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DENSITY AND REFRACTIVE INDEX OF SOME γ-IRRADIATED ALKALI SILICATE GLASSES

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The densities and refractive indices of some sodalime-silica glasses with replacements of CaO by either BaO or ZnO have been studied before and after being subjected to varying doses of γ-irradiation. Also, the effect of varying the Na_2O or Al_2O_3 content was investigated. The experimental results show that γ-irradiation produces a slight change in the density but a remarkable increase in the refractive index. These data are correlated with the way of housing of the cation introduced into the glass and its response on the compactness and flexibility of the glassy network. Also the effect of interaction of γ-rays with the glass and the creation of new induced defects in the glass network, which might affect the properties investigated, is considered.

Introduction

The specific volume of glass was among the first properties that were calculated[1,2] on the basis of the composition. The subject is well covered by the work of several authors.[2–5] Density is one of the properties which can be used for confirming the conclusions concerning the structure of glasses that are based on other properties. In addition, STANWORTH[6] had shown that the refractive indices of glasses would provide clues concerning their internal structure.

General aspects of radiation damage in the solid with reference to glassy systems have been reviewed by PRIMAK and BOHMANN.[7] BOPP et al.[8] showed that commercial borosilicate, soda lime and fused silica glasses, all are compacted [density is increased] under irradiation, while lead glass is expanded [density is decreased].

When glass is subjected to ionizing radiation (X or γ-ray photons), electrons are ionized from the valence band if the energy of the radiation is greater than the band gap, and the excess energy is converted to kinetic energy. Then, the electrons move through the glass matrix and will either be trapped by preexisting flaws to form defect centers in the glass structure, recombine with the positively charged holes, or in the case of high energy (Compton) electrons will produce a secondary electron cascade by knock-on collisions with the bound electrons. High energy electrons in the glass can also produce

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short range atomic displacements, resulting in closely associated vacancy-interstitial pairs which largely recombine. Of further consideration is the penetration depth of the radiation, since the observed radiation-induced effects may be either bulk or layer phenomena depending upon the thickness of the damage layer. The defects occur in solids because the free energy is minimized by admitting a certain amount of disorder in the structure.[9]

It has been proposed[9–11] that, when the structural R–O–R bond in SiO_2 is irradiated, one Si–O bond breaks, an electron is trapped by the Si, forming an E′ center, and a hole is trapped by the resulting nonbridging oxygen (NBO).

A common feature of many of these defect centers that has only recently been recognized is the set of local structural changes by which they are stabilized in the glass subsequent to irradiation, one means being structural relaxation of the matrix. For example, in the case of the E′ center, the RO_3 group that does not trap the unpaired electron releases to planarity. In the case of the peroxy linkage, the radical may twist away from the adjacent network-former after hole trapping, thereby inhibiting rebonding.[12] The second means, is diffusivity of the modifying cation (either to the defect of away from it) after trapping in order to maintain charge neutrality and hence to stabilize the trapping site.

In the present communication, the densities and refractive indices of some selected alkali-silicate glasses were measured. Special attention is given to the changes obtained when comparing the density and refractive index values before and after several accumulated γ-doses. The change in glass composition was also considered.

Experimental

Glass preparation

Raw materials used were of the purest grade available. Silica was added as finely pulverized Dutch silver sand washed with 1:1 HCl followed by washing with 4% HF. Sodium, calcium and barium oxides were introduced in the form of their respective carbonates. Zinc and aluminium oxides were introduced as such.

The glasses were melted in platinum (2% rhodium) crucibles in an electric furnace at a temperature of 1450 °C. Melting was continued until the glass was well refined and homogeneous. The melts were cast into slabs of rectangular shape of about 1 cm^2 in cross-section and 4 cm in length, and were given proper annealing.

Irradiation procedure

In the present work, the ^{60}Co γ-source used was a Gamma Chamber 4000A manufactured by the Atomic Energy Agency of India. The dose rate for irradiation was 1.5 Gy/s. The glass samples were placed in the γ-cell in a manner that each sample was subjected to the same dose, the given doses are 5.4, 16.2, 32.4, 54 kGy.

Measurenments

Density. The density of the glass was determined by the Archimedes method in which the sample was weighed both in air and immersed in xylene at 20 °C. The density was calculated from the formula d = a/(a – b) 0.86, where d is the density of the glass, a and b, the weight of the sample in air and in xylene, respectively, and 0.86 is the density of xylene at 20 °C.

Refractive index. For refractive index measurements, the samples were ground and polished with the minimum amount of water. The refractive index of the glass was determined by an Abbe refractometer model G Carl Zeiss Jena (Germany). The measurements were undertaken using sodium light (λ = 589.3 μm) as an index in which the refractive index is related to the wavelength. The experimental data were found to be reproducible within ± 2%.

Results and discussion

Density

Effect of glass composition. Figure 1 and Table 1 show the densities of some silicate glasses of different compositions. Since silicon and sodium oxides form the main bulk of the glasses studied, the density of theses glasses is essentially determined by the

Table 1
Glass composition (wt.%)

Glass No.	SiO_2	Na_2O	CaO	Al_2O_3	BaO	ZnO
1	68	20	8	2	2	–
2	68	20	4	2	6	–
3	68	20	2	2	8	–
4	68	20	–	2	10	–
5	68	20	8	2	–	2
6	68	20	4	2	–	6
7	68	20	2	2	–	8
8	68	20	–	2	–	10
9	70	15	6	5	4	–
10	73	15	8	2	–	2
11	73	15	6	2	4	–

properties of these two oxides. In the alkali silicate glasses, the introduction of soda to silica results in the formation of single-bonded or non-bridging oxygen atoms, i.e., oxygen atoms linked to only one silicon atom.[13] The sodium ions are linked to the surrounding oxygens by bonds which are much more ionic and also much weaker than the silicon-oxygen bonds. Thus the structure of sodium silicate glass is weaker than that of vitreous silica.[14] As the soda content is increased, non-bridging oxygens are formed until eventually the network consists of isolated SiO_4 tetrahedra linked together by ionic Na–O bonds. Accordingly, the increase of the soda content in the glass studied results in an increasing number of non-bridging oxygens, and this may cause a decrease in the volume of the glass network structure. This will consequently explain the observed increase in density with increasing soda content in the sodium lime silicate glass studied.[15] Moreover, the experimental results obtained for glasses containing different concentrations of alumina can be explained by assuming that, whith the increase of Al_2O_3, the opportunity arises for Al^{3+} ions to assume four-fold coordination as AlO_4 groups, which strengthen and compact the glass network leading thus to the observed densities.

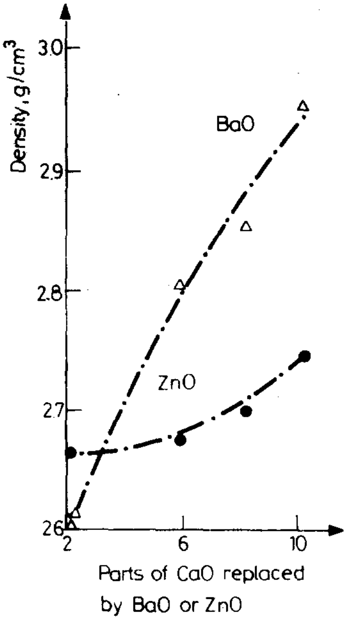

Fig. 1. Relationship between density and parts of CaO replaced by BaO or ZnO

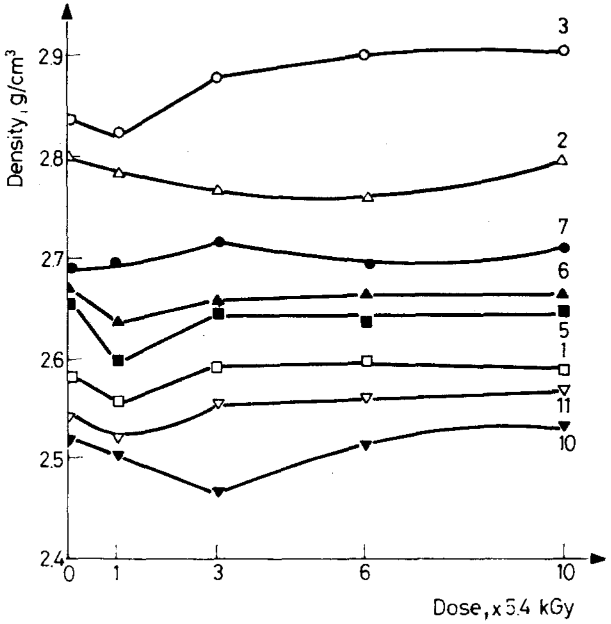

Fig. 2. Effect of γ-irradiation on the density ot glasses Nos 1, 2, 3, 5, 6, 7, 10 and 11

Table 2
Effect of irraiation on density and refractive index of the glasses investigated

Glasp. No.	Pre-irradiated	Density, g/cm^3				Refractive index (η_o)	
		5.4 kGy	16.2 kGy	32.4 kGy	54 kGy	Pre-irradiated	54 kGy
1	2.583	2.558	2.595	2.603	2.580	1.5000	1.6752
2	2.807	2.785	2.773	2.763	2.803	1.5023	1.6772
3	2.848	2.835	2.880	2.908	2.909	1.5038	1.6801
4	2.955	2.888	2.975	2.979	3.003	1.5042	1.6832
5	2.664	2.608	2.650	2.640	2.657	1.5005	1.5104
6	2.672	2.634	2.660	2.664	2.663	1.5010	1.5157
7	2.697	2.699	2.722	2.695	2.715	1.5018	1.5194
8	2.738	2.671	2.718	2.812	2.700	1.5020	1.5125
9	2.580	2.568	2.596	2.606	2.589	1.5015	1.6783
10	2.522	2.514	2.468	2.518	2.539	1.5002	1.5100
11	2.549	2.523	2.555	2.557	2.579	1.5013	1.6621

Effect of irradiation. From the results shown in Fig. 2 and tabulated in Table, 2, the density of silicate glasses have nearly the same trend in which a slight decrease in density occurred at the first irradiation stage. The subsequent increase in the radiation dose, however, resulted in a slight increase in density, although the density values of most of the glasses remained close to the value of the pre-irradiated glass.

This slight change in density may be due to the possible atomic displacements that resulted from γ-collision with the glass, which may materially alter the stresses in the glass. Also, the recoiled oxygen ions from the sample may give an explanation for the volume changes.

If a glass has been compacted by external pressure, radiation will decrease its density; however, it will not completely restore the equilibrium density. PRIMAK et al.[16,17] suggested that the irradiated state is a separate state for each glass, which is attained independently of the original state. A further conclusion is that the radiation-compacted structure is different from the pressure-compacted one, which is also supported by annealing experiments.

Towards the end of its track the γ-irradiation produces a large number of displacements creating an area of highly disturbed material. Within these "displacement spikes" individual displacements have no meaning.

BRINKMAN[18] proposed that this disturbed region can be considered as quenched glass and is, therefore, an area of volume expansion. This expanded region will exert pressure on the surrounding material which will become compacted, while any resulting strain is released by plastic flow. The outer area, therefore, can be considered a region of annealed glass of higher density. These effects do not reach their maximum at the same level of irradiation. Depending on the size of the displacement spikes, their zones of compaction and expansion and the overlap of these zones, the glass will either contract or expand upon irradiation.

Refractive index

Effect of composition. The results of refractive index measurements on glasses of different compositions are plotted in Fig. 3. This figure shows that the calcium to barium ratio in the glass has a considerable effect on its refractive index. The refractive index of the glass sample containing a CaO to BaO ratio of 8:2 (glass No. 1) is lower than that of the glass with a calcium to barium ratio of 4:6 (glass No. 2).

In glasses containing calcium and zinc oxides, the ratio of theses two oxides has the same effect on the refractive index of the glass, although of much smaller magnitude than the calcium to barium ratio. The glass sample containing 10% ZnO (all CaO are replaced by ZnO; glass No. 8) has a higher refractive index than the sample with a CaO to ZnO ratio of 8:2 (glass No. 5).

The higher refractive index of glass containing a high proportion of ZnO can be attributed to the presence of part of ZnO in $[ZnO_4]$ groups as building units which lower the average coordination number of oxygen. This results in compacting of the struture, which is, in turn reflected in the increase of the refractive index. Moreover, the introduction of Zn^{2+} ions leads to a high polarization of neighboring oxygen ions. As a result the electromagnetic waves passing through the glass containing zinc-oxide suffer higher refraction due to the presence of oxygen ions with higher polarizability.

Ba^{2+} ions are normally housed in the glas interstices and these divalent Ba^{2+} cations become more strongly held in the interstices than the Na^+ ions. The groups of SiO_4 tetrahedra around the divalent cations become more stable than the same groups which might be formed around the monovalent cations. Consequently, the structure is expected to develop a series of interstices of more or less regular type surrounding the Ca^{2+} and Ba^{2+} cations with a proportion of large, irregular intersices in which Na^+ ions has to be housed, possibly with more than one Na^+ ion in each of the large, irregular rings. As a result, sodium ions are comparatively weakly held in the structure, and most of the more regular interstices are occupied by divalent cations.[19] When the number of Ba^{2+} ions incrases, they may be associated with two oxygen ions bonded to SiO_4 tetrahedra, thus forming ionic bridging linkages between the SiO_4 tetrahedra. The increase observed in the refractive index could be attributed to the volume contraction or compacting influence of ions.

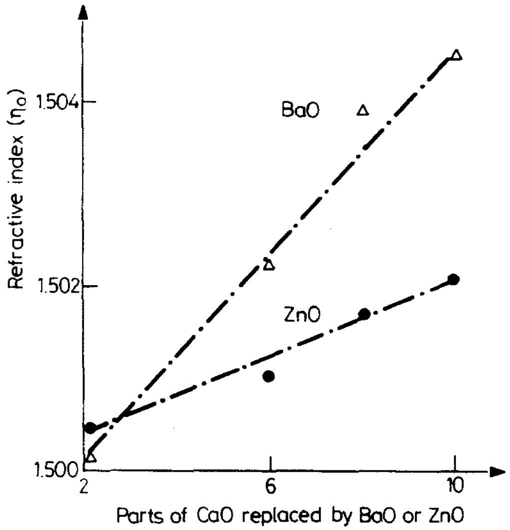

Fig. 3. Relationship between refractive index and parts of CaO replaced by BaO or ZnO

Effect of irradiation. From the results tabulated in Table 2, the remarkable increase in the value of refractive index of the glass samples exposed to 54 kGy can be explained as follows. At a low irradiation doses, the refraction lines become increasingly diffuse, and at higher doses, they can hardly be distinguished from the background, resembling the refraction lines of the unirradiated base glass. In addition, the difference between the unirradiated and irradiated silicate glass lies not in the Si–O bond length, which is the same in the two cases, but rather in the decreased Si–Si distance, indicating a smaller Si–O–Si bond angle. Moreover, the formation of magnetic centers during irradiation can reasonably be taken to mean rupture of covalent bonds. STEVENS et al.[20] measured the increase in magnetic succeptibility with neutron irradiation, and determined a rate of 3.7 centers formed per incident fast neutron before reaching saturation. It seems significant that the concentration of magnetic centers approaches the same saturation value in silica and in quartz.[21]

Conclusions

Density and refractive index measurements were performed on some silicate glasses before and after γ-irradiation. Experimental results show changes upon substitution of CaO by BaO or ZnO or increasing the Al_2O_3 or Na_2O content, or increasing the γ-dose. Experimental results reveal that the density is only slightly affected while the refractive index shows a remarkable change.

The data are explained on the basis of the assumption of the expected change in glass structure upon varying the chemical composition together with the introduction of induced defect centers when the glasses are subjected to γ-rays.

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