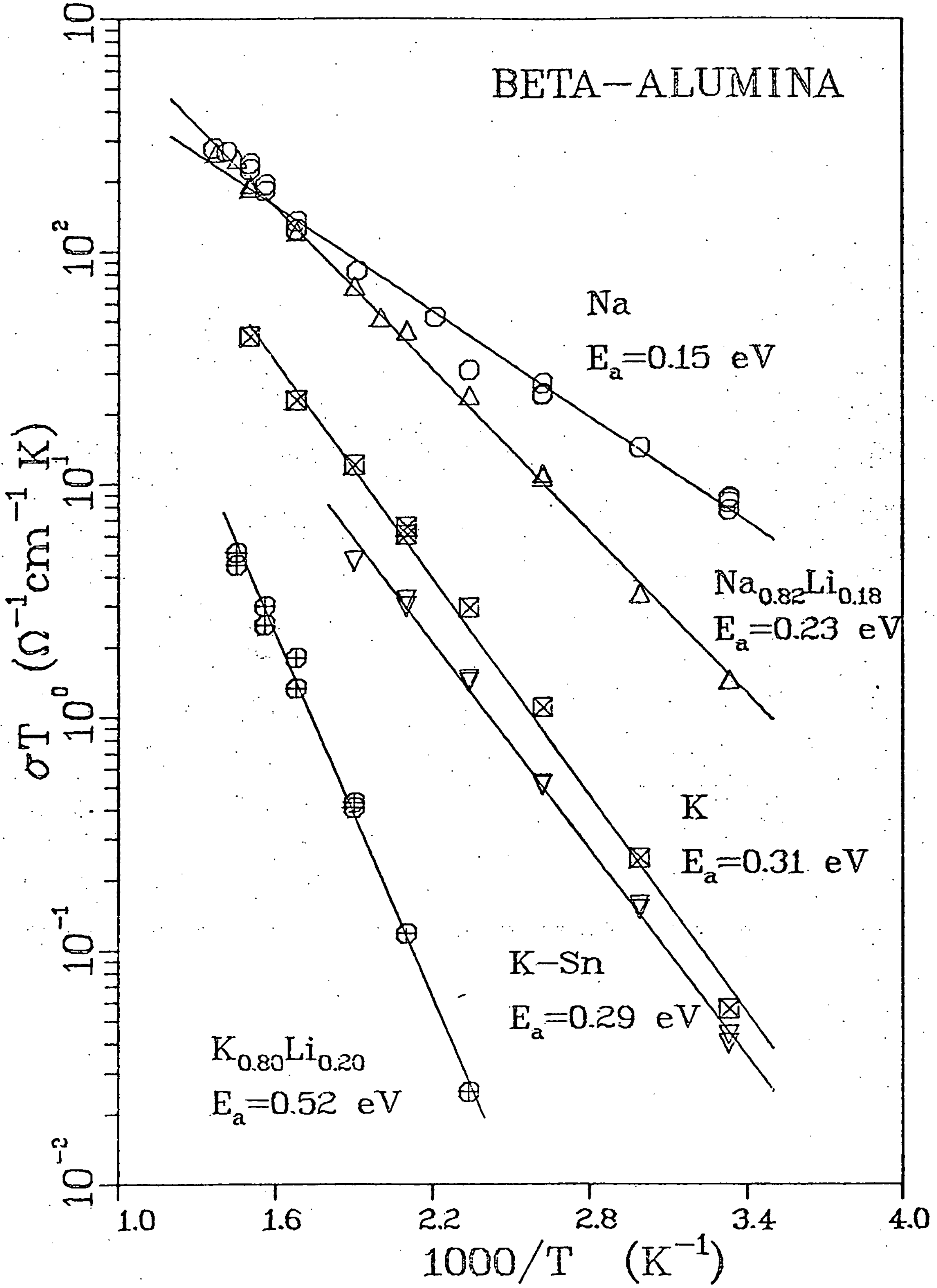

BETA-ALUMINA
Na
E_a=0.15 eV
$Na_{0.82}Li_{0.18}$
E_a=0.23 eV
K
E_a=0.31 eV
K-Sn
E_a=0.29 eV
$K_{0.80}Li_{0.20}$
E_a=0.52 eV
σT $(\Omega^{-1}cm^{-1}K)$
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
1.0
1.6
2.2
2.8
3.4
4.0
1000/T (K^{-1})

Fig. 2

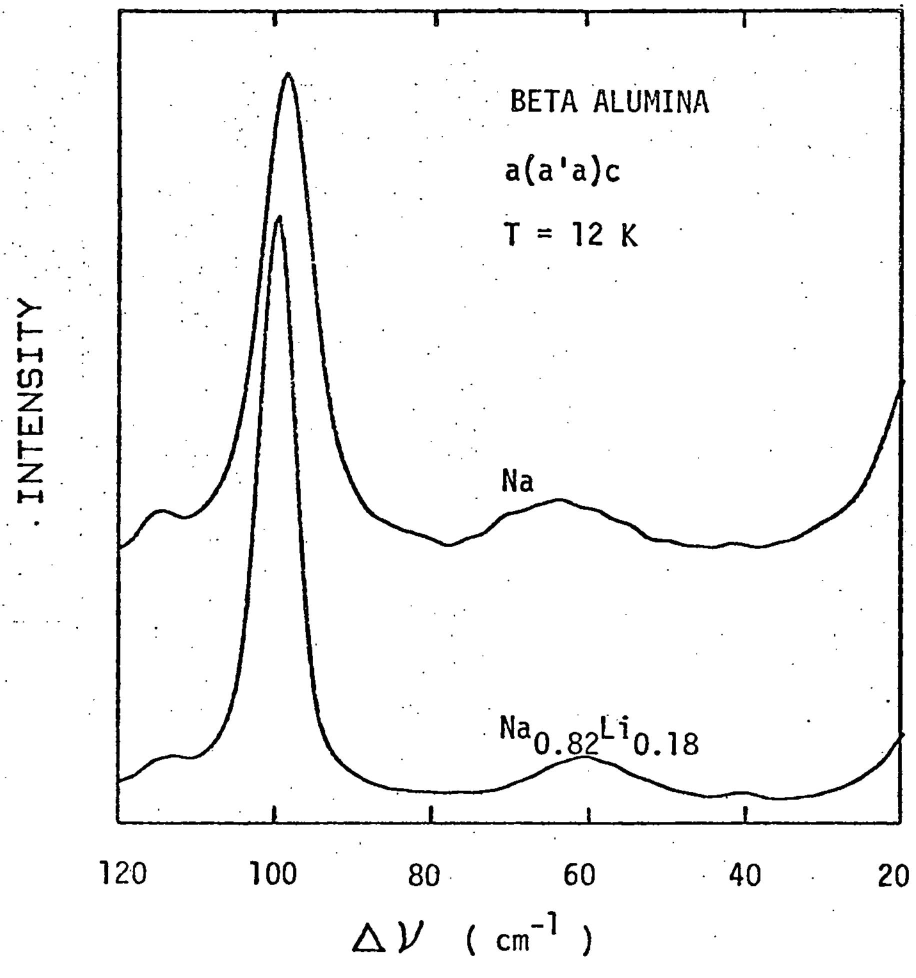
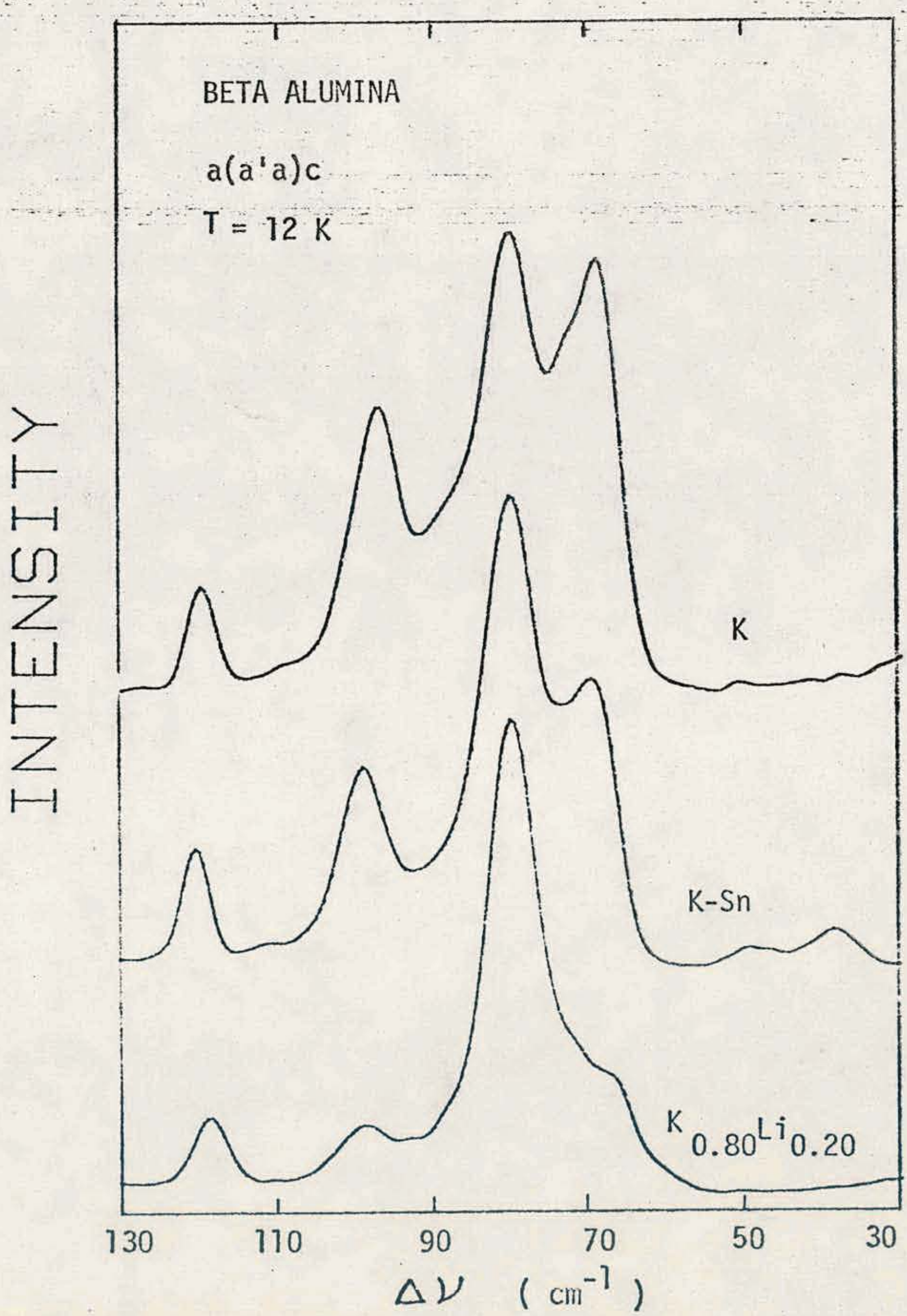

BETA ALUMINA
a(a'a)c
T = 12 K
INTENSITY
Na
Na$_{0.82}$Li$_{0.18}$
120
100
80
60
40
20
Δν (cm^{-1})

Fig. 3


BETA ALUMINA
a(a'a)c
T = 12 K
INTENSITY
K
K-Sn
$K_{0.80}Li_{0.20}$
130
110
90
70
50
30
Δν (cm⁻¹)