A New Infrared Technique for Characterizing Partially Amorphous Solids

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Infrared reflection measurements on pelletized spinel alumina powder yield sharp peaks with frequencies dependent upon the pretreatment of the alumina. A qualitative theory is proposed by which information about the participation in the bulk phase of foreign ions and the degree of sintering in the activated aluminas can be determined from this exceedingly simple experimental method.

The characterization of semiamorphous solids by infrared spectroscopy has long been extremely tenuous despite the probable existence of discrete vibrational modes in the material. In typical preparations of solids of this sort, an amorphous gel is dehydrated giving a high-surface-area, small-particle-size material of commercial value for catalysis, ion exchange, etc. Unfortunately, the ultimate particles, having sizes typically of the order of the wavelengths associated with vibrational motion, scatter the infrared radiation to the extent that transmission experiments have been performed only on very specially prepared solids. The aim of this work has been the development of an infrared reflection technique which yields some information about the physical properties of a typical semi-amorphous solid, in this case an activated alumina of the spinel modification.

The precursor material studied was Kaiser alumina KA-101, a primarily amorphous transition alumina. This was converted to a more crystalline spinel-structure alumina by heating for 5 hr at temperatures between 600° and 1000°C in a carefully regulated oven. Prior to calcination, samples were impregnated with varying concentrations of either K^+, Na^+, Li^+, Ce^{4+}, or Mg^{2+} using reagent grade nitrate salts in a volume of water just suffi-cient to be absorbed completely by the dry alumina. The treated aluminas were characterized by measurements of surface area, pore volume, density, and X-ray diffraction pattern. The results of these investigations are reported elsewhere (1).

Infrared transmission measurements were attempted on the samples as a complementary method for discerning fine differences among the variously pretreated aluminas. However, the O–H stretching region at around 3750 cm^{-1} was masked by scattering due to small particle sizes, and the lower-energy absorption band at about 1000 cm^{-1} led to imprecise energy determination and displayed spectral characteristics very sensitive to the details of the grinding and mulling of the alumina.

The latter experimental difficulties were not encountered in reflection experiments. The samples were thoroughly ground with a clean agate mortar and pestle, and the powder pressed, at 46 000 psi for 1 min, into a pellet 1 inch in diameter and approximately 1 mm thick. The pellet was mounted, with a system of mirrors, such that the sample beam of a Beckman IR-5 infrared spectrometer struck it at an angle close to grazing incidence and was reflected into the detector. Spectra exemplified by Fig. 1 were obtained. Duplicate runs and careful checks showed that the position and
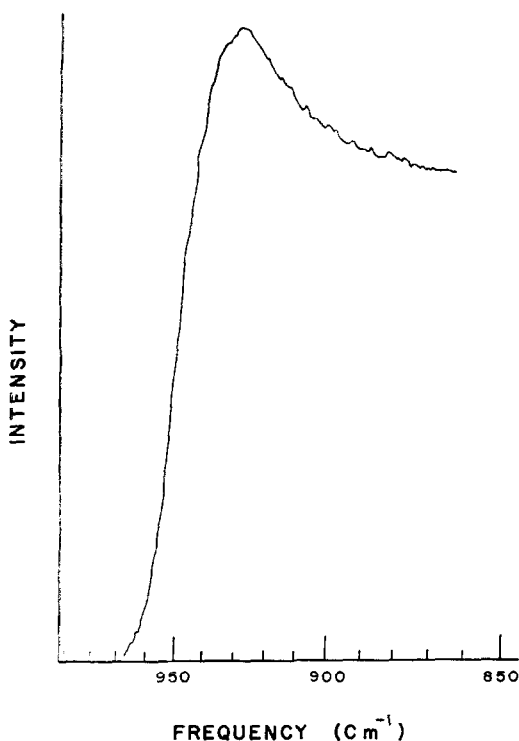
FIG. 1. Infrared reflection spectrum for high-surface-area, spinel-structure alumina.
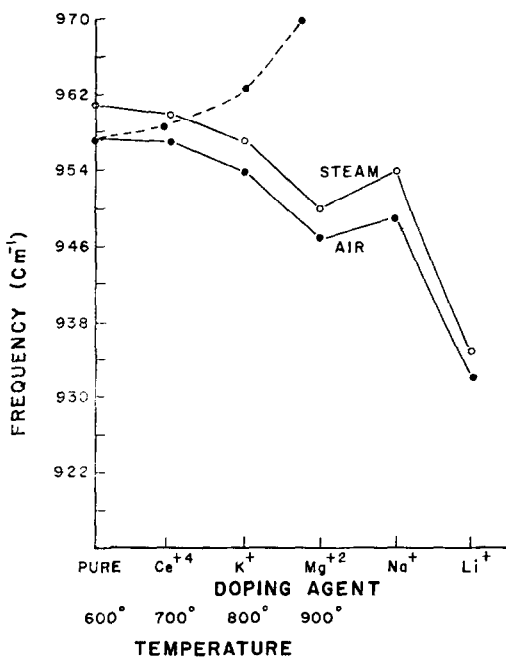

FIG. 2. The effect of sintering upon the position of infrared reflection maxima. The approximately parallel curves reflect the relative sintering in steam and in air for aluminas doped with 0.03 ion ratio of different foreign ions and calcined at 600°C. The dashed curve shows the temperature dependence of peak position for undoped alumina heated in air.

shape of the reflection maximum were independent of the pelletizing pressure or time, and of the angle of incidence.

There was a reproducible variation in the position of the reflection maximum as a function of the pretreatment of the sample. In general, the frequency where maximum reflection occurred varied proportionally with the degree of sintering and loss of surface area which the sample incurred. Thus calcination conditions conducive to sintering, high temperatures, and high moisture content (2, 3), led to aluminas with reflection maxima at progressively higher frequencies. The dependence of this peak upon temperature and upon moisture content for similarly doped aluminas is shown in Fig. 2.

Functional dependence of the position of the reflection maximum on the concentration of K^+, Li^+, and Mg^{2+} impregnates is summarized in Fig. 3. A general downward trend in energy with increasing foreign-ion concentration was observed.

The broad vibrational bands in solids have been comprehensively characterized and theoretically treated in the past. In the simplest cases, it can be shown that in an infinite ionic crystal the energy of the onset of the absorption continuum in the infrared is proportional to the force constant and inversely proportional to the reduced mass of the components vibrating against one another (4). This frequency may be computed in a first approximation by considering only nearest neighbors in harmonic oscillation with respect to one another. However, for a precise calculation, all of the atoms in the crystallite, their mass, their position, and their mutual force constants must be taken into account.

Although such a rigorous treatment is impractical, some qualitative interpretations of the small but reproducible energy shifts observed in our work are suggested
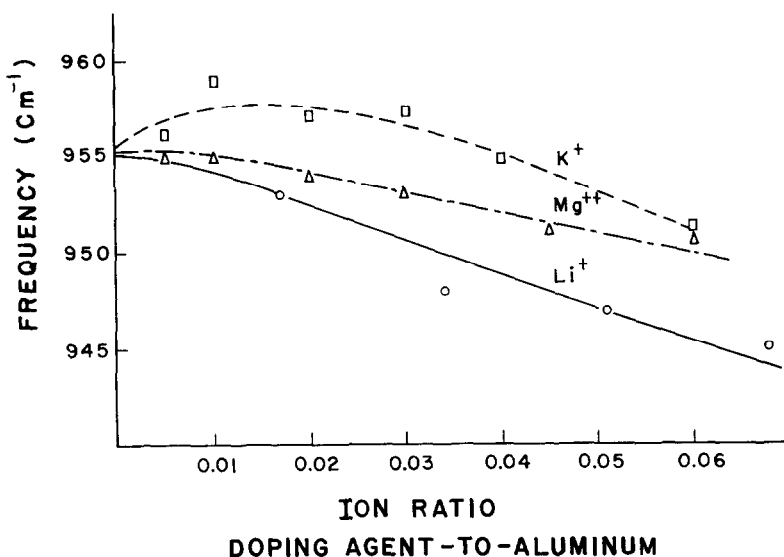
FIG. 3. Infrared reflection maximum as a function of concentration and identity of doping agents in a spinel alumina calcined at 600°C.

by this reasoning. The continuous variation of the reflection-peak energy with degree of sintering, for example, implies a correlation with the compaction of material and increase in continuity implicit in the sintering process. It is generally accepted that the mechanism of sintering in alumina, under the conditions imposed in these experiments, is surface diffusion, leading to the formation of fillets of material between previously separated particles, and the consequent widening of pore diameters as surface area diminishes (2, 3). On an atomic level, this may be pictured as the formation of atomic bridges, e.g., oxygen bridges between neighboring aluminum ions. With such a mechanism of thermal equilibration, therefore, the reflection maximum appears to be quite a sensitive measure of the completeness of the organization of matter into a continuous three-dimensional lattice for materials of like atomic constitution, or, stated differently, of the mean aluminum-to-oxygen distance.

The data on the aluminas impregnated with small amounts of foreign atoms portray a contrary situation and indicate a strong potential utility of the infrared reflection technique.

It has been found and substantiated comprehensively that for lithium doping, small concentrations lead to a stabilization of surface area through incorporation of the lithium into vacant cation sites in the spinel lattice (5). A lithium-aluminum mixed spinel with the stoichiometry $5Al_2O_3 \cdot Li_2O$ has been detected and reported to have a lattice constant of 7.90 Å, within 0.01 Å of the undoped alumina spinel (5). Thus residency by lithium in the bulk-phase spinel lattice requires little reorganization of the oxygen network during impregnation and occurs quite favorably, stabilizing the material. The resultant spinel, if in completely equilibrated stoichiometry, would contain positive charges equally distributed over all the interstitial vacancies, leading to a lattice of a more polar, ionic nature than pure spinel alumina. Reduced masses and degree of sintering being equal, an increase in ionicity would generally lead to a decrease in the average force constant, which would be manifest in the lowering of vibrational energies (4). A trend in this direction for our lithium-doped samples is observed, suggesting the increasing participation of lithium in the bulk spinel phase.

Incorporation into the bulk lattice becomes more difficult for magnesium and

potassium. The former exists in a mixed spinel of stoichiometry $Al_2O_3 \cdot MgO$. However, the slightly larger unit-cell lattice constant of 8.07 Å (5) indicates that in our method of impregnation some stretching of the existing lattice must occur to allow entry of the Mg^{2+} into the bulk phase. That bulk occupancy is energetically less favorable than with Li^+ is attested by the slower decrease in the energy of the reflection maximum with increasing impregnate content.

A mixed potassium-aluminum spinel structure has never been reported (6), and, from mineralogical principles developed by Pauling in 1928 (7), K^+ would be expected to squeeze into the existing Al_2O_3 lattice only with the greatest difficulty. Again we observe a smaller change in the position of the reflection maximum as potassium content increases.

The observations and interpretations reported here concerning bulk occupancy by foreign ions are completely consistent with the schema derived from physical-property and spectroscopic measurements on the same samples. We thus feel that infrared reflection potentially provides a simple and valuable means of characterization of participation in the bulk phase by foreign atoms and of the relative degrees of continuity in poorly crystalline solids.

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