Refractive index measurements on CaF_2 single crystal and melt using ellipsometry

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Abstract:

Refractive indices of CaF_2 have been determined by ellipsometry and factors determining the temperature dependence have been discussed. Measurements were made on CaF_2 single crystal and melt in dehydrated He atmosphere in the temperature ranges room temperature-1050 K and 1600-1800 K, respectively. The standard deviation in the measured refractive indices was within ± 0.001. The refractive indices obtained have been approximated to the following equations:

Single crystal: $n = n_{298} - 1.541\times10^{-5}(T - 298)$ 298 – 1050 K

Melt: $n = n_{1600} - 4.667\times10^{-5}(T - 1600)$ 1600 – 1800 K

where $n_{298} = 1.429$ and $n_{1600} = 1.409$.

It is likely that the temperature coefficients are determined predominantly by those of the densities.

Key words: calcium fluoride, refractive index, ellipsometry, density and molar electronic polarisability.

Introduction:

The very-large-scale-integrated-circuit (VLSI) technology has enabled one to manufacture silicon chips which can operate at ultra high-speed even by low electric power and aims at producing further integrated circuit devices with 50 nm wide metal interconnects. For this production, photolithography used for interconnect formation is a key technology; however, steppers currently used as the projection system are approaching the limits because the space resolution is determined by the wavelength of the light source, which is limited down to 248 nm at the present time. One solution to this problem is to shorten the wavelength of the light source into the ultraviolet (UV) region, for example, using F_2 lasers with 157 nm wavelength emission. However, the use of F_2 lasers requires commonly used fused silica optical components to be replaced because this material has high absorption losses in the UV region. Single crystalline CaF_2 is considered to be an alternative to fused silica because of its excellent transmission characteristics down to deep UV.

It is indispensable to lens making to produce single crystals of CaF_2 having a large diameter. Simultaneously, high laser durability, low stress birefringence and high uniformity of refractive index as well as low impurity concentrations are strongly required to the crystals. Accordingly,

CaF_2 single crystals should be produced so as to have extremely low defect densities because all types of crystal defect, *i.e.*, dislocations and low angle grain boundaries affect the optical quality of the crystals and, thus, thermal stress in CaF_2 should be controlled to levels as low as possible in the crystal growth process. To meet all such requirements, strict process design and control are indispensable on the basis of the process modelling for the crystal growth.

For the modelling of heat flow in the crystal growth process of CaF_2, heat transfer by radiation should also be taken into account because radiation as well as thermal conduction contributes to heat transfer through semitransparent media such as CaF_2 at high temperatures (Susa *et al* 1993). Thus, the effective thermal conductivity (k_{eff}) containing thermal conductivity (k_{th}) and radiation (k_{rad}) is required for the modelling. These values are related by the following equation.

$$k_{eff} = k_{th} + k_{rad} \tag{1}$$

Values of k_{th} for CaF_2 have been reported by several workers (Charvat and Kingery 1957, Mitchell and Wadier 1981, Taylor and Mills 1982, Nagata *et al* 1984). On the other hand, for optically thick conditions, k_{rad} can be derived using the refractive index (n) from Eq.(2) in the manner called diffusion-approximation (Gardon 1961, Gardon 1962, Siegel and Howell

1972).

$$k_{rad} = \frac{16\sigma n^2 T^3}{3A} \qquad (2)$$

where σ is the Stefan-Boltzmann constant, A is the absorption coefficient and T is the thermodynamic temperature; actually, Vizman *et al* (1996) have applied the similar approximation to CaF_2 using the refractive index at room temperature. However, there are no extant data for CaF_2 single crystal at high temperatures and its melt.

Refractive index measurements can be made relatively easily on samples at room temperature, for example, using an Abbé refractometer; however, it is very difficult to measure on samples at high temperatures, including melts. Nevertheless, several workers have attempted measurements of refractive indices for liquid metals (Bruckner *et al* 1989, Krishnan *et al* 1990, Krishnan and Nordine 1996) and semiconductors (Jellison and Lowndes 1987) at high temperature by ellipsometry. In addition, Yagi *et al* (2002, 2003a, 2003b) have also determined refractive indices for glass/slag melts using an ellipsometer equipped with a furnace system. Consequently, the aims of the present work are to determine refractive indices of CaF_2 single crystal and melt as functions of temperature using ellipsometry and to discuss factors determining the temperature dependence of the refractive indices.

Experimental:

Sample preparation

Samples used were CaF_2 single crystal and melt. For measurements on the single crystal, samples in the shape of a disc (20 mm diameter and 5 mm height) were used. For measurements on the melt, samples were prepared from the reagent grade CaF_2 powders. The powders were dried in air at a temperature of 423 K, melted in a platinum crucible at 1823 K for 15min in a flow of dehydrated Ar gas and then poured onto a copper plate to obtain samples.

Measurement

The refractive indices were measured using a rotating-analyser type ellipsometer equipped with an electric furnace, as shown in Figure 1. This ellipsometer has a He-Ne laser (632.8 nm wavelength and 1 mm beam diameter) as the probe light, whose angles of incidence and reflectance were adjusted to 60 deg with respect to the sample surface. To reduce radiation effects from the sample and the heating elements, two diaphragms (5 and 2 mm diameter) were placed in the optical path and, furthermore, an interference filter for 632.8 nm was attached to the analyser. In the measurement, the linearly polarised probe light was incident onto the sample surface and the polarisation state of the reflected light was analysed with the rotating analyser, providing the ellipsometry parameters, *i.e*., Δ and Ψ. The values of Δ and Ψ were then converted to the refractive index (n) using the angle of incidence. More details of the apparatus and its performance were described previously (Yagi *et al* 2003a).

For measurements on the single crystal, the samples were placed on the stage in the furnace and refractive index measurements were started at room temperature, being made at intervals of about 100 K during the heating cycle up to about 1050 K. For measurements on the melt, the previously prepared samples were placed in a platinum crucible (60 mm diameter and 20 mm depth) and heated up to about 1800 K. Measurements were carried out during the cooling cycle in the temperature range 1800-1600 K. For both cases, about 20 runs were carried out at each temperature to confirm the reproducibility of the measurements. The temperature of samples was measured with an R-type thermocouple positioned near the sample stage. To avoid the fluctuation of the laser beam due to convection of air, the pressure in the furnace was reduced to about 0.6 atm. Prior to refractive index measurements, investigations were made about the effect of the polarisation angle of the probe light on the refractive index and the effect of atmosphere on the refractive index to determine suitable experimental conditions, which are mentioned in the “Results and discussion” section.

Results and discussion:

Effect of polarisation angle of probe light on refractive index

The optimum polarisation angle of the probe light varies from 45 to 10 deg depending upon the material. Prior to the measurement, it was necessary to optimise this angle to CaF_2 single crystal and melt. Figures 2(a)-2(d) show the distribution of refractive indices for CaF_2 single crystal at room temperature measured at various polarisation angles of the probe light. In these figures the dashed line represents the refractive index of the same material measured at 632.8 nm with an Abbé refractometer and the abscissa represents the frequency where a certain refractive index value was recorded. Values measured at angles of 10 and 20 deg by ellipsometry are in good agreement with that with the Abbé refractometer, where the discrepancy is approximately 0.0005; however, the refractive index by ellipsometry deviates from the value with the Abbé refractometer as the polarisation angle increases to 30 or 40 deg. This suggests that smaller angles provide better experimental conditions but, for an angle of 10 deg, the intensity of the reflected probe light was too weak to measure the refractive index of CaF_2 melt, probably due to the instability of liquid surface and the high intensity of background radiation. Consequently, the polarisation angle was determined to be 20 deg.

Effects of atmosphere on refractive index

Figure 3 shows values of refractive index measured in Ar and in dehydrated He as functions of temperature. It can be seen that values measured in Ar are greater than those in dehydrated He. This difference would arise from the change of CaF_2 to CaO by the chemical reaction with moisture contained in Ar as an impurity

$$CaF_2(l) + H_2O\ (g) \rightarrow CaO\ (l) + 2\ HF\ (g) \qquad (3)$$

because CaO has refractive index greater than CaF_2. There were two measurements made in Ar, giving different results, which is due to the difference in the measurement time: the measurement giving greater values took longer time. Generally, He gas is more purified than other gases and thus it is likely that dehydrated He is the most reasonable atmosphere for this measurement. Consequently, measurements of refractive indices were conducted for both single crystal and melt in dehydrated He atmosphere.

Temperature dependencies of refractive indices for CaF_2 single crystal and melt

Table 1 gives refractive indices of CaF_2 single crystal and melt measured at various temperatures in the present work, which are plotted against temperature in Figure 4. The refractive indices recorded for CaF_2 single crystal are 1.429 at 298 K and 1.416 at 1054 K and those for the melt are

1.396 at 1638 K and 1.389 at 1788 K, where the standard deviation is within ± 0.001. The value for room temperature is in very good agreement with that (1.433) recorded using a modified Gaertner precision spectrometer by Malitson (1963). The refractive indices decrease with temperature in both the crystal and the melt, and the temperature coefficients of refractive indices are about -1.541×10^{-5} for the crystal and about -4.667×10^{-5} for the melt. These refractive indices can be approximate to the following equations:

Single crystal: $n = n_{298} - 1.541\times10^{-5}(T - 298)$ 298 – 1050 K (4)

Melt: $n = n_{1600} - 4.667\times10^{-5}(T - 1600)$ 1600 – 1800 K (5)

where n_{298} = 1.429 and n_{1600} = 1.409. The extrapolation of the data for the crystal to the melting point suggests a small, discontinuous change in refractive index with melting.

Here, discussion is directed to factors determining the temperature dependence of the refractive indices. The refractive index is related to the density (d) and the molar electronic polarisability (α_m) by the Lorentz-Lorenz equation:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N_A \alpha_m \frac{d}{M} \quad (6)$$

where N_A is Avogadro's number and M is the molar mass. The term

$(n^2 - 1)/(n^2 + 2)$ increases monotonically with increasing the value of n where $n > 0$. Accordingly, the temperature dependence of n is the same as that of $(n^2 - 1)/(n^2 + 2)$. Thus, n is dependent upon temperature through d and α_m because N_A and M are independent of temperature. Thermal expansion due to a temperature rise decreases the value of d but increases that of α_m since further separation of the ions reduces the overlap of electron clouds. Accordingly, it is likely that the negative temperature coefficients of the refractive indices would be due to those for the densities.

More quantitative discussion is made about the temperature dependence of the refractive indices: As Prod'homme (1960) indicated, the derivative of Eq.(6) with respect to T can give the temperature coefficient of refractive index (dn/dT) as

$$\frac{dn}{dT} = \frac{(n^2 - 1)(n^2 + 2)}{6n} \quad (\varphi - \beta) \qquad (7)$$

In this equation β is the thermal expansion coefficient, *i.e.*, $\beta = (dV_m/dT)(1/V_m)$, where V_m is the molar volume and expressed by the equation $V_m = M/d$, and φ is the polarisation coefficient, *i.e.*, the temperature coefficient of molar refractivity defined by the equation $\varphi = (dR/dT)(1/R_m)$ and R is expressed using α_m as $R = (4/3)\pi N_A \alpha_m$. Thus, $\varphi = (d\alpha_m/dT)(1/\alpha_m)$. The term $(n^2 - 1)(n^2 + 2)/6n$ in Eq.(7) is always positive where $n > 1$, and consequently, the difference in magnitudes of φ and β determines the sign of dn/dT, *viz*., the temperature dependence of refractive index.

Values of β for CaF_2 are derived from the density data reported by Minato *et al* (2004). On the other hand, values of φ are derived from α_m determined as a function of temperature from Eq.(6) using the refractive index and density data. First, calculation from Eq.(6) provides α_m for the CaF_2 melt, as shown in Figure 5. It can be seen that the α_m values increase roughly linearly with an increase in temperature. The slope of this straight line gives values of φ *via* $\varphi = (d\alpha_m/dT)(1/\alpha_m)$, which are shown as a function of temperature in the temperature range1600-1800K along with values of β in Figure 6. The value of β increases but the value of φ decreases with increasing temperature. It is obvious that the value of (φ - β) is negative, giving negative sign to dn/dT *via* Eq.(7). This discussion confirms that the temperature dependence of the molar volume, *i.e*., the density dominates that of the refractive index for CaF_2 melt, and similar discussion could be applied to the refractive index of CaF_2 single crystal as well.

Systematic error in refractive indices

The angles of incidence and reflection of the probe light were adjusted to an angle of (60 ± 0.0083) deg in the present ellipsometer and the uncertainty of 0.0083 deg would be a factor giving the systematic error to refractive index values. On the other hand, the reflected probe light of 1 mm diameter travels through the diaphragm of 2 mm diameter positioned at a distance (l) of 520 mm away from the sample surface. Because of this construction, the deviation (δ) of the probe light should be within ± 0.5 mm at the diaphragm to enable the measurement to be made. The deviation (θ in deg) acceptable to the measurement can be estimated as 0.055 deg at most from the geometric relation $\theta = 180\delta/\pi l$. This uncertainty is greater than that (0.0083 deg) in the adjustment of the angles of incidence and reflectance, and thus there is a possibility that the deviation of 0.055 deg dominates the systematic error. Calculation by inputting an angle value of 60.055 deg instead of 60 deg gives rise to a difference of at most 0.003 in the refractive index and, consequently, the systematic error would be at most ± 0.003.

Conclusions:

The refractive indices for CaF_2 single crystal and melt have been determined by ellipsometry, respectively, in the temperature ranges room temperature-1050 K and 1600-1800 K. The standard deviation in measured refractive indices is within ± 0.001 and the systematic error has been estimated to be at most ± 0.003. The refractive indices obtained have been approximated to the following equations:

Single crystal: $n = n_{298} - 1.541\times10^{-5}(T - 298)$ 298 – 1050 K

Melt: $n = n_{1600} - 4.667\times10^{-5}\,(T - 1600)$ 1600 – 1800 K

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Figure 1 Ellipsometer for determination of refractive index at high temperature

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Figure 3 Refractive indices of CaF_2 melt at different atmospheric conditions

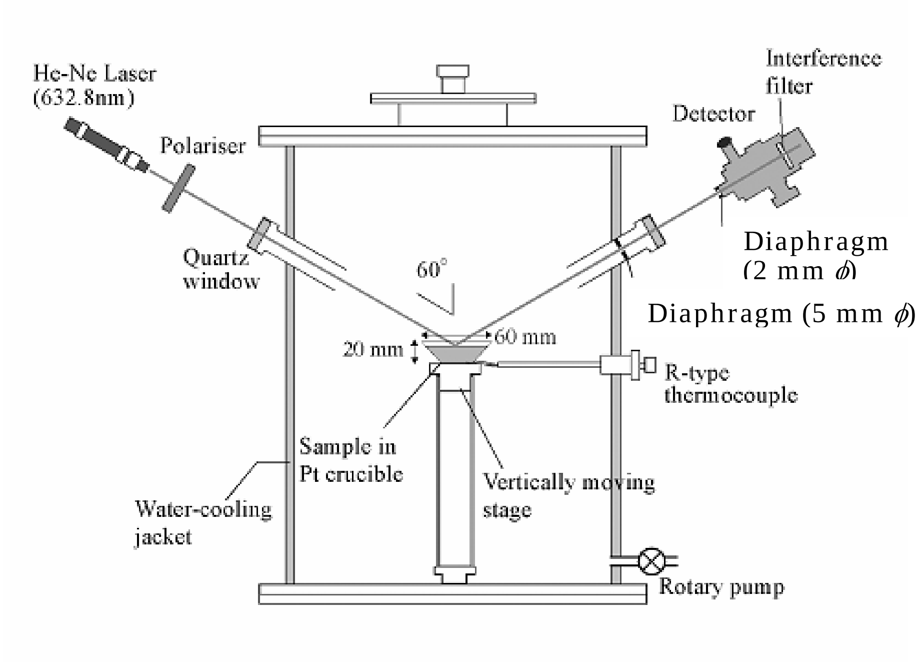
Figure 4 Refractive indices of CaF_2 single crystal and melt as functions of temperature

Figure 5 Molar electronic polarisability of CaF_2 melt as function of temperature

Figure 6 Thermal expansion coefficient (β) and polarisation coefficient (φ) for CaF_2 melt as functions of temperature

Table 1 Refractive index of CaF_2 single crystal and melt at various temperatures.

Temperature /K	Refractive index, *n*
298	1.429
473	1.425
573	1.423
673	1.422
756	1.423
847	1.423
952	1.419
1054	1.416
1638 (melt)	1.396
1670(melt)	1.394
1700(melt)	1.393
1750(melt)	1.390
1788(melt)	1.389



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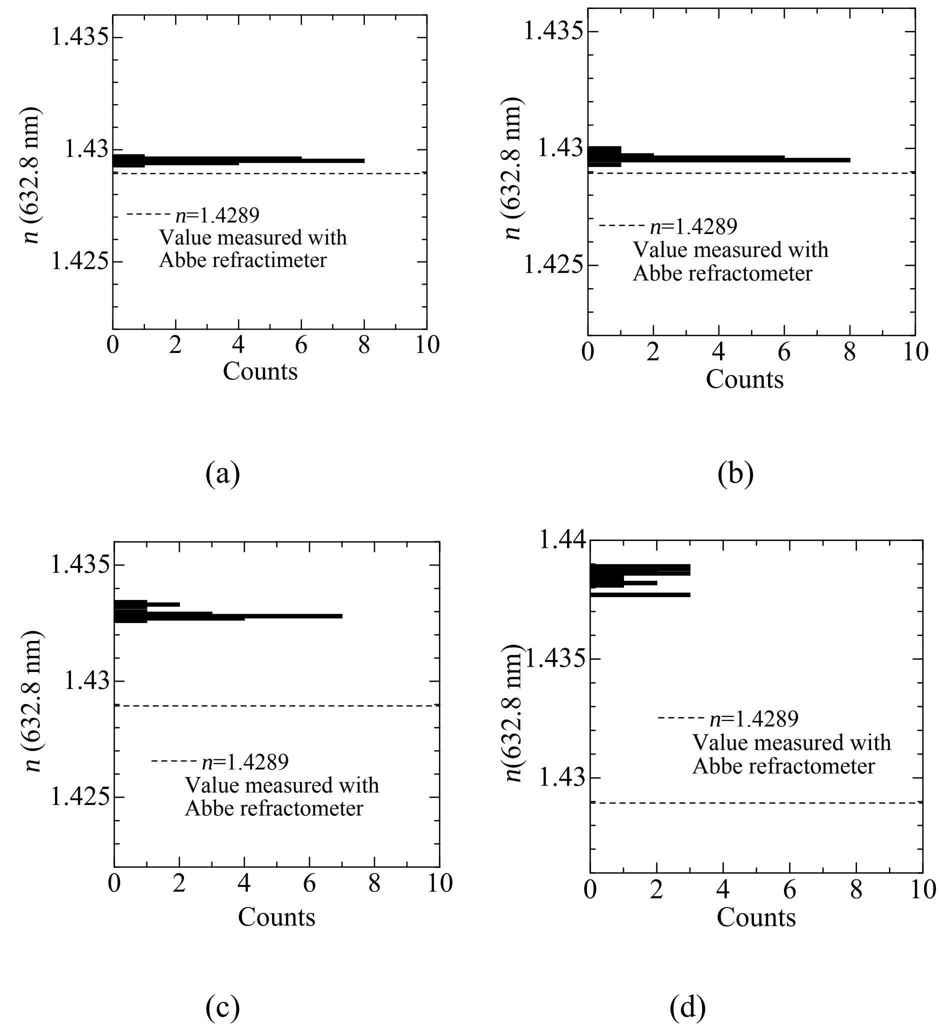

Figure 2 Dependence of refractive index of CaF_2 single crystal at room temperature on the angle of polariser, where the angle of the polariser is (a) 10^o, (b) 20^o, (c) 30^o and (d) 40^o.

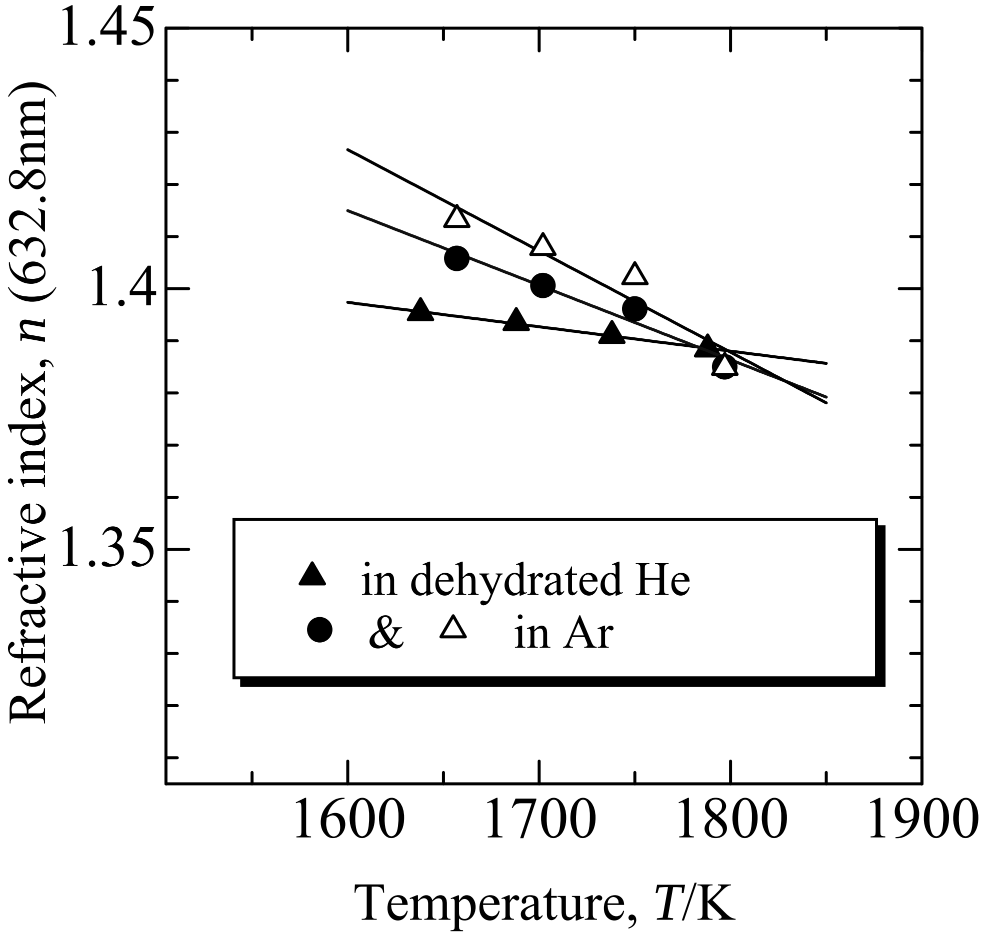

Figure 3 Refractive index of CaF_2 melt at different atmospheric conditions.

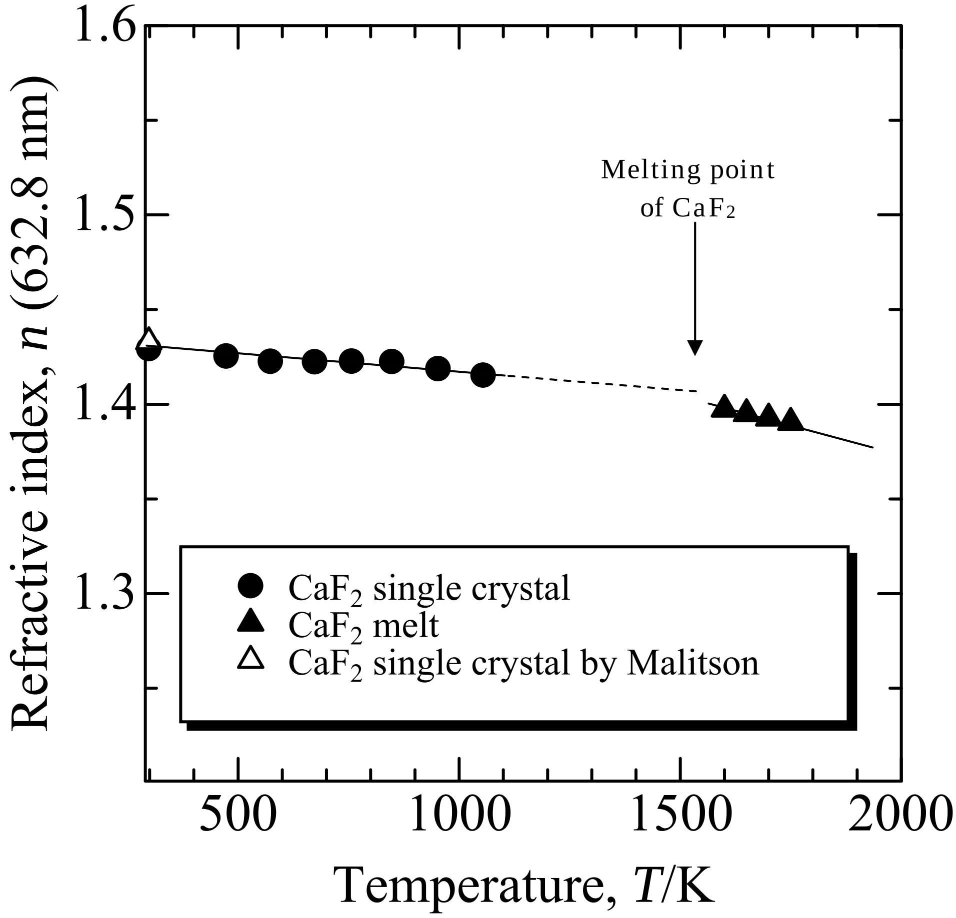

Figure 4 Refractive index of CaF_2 single crystal and melt as functions of temperature.

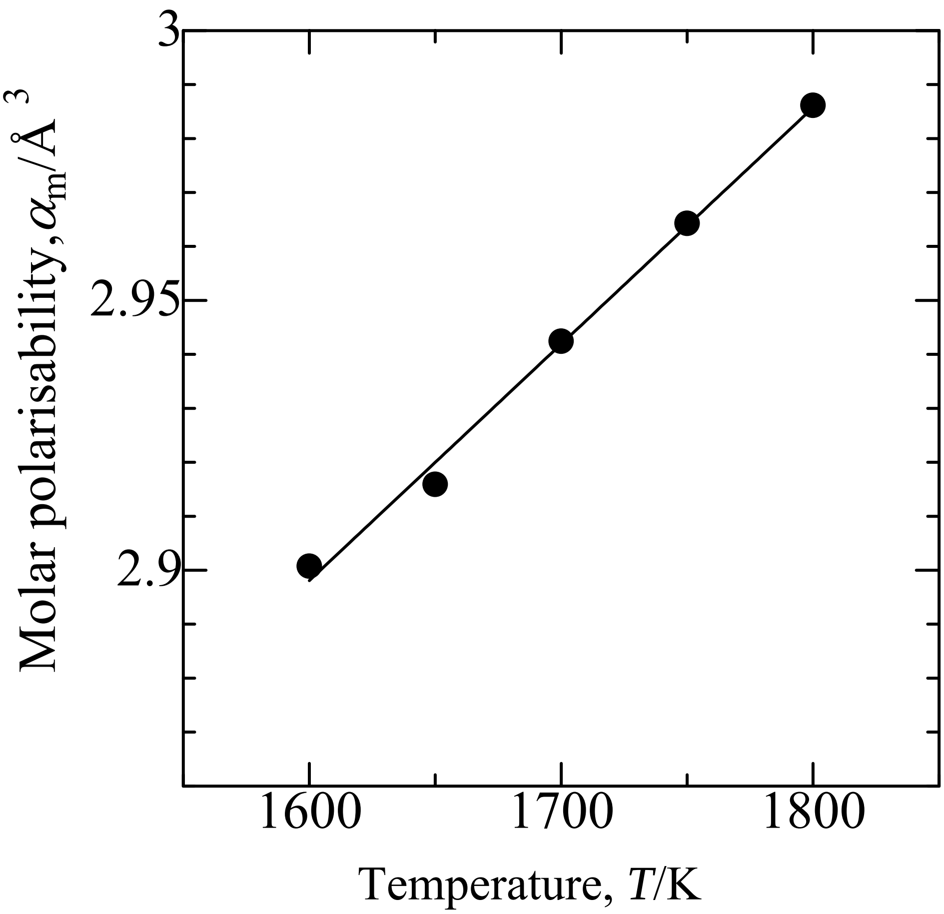

Figure 5 Molar electronic polarisability of CaF_2 melt as functions of temperature.

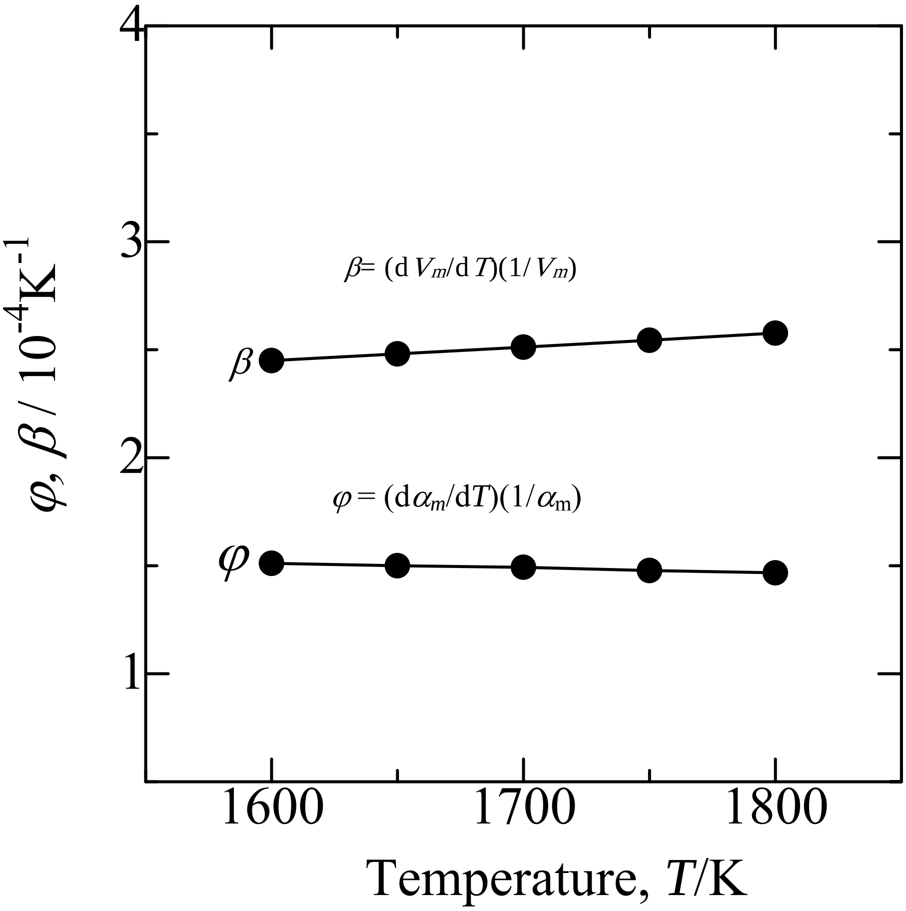

Figure 6 Thermal expansion coefficient (β) and polarization coefficient (φ) for CaF_2 melt as functions of temperature.