

Piezo- and Thermo-Optic Behavior of Spinel (MgAl_2O_4)*

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The piezo- and thermo-optic properties of oxides are extremely interesting and fascinating, since in some oxides such as vitreous silica, α -quartz, etc., the refractive index increases with hydrostatic pressure, while in some others such as MgO, SrTiO_3 , α - Al_2O_3 , etc., it decreases with pressure. Similarly, for MgO, α - Al_2O_3 , and vitreous silica the refractive index increases with temperature while for α -quartz it decreases. This paper reports the variation of refractive indices of both stoichiometric (*S*) and nonstoichiometric (*N*) spinel in the pressure range 0-14 kbars and in the temperature range 25-700°C determined by the interferometric technique. The refractive indices of both *S* and *N* spinels decrease linearly with pressure with the slopes $0.09_1 \times 10^{-3}$ and $0.06_5 \times 10^{-3}$ kbar^{-1} , respectively, and increase with temperature with the initial slopes of $0.90_3 \times 10^{-5}$ and $0.93_4 \times 10^{-5}$ deg^{-1} C, respectively. Since a unique value of polarizability cannot be attributed to the oxygen ion in oxides, it is impossible to predict the magnitude and sign of dn/dP and dn/dT unambiguously for an oxide. However, it is shown that an extension of the recent theoretical analysis of refractive behavior of ionic and covalent solids developed by Levine, leads to predictions of piezo- and thermo-optic properties of spinel which are in satisfactory agreement with experiment.

The piezo- and thermo-optic behavior of inorganic oxides presents a perplexing but fascinating study, for in some oxides such as α -quartz (1), vitreous silica (2), etc. the refractive index increases with hydrostatic pressure, while for MgO (3) and α - Al_2O_3 (4) the refractive index decreases with hydrostatic pressure. Similarly, for MgO, α - Al_2O_3 , and vitreous silica the refractive index increases with temperature, while for α -quartz it decreases (5). This result is rather surprising, since for these materials the optical behavior in the visible region of the spectrum is determined mainly by the oxygen ions. Hence, in order to understand this, a concerted effort has been undertaken to study the optical properties of a number of oxides with a

variety of cation-oxygen and oxygen-oxygen coordinations. The results of such measurements on spinel are reported in the article. Finally, these results are discussed along with similar data on MgO and α - Al_2O_3 .

Experimental

The experimental method and the computations involved in piezo-optic measurements at high pressures have already been discussed at length in regard to similar investigations with alkali halides (6). A schematic drawing of the experimental arrangement is shown in Fig. 1. In brief, the changes in the refractive indices were measured by observing the shift of the localized interference fringes across a fiducial mark on the crystal for $\lambda 5893 \text{ \AA}$. The change in the thickness of the sample was considered by using the elastic constants data of spinel as determined by Chang and Barsch (7) of this laboratory. No computations

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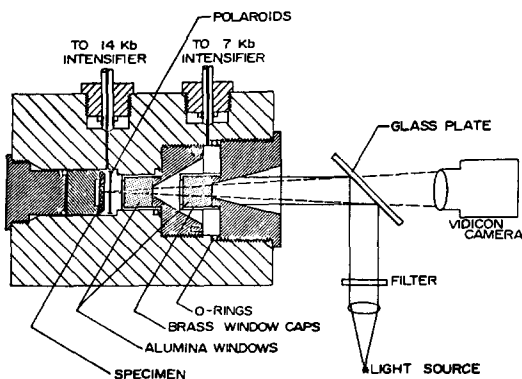


FIG. 1. Experimental arrangement used in the measurement of the change of the refractive index with hydrostatic pressure.

involving the third-order elastic constants were made since such data are not available in the literature. Nevertheless, the results of the present measurements indicate that the elastic behavior of spinel is quite linear in the entire pressure range (14 kbars) investigated. The change in the refractive index, Δn , was evaluated from the formula

$$\Delta n = (p\lambda - 2n\Delta t)/2t_0 \quad (1)$$

where p is the number of fringes shifted, t_0 is the initial thickness of the crystal, Δt is the change in thickness of the crystal under pressure, and λ is the wavelength of light employed.

The experimental arrangement for measurements on the variation of refractive index with temperature is exactly like Fig. 1, except that the high pressure optical vessel was replaced by a small tubular furnace with a small opening in its side. The crystal and a chromel-alumel thermocouple were arranged to be in proximity (no more than 1 mm apart). Since the furnace was essentially a closed unit, the temperature of the crystal as read by the thermocouple is estimated to be in error by no more than $\pm 1^\circ\text{C}$. The power to the furnace was supplied by a variac so regulated that the temperature of the furnace increased at about $1^\circ\text{C}/\text{min}$. The principle involved in these measurements on the change of index of refraction with temperature parallels that for the case of hydrostatic pressure. Thus, one can use Eq. (1) when Δt is considered as the change

in thickness of the specimen due to thermal expansion.

A single-crystalline boule of stoichiometric spinel grown by the Czochralski process was obtained from the Union Carbide Company. A crystal grown by the Verneuil process was also obtained from a commercial source. The compositions of the spinels were checked using spectrochemical analysis and it was found that the former was stoichiometric (28.4% MgO and 71.6% Al_2O_3), whereas the latter had 12.8% MgO and 86% Al_2O_3 by weight with minor amounts of Ti and Si. As no reliable data on the refractive index of spinel are available in the literature, and since its refractive index is much higher than the upper limit of the available refractometers, prisms of each crystal were prepared from the bulk samples used in the study, and their refractive indices were determined by the standard minimum deviation technique using a Gaertner research model spectrometer. The values obtained for the sodium D line at 22°C are given in Table I.

Results and Discussion

The variation of the refractive index with volume strain of spinel (stoichiometric-*S* and nonstoichiometric-*N*) is shown in Fig. 2. The stress necessary to produce this strain is also included in Fig. 2. The values of the elastic constants used for the computation of the strains are $c_{11} = 2.808 \pm 0.005$, $c_{12} = 1.532 \pm 0.005$ in units of 10^{12} dyn/cm².

It is seen from Fig. 2 that the refractive indices of both stoichiometric and nonstoichiometric spinels decrease linearly with pressure with slopes of 0.091×10^{-3} kbar⁻¹, respectively. Again from Fig. 2, the values of $\rho(dn/dp)$ were evaluated, since

$$\rho(dn/dp) = -\Delta n((\Delta V)/(V_0)) = B(\Delta n/\Delta P) \quad (2)$$

and are also entered in Table I. Table I lists also the strain polarizability parameter A_0 defined by

$$\rho(dn/dp)_{\text{obs}} = A(1 - A_0) \quad (3)$$

with

$$A_0 = -(\rho/\alpha)(\partial\alpha/\partial\rho). \quad (4)$$

TABLE I
THERMO-OPTIC PROPERTIES OF $MgAl_2O_4$, MgO AND Al_2O_3 , $\lambda = 5893 \text{ \AA}$ AND $P = 1 \text{ BAR}$

Crystal	n	$\rho \frac{dn}{dp}$	$\frac{dn}{dT}$ ($\times 10^5 \text{ deg}^{-1} \text{ C}$)	γ ($\times 10^5 \text{ deg}^{-1} \text{ C}$)	Drude			Lorentz-Lorenz		
					$\frac{\tau}{\lambda}$ ($\times 10^5 \text{ deg}^{-1} \text{ C}$)	$1 - A_0^D$	(τ^D/η)	$\frac{\tau}{\lambda}$ ($\times 10^5 \text{ deg}^{-1} \text{ C}$)	$1 - A_0^L$	(τ^L/η)
Spinel (S)	1.718	-0.181 ₅	0.90 ₅	2.03	0.94	-0.33	0.46	0.57	-0.19	0.28
Spinel (N)	1.724	-0.130 ₅	0.93 ₄	2.03	1.17	-0.23	0.58	0.71	-0.14	0.35
MgO	1.7379	-0.30 ₂	1.6	3.30	1.02	-0.52	0.31	0.63	-0.31	0.19
Al_2O_3 ω	1.768	-0.24	1.36	1.74	1.57	-0.42	0.90	0.92	-0.23	0.53
ϵ	1.760	-0.26	1.47		1.73	-0.43	0.99	1.09	-0.25	0.63

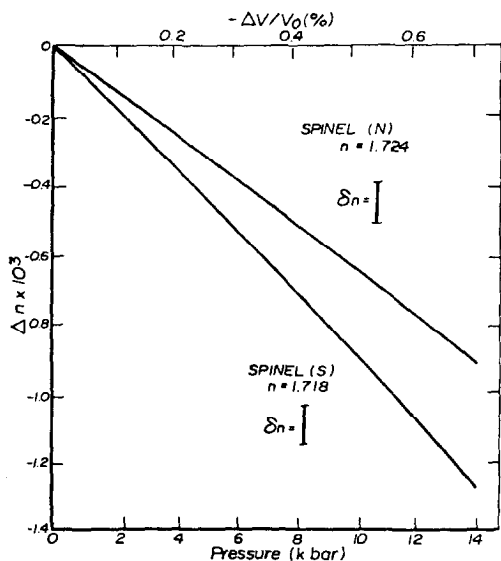


FIG. 2. Variation of the refractive index of MgAl_2O_4 (stoichiometric-S and Nonstoichiometric-N) with pressure and volume strain, $T = 22^\circ\text{C}$.

The factor A depends on the dispersion law used and is given by $(n^2 - 1)/2n$ or $(n^2 - 1) \times (n^2 + 2)/6n$ for the Drude or the Lorentz-Lorenz equations, respectively; α is the polarizability of the scattering ions. Since the contribution of the cations is negligible compared to the anions in these oxides, α can essentially be considered as the polarizability of the oxygen ion. It is seen that the value of A_0 is greater than unity for both Drude and Lorentz-Lorenz cases. This indicates that the change in ionic polarizability is greater than the effect of changing the number of ions per unit volume.

The function dn/dT can be related to the strain polarizability parameter A_0 by the equation

$$dn/dT = -\gamma A[(1 - A_0) - \tau/\gamma] \quad (5)$$

where γ is the coefficient of volume expansion, and $\tau = (1/\alpha)(\partial\alpha/\partial T)_V$, the pure temperature coefficient of the polarizability. The variation of the refractive indices of stoichiometric and nonstoichiometric spinels with temperature is shown in Fig. 3. The values of dn/dT and γ , the coefficient of volume expansion (8), used for evaluating dn/dT with the help of Eq. (5) are also given in Table I. It is seen

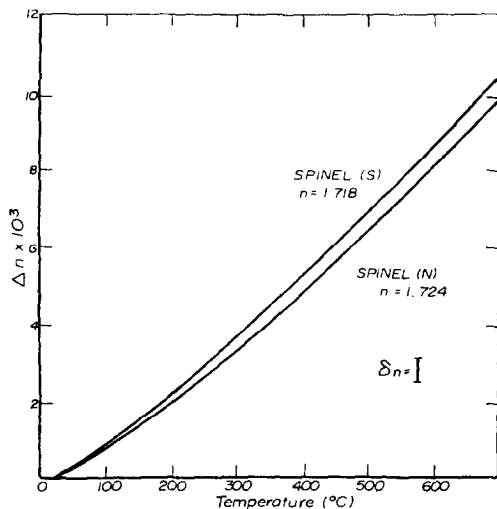


FIG. 3. Variation of the refractive index of MgAl_2O_4 (stoichiometric-S and nonstoichiometric-N) with temperature, $P = 1$ bar.

from Eq. (5) that dn/dT can be separated into two components, (i) $(1 - A_0)$ term—the change in refractive index due to volume expansion or thermal dilatation and (ii) τ/γ term—the pure temperature effect at constant volume. Table I lists these two components for all the materials studied. It is seen that in every case the $(\partial\alpha/\partial T)_V$ term is the dominant factor and thus determines the nature of observed dn/dT .

Table I also lists the values of the refractive indices and the observed values of $\rho(dn/d\rho)_T$ and dn/dT of MgO and $\alpha\text{-Al}_2\text{O}_3$ so that they can be compared with those obtained on spinel (MgAl_2O_4 or $\text{MgO} \cdot \text{Al}_2\text{O}_3$). It is seen that the refractive index of spinel—both stoichiometric as well as nonstoichiometric—is less than that of MgO and of $\alpha\text{-Al}_2\text{O}_3$. As mentioned earlier, in all these three materials the refractive index in the visible region of the spectrum is mainly determined by the oxygen ions. But since the crystal structure of these three compounds are very different, the coordination of the oxygen ions, the bond distances and bond angles are all quite different from each other. In the case of MgO , each oxygen is octahedrally bonded to six magnesium, with the Mg-O distance as 2.10 \AA , while in $\alpha\text{-Al}_2\text{O}_3$, each oxygen is bonded almost tetrahedrally to four Al with

Al-O distances of 1.86 and 1.97 Å. In the case of spinel, on the other hand, each oxygen is bonded to three Al along $\langle 100 \rangle$ directions with Al-O distance of 1.93 Å and also to one Mg along [111] with the Mg-O distance of 1.92 Å.

Tessman et al. (9) made an extensive study of the electronic polarizability of various ions in ionic and partially covalent crystals using a least-squares fit of index of refraction data. Naturally, the assumption of ions in partially covalent solids is only an approximation, but useful results can often be obtained. They found that unique values could be assigned to the polarizability of many ions with a precision of two decimal places. However, in the case of the doubly charged oxygen ion, the polarizability was found to range from 0.5 to 3.2 (Å³) in different crystals. Similarly, no unique value could be assigned to the other Group VI ions S²⁻, Se²⁻, and Te²⁻ as well.

Yamashita and Kurosawa (10), using quantum mechanical calculations find that the energy of the (2p)⁶ configuration of the O²⁻ ion is higher than the singly ionized oxygen ions O⁻. It is also well known (11) that the doubly charged oxygen ion has not been observed in the gaseous state. However, according to Yamashita, the doubly charged oxygen ion can exist in the solid state because of the stabilizing effect of the crystalline field. Therefore, it is expected that the oxygen wavefunction, which depends on the local crystal field of any particular crystal, will vary from oxide to oxide. This explains why Tessman et al. could not find a unique value of the optical polarizability of the O²⁻ ion, but concluded that the polarizability of the O²⁻ ion could vary in the wide range of 0.5–3.2 (Å³).

Thus it appears that it is almost impossible to predict, at the present state of our knowledge, the exact value of the polarizability of the oxygen ions in spinel, even though the polarizability of oxygen ions in α -Al₂O₃ and MgO are known. In other words, it is not always possible to arrive at the exact value of the refractive index of an oxide, even if the polarizability of the various constituent ions is known. Naturally, the values of dn/dP and dn/dT also cannot be predicted from such

an approach using the polarizability of the oxygen ions. Since these are derivatives of the refractive index, sometimes even the sign cannot be predicted from such an approach using the polarizability of oxygen ions.

In recent times, however, new approaches have been developed to interpret optical properties of solids. One is based on the concept of ionicity and the dielectric theory of covalent systems developed by Phillips and VanVechten (12). The other is the dispersion theory of refractive index behavior developed by Wemple and Didomenico (13). While both these theories are based on single oscillator models, they emphasize different ends of the spectrum and are therefore not identical. Neither theory can explain the pressure dependence of refractive index of ionic solids, without introducing additional parameters. Levine (14) has generalized the Phillips–VanVechten approach to complex inorganic oxides as well. He has shown that each metal–oxygen bond in such oxides can be characterized by attributes such as bond polarizability, ionicity, etc. We have extended this approach to understand the pressure and temperature variations of the optical properties of spinel.

According to Levine (14), the dielectric susceptibility χ of a system is given by

$$\chi = (n^2 - 1)/4\pi = \sum F_\mu \chi_\mu, \quad (6)$$

where χ_μ is the susceptibility of a crystal composed entirely of type μ bonds and F_μ is the fraction of such bonds. The subscript μ refers to corresponding quantities of the μ -type bond. The derivative with respect to pressure yields

$$(\partial\chi/\partial P)_T = \sum F_\mu (\partial\chi_\mu/\partial P)_T. \quad (7)$$

Similarly, for the temperature variation

$$d\chi/dT = (\partial\chi/\partial T)_V - \gamma\rho(\partial\chi/\partial\rho)_T, \quad (8)$$

where the first term describes the pure temperature effect and the second term gives the effect due to thermal expansion; γ is the coefficient of volume expansion. From Eq. (3) it follows that

$$\rho(\partial\chi/\partial\rho) = \mathbf{a}(1 - \Lambda_0), \quad (9)$$

TABLE II
THEORETICAL AND EXPERIMENTAL THERMO-OPTIC PROPERTIES OF SPINEL

Property	n_D	dn/dP (kbar ⁻¹)	dn/dT ($\times 10^5$ deg ⁻¹)	$1 - A_0$		τ/γ	
				Drude	Lorentz-Lorenz	Drude	Lorentz-Lorenz
Theoretical	1.71	-0.11	1.32	-0.37	-0.20	0.71	0.43
Experimental	1.72	-0.09	0.90	-0.33	-0.19	0.47	0.28

where

$$a = \chi \text{ or } 4\pi/3 \chi(\chi + (3/4\pi))$$

in terms of the strain polarizability parameter A_0 for the Drude and Lorentz-Lorenz equations, respectively. The pure temperature part $(\partial\chi/\partial T)_V$ is related to τ through

$$(\partial\chi/\partial T)_p = a\tau. \quad (10)$$

From the values of the A_0 and τ of MgO and α -Al₂O₃ given in Table I for the Drude and Lorentz-Lorenz cases, and using Eqs. (6)–(8) the refractive index of spinel (MgAl₂O₄), as well as its variation with pressure and temperature were calculated and are presented in Table II. It is seen that the agreement is satisfactory. Thus this approach using the metal-oxygen bond susceptibility to evaluate the piezo- and thermo-optic behavior of oxides appears to be promising. Extension of these calculations to other oxides is in progress.

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