

## Chapter 2

# Methods of Measuring Refractive Indices

Several methods for the RI measurement are available. RIs of bulk crystals and glasses can be measured very precisely using prisms cut-out of these materials [1–7] by the interference methods using a Michelson-type interferometer [8–10] or by the ellipsometer methods [11, 12]. RIs of solid *powders* are usually measured by the immersion method [13–15], whereas the optical diffraction method [16–18] is suitable for powders suspended in the liquid media. The authors' own works in this field are listed below.

### 2.1 Method of the Prism

A ray of light is directed on to a face of a prism at an angle of incidence  $\theta_i$ , in such a way that the ray is parallel to the principal cross-section of the prism. The ray is refracted at the entrance face and then deviates from the original direction by an angle  $\delta$ , forming an angle  $\beta$  with the normal to the exit face (exit angle) so that

$$\delta = \theta_i + \beta - \alpha \quad (2.1)$$

where  $\alpha$  is the angle between the faces of the prism. Then RI can be calculated [4] as

$$n = \sqrt{\sin^2 \theta_i + (\sin \beta + \cos \alpha \cdot \sin \theta_i)^2 / \sin^2 \alpha} \quad (2.2)$$

In practice, one of the three angles ( $\theta_i$ ,  $\beta$  or  $\delta$ ) is usually fixed and only two have to be measured. The most common method is Fraunhofer's method of minimum deviation. Here, the prism is positioned so that the deviation angle  $\delta$  reaches the minimum value ( $\delta_o$ ), the incident and exit angles are equal, and Eq. 2.2 is simplified to

$$n = \frac{\sin \frac{1}{2}(\delta_0 + \alpha)}{\sin \frac{\alpha}{2}} \quad (2.3)$$

Alternatively, the  $\theta_i$  angle is fixed at  $90^\circ$ , the light source being placed in the plane of the entrance face. With this geometry, one can observe the border between the illuminated and the dark fields, which corresponds to the complete internal reflection of the ray from the entrance face. Equation 2.2 then converts into

$$n = \sqrt{1 + \left( \frac{\cos \alpha + \sin \beta}{\sin \alpha} \right)^2} \quad (2.4)$$

The usual precision of RI measurements is  $\pm 1.5 \times 10^{-5}$  using standard goniometers with 2–5" angle readings. It can be increased to  $10^{-6}$ , although this requires special goniometers with 0.1" angle readings, careful thermostating and puts additional demands on the size and quality of the sample. The same method can be applied to measure RI in the UV and IR ranges adjacent to the visible range, using fluorescent eyepieces [8] or image-transforming tubes [9]. Measurements at non-ambient temperatures ( $-70$  to  $+90$  °C) are possible, albeit with reduced precision (several units of  $10^{-4}$ ). Various modifications of the prism method have been described [19]. A disadvantage of this method is the need to prepare prism-shaped samples, which is unsuitable for routine measurements.

## 2.2 Method of the Critical Angle

For the light to pass from a medium with higher RI to that with lower RI, the condition

$$\sin \theta_r = \frac{n_i}{n_r} \sin \theta_i < 1 \quad (2.5)$$

must be met. If  $\theta_i$  exceeds the critical angle (corresponding to  $\sin \theta_r = 1$ ) the light will experience total internal reflection (TIR) back into the high-RI medium. In this method, the sample is contacted to a reference prism with precisely known (high) RI and the critical angle, and hence, the sample RI is determined. It is impossible to measure RI higher than that of the measuring prisms, which for a long time were made of heavy flint glass ( $n = 1.78$ ), but the introduction of thallium halide alloys or high-RI composite materials raised this limit to 2.00–2.20. Using photoelectric measuring device [19], RI can be measured with the precision of  $10^{-5}$  in the visible and near-IR ranges.

Based on TIR of incoherent illumination, Abbé refractometers usually measure RIs of liquids but can also be used for solids with flat surfaces [20, 21]. Although TIR methods give good precision ( $10^{-4}$ – $10^{-5}$ ) for transparent liquids and solids, a small

loss in the sample or incomplete contact between the sample and the prism severely increases the uncertainty in the critical angle and in the resulting RI value [21].

## 2.3 Interferometric and Diffraction Methods

On the contrary, for the interferometric methods, the accuracy in the RI measurement is not affected by the small loss in the sample, since the actual path length difference is measured. Although these methods are usually employed to detect very small relative phase differences, they were extended to measuring absolute RI values. A standard Michelson interferometer (MI) is used to measure such values in transparent solid plates, because of its simplicity [22, 23]. In the MI method, a transparent plate sample is rotated in one of the two arms of the interferometer continuously changing the optical path length difference, and hence producing a fringe pattern (with respect to the angle of incidence). From this pattern, and knowing the sample thickness, RI can be easily determined with the accuracy of  $\sim 10^{-3}$ , the error arising mainly from the sample thickness measurement, because the RI and the thickness cannot be independently determined from a single fringe pattern.

The Fabry–Perot (FP) method is another interferometric technique used for the same purpose [24]. In this case, the fringe pattern is determined solely by the phase difference between the directly transmitted light wave and the collinearly propagating waves, therefore the FP fringe pattern is more stable against environmental perturbations than the MI fringes. However, in both methods, the thickness measurement limits the accuracy of the RI determination. Gillen and Guha combined the MI and FP methods and successfully determined both the RI and the thickness values from the two correlated sets of fringes [25]. Coppola et al. [26] also applied FP method to obtain both RI and the thickness with the relative uncertainty of *ca.*  $10^{-4}$ . A recent modification of the FP method [27] used two lasers with considerably different wavelengths, to measure the thickness and the RI with a relative uncertainty of  $10^{-5}$ . We used the FP method to determine the RI of agglomerated nanodiamond particles in water colloidal solutions, having measured the particle sizes by dynamic laser scattering [28]. For different sizes of agglomerates, RI varied from 1.74 to 1.79, showing the agglomerates to consist of diamond ( $n = 2.42$ ) and water ( $n = 1.33$ ), presumably with water shells of 0.5 nm thickness surrounding 5 nm diamond particles [28].

## 2.4 Immersion Method

The immersion method, commonly used to determine RIs of polycrystalline materials, is based on the phenomenon of ‘optical dissolution’, whereby a crystalline grain becomes invisible in a liquid with the same RI. The right liquid can be chosen using the following effect. When a heterogeneous system, i.e. crystal grains

in a liquid, is viewed under microscope in transmitted light, a bright rim (the Becke line) is visible around the phase boundaries. If the focal distance is increased, the Becke line always shifts towards the phase with higher RI, i.e. towards the centre of the particle if it has higher RI than the medium and vice versa.

Immersion liquids ('oils') with precisely known RI are commercially available. Standard sets have RIs ranging from 1.400 to 1.780, in 0.003–0.005 increments, and there are special compositions with higher RI, viz. S-As<sub>2</sub>S<sub>2</sub>-AsBr<sub>3</sub> (1:1:3) with  $n = 2.00$ , S-As<sub>2</sub>S<sub>3</sub>-AsBr<sub>3</sub> (1:7:12) with  $n = 2.07$  and Se-As<sub>2</sub>S<sub>2</sub>-AsBr<sub>3</sub> (1:1:3) with  $n = 2.11$ . Interim values of RI can be obtained by adding methylene iodide (CH<sub>2</sub>I<sub>2</sub>) with  $n = 1.74$  to standard oils. 'Fine-tuning' can be achieved by varying the temperature, because on warming RIs of liquids decrease much faster than those of crystals; so a crystal can be immersed into a liquid with higher RI and the whole warmed until the point of optical dissolution is reached.

Determination of higher RI presents considerable difficulties. Alloys of sulphur with selenium ( $n$  from 2.07 to 2.70) or thallium halides (TlCl  $n = 2.25$ , TlBr  $n = 2.42$ , TlI  $n = 2.78$ ) can be heated to a plastic state and used as immersion media for measuring very high RIs. If heating affects the sample (through thermal decomposition or chemical interaction with the alloy), cold compression of the alloy powder and the sample into thin transparent disks can be used instead [29, 30]. For this purpose, we also prepared solid solutions TlCl/TlBr and TlBr/TlI with the content of each component varying from 0 to 100 % in 10 % steps. The RI of these materials was calibrated by using them as immersion media for measuring the *already known* RI of some crystals. This allowed us to measure high RIs with the accuracy of  $\pm 0.01$ .

It is known that in IR spectra of powders, the intensity of absorption bands and of diffuse scattering depends on the difference between the RIs of the sample and the medium into which it is compressed [31]. To account for these effects, we studied [32] the IR spectra of several substances with known RIs compressed into transparent tablets with KBr, TlCl and TlBr and elucidated the dependence of the intensity of diffuse scattering on the difference of RIs in the samples and the immersion medium,  $\Delta n_{s-m}$ . Using these dependences, we determined for the first time the RIs of the powders of Mn<sub>2</sub>O<sub>3</sub> (2.33),  $\gamma$ -MnS (2.45),  $\alpha$ -MnS (2.67), MnSeS (2.79), MnSe (3.12), SnO (2.78), SnOS (2.67), Sn<sub>5</sub>O<sub>6</sub>Se<sub>4</sub> (2.75), Sn<sub>2</sub>O<sub>3</sub>I<sub>2</sub> (2.36) and PtCl<sub>2</sub> (2.24). These values are the exact RIs for optically isotropic and the average RIs for optically anisotropic materials.

The dependence of the intensity and shape of the IR valence vibration band  $\nu_3(\text{N-O})$  at 1400 cm<sup>-1</sup> on the medium has been studied on optically isotropic crystals of Sr(NO<sub>3</sub>)<sub>2</sub> and Pb(NO<sub>3</sub>)<sub>2</sub> [33] pressed into powders of KBr, KCl, CsCl, CsI, AgCl, CuCl, TlCl and TlBr as the immersion media with the RIs ranging from 1.490 to 2.302. It was found that when  $\Delta n_{s-m}$  decreases, the diffuse background in IR spectra decreases but the intensity of absorption bands and their fine structures improve. Because, in an absorption band, the anomalous dispersion occurs and the RI of a substance increases, it may become equal to that of the immersion medium. At this point, the mixture becomes transparent, i.e. the system acts like a Christiansen optical filter. Then, fixing the frequency at which the maximum

transparency occurs and knowing the RI of the immersion medium at this frequency, the anomalous dispersion of the sample can be investigated, as has been done for  $\text{Sr}(\text{NO}_3)_2$ . In principle, using as the immersion medium a liquid with absorption bands in the visible range (where  $n \rightarrow \infty$ ), one can determine the RI of any high-RI substance by varying the wavelength and measuring the light scattering in this liquid.

The dependence of the intensity of  $\nu(\text{C}-\text{O})$  absorption bands on  $\Delta n_{s-m}$  has been studied [34]. For optically uniaxial crystals of  $\text{MgCO}_3$ ,  $\text{CaCO}_3$  and  $\text{PbCO}_3$ , it revealed two maxima, corresponding to the two principal RIs,  $n_e$  and  $n_o$ ; for optically biaxial  $\text{KHCO}_3$ , there were three maxima corresponding to three principal RIs ( $n_g$ ,  $n_m$ ,  $n_p$ ). In the crystals of  $\text{NH}_4\text{SCN}$  and  $\text{Y}(\text{OH})_3$ , in which quasi-isotropic ammonium cation and  $\text{YO}_6$  polyhedron are combined with anisotropic SCN and OH ions, the intensities of the  $\nu(\text{N}-\text{H})$  and  $\nu(\text{Y}-\text{O})$  bond vibrations show ‘isotropic’ dependence on  $\Delta n_{s-m}$ , while the vibrations of SCN and OH follow the ‘anisotropic’ trend [35].

For an optically anisotropic crystal (see Chap. 1), RI depends on the direction, i.e. aspect of the crystal, and for a given aspect, on the direction in which the light is polarised. In optically uniaxial crystals, the ordinary ray (governed by  $n_o$ ) is always polarised perpendicular to the optic axis, and the extraordinary ray (governed by  $n_e$ ) in the direction parallel to the optic axis. Thus,  $n_o$  can be measured in any aspect, but  $n_e$  only in the plane parallel to the optic (=main crystallographic) axis, the chances of finding which incidentally are slim. In an arbitrary aspect, one would observe  $n'_e$  instead, which can vary from  $n_e$  to  $n_o$ . The standard routine is to inspect a sufficient number of variously oriented crystal grains, find the limit of  $n'_e$  and assume it to be  $n_e$ . Similarly, for a random aspect of a biaxial crystal, one can measure two RIs,  $n'_g$  and  $n'_p$ , related to the principal RIs of the crystal as  $n_g > n'_g > n_m > n'_p > n_p$ . Note that the sufficient number of observations [36] should be at least equal to the birefringence  $\Delta n$  divided by the precision of the immersion method, i.e. usually  $\Delta n/0.002$  for uniaxial and  $\Delta n/0.003$  for biaxial crystals [36]. Hence, a reliable characterisation of a material may require tens or even hundreds of observations, even assuming fully random grain orientations. The latter is unlikely, as optically anisotropic grains tend to have also anisotropic shapes and mechanical properties, thus making the task even more difficult.

## 2.5 Optical Homogeneity

If a solid is heterogeneous but the grain sizes of the components are smaller than the wavelength of light, for crystal-optical investigation, it will appear as homogeneous with a uniform RI – although other methods, such as X-ray diffraction, may recognise the presence of different phases. The phenomenon was first described by Belyankin [37] with respect to nuclei of the mineral mullite formed within a glass and was extensively explored since then [38–50]. Over 400 cases have been

described so far of this effect, known as ‘optical homogeneity’ in Western literature, while the term ‘optical mixing’ [38] is used in Russian. Obviously, it becomes increasingly relevant with the current intense interest in sub-micron and nano-size powders. A similar effect was observed in solid products of shock compression, when partial phase transformations took place under certain thermodynamic conditions [50].

The usual sources of optically homogeneous systems are as follows: (i) high purity solid-phase processes which do not involve melting, (ii) chemical transformations with melting of initial components and the reaction products and (iii) physical transformations at temperatures above the melting point. It can occur both when a crystal undergoes a partial amorphisation (on heating) and when an amorphous solid or gel undergoes partial crystallisation, as well as during a concomitant or consequent crystallisation of different phases, one of them crystallising on the surface of another. In fact, the effect can be modelled by deliberately mixing fine-grain components. This has important implications for the immersion method, where a sample is always ground up prior to investigation, and optical homogenisation may occur at this stage.

It is also important that crystallisation of a new phase, microscopically intergrown with the starting material, is always oriented in certain directions with respect to the latter, in accordance with the elements of structural similarity between the two. Such intergrowth typically results in optical homogeneity. Thus, we observed a pseudomorphic optically homogeneous phase during crystallisation of alkali aluminates of the  $\beta$ -alumina type, when the structures of both the initial  $\Theta$ - $\text{Al}_2\text{O}_3$  and the product have common layered blocks of a layered spinel type. An optically homogeneous phase was observed in the products of the interaction between  $\beta$ -eucryptite and dolomite, where prismatic crystals with an RI intermediate between those of  $\gamma$ - $\text{LiAlO}_2$  and  $\beta$ - $\text{Ca}_2\text{SiO}_4$ , were observed.

In hydrothermal systems, we have observed generation of optically homogeneous phases in various forms, e.g. needle-shaped. The most probable reason for the formation of metastable combined phases seems to be the existence of similar structural elements in the two phases. The duration of optically homogeneous phase existence depends on temperature, the degree of structural likeness and the ability of the more disperse phase to crystallise. The available data suggest that optically homogeneous phases can be much more widespread than commonly recognised, and may emerge in any method of synthesis, even simple mechanical grinding. On the other hand, the existence of such phases can provide insight into the structural elements of the intergrown components.

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Batsanov, S.S.; Ruchkin, E.D.; Poroshina, I.A.

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