LASER CHARACTERISTICS OF KCL:O_2^-

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Amplified spontaneous emission and laser action have been observed at 77 K in KCl crystals containing the superoxide ion (O_2^-). The laser operates in two bands of width ~50 Å centered at 6350 Å and 5984 Å. These bands are the (lattice) phonon sidebands of vibronic transitions of the superoxide ion. At lower temperatures (~6 K) amplified spontaneous emission is observed in the zero phonon line at 6294 Å.

In this letter we report the observation of amplified spontaneous emission (ASE) and laser action at 77 K in single crystals of KCl containing the superoxide ion (O_2^-). Previously, superradiance had been reported in KCl:O_2^- by Florian et al. [1], but only for temperatures below 30 K. Our observation of laser action at 77 K suggests the potential usefulness of this system as a source of tunable visible radiation.

The physical and optical properties of O_2^- have been the subject of considerable investigation [2,3]. The superoxide ion has been reported to be ellipsoidal [4] and enters the KCl lattice by substituting for a Cl^- ion, orienting itself along a (110) direction [5] as shown in fig. 1. The O_2^- ion is stable under modest illumination, even at room temperature, and emits visible light when excited by ultraviolet radiation. The absorption and excitation spectra of KCl:O_2^- are characterized by broad and featureless bands peaked at 2420 Å. At 77 K the fluorescence thus excited appears as a series of broad (~100 Å) peaks separated by ~300 Å and defined by an envelope centered near 6000 Å (see fig. 2). As the temperature of the crystal is lowered, the emission is gradually channeled into a series of sharp zero (lattice) phonon lines lying to the high energy side of the peaks shown in fig. 2. The quantum efficiency of the emission is nearly unity for temperatures lower than 200 K, above which it drops rapidly.

We grew single crystals of KCl:O_2^- by the Czochralski method. The melt was contained in an

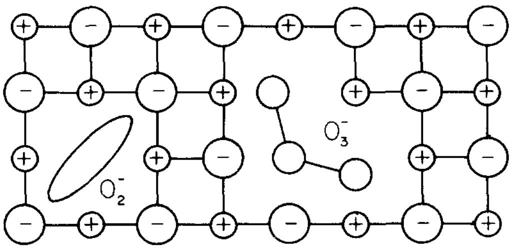

Fig. 1. O_2^- center and proposed model of O_3^- center in an alkali halide lattice.

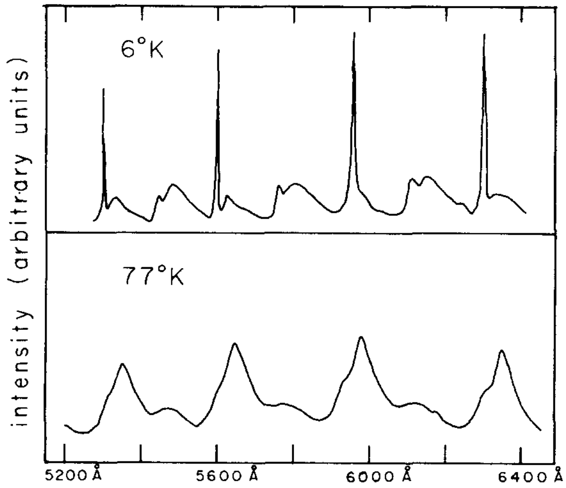

Fig. 2. Emission spectrum of KCl:O_2^- at 6 K and 77 K.

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alumina crucible and consisted of KCl to which 1 mole % potassium superoxide (KO_2) had been added. The superoxide concentration of the crystals could be determined from the measured absorption spectra using Smakula's equation [6] and the known [7] value (0.057) of the oscillator strength. Crystals used in our experiments had 10^{17}–10^{18} O_2^- ions/cm^3. The boules were cleaved into samples measuring 10 × 10 × 2 mm and stored under dessicant until used.

Most of our experimental work was performed at a temperature of 77 K in a glass cryostat equipped with two Brewster windows and a quartz pumping window. A Lumonics TE-861S-3 excimer laser charged with KrF was used as the excitation source. The pump wavelength was 2490 Å, the pulse duration was 12 ns, and the maximum pulse energy was 200 mJ. The beam was focused to a line of dimensions 1 × 10 mm using a quartz cylindrical lens. Samples so excited showed an enhanced red fluorescence, which had its maximum at the peak of the phonon-assisted sideband at 6350 Å, and a bandwidth in excess of 50Å. The light was emitted in a cone whose half angle was 30°. Due to the broad emission linewidth, we believe that this emission is due to ASE and not superradiance. This interpretation is consistent with the observation of Florian et al. that superradiance disappears as the temperature is raised above 30 K, probably due to the onset of rotational broadening at the higher temperatures. This red emission died away after approximately 20 shots, due to the destruction of the O_2^-, as explained below.

A laser cavity was constructed by placing flat dielectric mirrors on either side of the cryostate as shown in fig. 3. The mirrors were 90% reflecting over the range 5800–6400 Å. With this cavity laser emission occurred centered at 6350 Å, with a width of ~20 Å. We have measured the output energy as a function of input energy by attenuating the pump beam with filters. The declining output power due to bleaching was compensated for by taking control shots with an attenuated pump beam after each data point. We were thus able to normalize our data to a standard output. From the slope and intercept of the graphs thus obtained we could determine that the slope efficiency was 0.09 ± 0.01%, threshold energy was 9.7 ± 1.9 mJ. The high threshold and low efficiency possibly result from high losses due to reflection and scattering.

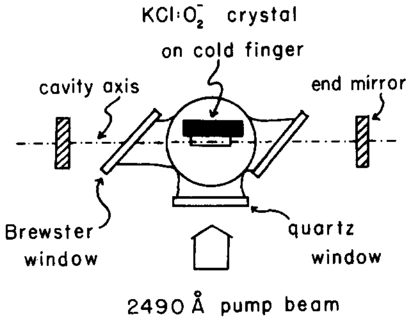

Fig. 3. KCl:O_2^- laser cavity.

The rapid loss of the amplified red emission has been found to be due to the transformation of the superoxide ion (O_2^-) to the ozonide ion (O_3^-). Samples of KCl:O_2^- that have been heavily irradiated by the KrF laser at low temperatures show a distinctly brown shading upon removal at room temperature. The discoloration is due to the structured absorption band peaking near 4500Å shown in fig. 4. This absorption band is identical to that reported for ozonide and is due to transitions from the $^2B_1$ ground state to the symmetric stretch $^2A_2$ excited state [12]. Although ozonide has been reported in a wide variety of hosts, ours appears to be the first observation of it in the alkali halides. It is likely that the configuration of O_3^- in KCl is similar to that of S_3^- in KCl [10,11] and consists of three oxygen atoms joined to form a 110° angle and nested in a trivacancy as shown in fig. 1.

We have formed ozonide directly in KCl:O_2^- crystals by exposing them to 2537 Å light at room temperature. At 77 K such exposure leads to the forma-

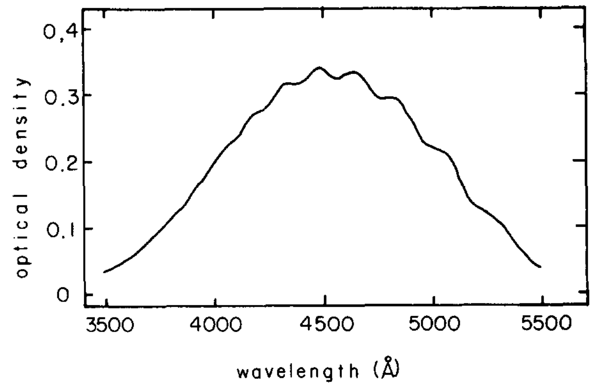

Fig. 4. Absorption spectrum of O_3^- in KCl at 300 K.

tion of absorption bands at 5400 Å and 3080 Å (as well as the destruction of the 2420 Å O_2^- band). The 5400 Å band is due to the F center, which normally forms in KCl exposed to ultraviolet light, and may not be connected with the transformation of the O_2^- center. The 3080 Å band, however, disappears and is replaced by the O_3^- band when the crystal is exposed to room light at room temperature. These observations, along with studies by Hiller and Vesta [13] and Iwamoto and Lunsford [14] suggest the following reactions leading to the formation of O_3^- in KCl:

$$O_2^- + h\nu \rightarrow O^- + O\,, \quad O_2^- + O \rightarrow O_3^-\,.$$

The observation that enhanced red fluorescence lasts longer at 6 K than at 77 K may be due to a slower ionic diffusion rate, and hence greater stability at O_2^-, at reduced temperatures. Irradiation into the 4500 Å O_3^- absorption band does not cause any reduction in the ozonide concentration, so the ozonide center is very stable. It might be possible to prevent O_3^- formation by some operation on the intermediate products, O^- and O.

In addition we have studied the emission characteristics of our sample at 6 K, at which temperature Florian et al. report superradiant emission of the 6294 Å zero phonon line. In their experiment a modelocked laser pulse of duration ~30 ps and energy of up to 100 μJ excited the sample, and superradiant pulses of duration ~100 ps were emitted delayed by as much as 1 ns from the exciting radiation. We also observed enhanced, directional emission of the 6294 Å zero phonon line. This radiation was emitted in a cone of half angle 20° from both ends of the crystal. The linewidth of this radiation was measured to be ~0.5 Å by a Fabry–Perot interferometer. The broad emission linewidth implies a short dephasing time, on the order of 10 ps, which is much shorter than the superradiant pulse length and delay times reported by Florian et al. We therefore believe that the radiation seen by ourselves is ASE and not superradiance. It is possible that the cause of the discrepancy between our results and those of Florian et al. lies in our different experimental conditions. In particular, our exciting pulse was longer (10 ns), more energetic (~100 mJ), and we used transverse rather than longitudinal excitation. In addition, our broad emission linewidth might be the result of high dislocation density or high superoxide concentration. Broadening of the zero phonon lines to widths of 1 Å or more as a result of such causes has been reported by Freiburg and Rebane [15,16].

In conclusion, we have demonstrated lasing at two wavelengths in KCl:O_2^- at 77 K and have measured the slope efficiency and threshold energy of this laser. The laser should exhibit tunability near 6350 and 5984 Å. The crystal can be stored at room temperature for long periods of time prior to use. The most serious obstacle to the use of this laser is the conversion of the active O_2^- centers to O_3^- under intense pump radiation.

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