

## INFRARED AND MAGNETIC PROPERTIES OF $Ba_{1-x}K_xBiO_{3-y}$

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### Abstract

Results from magnetic ac susceptibility, x-ray diffraction and infrared reflection measurements on  $Ba_{1-x}K_xBiO_{3-y}$  are reported. We demonstrate the strong dependence of the superconducting as well as the normal state properties on the K content.

### Introduction

The high- $T_c$  superconductor  $Ba_{1-x}K_xBiO_{3-y}$  became famous because of its unique features. It is copper-free and has a cubic structure [1,2], unlike the other high- $T_c$  materials. Its transition temperature  $T_c = 30$  K is only 8 K below the La-based copperoxides. The question whether  $Ba_{1-x}K_xBiO_{3-y}$  can be described by the BCS model is of particular interest. Even in the copperoxides phonon mediated pairing seems to contribute to the superconducting properties. Understanding of the mechanism in  $Ba_{1-x}K_xBiO_{3-y}$  could help to understand at least those phonon contributions, too.

In this paper we present first results from magnetic susceptibility and infrared reflection measurements on samples prepared by a method reported by Hinks et al. [8].

### Sample Preparation

Powder mixtures of  $BaO$ ,  $KO_2$  and  $Bi_2O_3$  were reacted at  $710^\circ C$  for one hour in flowing nitrogen. The oxygen anneal was carried out at  $450^\circ C$  for 4 hours. The quality of our samples improved on adding 25 % extra  $KO_2$ , in contrast to the results in [2], but never reached the  $T_c$  values in this paper. Probably the procedure has to be adapted to the special conditions of our technical equipment in order to get similar results.

### Magnetic ac susceptibility and X-ray diffraction

The superconducting properties of our samples were examined by ac susceptibility measurements using a mutual inductance method described in [4]. A starting composition of  $x = 0.4$  leads to  $T_c = 22$  K and about 50 % of ideal diamagnetism. None of our samples without any excess potassium showed larger critical temperature. Adding 25 % excess  $KO_2$  results in  $T_c = 25$  K with nearly the same diamagnetism. Adding

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50 %  $\text{KO}_2$  lowers  $T_c$  dramatically to about 12 K, whereas the fraction of ideal diamagnetism is increased to about 80 %. This dependence on  $x$  is in agreement with the phase diagram given in [2]. The lattice constants  $a$  of the three samples were determined by x-ray diffraction using a Siemens D 501 diffractometer. We found  $a=4.282 \text{ \AA}$  and  $a=4.265 \text{ \AA}$  for  $x = 0.5$  and  $x = 0.6$ , respectively. No other crystalline phases seem to be present. The  $x = 0.4$  sample is multiphase, with two cubic phases with  $a = 4.283 \text{ \AA}$  (I) and  $a = 4.314 \text{ \AA}$  (II). According to the phase diagram [2] phase II is not superconducting. We estimate the actual K content of the single phase samples from the diagram to be  $x = 0.33$  and  $x = 0.44$ .

### IR-Reflection Spectra

Reflection spectra of the samples were taken with two Perkin Elmer Spectrometers ( $\lambda$  9 and Type 684) in the region between 0.05 eV and 3 eV. An Al mirror served as a reference. Prior to the measurements the samples were polished on a soft cloth, but the surfaces were still rough after this treatment. Figure 1 shows the spectra for  $x = 0.5$  and  $x = 0.6$ .  $x = 0.5$  and  $x = 0.4$  (not shown) have nearly the same spectra.

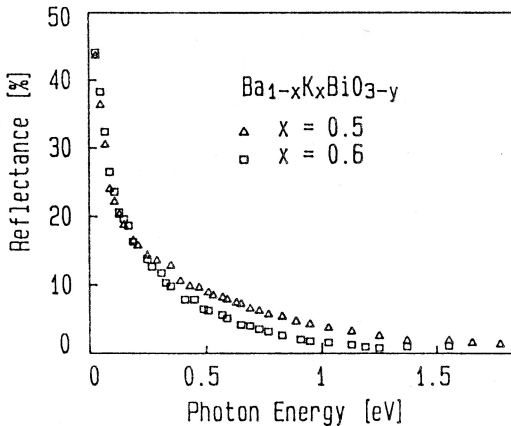


Fig.1: Reflection spectra of  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-y}$  shown in a wide energy range

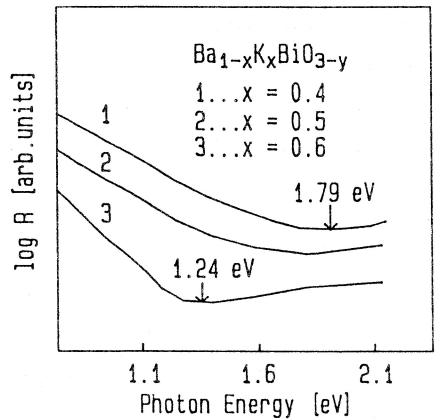


Fig.2: Reflectance in the region of the minima (logarithmic scale and displaced vertically)

The reflectivity rises monotonically with decreasing photon energy, starting at different points for the two K concentrations. Contrary to the results from thin films [5] there is no simple Drude behaviour. We believe that this difference is due to the rough surfaces of our samples. Nevertheless, the spectra exhibit minima near the starting point of the rise, which is typical for plasma edges (Figure 2). We took these minima to estimate the free carrier parameters, i.e. plasma frequency  $\omega_p$ , scattering rate  $\gamma$  and

background dielectric constant  $\epsilon_\infty$ . The minimum  $R_{min}$  appears at a frequency  $\omega_{min}$  where the real part of the dielectric function  $\epsilon_r = n^2 - k^2 = 1$  [6] (n... refractive index, k...extinction coefficient). In the case of small k the imaginary part of the dielectric function  $\epsilon_i \approx 2k$ . These two conditions applied to the ordinary Drude formula for  $\epsilon_r$  and  $\epsilon_i$  [6] leads to the equations:

$$\omega_{min} = \sqrt{\alpha\omega_p^2 - \gamma^2}, \quad \gamma = 2\alpha\omega_{min} \sqrt{\frac{R_{min}}{1 - 3R_{min}}}, \quad R(\omega \rightarrow \infty) = \left( \frac{\sqrt{\epsilon_\infty} - 1}{\sqrt{\epsilon_\infty} + 1} \right)^2$$

Here  $\alpha = \epsilon_\infty / (\epsilon_\infty - 1)$ . Evaluation of the spectra of the single phase samples yields  $\omega_p = 1.32$  eV,  $\gamma = 0.94$  eV,  $\epsilon_\infty = 1.7$  for x = 0.5 and  $\omega_p = 0.89$  eV,  $\gamma = 0.50$  eV,  $\epsilon_\infty = 1.5$  for x = 0.6. These values are of course subject to errors due to inaccurate reflectivities  $R_{min}$  and  $R(\omega \rightarrow \infty)$ . For example, an error of a factor of 3 in R would result in an error of about 30 % in  $\omega_p$  and about 40 % in  $\gamma$ . Nevertheless the agreement with the results in [5] is satisfying.

The main result from this analysis is that the plasma frequency decreases when the K content exceeds the optimum value. This means that the effective carrier mass increases more rapidly than the carrier concentration. A possible reason is a nonparabolic conduction band. Increasing K content leads to filling of the conduction band, so that the fermi level shifts to the nonparabolic region of the band, resulting in larger effective masses.

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