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Long Wavelength Optical Phonons in Mixed  
Alkali Halide Powder Crystals

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Introduction Although substantial work has been done on alkali halide mixed crystals grown from the melt, measurements on mixed crystals prepared from powders are rare /1/. In this note we discuss the infrared active lattice modes of the powder mixed crystal  $\text{KCl}_{1-x}\text{Br}_x$  measured by dispersive Fourier transform spectroscopy /2/ (DFTS).

It is well known that crystalline alkali halides have a single lattice vibrational frequency (the reststrahlen band), which depends on the atomic masses and the interatomic forces. The vibrational behavior of a mixed alkali halide crystal depends on the concentration of the components /3/. The conditions necessary for the two types of behavior observed in mixed crystals, e.g., one-mode or two-mode behavior, and the condition necessary for the existence of a localized and gap mode have been discussed in detail previously /4 to 8/. In our system, there is a frequency overlap between the reststrahlen bands of the constituents, and a single lattice mode appears whose frequency lies between the vibrational frequencies of the constituents.

Far-infrared techniques Measurements were carried out on the far-infrared asymmetric Fourier spectrometer described by Russell and Bell /9/. By replacing the fixed mirror with the mixed-crystal sample, we were able directly to measure the amplitude reflectivity and the phase shift upon reflection from the sample. To cover the frequency spectrum of 30 to  $300\text{ cm}^{-1}$ , beam splitters of thicknesses 6.25 and  $12.5\text{ }\mu\text{m}$  were used. The detector was a liquid helium cooled bolometer. Measurements were made at ambient temperature with  $2\text{ cm}^{-1}$  resolution. The average standard deviation of the interferogram points was 0.1%.

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Sample preparation Pure KCl and KBr crystals (Harshaw) were ground into a fine powder by milling them several times at 77 K (Spex Freezer Mill). KCl and KBr are hygroscopic, so the powders were baked for 24 h in vacuum at 400 °C to remove water absorbed during the milling process. The powders then were mixed to an appropriate mole fraction to make the sample  $\text{KCl}_{1-x}\text{Br}_x$ . To improve homogeneity the mixed powder was again ground and baked. The powders were then compressed in an evacuated die to form a glass-like, transparent pellet of 1.6 cm diameter and 3 mm thickness. The pellets were glued in a brass holder and polished optically flat, flatness being an essential requirement of amplitude spectroscopy /10/. Because of the hygroscopic nature of the sample and the high humidity of the environment it is possible that some water vapor was absorbed during the polishing step.

Results and discussion The reflectivity of mixed powder pellets of  $\text{KCl}_{1-x}\text{Br}_x$  retains the overall shape as the mixed crystal of the same composition grown from the melt /11/. The phase appears to be higher at frequencies below the transverse optic mode (TO), and above the longitudinal optic mode (LO) frequencies, as compared to the phase spectra of the individual KCl and KBr crystals /9, 10/.

The results for the amplitude and phase of the reflectivity were used to determine the complex and dielectric function of the mixed system, using the well known Fresnel relation /12/. Fig. 1a, b presents the complex dielectric function of  $\text{KCl}_{1-x}\text{Br}_x$ . The long-wavelength ( $q = 0$ ) frequencies of the TO and LO modes are indicated in Fig. 1. The TO frequency is the wave number where the conductivity  $\sigma_1 = \nu \epsilon_2 / 2$  has its maximum value and the LO frequency is the wave number where  $\epsilon_1 = N^2 - K^2$ , is zero. In the expressions above, N and K are real and imaginary parts of complex refractive index, and  $\epsilon_1$  and  $\epsilon_2$  are the real and imaginary parts of the complex dielectric function. The values of TO and LO for mixed powder pellets of  $\text{KCl}_{1-x}\text{Br}_x$  as well as those of the same composition grown from melt by Fertelano and Perry /11/ are listed in Table 1.

The anharmonic damping function /13/,  $\Gamma(0j, \nu)$ , is shown in Fig. 2. This quantity is calculated using the modified relation /14/

$$\Gamma(0j, \nu) = \frac{\nu_{0j} [\epsilon_1(0) - \epsilon(\infty)] \epsilon_2(\nu)}{2[\{\epsilon_1(\nu) - \epsilon_2(\nu)\}^2 + \epsilon_2(\nu)^2]},$$

Table 1

Comparison of room temperature long wavelength optical phonons in  $\text{KCl}_{1-x}\text{Br}_x$  mixtures (frequencies are in  $\text{cm}^{-1}$ )

mole fraction $x$	$\text{KCl}_{1-x}\text{Br}_x$ mixed powder pellets		$\text{KCl}_{1-x}\text{Br}_x$ grown from melt /11/	
	$\nu_{\text{TO}}$	$\nu_{\text{LO}}$	$\nu_{\text{TO}}$	$\nu_{\text{LO}}$
0.50	$142 \pm 2$	$192 \pm 2$	140	196
0.25	$144 \pm 2$	$196 \pm 2$	142	197.5

here  $\epsilon_1(0)$  and  $\epsilon(\infty)$  are the static and limiting high frequency values of the dielectric constant, and  $\nu_{0j}$  is the harmonic frequency of the TO phonon at wave vector  $q = 0$ . The values of  $\epsilon_1(0)$  and  $\epsilon(\infty)$  were taken from Fertelano and Perry /11/; they are in accord with our estimates from the low and high frequency data of Fig. 1. The close agreement between our values of phonon frequencies and dielectric constants and those of Fertelano and Perry /11/ shows the validity of the mixed powder pellet as a mixed crystal.

The overall anharmonic damping function of mixed powder pellets is higher than the average anharmonic damping function of pure KCl and KBr crystals /15, 16/ previously measured in our frequency range ( $30$  to  $300 \text{ cm}^{-1}$ ). We attribute this difference to the absorption of water vapors by our samples from

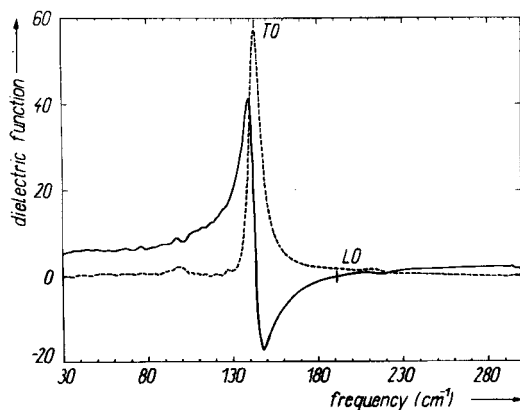


Fig. 1. Measured real  $\epsilon_1$ (—) and imaginary  $\epsilon_2$ (---) far-infrared dielectric function of  $\text{KCl}_{1-x}\text{Br}_x$ , for  $x = 0.5$

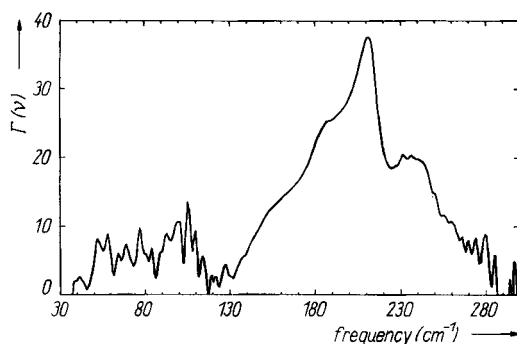


Fig. 2. The phonon self-energy function  $\Gamma(\nu)$  for  $\text{KCl}_{0.5}\text{Br}_{0.5}$

the high humidity (80 to 90%) environment during the process of polishing the samples. As we can see from Fig. 1, there is a single vibrational frequency, which shifts slightly as the mole fraction varies. Note also that the reflection spectra show the side lobe at the high frequency side which is a peculiarity of alkali halide crystals. Our mixed powder pellets possess all the optical properties of a mixed crystal. Thus, it is not correct to say that the mixed powder pellet does not behave like a mixed crystal /1/. Given these results, we propose that the optical constant of mixtures can be derived from those of the constituents. The critical point analysis /17/ of the anharmonic damping functions for the mixture is in progress and will be presented elsewhere.

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