Int. J. High Techology Ceramics 3 (1987) 285–295

Hot Pressing of Lead Fluoride PbF_2

M. Gendry, R. Soria, A. El Mansouri and L. Cot*

Laboratoire de Physicochimie des Matériaux (UA 407),
Ecole Nationale Supérieure de Chimie, 8 Rue de l'Ecole Normale,
34075 Montpellier Cedex, France

SUMMARY

The hot pressing of lead fluoride powders below 300°C is described. The fabrication of high-density shapes of lead fluoride for infrared transmitting applications is possible by this process. The hot pressing model of Murray et al., *with a relation expressing densification as a function of viscosity, time, applied pressure and temperature, is used for the analysis of the lead fluoride densification kinetics. It is shown that the density, which is closely correlated to the transmission, is sufficient for infrared transmitting applications, but too low for transmitting applications in the visible range.*

1 INTRODUCTION

With its large transparency range to electromagnetic radiation (0·3–36 μm), lead fluoride is an interesting transmitting material for infrared, but also for combined visible and infrared spectroscopy. This compound is not a glass former[1] and it is difficult to involve the growth of lead fluoride crystals from the melt[2] because of its tendency to oxidation at temperatures higher than 300°C. Therefore, hot pressing appears to be a better process for preparing lead fluoride windows. The hot pressing parameters (temperature, pressure and time) influencing their relative density and their transmission in the 3–5 and 8–14 μm infrared ranges are investigated.

* To whom all correspondence should be addressed.

Int. J. High Technology Ceramics 0267-3762/87/$03·50

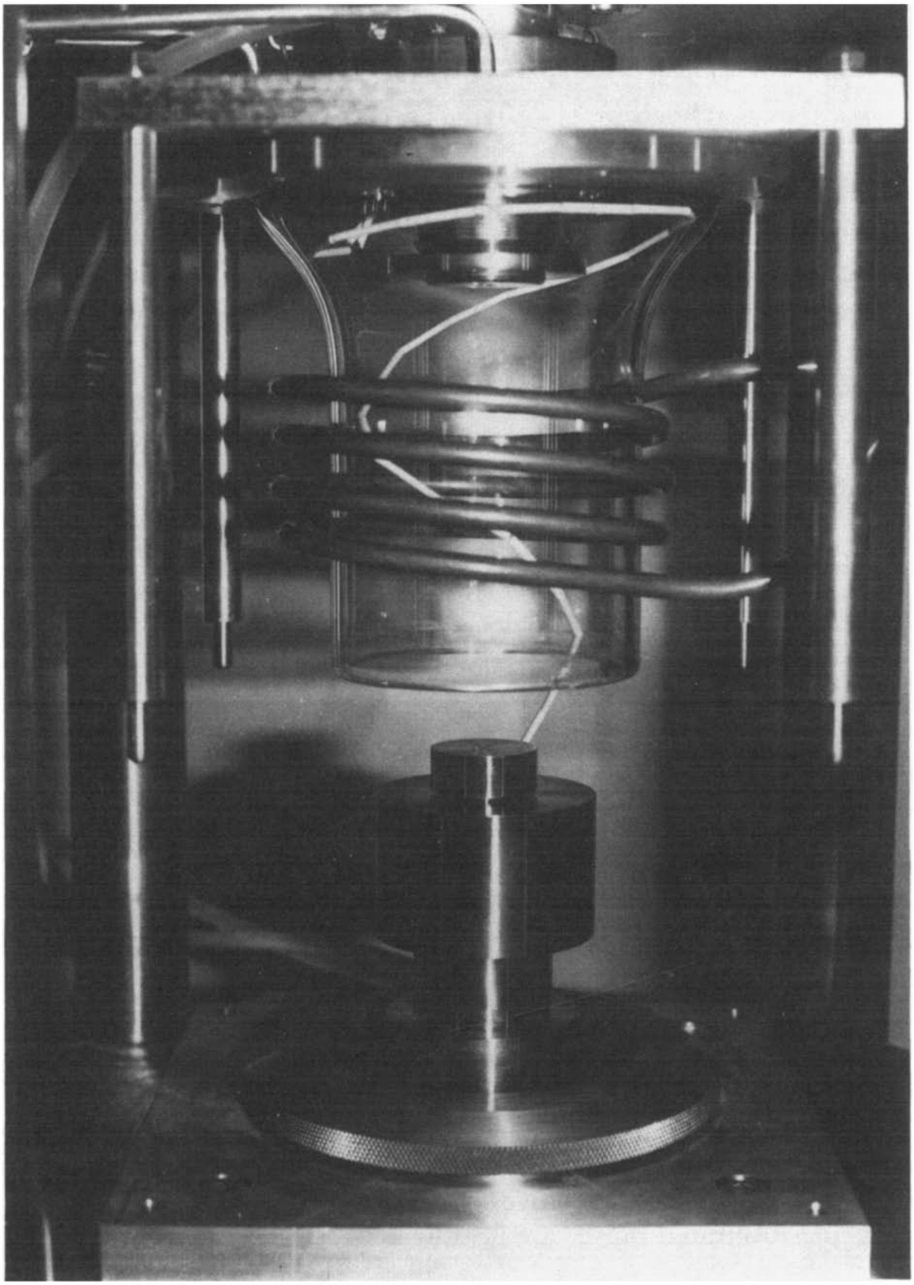


Fig. 1. Photography of hot pressing rig.

2 EXPERIMENTAL PROCEDURE

2.1 Hot pressing unit

It is generally accepted that the sintering temperature of a substance must be higher than two-thirds of melting point, T_m, in degrees Kelvin. With T_m (PbF_2) = 1095 K, the sintering temperature of lead fluoride must be higher than 460°C; but above 300°C lead fluoride easily oxidizes, except in inert atmospheres not readily applicable on an industrial scale. Thus, the upper temperature for hot pressing of lead fluoride powders has been fixed at 300°C, and we have built a hot pressing unit able to apply a pressure of 780 MPa to a sample of 20 mm diameter.

The hot pressing unit (Fig. 1) consists of:

—a 120-ton press
—an induction heater (80 kHz)
—a quartz envelope able to carry out the hot pressing in a controlled atmosphere
—a stainless steel die

The faces of the die in contact with the lead fluoride powder being pressed are smooth and chemically protected by a thin electrolytically deposited gold layer.

2.2 Lead fluoride powder preparation

Lead fluoride shows an irreversible allotropic transition[3] from the orthorhombic α form to the cubic β form, at 350°C and 10^5 Pa. In this work, the cubic form was used. The allotropic transition of initial powder (orthorhombic form) is realized at $T = 360$°C under nitrogen flow,

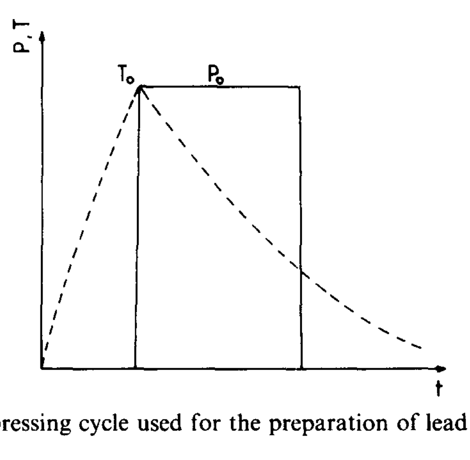


Fig. 2. Hot pressing cycle used for the preparation of lead fluoride discs.

dehydrated by phosphorus pentoxide and deoxygenated by manganese monoxide. Then, the lead fluoride powders were screened to $<20\,\mu m$. The average particle size is about $10\,\mu m$, estimated by scanning electron microscopy.

2.3 Hot pressing cycle

Different hot pressing cycles (P, T) have been proposed by Pastor.[4] None of these led to homogeneous lead fluoride discs. Therefore, the cycle shown in Fig. 2 has been utilized with the pressure being maintained during cooling. This cycle leads to homogeneous discs as shown in Fig. 3.

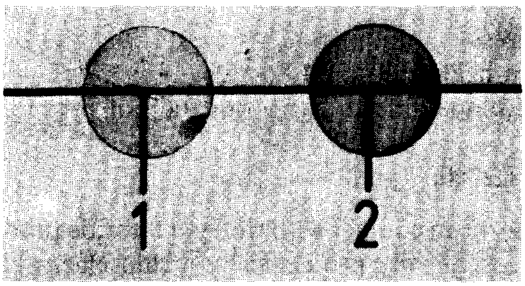


Fig. 3. Photography of lead fluoride discs (thickness: e (mm)).

3 LEAD FLUORIDE DENSIFICATION DEPENDENCE ON HOT PRESSING PARAMETERS

Experiments were performed for studying how the hot pressing parameters (temperature, pressure and time) affected the relative density, D, of windows and their spectral transmission in the 3–5 and 8–14 μm ranges (Figs 4, 5 and 6). Relative density, D, is given by d_{exp}/d_{theo} ratio.

The theoretical density of the high pressure orthorhombic form of lead fluoride which is that of the hot pressed lead fluoride powder is $d_{theo} = 8{\cdot}44\ g/cm^3$.[5] Transmission T_n(%) was calculated by integration (by weighing of the recording paper) of the area under the transmission curve in the 3–5 and 8–14 μm ranges, for discs of 1 mm thickness (Fig. 7).

3.1 Discussion of results

(1) For increasing time t (Fig. 6), at fixed T and P, there is a limiting relative density, as encountered in the model of Murray *et al.*,[6] which characterizes a plastic flow deformation mechanism.

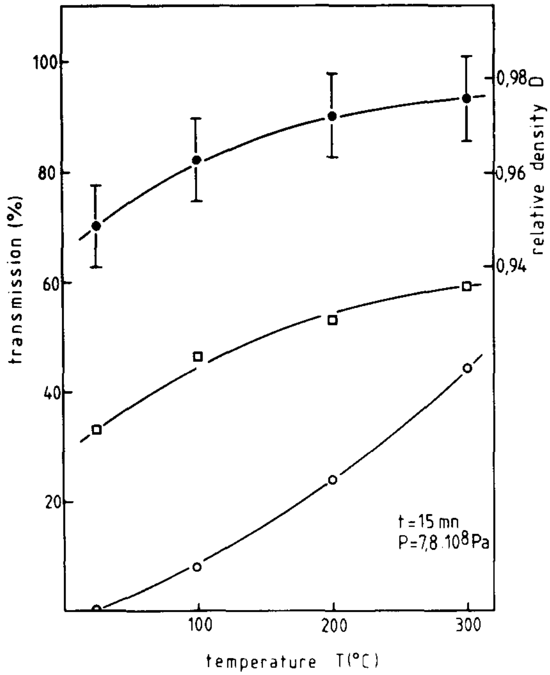


Fig. 4. Temperature dependence of: ●, relative density D; □, transmission in 8–14 μm range; ○, transmission in 3–5 μm range.

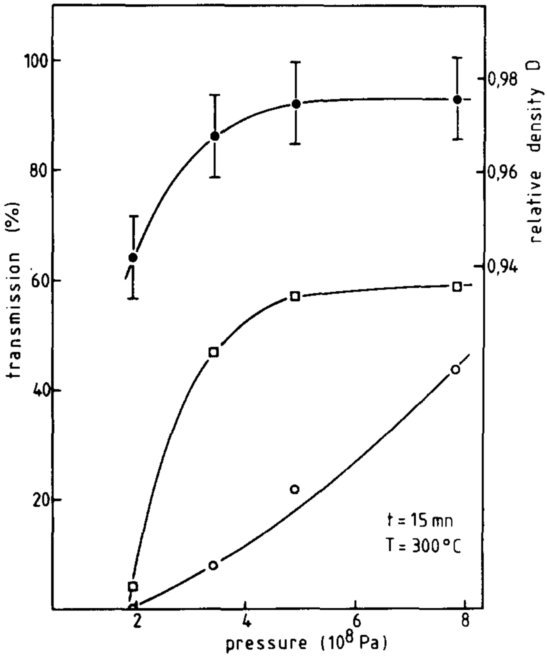


Fig. 5. Pressure dependence of: ●, relative density D; □, transmission in 8–14 μm range; ○, transmission in 3–5 μm range.

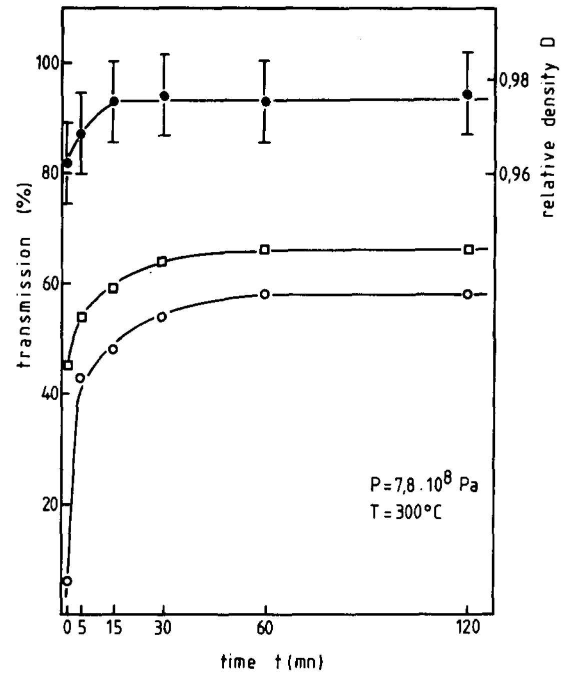


Fig. 6. Time dependence of: ●, relative density D; □, transmission in 8–14 μm range; ○, transmission in 3–5 μm range.

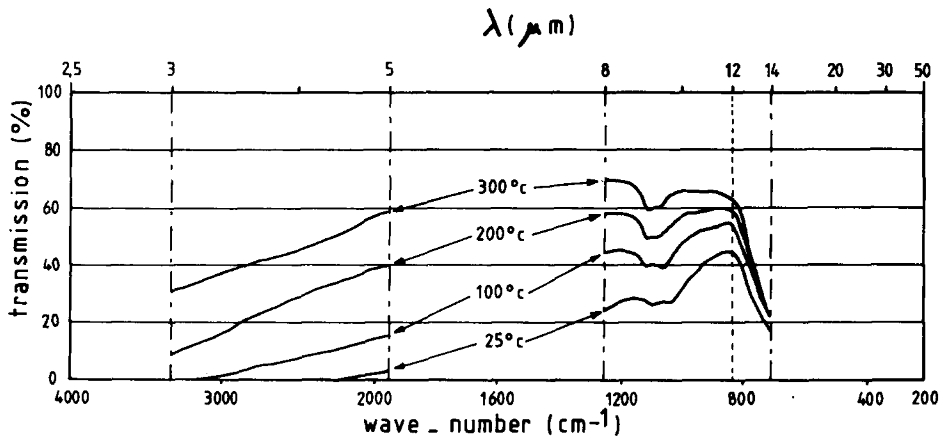


Fig. 7. Transmission spectra of lead fluoride discs (thickness 1 mm) for different hot pressing temperatures ($P = 780$ MPa; $t = 15$ min).

(2) Similar influence of different parameters T, P and t on relative density and transmission in 8–14 μm range is observed.

(3) Transmission in the 3–5 μm range is only efficient when the relative density is $>0{\cdot}97$.

If we consider the scattering losses as responsible for decreasing the transmission, according to the wavelength range, it follows that, in the 8–14 μm range, the 10 μm average grain size of the discs (Fig. 8(a)) is responsible for the scattering losses in the 8–14 μm range; the transmission increases with the progressive disappearance of individuality of each grain by coalescing into a homogeneous matrix (Fig. 8(b)).

In the 3–5 μm range, in the case of sintering of spherical particles, the size of the generated closed pores has been established as:[6]

$$r = R\left(\frac{1-D}{D}\right)^{1/3}$$

where r = radius of closed pores, R = original particle radius, and D = relative density.

With our lead fluoride powder ($2R = 10$ μm) and when $D = 0{\cdot}97$ (Fig. 8(b)) the pore size is $2r = 3{\cdot}1$ μm. In the 3–5 μm range, the closed pores must now be considered as the scattering centres, and the transmission will increase with decreasing size of porosity in the last phase of the hot pressing, for relative density $>0{\cdot}97$ (Fig. 8(c)).

4 KINETICS OF DENSIFICATION

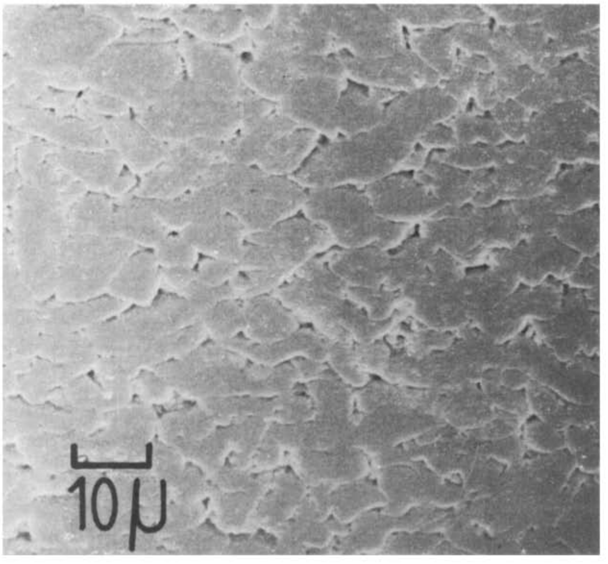
A model has been proposed by Murray *et al.*[6] for the kinetic densification of Bingham's solid by hot pressing. The rate equation for hot pressing depends on pressure, time and densification according to:

$$\frac{\mathrm{d}D}{\mathrm{d}t} = \frac{3}{4}\frac{(1-D)}{\eta_\infty}\left[P - \sqrt{2}\tau_c \ln\left(\frac{1}{1-D}\right)\right] \quad (1)$$

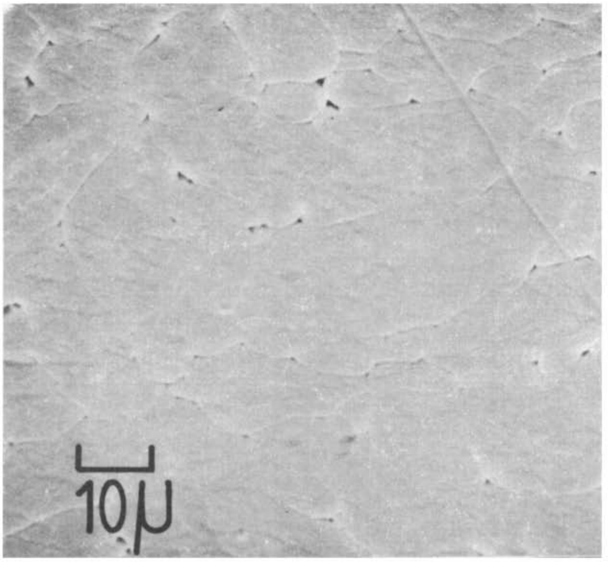
where D = relative density at time t (s), P = applied pressure (dyne/cm^2), η_∞ = viscosity (in poises) at infinite strain rate, and τ_c = limiting shear stress.

For a viscous material ($\tau = 0$) eqn (1) becomes:

$$\frac{\mathrm{d}D}{\mathrm{d}t} = \frac{3P}{4\eta}(1-D) \quad (2)$$

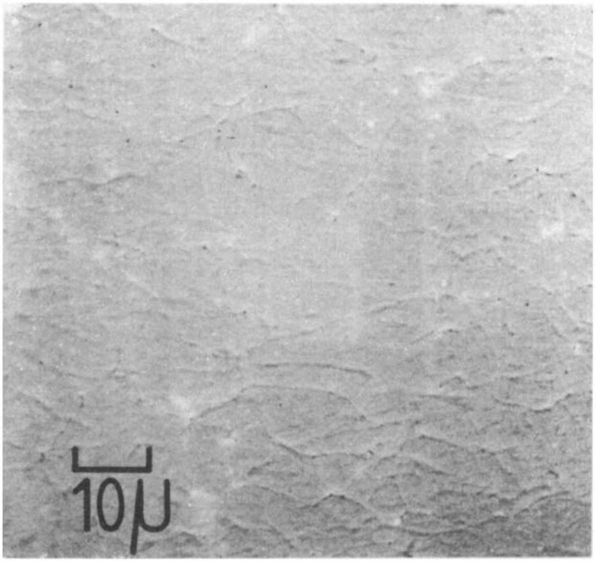


(a)



(b)

Fig. 8. Microstructure of the hot pressed discs with different relative densities, *D*. (a) $D = 0{\cdot}90$; (b) $D = 0{\cdot}97$; (c) $D = 0{\cdot}98$.



(c)

Fig. 8.—*contd.*

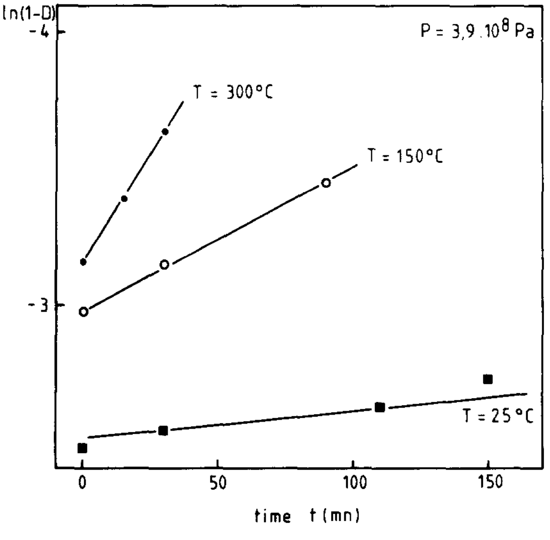


Fig. 9. Plot of $\ln(1-D)$ vs. time for pressure $P = 390$ MPa.

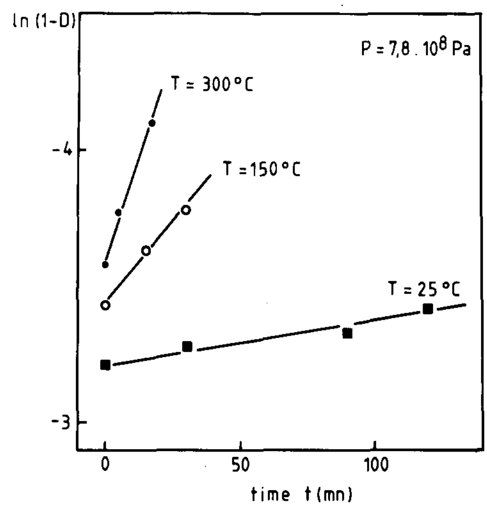


Fig. 10. Plot of $\ln(1-D)$ vs. time for pressure $P = 780$ MPa.

Thus, for appreciable external pressures the rate equation takes the form of a first-order kinetic curve. Integration of eqn (2) gives

$$\ln(1-D) = 3/4P/\eta t + C \tag{3}$$

and shows that a plot of $\ln(1-D)$ vs. t should give a straight line, with integration constant equals $\ln(1-D_0)$ if for $t=0$, $D=D_0$ (the initial pressed density in the die).

Plots of $\ln(1-D)$ vs. t for hot pressing of lead fluoride are shown in Figs 9 and 10 for applied pressures of 390 and 780 MPa, respectively. Whatever the temperature may be, the linear relationship between these two quantities indicates a viscous flow mechanism as responsible for hot pressing densification of lead fluoride.

TABLE 1
Ratio of $\ln(1-D)$ vs. Time, t

T (°C)	*Theoretical ratio*	*Experimental ratio*
25	2	1·6
150	2	2·2
300	2	1·8

Since the isothermal (viscosity is constant) hot pressing experiments were carried out at different pressures, the slopes of straight lines on the $\ln(1-D)$ vs. t plots should be in the ratio of the pressures. The results shown in Table 1 approximate the theoretical values i.e. the ratio of the pressures.

5 CONCLUSIONS

This study has shown that fabrication of lead fluoride windows is feasible by hot pressing. Reaching a limiting relative density for the lead fluoride discs is characteristic of plastic flow as a densification mechanism, but the rate of densification shows, however, that the effect of external pressure is to widen the range over which this material behaves as a viscous solid.

The transmission of discs (with relative density equal to 0·98) is better than 65% in the 8–14 μm range and 55% in the 3–5 μm range, for a maximum theoretical transmission of 85%, if we consider the reflection losses with $n_D PbF_2 = 1{\cdot}7663$.[2] It is generally accepted that the relative density of the samples must be at least 0·99 to minimize scattering losses and to reach the maximum theoretical transmission. To obtain such relative density and to optimize transmission in the 3–5 and 8–14 μm infrared ranges and extend transmission to the visible range, this work has shown that it is necessary to synthesize lead fluoride powders of smaller particle size. The results obtained with such powders will be given in another paper.

REFERENCES

1. Baldwin, C. M. and Mackenzie, J. D., Fundamental condition for glass formation in fluoride systems, *J. Am. Ceram. Soc.*, **62** (1979) 537–8.
2. Jones, D. A., Growth of lead fluoride crystals from the melt, *Proc. Phys. Soc.*, *(London)*, **B68** (1955) 165–70.
3. Klement, W. and Cohen, L. H., Solid-solid transition temperatures in PbF_2 from differential thermal analyses under hydrostatic pressures $\lesssim 6$ Kb, *J. Electrochem. Soc. Solid. State Sci. Technol.*, **126** (1979) 1403–5.
4. Pastor, H., Kinetics of pressure sintering, *Rev. Int. Hautes Temper. Refract.*, **9** (1972) 251–64.
5. Sauka, Ya. Ya., Crystal modifications of lead fluoride, *Zh. Obshch. Khim.*, **19** (1949) 1454–8.
6. Murray, P., Rodgers, E. P. and Williams, E. A., Practical and theoretical aspects of the hot pressing of refractory oxides, *Trans. Brit. Ceram. Soc.*, **53** (1954) 474–510.

Received 7 February 1987; revised version received 15 September 1987; accepted 12 October 1987