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# Study of the reflectivity of ceramic materials for laser-cavity mirrors

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High power lasers for industrial applications necessitate easy handling and ability to be subjected to fast movements. Thus, small volume and weight for these devices without prejudicing their accuracy of beam-fire and their integrity during the time is required. Solid state crystal Nd:YAG lasers were consequently considered. An important aspect under high power irradiation, is the system of mirrors of the cavity that must reflect back towards the laser active crystal source a sufficient radiant energy to activate laser pumping. At the same time the material of these mirrors must not degrade in short times (in the sense of industrial applications) and be sufficiently able to dissipate the produced heat. Ceramics are obvious candidates in particular alumina ceramic. After the test concerning the reflectivity of a wide range of white materials, it was realized that alumina ceramic is up to now the better and about which current technology allows easy manufacture of these mirrors. Certain rules must be followed to prepare white alumina mirrors able to maintain for sufficiently long times their reflectivity such as sintering at suitably high temperature in reducing atmosphere using very pure corundum-like spheroidal grains, correct granulometry of the utilized powders and treatment of the surface with a specific porcelain-like glaze before firing.

## 1. Introduction

The utilization in the industrial field of apparatus that depends upon laser devices as the heart of their activity is rapidly increasing as their technological evolution improves. Lasers are now commonly used in training devices to reach the highest precision possible on the positioning of pieces during their machining. This is currently a particularly important technology on robotized working and assembly lines. Lasers are also utilized by the electronics industry to help in mass production on the surface of machining pieces, microwelding, micromelting or localized chemical transformation (these reactions are carried out under a suitable gaseous atmosphere and are induced solely by laser-beam radiation at a specific wavelength). In many cases, a laser beam is also utilized to obtain straight, thin and burrless cuts on ceramics (e.g. on alumina substrates in the thick-film electronic industry) or on metals (e.g. in the steel plate coils industry). In every kind of application the result obtained depends on the laser power. To cut slabs, the requested power of the utilized laser increases as the thickness of the slab increases.

Up to now the most used laser source for high-power industrial application was the $CO_2$ laser. The $CO_2$ laser is already available for average power in excess of 10 kW. Recently, a growing interest has been shown in industrial processes involving high average-power solid-state lasers, mainly lasers that use a large cylinder-shaped monocrystal of yttrium–aluminium garnet doped with neodymium (Nd:YAG) as the laser exciting element. The advantage of the Nd:YAG laser is its short operating wavelength (1.06 μm), compared with that of the $CO_2$ laser (10.6 μm). This leads to many advantages in processing most materials. First, the spot size of the focused laser beam can, in principle, be ten times smaller, increasing the cutting and drilling speed. The radiant absorption of many metallic or non-metallic materials is also much higher at shorter wavelength. Moreover the biggest advantage, in terms of laser integration in the production plant, is the possibility of propagating the laser beam through optical fibres. An average power output of more than 2 kW of a Nd:YAG laser from a 1 mm fused silica optical fibre was recently demonstrated [1]. The laser head can then be placed far away from the machine tool and several machines can also share the same laser head, thus reducing the costs. The main disadvantage of the Nd:YAG laser with respect to the $CO_2$ laser is its lower overall efficiency. The efficiency of $CO_2$ lasers, defined as the laser optical output power divided by the laser electrical input power, is in the range 10%–15%. The efficiency of Nd:YAG lasers is instead usually lower than 4%. The main reason is that $CO_2$ lasers are directly excited by the electrical discharge, while solid-state lasers are optically pumped by rare gas arc discharge lamps. The excitation light is transferred from the lamp to the laser crystals

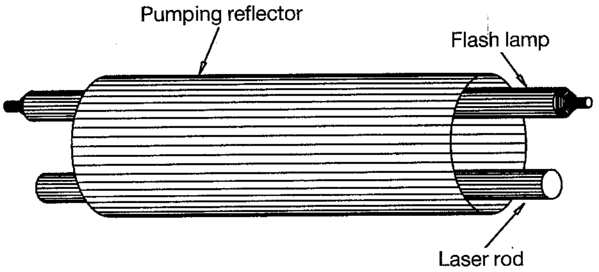

*Figure 1* A typical arrangement of the laser camera to achieve laser excitation of an Nd:YAG monocrystal (laser rod) where ceramic reflecting mirrors have application as pumping reflectors of the radiation emitted by the flash lamp.

by a suitable reflector, forming the so-called "pumping chamber" of the laser, as shown in Fig. 1. The efficiency of the light transfer is a critical point in a solid-state laser, because it involves not only the overall laser efficiency, but also the quantity of heat to be removed from the laser head in order to maintain its temperature at a safe level for all the components involved. This is a very important feature in a high-power industrial laser, where average power in excess of 10 kW is dissipated into the laser head. Requirements for the material used for the pumping chamber are, therefore high reflectivity in the required wavelength range, good mechanical strength, and high thermal conductivity. Because heat removal is achieved by the passage of a suitable fluid (usually deionized $H_2O$) inside the laser head, chemical resistance to the cooling fluid under intense ultraviolet irradiation is also required.

Two different technologies are now used for solid-state laser pumping chambers. The oldest one, still used for low-power lasers, uses metallic reflectors, polished to make a specular reflecting mirror. The surface shape is usually an elliptical cylinder, which focuses the flashlamp image on to the laser crystal. The reflectivity of the metallic surface is enhanced by a suitable reflective coating. For Nd:YAG lasers, the most commonly used coating is electroplated gold. High-purity gold shows a high reflectivity in the 500–900 nm spectral region, where the main absorption bands of neodymium are found. Gold also does not suffer from oxidation and it is quite resistant to most chemical attack from cooling fluids.

The most important disadvantage of gold-plated reflectors is their low resistance to scratches and other mechanical damages. This point is very important on high-power industrial lasers, because lamp replacement is required quite often, at least once a week. The probability of damaging the reflector is then rather high. For the same reason, gold-plated reflectors are also nearly impossible to clean, because any attempt to clean the soft gold surface will result in scratching it, even using the softest lens cleaning tissue.

New technologies are now emerging to solve these problems. They use diffuse reflecting surfaces, placed around the lamps and the crystal, in the so-called "close coupled geometry". The light transfer between the flashlamp and the crystal is made by a statistical process induced by the random scattering of light on the reflector walls.

The first diffusive reflectors were made of metal oxide powders, contained in a glass or fused silica envelope. Some of these materials, such as MgO, show a very high diffuse reflectance in a very wide band, leading to a high laser overall efficiency. The main disadvantage of the powder-type reflector is its low thermal conductivity. Cooling of this kind of reflector was found to be possible for a lamp input average power of less than about 1 kW. The maximum average output power of the laser is then limited to between 20 and 40 W.

Higher average power can be obtained from lasers with diffusing reflectors when reflectors are made with white ceramics. The thermal conductivity of the ceramics can be orders of magnitudes higher than that of the powder. The ceramic reflectors are also very rugged, easy to clean, and can be easily cooled by means of flowing water around the reflector itself.

The main technological problem is manufacturing the reflector, using proper, high-reflectivity base materials, and maintaining the reflectivity up to the end of the process. Although very thin, a vitreous glaze layer is also required for protection from the cooling fluid.

The requirements for the spectral region where the reflectivity of the material should be high depend on the kind of laser crystal and the type of lamps used. For high-power solid-state lasers for industrial applications, Nd:YAG and krypton flash-lamps are by far the most common choices.

The Nd:YAG absorption spectrum is shown in Fig. 2. The main absorption bands are located in the near infrared, around 800 nm. Other strong absorption lines are, however, present at 750 nm and between 500 and 600 nm. The strong absorption below 300 nm is due to the crystal bulk absorption. Irradiation of the crystal in this spectral region is to be avoided, because it does not contribute to the laser emission, but simply heats the crystal.

The emission spectrum of the krypton flash-lamp is shown in Fig. 3. As usual in gas discharge lamps, the spectrum is made up of several narrow lines and a continuum emission. Both extend from the infrared to the cut-off wavelength of the lamp cooling flow tubes. The UV spectrum is usually avoided using a cooling jacket made of Pyrex glass, which is responsible for

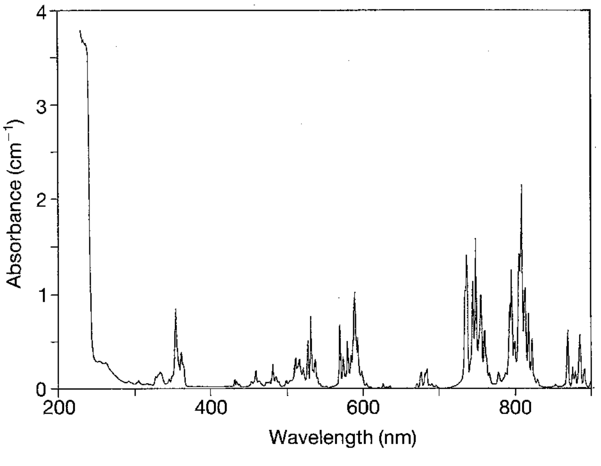

*Figure 2* Absorbance spectrum of a typical Nd:YAG monocrystal.

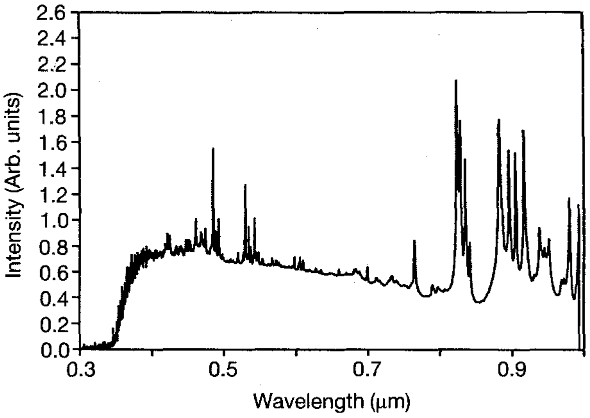

*Figure 3* Spectrum of radiant emission of a normal gas-discharge flash lamp, peak current 80 nm.

the cutoff at about 350 nm shown in Fig. 3. The ultraviolet spectrum is, in fact, responsible for overheating the laser rod and for damage of all other components inside the laser cavity, including reflectors.

For all the above-mentioned reasons, the spectral band, where high reflectivity is required, ranges from about 400–900 nm. This work investigated the reflectance properties of some substances used as possible components of high-reflectance ceramics, suitable for laser pumping chambers. The results are compared with those of other materials, well known for their high laser efficiency, but not suitable for high-power operation for some of the above-mentioned reasons.

## 2. Notes about the materials used

At present some good materials are available on the market to produce diffuse reflecting cavities of lasers at a pumping power less than 5 kW. One of the best is SPECTRALON SRM-99, a very white polymer that reflects with an absolute efficiency greater than 95%, over practically all the interesting range of the electromagnetic spectrum. Its ultrapure production is even utilized as standard material to have a reference marker in evaluating the reflectance degree of other materials. Our X-ray diffraction (XRD) analysis on a very good sample coming from the market, shows that it is a highly fluorinated organic compound that contains significant amounts of calcium and potassium and traces of compounds of chlorine, silica and alumina. Fig. 4 shows the reflectance spectrum of this commercial SPECTRALON SRM-99, together with those of other reflecting materials utilized to make laser reflectors: other polymer metallic films and MACOR. This last material is a machinable ceramic that, because of this property, could be considered ideal. However, all polymers are hardly utilized in lasers of some power; even a weak radiant energy in play inside a cavity is sufficient to induce their evaporation or oxidation.

The majority of front-surface mirrors used in precision optics are produced by evaporating metals on to a polished surface of glass or quartz in a high vacuum. The spectral reflectance of a good vacuum-deposited metal coating is always higher than that of an electroplated or of a polished surface of the same metal, except gold. Spectral curves of absolute reflectivity of freshly vacuum-deposited coatings of aluminium, silver, gold, copper and rhodium metallic films [2], are reported as examples of standard substances [3]. Silver films exhibit a reflectivity that is similar to or even slightly better than that of aluminium films; however, both are easily oxidizable simply by their exposure to the atmosphere, but whilst aluminium oxide is white (or transparent in its corundum phase), silver oxide is dark and highly absorbant. So both are usually unused, but in case of need, aluminium films alone may be used. Gold-protected silver films (that exhibit a slow rate of oxidation) deposited on ceramic, or metal, substrates have however, shown, an overall lesser efficiency than the simple films of aluminium (compare the reflectance curve of vacuum-deposited aluminium in Fig. 4 with those of gold-protected silver films show in Fig. 5). In any case, the potential efficiency of utilizable metal surfaces is less than that of other possible different materials, without taking account of problems connected with their use in lasers of powers greater than 5 kW. In such power ranges, it is best to turn to white refractory ceramic mirrors.

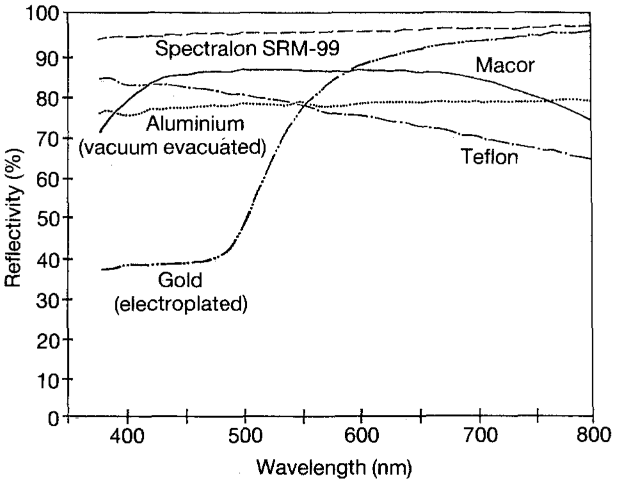

*Figure 4* Reflectivity spectrum of some substances still utilized for the production of reflecting mirrors for weak powers of irradiation.

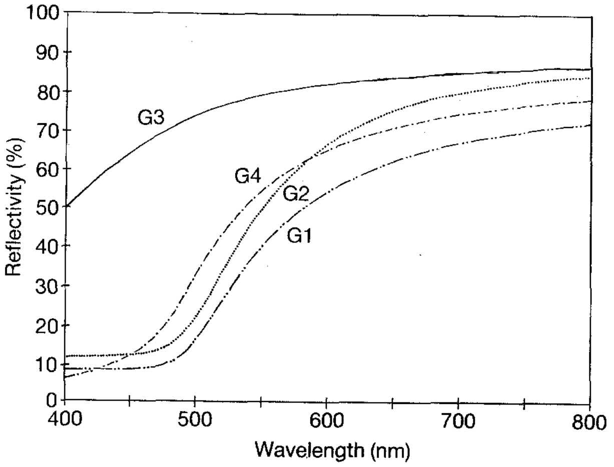

*Figure 5* Reflectivity spectra of some samples of gold protected silver films deposited on ceramic mirrors. G1, Galvotek (15 µm Ag + 0.03 µm Au); G2, Galvotek (15 µm Ag + 0.5 µm Au); G3, Galvotek (15 µm Ag + flash Au); G4, Galvotek (3 µm Ag + 0.2 µm Au).

The response of optical reflectivity of some ceramic powders has been studied in the past. The users' experiences, coming from industrial utilization of ceramic mirrors produced in the past, suggested that the spectral curves of the powders are not always such that the corresponding ceramic will have the same optical behaviour. Here we outline some of the known factors that lead to different optical behaviour of a ceramic compared to that of the powders with which it was made.

First, it is well known that white powders of some substances, such as $BaSO_4$, $MgCO_3$, MgO and Vitreolite glass, are highly reflective. However, either because of thermochemical decomposability of the first two, or because of the fusibility behaviour of the glass, only powders of MgO are suitable to produce a ceramic. It should be noted that MgO has one of the highest optical reflectivities with its absolute per cent reflectance of about 98% over a very wide band of wavelengths; it has been considered as a standard for reflectivity measurements by the "Commission International de l'Eclairage (CIE)" since 1931 and formally accepted in 1964 within the Large-Field Standard Observer for Colorimetry [4]. This standard is prepared by deposition of a smoke of molecular MgO produced instantly (preferably by autocombustion of metallic powders of pure magnesium in an atmosphere of pure oxygen), fluxed upon the finely polished surface to be covered (generally a slab of glass). The obtained reflectance values are nevertheless shown to depend rather on the method by which the film deposited on the reflecting surface was prepared and on the thickness of this film. The obtained value of reflectance for whichever ceramic is utilized as the reflecting mirror, depends also on the impurities contained and even on the ageing time, as well as on the overall time of exposure to ultraviolet radiation. The ageing with time (that, is the progressive loss with time of the original spectral properties of reflectance) of reflecting ceramic surfaces is a second factor that appears to differentiate the behaviour of a ceramic from that of the powders with which it is made. A third factor can also be taken into consideration: a sintered material can have a colour different from that of the starting powders. This phenomenon is known in the field of mineralogy as allochromatism, in which powders scraped from a mineral of one colour can exhibit a different colour. Allochromatism depends on the presence of impurities, lattice defects and/or polarization factors, all eventually connected with tribochromy, triboluminescence, paramorphosis, the dimension of the powder grains, etc. Porosity, carbon diffusion and other effects depending on the sintering process adopted, can also play a role in this third factor.

## 3. Materials and methods

All the spectral measurements reported in this paper were carried out using the same procedure on the total reflectance (collecting the emitted radiation over a total angle of 180°), except for different signals. A Pye Unicam PU 8800 spectrometer, equipped with tungsten and deuterium lamps, was used, which had a double beam with chopper and integrating sphere.

All the total reflectance measurements are relative and were carried out by comparison of a sample of diffuse reflectance with a certificate of NBS calibration. All the values were then corrected for the absolute reflectance of such samples.

The measurements on metallic film samples (including those reported in Figs 4 and 5) were carried out using the same spectrophotometer, but with a device for measurement of specular reflectance. No recourse to a standard sample reflectance is made, thus the absolute reflectance is given directly.

Measurements of diffuse reflectance under a small angle ( ~ 4°) were made using a spectroradiometer PR 704 Spectrascan (PhotoResearch Co.), equipped with a tungsten lamp as light source. The spectrum is shared into 256 channels. Also in this case the reflectance value was collected by comparison with the white light value coming from a Spectralon SRM-99 standard, calibrating the device under NBS conditions.

## 4. Results

The present work examined the reflectivity behaviour of many ceramic substances, each a potential candidate to make reflectors, either alone as a ceramic or in combination with others in an enamel. Whilst dealing in this work with commercial powders, the measurements also concerned those substances for which there is wide literature because they have been studied as pure substances in the past. Spectra for MgO, $SiO_2$, $Al_2O_3$ and $TiO_2$ powders are shown in Fig. 6. Ceramic discs of MgO and $Al_2O_3$ produced with the same powders showed spectra similar to those seen in this figure. These are substances whose ceramics can be considered for potential use in high-power lasers because of their high refractivity. Other preliminary measurements were carried out on laser cavities made of alumina, at present utilized for low-power lasers. The measured reflectivity is not high, but is sufficiently good in the region of greatest interest for laser photonic pumping of the Nd:YAG monocrystal, at about

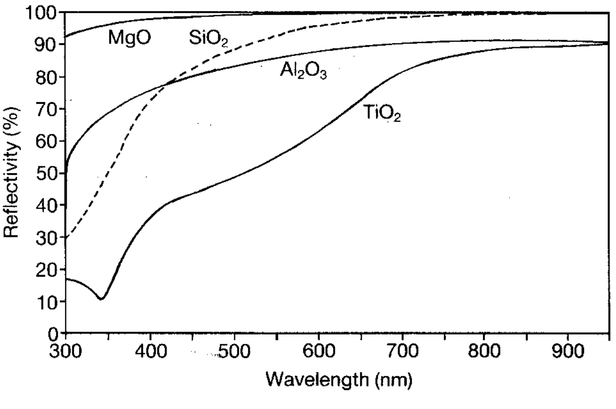

*Figure 6* Reflectivity spectra of very pure commercial powders as indicated. $SiO_2$ is from powdered pure quartz free from chromophorous ions.

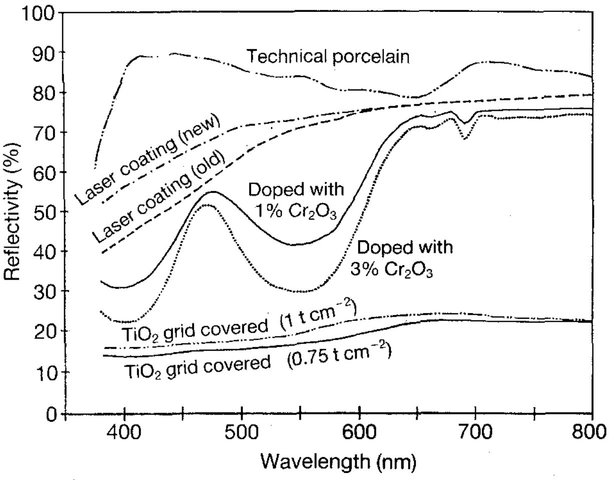

*Figure 7* Spectra of various samples of alumina ceramic subjected to different treatments. Laser coating new and old refer to plasma-sprayed alumina coating finely polished, just produced, and after 200 h use as a reflector inside a 5 kW Nd : YAG laser. The two lower curves are for alumina covered with titania at different surface concentrations.

800 nm. Measurements on an equivalent sample used as a cavity for about 2 years indicated a progressive yellowing of its surface under the influence of ultraviolet radiation. Fig. 7 shows a series of spectra of alumina treated differently. Alumina coatings by plasma spraying on stainless steel substrata also show a lowering of efficiency with time. In addition, in some technical porcelains, selected for their highest whiteness, a progressive decay into a yellowish colour takes place.

A new approach to the solution of this problem was also taken into consideration, in an attempt to increase in a different way the efficiency at high-power irradiation of the reflecting cavity of solid-state lasers. This new approach is based on advantages of utilizing substances capable of collecting absorbed radiation over a wide band of wavelengths (otherwise lost as heat) and which can re-emit the radiation as fluorescence over a narrower band corresponding to the absorption band of the excited laser monocrystal used. In particular, the doping of alumina ceramic with chromium trioxide was considered, by exploiting its crystallographic isostructural similarity with alumina and obtaining green-coloured ceramics. The $Cr^{3+}$ cation has, in fact, an emission band centred at 695 nm, thus, in principle, it is a possible candidate for this new approach. Unfortunately, measurements have indicated wide bands of absorption of $Cr^{3+}$ (Fig. 7) which strongly reduce the reflectance of the obtained mirror between 400 and 600 nm. The loss of excitation due to this reason is not sufficiently compensated by the gain from the re-emission by fluorescence. This absorption is shown to be proportional to the concentration of the dopant introduced, even if followed by a corresponding proportionate small increase of selectivity.

Another possible candidate was the $Ti^{3+}$ ion, but in this case difficulties arose in producing a stable sintered material starting from $TiO_2$. This new system was also aborted, because of its comprehensive very low reflectivity over the whole spectrum (Fig. 7).

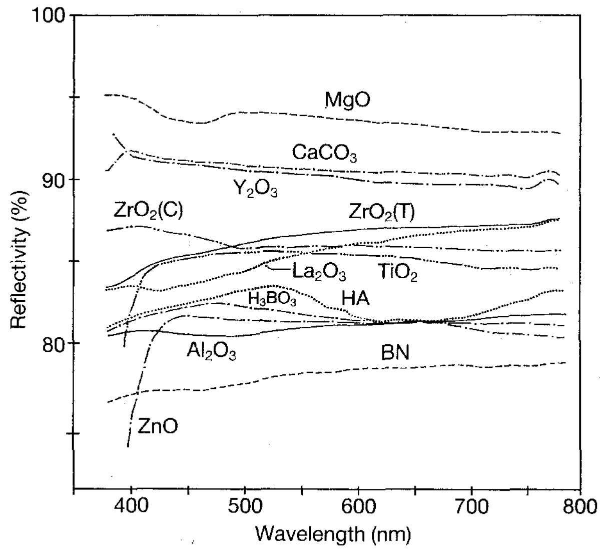

*Figure 8* Reflectivity spectra of the indicated substances. For $ZrO_2$: T = Tetragonal; C = Cubic.

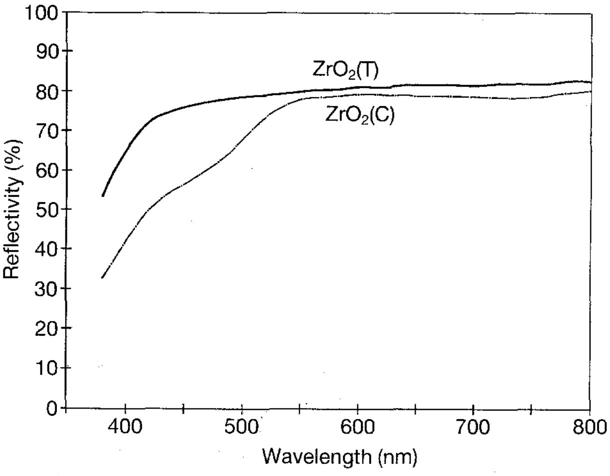

*Figure 9* Comparison between two reflectance spectra of ceramic samples with low (T) and high (C) contents of $Y_2O_3$ phase stabilizer.

Total reflectance spectra of other substances examined are shown in Fig. 8. It is easily seen that the best substances are MgO, $CaCO_3$ and $Y_2O_3$. $ZrO_2$ is also good enough; some differences connected with the crystalline phase involved may be seen. The tetragonal powders appear to be more efficient than the cubic ones. The difference in efficiency can be ascribed either to the phase stabilizer ($Y_2O_3$), or to the different atomic arrangement in the crystalline lattice, or even to the presence of microdefects. To verify if such a behaviour is also maintained for zirconia ceramics, and to evaluate to which of the cited reasons the decreasing efficiency may be ascribed, two ceramic discs were prepared using $ZrO_2$ powders, the first at low (3%) and the second at high (11%) $Y_2O_3$ stabilizer content, and their flat surfaces were accurately polished as mirrors. The ceramic samples were sintered with the same procedures and had no porosity at all, the first being tetragonal (T) stabilized, and the second cubic (C) stabilized. In spite of the fact that $Y_2O_3$ give rise to a reflectance spectrum that is better than those for $ZrO_2$ (Fig. 8), it is observed in Fig. 9 that as the $Y_2O_3$ stabilizing agent content increases, there is a noticeable decrease in reflectance efficiency in these ceramics at the shortest wavelengths.

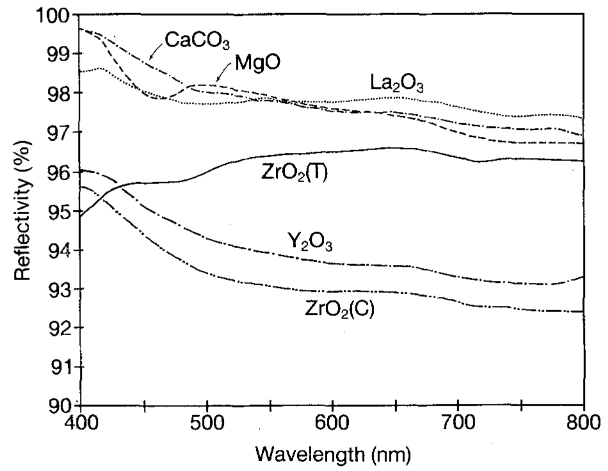

*Figure 10* Reflectance spectra at small angle ( ~ 4°) of powders of the substances considered in Fig. 8 which answer better to the purposes of this study.

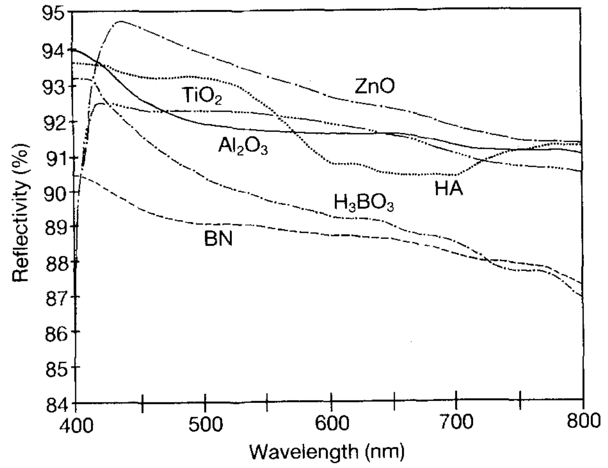

*Figure 11* Reflectance spectra at small angles ( ~ 4°) of the other substances considered in Fig. 8 but excluded from Fig. 10.

Fig. 10 shows the most significant spectra of diffuse reflectance at small angles ( ~ 4°); the remainder are shown in Fig. 11. The spectra of Fig. 10 confirm the highest efficiency of substances such as MgO and $CaCO_3$ known from the literature and also the higher efficiency of tetragonal $ZrO_2$ in comparison with cubic $ZrO_2$ observed here.

On examining the spectra in Fig. 10, they appear in general to be more efficient than those at total reflectance. These spectra are, in fact, simply shifted upwards, but maintain the same proportionality in the distribution of their reciprocal distances, except for the ambiguous case of $La_2O_3$. This latter substance behaves as an optimum material at small angle reflectivity, whereas its efficiency decreases substantially at total angle reflectivity, joining the fairly good one of tetragonal $ZrO_2$ (Fig. 8). The differences in reflectance (%) observeable between total and small angle reflectance can be explained by considering that not all the materials behave as perfect diffusers (Lambertian) of light, but often exhibit a lobe of radiation that is pronounced, at the edge of the specular reflection.

Some white enamels were also prepared to cover a titanium alloy (Ti/6Al/4V) substrate. These enamels contain alumina powder as a white opacifier of the glassy matrix. The composition of such enamels is approximately as follow: $SiO_2$ 50%–60%; $Na_2O$ 15%–20%; $K_2O$ 5%–10%; MgO 1%–3%; $P_2O_5$ 1%–3%; $ZrO_2$ 1%–3%; $Al_2O_3$ 3%–5%. The concentration of impurities CaO and ZnO is less than 1%, whereas that of chromophoric agents is less than 0.1%. This kind of enamel showed a fairly good efficiency, similar to that of the porcelain in Fig. 7.

## 5. Discussion and conclusion

We have confirmed the optimum reflectivity behaviour of the well-known high-purity MgO, even that commercially available. Other substances, such as $SiO_2$, $La_2O_3$ and tetragonal $ZrO_2$ have also been shown to be good.

In zirconia, a sufficiently substantial influence comes from the presence of the network stabilizer $Y_2O_3$, probably due to non-conservative relaxation phenomena. It probably depends on the formation of defects inside the crystallographic lattice of $ZrO_2$. In fact, ionic substitution of $Y^{3+}$ for $Zr^{4+}$ in its crystallographic site inevitably involves the presence in the neighbourhood of a vacancy in an $O^{2-}$ crystallographic site to maintain the electrical charge neutrality, because of the difference in charge of the two cations. This determines the onset of a local discontinuity inside the crystallographic lattice. The composition of many such defects gives rise to a network structure in which non-conservative vibrations at short wavelengths are allowed, that involve the atoms at the boundary of the vacancies. These vibrations, non-tunable with those of the predominant lattice of $ZrO_2$, soon scatter and change into heat. The greater the amount of introduced $Y_2O_3$, the greater are the numbers of these vacancies and consequently the greater is the absorption at the high frequencies, exactly in agreement with the observations. It is clear that in the reflectance at small angles the $Y_2O_3$ spectrum practically traces the outline of that of cubic $ZrO_2$ (which has a high content of this stabilizer).

From the spectra for alumina of Figs 8 and 11 it appears that all considered, alumina is not an ideal substance from which to obtain a ceramic suitable to give rise to reflecting mirrors. The original high reflectance of the surface of an $Al_2O_3$ ceramic is lost with time, because the surface itself yellows in relation to the time of exposure to high fluxes of light radiation. Other factors excepted, this could be due to an original micronic layer of an allotropic phase of alumina that forms during sintering for particular reasons (hydration of the surface, migration of impurities, ultrathin dimensions of the ceramic grains, etc.). Under the action of the continuous photonic bombardment and thermal stress, sintering of the surface grains continues and the grains enlarge. The typical microstructure of alumina ceramic is thus also restored in the surface of the mirror, and consequently its colour characteristic which is not white, but yellowish. Electronic paramagnetic resonance (EPR) analyses carried out on flat samples of alumina ceramic, manufactured for such uses, indicate a general alignment of the basal planes of the grains on the surface, with the principal crystallographic six-fold $c$-axis disposed not really perpendicular to the surface, but inclined, forming an angle of about 94°. This is just as if the single grains arrange themselves with their crystallographic basal [0 0 0 1] planes slightly inclined at 4°, in the comparison to the mean profile of the surface, rather than flanked, giving rise to a saw-toothed microstructure.

$TiO_2$ does not show any good potential use as reflecting material. This is probably because of its pale yellow colour (visibly much more perceptible than that of alumina) which contains all three phases which crystallize.

On the other hand, even substances which are visibly very white, such as hydroxyapatite [$Ca_5(PO_4)_3OH$], boron nitride [BN] and boric acid [$H_3BO_3$], display rather poor reflectance spectra (Figs 8 and 11). This is proof that the perception by the naked eye of white reflected from a sample does not always correspond to the real optical behaviour of white body instrumentally achievable.

It is difficult to visualise the use of quartz ($SiO_2$) as a ceramic, because it has a tendency to give rise to transparent glassy quartz during heating at high temperature. It will be useful as a component of enamels, owing to its high efficiency in reflecting, and its transparency as a glass. Any improvement in the efficiency of enamels is difficult to perceive when utilizing MgO, or $La_2O_3$ or also tetragonal $ZrO_2$ instead of $Al_2O_3$ as opacifier. $CaCO_3$ is not useful because it is not sinterable to obtain a ceramic, and introduces bubbles inside the glassy body of an enamel. Its spectra, however, show that the eventual introduction of the $Ca^{2+}$ ion as an oxide (CaO) in the composition of an enamel should not depress the reflective efficiency of the glassy matrix of the enamel.

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