INFRARED PHOTOACOUSTIC SPECTROMETRY OF POWDERED SAMPLES.
CALIBRATION CURVES OF SULFATE COMPOUNDS

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Photoacoustic signal intensities were measured at ν_3 band of sulfate ion on powdered sulfate/NaCl mixtures of a variety of particle sizes and sulfate compositions. It was found that (1) the slope of the calibration curves for potassium aluminum sulfate dodecahydrate was the steepest, then the next for calcium sulfate dihydrate, and the least for potassium sulfate, and that (2) the slope increased with decreasing particle size for sulfate compounds except for calcium sulfate dihydrate. The first result was shown to reflect the difference in molar concentration of sulfate ion in sulfate crystal, and the second result to come from the difference in crystal form among sulfate compounds.

There are many reports on photoacoustic spectrometry of homogeneous solids, and in many cases phenomena observed on these samples have successfully been explained by the theory of Rosencwaig et al.¹⁾ However, the theory can not be applied straightforward to heterogeneous solids, including powdered samples. Several reports have dealt with powdered samples in quantitative aspects. Some treated the spectral saturation effect in optically thick cases²⁾, and some did the light scattering effect of powdered sample³⁾. However, no comparative study has been made on the calibration curves among different compounds containing the same light absorbing group.

In our investigation of infrared photoacoustic spectrometry of powdered sulfate compounds, the spectral intensity was measured by exciting them at ν_3 band of sulfate ion with a tunable carbon dioxide laser. It was found that the slope of the calibration curves was varied among different sulfate compounds even under the same experimental conditions. In the present report, the behaviors of the calibration curves of three different sulfate compounds, potassium aluminum sulfate dodecahydrate, calcium sulfate dihydrate, and potassium sulfate are investigated under various conditions, and interpretation of experimental result is undertaken.

EXPERIMENTAL

Materials

Potassium aluminum sulfate dodecahydrate, calcium sulfate dihydrate, and potassium sulfate were all of reagent grade. (Hereafter they will be stated without specification of the water of crystallization for convenience.) Sodium chloride which was used as diluent of sulfate was also of reagent grade. Sulfate was ground in an agate mortar and pestle, passed through a set of wire mesh sieves, and classified into the following particle size fractions: (a) 100-150 mesh, (b) 200-270 mesh, and (c) 325-400 mesh. Powdered sulfate was analyzed for sulfate ion contents by barium sulfate gravimetry. A portion of the classified sulfate powder was added to sodium chloride (200-270 mesh) prepared in the same way as sulfate, and fully mixed in a plastic vial with a Wig-L-Bug mixer, SPEX Industries Inc..

Apparatus and measurements

Photoacoustic spectra were measured with an infrared photoacoustic spectrometer constructed in our laboratory, which is shown in Fig. 1. The infrared beam from a tunable carbon dioxide laser, the Laakmann Electro-Optics, Inc., Model RF-4400, was split into two beams with germanium plates. The wavelength of the emitted line was monitored with a carbon dioxide laser spectrum analyzer, Optical Engineering, Inc., Model 16-A. The beam was chopped with a light chopper, Ithaco, Inc., Model 218, at 60 Hz. The output from a sample cell and a reference cell was fed to a lock-in amplifier, the EG&G PAR Corp., Model 5101. The photoacoustic signal intensities were measured alternately with a selector switch. The sample signal intensity was normalized by dividing it by the reference signal intensity. As shown in Fig. 2, the sample cell was fitted with a Sony electret condenser microphone, type ECM-16, and a barium fluoride window. The sample powder was filled in an aluminum sample tray 1mm deep and then the surface was leveled gently. Infrared absorption spectra were measured with a Hitachi infrared spectrometer, Model 260-10, by a potassium bromide pellet method.

Fig. 1 Schematic diagram of infrared photoacoustic spectrometer

L: Tunable carbon dioxide laser; SA: Carbon dioxide laser spectrum analyzer; GP: Germanium plate; LC: Light chopper; SC: Sample cell; RC: Reference cell; SS: Selector switch; LA: Lock-in amplifier

Fig. 2 Sample cell

W: BaF₂ window; ST: Sample tray; CM: Condenser microphone

RESULTS AND DISCUSSION

Optical absorption properties

Infrared absorption spectra of three sulfate compounds were measured, and the absorption peak of ν_3 band of sulfate ion was found to appear at around 1120 cm^{-1} . A spectrum of potassium sulfate is shown in Fig. 3. The molar absorption coefficient, ϵ , at the absorption peak was determined by applying the Lambert-Beer's law to sulfate ion in potassium bromide pellet. The values of ϵ were approximately 470 , 500 , and $130\text{ M}^{-1}\cdot\text{cm}^{-1}$ for potassium aluminum sulfate, calcium sulfate, and potassium sulfate, respectively. From the value of ϵ and the data of molecular weight, M_r , and density, ρ , the absorption coefficient, β_0 , can be calculated according to the relation $\beta_0 = 2.3\epsilon\rho/M_r$. In Table 1 are shown the values of β_0 and its reciprocal, that is, the optical absorption length, μ_0 , together with the values of M_r , ρ , and the molar concentration of sulfate ion in sulfate crystal, c .

The tunable carbon dioxide laser emits several tens of vibrational-rotational lines in the wavelength range of 9.2 to $10.8\text{ }\mu\text{m}$. In the present study, an R-24 line at 1081 cm^{-1} , which is near the absorption peak of the ν_3 band and relatively intense, was chosen to excite sulfate ions. From the infrared absorption spectra, the absorption coefficient and the optical absorption length, μ_1 , at 1081 cm^{-1} were recalculated for each compound. In Table 1 are presented the values of μ_1 , which range from 2 to $5\text{ }\mu\text{m}$. All the incident light is practically absorbed within a few optical absorption lengths. It was found from microscopic observation of sulfate particles of 325-400 mesh fraction that potassium aluminum sulfate and potassium sulfate were composed of granular particles of around $40\text{ }\mu\text{m}$ in diameter, while calcium sulfate consisted of clusters of columnar crystals several μm thick. Therefore, all the light incident to a sulfate particle is practically absorbed by the particle, and so the sulfate particle can be taken as optically opaque solid, as defined by Rosencwaig et al.¹⁾. Accordingly in the present case, the amount of light absorbed, irrespective of difference in the absorption coefficient, is unchanged under the same measuring conditions.

Fig. 3 IR absorption spectrum of potassium sulfate

Table 1 Optical absorption properties and other data of sulfate compounds

Compounds	$M_r/\text{g}\cdot\text{mol}^{-1}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$c/\text{mol}\cdot\text{cm}^{-3}$	β_0/cm^{-1}	μ_0/cm	μ_1/cm
$\text{KAl}(\text{SO}_4)_2\cdot 12\text{H}_2\text{O}$	474.4	1.75	0.00369	3970	2.52×10^{-4}	4.78×10^{-4}
$\text{CaSO}_4\cdot 2\text{H}_2\text{O}$	172.2	2.32	0.0135	15600	0.64×10^{-4}	2.14×10^{-4}
K_2SO_4	174.3	2.66	0.0153	4570	2.19×10^{-4}	5.06×10^{-4}

Thermal properties

The photoacoustic signal is dependent on the thermal properties as well as the optical absorption properties. From the data of thermal conductivity⁴⁾⁻⁶⁾, thermal diffusion lengths at 60 Hz, μ , were calculated to be 68, 49, 140, and 340 μm for potassium aluminum sulfate, calcium sulfate, sodium chloride, and air, respectively. Since the optical absorption lengths of the sulfate compounds are one order of magnitude smaller than the thermal diffusion lengths, all the heat generated at the sites of sulfate ion in a particle can be transferred out of the particle.

Sulfate particles are surrounded by a heterogeneous medium composed of sodium chloride powder and air. The effective thermal diffusion length, μ_e , of the medium was estimated to be approximately 160 μm in the same manner as has been applied to powdered sample of asbestos⁷⁾. Here the packing fraction of sodium chloride powder was estimated to be 0.75 from the average weight of sodium chloride powder required to fill a sample tray. The heat generated in sulfate particles can reach the surface from the particles within a few effective thermal diffusion lengths.

Concentration dependence of photoacoustic signal

The photoacoustic signal intensity was measured on 200-270 mesh sulfate/NaCl mixtures containing 0 to 100 % of sulfate ions. The plot of the normalized intensity against mole fraction of sulfate ion showed a similar tendency for all three sulfate compounds. An example of the plot is illustrated in Fig. 4. The sample containing no sulfate gave some background intensity. The intensity rapidly increases with increasing sulfate ion fraction in very low fraction, and afterwards shows a gentle rise. The nonlinear behavior seems to be compared with the case of the mechanical mixtures of sample powder and diluent powder reported by Bacconsall et al.⁸⁾. In their study, powder mixtures of a sample and a diluent gave the nonlinear behavior, which was attributed to optical and thermal interactions between the sample and the diluent. According to them, the diluent produces considerable scattering of the incident light. Some of the scattering light is absorbed by the sample, and generates an additional photoacoustic signal. The additional photoacoustic signal will diminish as the fraction of the more strongly scattering component (diluent) is reduced. In addition, thermal interactions contribute to nonlinearity.

These both effects by the diluent might work similarly in our experiments. Additionally an overlap effect, which occurs when a sample particle hides behind another particle and can not take part in light absorption, can not be neglected in the present case.

Fig. 4 Photoacoustic signal intensity of sulfate ion as a function of its mole fraction

Assuming sulfate particles to be uniformly dispersed in the matrix, the sulfate content at which the overlap effect begins to occur can be calculated from the amount of sodium chloride filled in a sample tray ($1\text{mm} \times 13\text{mm}$) and the number of sulfate particles required to cover the tray in a single particle layer. For the powder mixture of 200–270 mesh, the content are approximately 0.006 and 0.02 mole fraction for potassium aluminum sulfate and potassium sulfate, respectively. As sulfate particles begin to overlap each other, the particles incapable of absorbing the light coming from the front increase in number, which results in the nonlinear behavior. Thus the overlap effect could be an alternative explanation of the nonlinearity. The scattering coefficient, S , is expected to vary in inverse proportion to both the particle diameter, d , and the wavelength, λ , in the present experimental conditions where $d \approx \lambda$ ³⁾. Accordingly, in the wavelength region of carbon dioxide laser the scattering effect would not be so significant as in the visible region, but instead the overlap effect seems to be important.

Slope of calibration curve

All of the three sulfate compounds gave linear calibration curves in the sulfate ion concentration range less than several tenths mole %, that is, several thousandths mole fraction. However, their slopes were diverse. In Fig. 5 are shown their calibration curves obtained for different particle sizes in the range of 0 to 0.2 mole %. The figure shows that (1) the slope for potassium aluminum sulfate is the steepest, then the next for calcium sulfate, and the least for potassium sulfate, and (2) the slope increases with decreasing particle size for sulfate compounds except calcium sulfate, which always gives a constant slope within an experimental error.

In our experimental condition a sulfate particle of the same size absorbs the same amount of light, irrespective of difference in the absorption coefficient. Consequently photoacoustic signal intensity should be determined by the number of sulfate particles, n . As obvious from the fourth column in Table 1, the molar concentration of sulfate ion in sulfate crystal is the lowest for potassium aluminum sulfate and the highest for potassium sulfate. Conversely sulfate crystal containing equimolecular amounts of sulfate ions has the

Fig. 5 Calibration curves of three sulfate compounds

largest volume for potassium aluminum sulfate and the smallest volume for potassium sulfate, and so, when divided into the same size of particles, the largest number of particles will be obtained from the former and the smallest from the latter. Eventually the former would give the highest photoacoustic signal intensity, and the latter the lowest. This inference is consistent with the experimental results shown in Fig. 5, and so the difference in the molar concentration of sulfate ions in sulfate crystal seems to cause the difference in slope of calibration curves.

It is commonly explained that a reduction of particle size results in enhancement of photoacoustic signal owing to increase in overall surface area. However, it should not be overlooked that the size reduction is related to increase in overall cross section viewed from the front, $nmd^2/4$ (n and d are as defined in the preceding page), especially when the scattering effect is unimportant and only a part of the surface facing the front takes part in light absorption. The results of calculation represent that the overall cross section is approximately doubled by particle size reduction from 100-150 mesh to 200-270 mesh and further increased approximately 50 % in the reduction from 200-270 mesh to 325-400 mesh. Just in such a manner the slope of the calibration curves increases with decreasing particle size for potassium aluminum sulfate and potassium sulfate, as shown in Fig. 5.

In the case of calcium sulfate, the narrower sieve fraction gave the same magnitude of photoacoustic signal as the wider sieve fraction within an experimental error. This fact seems to be connected with the crystal form of calcium sulfate which belongs to the monoclinic crystal system. This compound as received was composed of columnar crystals several μm thick. It was found from microscopic observation that mechanical grinding was effective only in breaking thin crystals, making no substantial contribution to increase in the overall surface area or the overall cross section. It seems to be a phenomenon characteristic of fibrous crystals that mechanical grinding did not lead to change in slope of the calibration curve.

CONCLUSION

In photoacoustic spectrometry of powdered samples, the calibration curves should be constructed for each compound, if the molar concentration of a light absorbing group in crystal is not the same among different compounds containing the light absorbing group. Powdered sample in a granular state increases the signal intensity with decreasing particle size nearly in proportion to the overall cross section. Powdered sample composed of fibrous crystals hardly changes the signal intensity with change of particle size for the fractions obtained through mesh not so fine as the fibrous crystals.

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