TABLE I Tensile properties

Alloy	Temperature (° C)	0.1% yield stress (10^3 psi)	Ultimate tensile strength (10^3 psi)	Elongation (%)
Co–W–Si	room	122	157	9.3
	900	40.3	42.1	35
	1000	28.9	30.4	38
Co–Mo–Si	room	280	280	0
	900	107	107	0
	1000	74.2	75.5	0.8
Co–Ti–Si	room	108	108	0
	900	54.4	54.4	32
	1000	26.5	26.5	34
Co–Nb–Si	room	157	157	0
	900	108	108	0
	1000	69.9	71.1	47

eutectics. Probably a rod morphology is necessary, perhaps with a lower volume fraction of silicide than contained in the present Co–Mo–Si alloy.

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Some physical properties of hot-pressed CaF_2

Alkali halides heated to high temperatures and pressed under high pressure were termed hot-pressed. In their physical appearance, as well as in some of their physical properties, the hot-pressed samples resemble single crystals of the same material. Attempts are being made to use these samples in place of single crystals. The aim of the present study is to show that in some important physical properties the hot-pressed samples differ considerably from the single crystals. In this communication we report measurements of the dielectric constant (K) and loss ($\tan \delta$) for hot-pressed CaF_2 in the frequency range 10^2 to 10^6 Hz and in the temperature range 30 to 450° C. The optical absorption data of these samples before and after irradiation and thermoluminescence are also presented.

The samples used in the present work were donated by Professor A. Smakula. The density of these samples is reported to be $3.179\,27\,\mathrm{g\,cm^{-3}}$ and lattice parameter 5.463 65 Å (these values are $3.179\,34\,\mathrm{g\,cm^{-3}}$ and 5.463 42 Å, respectively, for CaF_2 single crystals [1]).

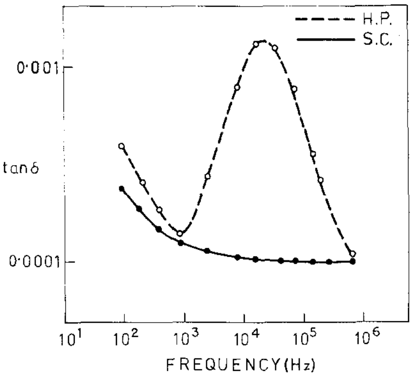

Figure 1 Dielectric loss (tan δ) at 30° C as a function of frequency for hot-pressed (H.P.) and single crystal (S.C.) CaF_2.

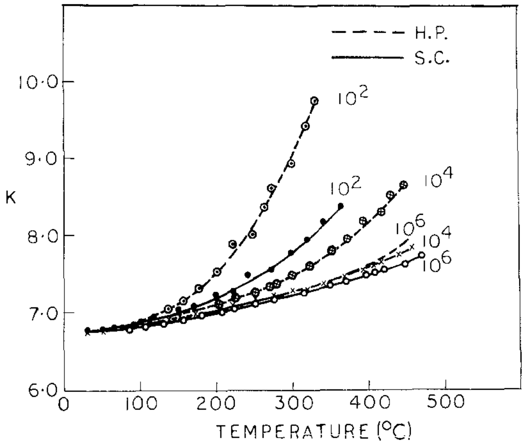

Figure 2 Variation of dielectric constant (K) with temperature at different frequencies for hot-pressed and single crystal CaF_2.

The dielectric measurements were taken using a GR 716 capacitance bridge in the frequency range 10^2 to 10^5 Hz [2] and a Marconi Circuit Magnification Meter type TF 329 G for the range 10^5 to 10^6 Hz [3]. The accuracy in measurement of K is 2% and for tan δ is 5%, the detection level in tan δ value is about 0.0001. Optical absorption measurements were made using a spektromom 202 over the wavelengths 200 to 300 nm at room temperature (≈ 30° C). The thermoluminescence output (after X-ray irradiation) was recorded on an Esterline-Angus recorder using conventional apparatus [4]. The temperature measurement was accurate to 4° C.

X-ray irradiation of the samples was carried out at 35 kV, 10 mA for 2 h at room temperatures (1 h on either side of the sample) using a Philips Norelco unit; the samples were positioned 2 cm from the window of the X-ray tube.

The value of the dielectric constant at room temperature for hot-pressed CaF_2 is 6.8 and is independent of frequency, which is in exact agreement with that of CaF_2 single crystals [5]. Fig. 1 gives dielectric loss (tan δ) as a function of frequency for these samples. The tan δ values exhibit a peak around 4×10^4 Hz which is not present in CaF_2 single crystals.

The variation of K with temperature at different frequencies for hot-pressed CaF_2 is shown in Fig. 2; this figure also gives data for single crystals. Although both varieties of samples exhibit similar behaviour, the rate of change of K with temperature is considerably larger, as is the frequency dependence of K, compared to the single crystals. Similar behaviour was observed in the graphs for tan δ as a function of temperature; as such these data are not presented. It may, however, be pointed out that the dielectric loss peak observed in hot-pressed CaF_2 at 30° C shifts to higher frequencies at higher temperatures.

The optical absorption of hot-pressed samples before and after X-ray irradiation is presented in Fig. 3. It can be seen that the absorption coefficient (α) has larger values compared to the single crystals both before and after X-ray irradiation. There is an absorption band at 370 nm in the hot-pressed sample (this seems to correspond to the α band of CaF_2 single crystals which is supposed to be similar to the F band in alkali halide crystals). This band is not formed in CaF_2 single crystals when irradiated at room temperature with X-rays [6].

The thermoluminescence curves for both hot-pressed and single crystal samples are given in Fig. 4. We find that although the TL pattern remains the same, the total thermoluminescence output is about ten times larger in the hot-pressed sample.

It may be mentioned here that the hot-pressed samples after X-ray irradiation exhibited an intense afterglow which lasted for more than an hour, whereas single crystal CaF_2 exhibits no afterglow. These measurements have been carried out on four hot-pressed samples of CaF_2 and the features reported here are always reproducible.

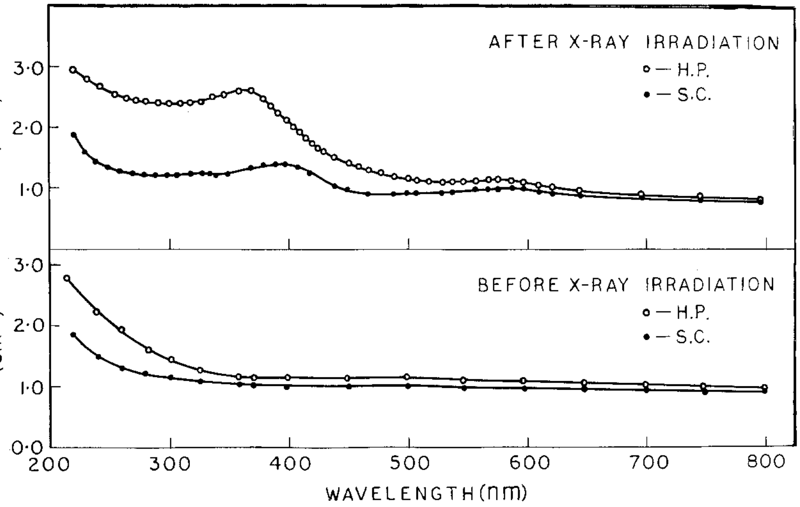

Figure 3 Absorption coefficient (α) at 30° C as a function of wavelength for hot-pressed and single crystal CaF_2 before and after X-ray irradiation.

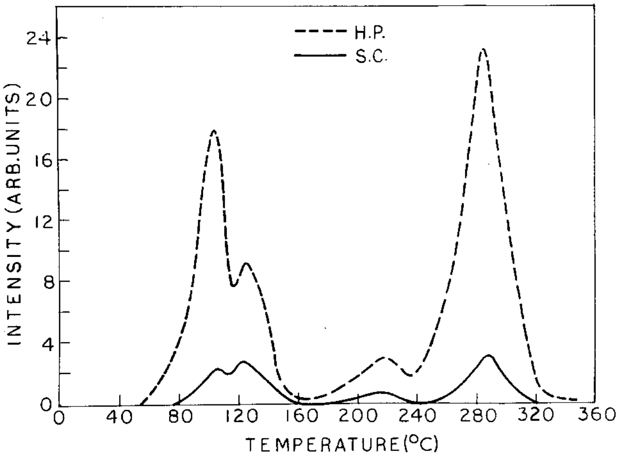

Figure 4 Thermoluminescence curves for hot-pressed and single crystal samples of CaF_2.

More measurements along these lines as well as on the afterglow decay characteristics, etc., are in progress; as such no attempt is being made to go into the understanding of these data now. It is intended to communicate these findings in due course.

In conclusion it may be stressed that hot-pressed samples exhibit considerable divergencies in their physical properties compared to single crystals; judging from their behaviour, the hot-pressed samples seem to contain more defects and even impurities.

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The influence of iron and hydrogen in the nitridation of silicon

Interest in the presence of both iron [1, 2] and hydrogen [1, 3–5] in the silicon–nitrogen system has arisen in part because of their recognized capacity for accelerating the nitridation reaction. Dawson amd Moulson [6] have reported on the combined effect of iron and hydrogen, and comment on the apparently very fast kinetics observed as a result of a cumulative effect. We have recently examined a series of silicon powders of constant particle size distribution (10 to 20 μm; 350 $m^2 kg^{-1}$) but of varying iron content, nitrided both under purified nitrogen and under nitrogen–5% hydrogen. These powders were obtained by crushing semiconductor-grade silicon billet in a cast-iron mill, followed by leaching in boiling 1 M hydrochloric acid for different lengths of time to remove different proportions of the iron introduced during comminution. The minimum level of iron obtainable was 2.5×10^{-3} at.% and the maximum level used was 0.28 at.%. This iron was, therefore, "residual" iron, in contrast to the iron of Dawson and Moulson [6] which was added as ferric nitrate to acid leached silicon powder. Nitridations of small compacts (approximately 500 mg) were carried out in a molybdenum wound alumina tube furnace at 1630 K with a gas flow rate of 50 ml min^{-1}. The recorded water and oxygen partial pressures in the outlet gas from the reaction tube were 5×10^{-4} and 10^{-16} atm, respectively, for nitrogen, and 5×10^{-4} and 3×10^{-19} atm for nitrogen–5% hydrogen.

Nitridation data are presented in Figs. 1 and 3 using a linear time axis, and in Figs. 2 and 4 with a logarithmic time axis. The fraction of silicon reacted only is plotted; the α/β phase ratio in the product nitride remained constant, within experimental error, under all conditions at 85 : 15. The semi-logarithmic treatment provides a reasonable fit to most of the data points after an initial induction period. This indicates an experimental rate law over much of the time scale of the direct logarithmic type:

$$\alpha = k \log [at + 1]$$

where α is the fraction of reaction and k and a are constants, with departures also at very large values of t, as α approaches 1.0. A physical basis for this type of equation is provided by the mutual pore closure mechanism [7] in which reaction occurs only at a limited number of active sites, the number of which diminishes with time at a rate proportional to the reaction rate. However, while a pore closure mechanism might appear to provide a realistic model for the nitridation process in view of information available on the growth patterns of silicon nitride at clean silicon surfaces [8], and although earlier publications [9–11] suggests some generality for a logarithmic rate law, there are dangers in trying to deduce a reaction mechanism solely on the basis of an experimental rate equation. At this stage, therefore, we use this form of compressed time axis presentation as a matter of convenience, and without implying a particular nitridation mechanism. The practical merit of this form of presentation is that it allows quantitative comparisons to be made between different reaction curves over a considerable time scale, and especially after time intervals where the reaction rate is becoming very slow.

One feature of interest in these results, and shown clearly by Figs. 2 and 4, is that they confirm that an important acceleratory effect of hydrogen is due to a marked reduction in the length of an induction period (from the order of 10^3 to 10^2 sec), with subsequent fast initial