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Characterization of Fluorophosphate Optical Glasses

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This paper reports different physical properties concerning Abbe numbers (ϑ_e), nonlinearity refractive indices (n_2) and coefficients (γ), electronegativities (ΔX), ionic characteristics (I_c), and the nonlinear susceptibilities ($\chi_{1111}^{e(3)}$) derived from the measured refractive indices at λ_e = 5461 Å, $\lambda_{F'}$ = 4800 Å, and $\lambda_{c'}$ = 6438 Å and also the densities of the optical glasses based on $Pb(PO_3)_2$ and $Ba(PO_3)_2$ by varying the CaF_2 and NaF contents as the network modifiers (NWM).

Introduction

About a decade ago, a theoretical formulation was made by Boling *et al.* (*1*) to predict the nonlinear refractive index changes in optical materials. According to these authors the nonlinear refractive index coefficient n_2 must be small enough to minimize the environmental effects on the dopant ion in its laser operation. From the Lawrence Livermore Laboratories a review article was published in 1975 declaring the prepared materials optically active on the basis of the magnitudes of their dispersive power which has been popularly known as the Abbe number with values between 50 and 100 (*2*). In the same paper a simple empirical formula was given to define the nonlinear refractive index parameter n_2 through the measured refractive indices at three different wavelengths. About 5 years ago two new sets of glasses involving $Ba(PO_{3)2}$ and $Pb(PO_3)_2$ as major constituents were formed by changing the concentrations of the alkali and alkaline fluorides as the network modifiers (*3*). Although these authors could report the formation details of these fluorophosphate glasses, they did not carry out any property characterization. Therefore, we have undertaken a study to understand the different physical properties in order to verify the optical efficiencies of these glasses.

Theoretical Considerations

Nonlinear properties. The optical quality defining parameter known as the Abbe number (ϑ_e) is obtained from (*4*)

$$\vartheta_e = \frac{n_e - 1}{n_{F'} - n_{c'}},$$

where n_e is the refractive index at λ_e = 5461 Å, $n_{F'}$ at $\lambda_{F'}$ = 4800 Å, and $n_{c'}$ at 6438 Å. The reciprocal of ϑ_e gives the dispersive power of the glass of interest in the study.

Another important optical characteristic parameter that is normally called the nonlinear refractive index (n_2). A simple mathematical expression used in evaluating the value of n_2 is given below through the values of the Abbe number and n_e as (*2*)

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TABLE I

PHYSICAL PROPERTIES SUCH AS THE MOLECULAR WEIGHT (MW), DENSITY (D), REFRACTIVE INDEX (n_e), DIELECTRIC CONSTANT (ε), ABBE NUMBER (ϑ_e), AND DISPERSIVE POWER ($1/\vartheta_e$) OF $Pb(PO_3)_2$ AND $Ba(PO_3)_2$ GLASSES WITH BOTH NaF AND CaF_2 AS THE NETWORK MODIFIERS

Glass type	Chemical composition	MW (g)	D ($g \cdot cm^{-3}$)	n_e	ε	ϑ_e	$1/\vartheta_e$
Pb glass							
(A)	100 $Pb(PO_3)_2$	365.13	4.640	1.738	3.021	35	0.028
(B)	80 $Pb(PO_3)_2$ + 20 CaF_2	307.72	4.660	1.738	3.021	33	0.030
(C)	80 $Pb(PO_3)_2$ + 10 CaF_2 + 10 NaF	304.02	4.655	1.734	3.007	35	0.029
(D)	80 $Pb(PO_3)_2$ + 20 NaF	300.50	4.651	1.731	2.995	35	0.028
(E)	70 $Pb(PO_3)_2$ + 30 CaF_2	279.02	4.650	1.732	3.000	36	0.027
(F)	60 $Pb(PO_3)_2$ + 20 CaF_2 + 20 NaF	243.09	4.610	1.728	2.987	41	0.025
(G)	60 $Pb(PO_3)_2$ + 40 NaF	235.87	4.605	1.717	2.949	41	0.024
(H)	50 $Pb(PO_3)_2$ + 25 CaF_2 + 25 NaF	212.58	4.560	1.713	2.935	45	0.022
(I)	50 $Pb(PO_3)_2$ + 50 NaF	203.56	4.520	1.712	2.930	48	0.021
Ba glass							
(A)	100 $Ba(PO_3)_2$	295.28	3.673	1.589	2.528	64	0.016
(B)	80 $Ba(PO_3)_2$ + 20 CaF_2	251.84	3.760	1.605	2.575	61	0.016
(C)	80 $Ba(PO_3)_2$ + 10 CaF_2 + 10 NaF	248.23	3.735	1.594	2.541	64	0.016
(D)	80 $Ba(PO_3)_2$ + 20 NaF	244.62	3.695	1.592	2.534	64	0.016
(E)	60 $Ba(PO_3)_2$ + 40 CaF_2	208.40	3.743	1.599	2.555	64	0.016
(F)	60 $Ba(PO_3)_2$ + 20 CaF_2 + 20 NaF	201.18	3.710	1.587	2.517	65	0.015
(G)	60 $Ba(PO_3)_2$ + 40 NaF	193.96	3.660	1.582	2.502	65	0.015
(H)	50 $Ba(PO_3)_2$ + 50 CaF_2	186.68	3.713	1.584	2.510	66	0.015
(I)	50 $Ba(PO_3)_2$ + 25 CaF_2 + 25 NaF	177.66	3.633	1.576	2.484	68	0.015

$$n_2(10^{-13}\text{esu}) = \frac{68(n_e - 1)(n_e^2 + 2)^2}{\vartheta_e \left[1.517 + \dfrac{(n_e^2 + 2)(n_e + 1)\,\vartheta_e}{6n_e}\right]^{1/2}}.$$

Once this n_2 is estimated it becomes easy to determine the nonlinear refractive index coefficient (γ) as shown below (5)

$$\gamma\,(\text{cm}^2/\text{W}) = \frac{4\pi \times 10^7}{C\,n_e}\,n_2\,(\text{esu}),$$

where C is the velocity of light.

Bonding properties. The bonding nature of the glasses could be defined through the ionic characteristic parameter (I_c). This parameter is easily obtained from the estimated electronegativities (ΔX) of the glasses (6):

$$I_c = [1 - e^{-(\Delta X)^2/4}] \times 100.$$

If the factor I_c approaches a value of 50, it means that the material is said to be having both ionic and covalent bonding characteristics.

Susceptibility properties. The expression for a nonlinear susceptibility of material is given by (7)

$$\chi_{1111}^{e(3)} = \frac{g}{4}\left(\frac{n_e^2 + 2}{3}\right)^2 \left(\frac{n_e^2 - 1}{4\pi}\right)^2 \frac{1}{N\hbar\omega_0}$$

$$g \simeq 3 \text{ (for glassy materials)}$$

$$N = \frac{\pi}{r_o}\frac{(n_e^2 - 1)(n_e + 1)(X_{F'} - X_{c'})\vartheta_e}{2\,n_e}$$

$$r_o = 0.528 \times 10^{-8}$$

TABLE II

NONLINEAR REFRACTIVE INDICES (n_2), NONLINEAR REFRACTIVE INDEX COEFFICIENTS (γ), NONLINEAR FACTORS N AND ω_0, AND NONLINEAR SUSCEPTIBILITIES ($\chi_{1111}^{e(3)}$) OF $Pb(PO_3)_2$ AND $Ba(PO_3)_2$ OPTICAL GLASSES WITH NaF AND CaF_2 AS THE PROPERTY MODIFIERS

Glass type	n_2 (10^{-13} esu)	γ 10^{-11} (cm^2/W)	N ($\times 10^{-16}$)	ω_0 ($\times 10^{-3}$)	$\chi_{1111}^{e(3)}$
Pb glass					
(A)	5.1506	1.2417	646.67	96.59	82.44
(B)	5.5380	1.3353	609.95	93.93	89.81
(C)	5.2275	1.2633	631.68	95.71	83.47
(D)	4.6933	1.1364	635.74	96.17	81.23
(E)	4.8668	1.1774	658.82	97.77	77.63
(F)	4.1136	0.9974	728.79	102.85	65.49
(G)	3.9578	0.9657	721.99	102.96	62.61
(H)	3.4178	0.8359	793.03	107.98	53.27
(I)	3.1196	0.7637	838.41	111.04	48.61
Ba glass					
(A)	1.4416	0.3800	910.89	124.31	21.13
(B)	1.6364	0.4270	890.44	121.73	23.96
(C)	1.4412	0.3789	924.79	124.90	21.18
(D)	1.4601	0.3844	909.95	124.08	21.42
(E)	1.5241	0.3995	926.77	124.65	21.71
(F)	1.3821	0.3651	925.07	125.54	20.21
(G)	1.3848	0.3669	906.86	124.74	20.19
(H)	1.3390	0.3544	937.03	126.51	19.56
(I)	1.2707	0.3378	940.72	127.49	18.46

$$\omega_0 = X_e + \left[\frac{(n_e + 2)(n_e + 1)(X_{F'} - X_{c'})\vartheta_e}{6\, n_e},\right]$$

where $X_{F'} = 10^{16}/(4800)^2$, $X_e = 10^{16}/(5461)^2$, and $X_{c'} = 10^{16}/(6438)^2$.

Reflection losses ($R\%$). The loss of incident light energy by reflection from the glass surface is an important property, useful in the measurement of surface coating uniformity and in the measurement of the light transmission characteristics of various colors of glasses. For normal (or) perpendicular incidence of light on a glass surface, the fraction reflected by a single surface can be calculated from Fresnel's formula which states that the reflection losses (R) of a glass (*8*)

$$R\% = \left[\frac{(n_e - 1)}{(n_e + 1)}\right]^2 \times 100,$$

where R = light fraction reflected, n_e = glass refractive index.

Molar refractivity R_M, defined through the refractive index (n_e), molecular weight (MW), and density (D) of the material studied, is given as (*9*)

$$R_M = \left[\frac{(n_e^2 - 1)}{(n_e^2 + 2)}\right]\frac{MW}{D}.$$

By the use of Clausius–Mosotti equation (*10*) the molecular electronic polarizability is determined as

$$\alpha_e = \left[\frac{(\varepsilon - 1)/(\varepsilon + 2)}{\frac{4\pi}{3}\left(\frac{D \times N_A}{M}\right)}\right].$$

Field strengths (F). In order to understand the effects of ionic field strengths gen-

TABLE III

THE VALUES OF ELECTRONEGATIVITIES CONCERNING THE ANIONS(X_a), THE CATIONS (X_c), THE GLASS (ΔX), AND THE MAGNITUDE OF IONIC BONDING CHARACTERISTICS OF $Pb(PO_3)_2$ AND $Ba(PO_3)_2$ GLASSES TO STUDY THE INFLUENCES OF CaF_2 AND NaF

Glass type	X_a	X_c	ΔX	I_c%
Pb glass				
(A)	3.440	2.210	1.230	32
(B)	3.548	1.968	1.580	46
(C)	3.548	1.961	1.587	47
(D)	3.548	1.954	1.594	47
(E)	3.602	1.847	1.755	54
(F)	3.656	1.712	1.944	61
(G)	3.656	1.698	1.958	62
(H)	3.710	1.588	2.123	68
(I)	3.710	1.570	2.140	68
Ba glass				
(A)	3.440	1.525	1.915	60
(B)	3.548	1.420	2.128	68
(C)	3.548	1.413	2.135	68
(D)	3.548	1.406	2.142	68
(E)	3.656	1.315	2.341	75
(F)	3.656	1.301	2.355	75
(G)	3.656	1.287	2.369	75
(H)	3.710	1.263	2.448	78
(I)	3.710	0.938	2.773	85

erated by the Na^+ and Ca^{+2} ions in the glass matrices studied here, we have estimated the concentration of these ions. The alkali and alkaline ion concentration is derived from the measured densities (D), the molecular weight (MW), and the molarity of these ions available in the glass matrix (*11*),

$$(N)\ Na^+ \text{ or } Ca^{+2}/cm^3 = \frac{N_A \times M\% \text{ of ion} \times D}{MW}.$$

With these obtained N values of Na^+, Ca^{+2}, the ionic radius (r_p) and ion–ion spacing (r_i) can be evaluated from the relations (*12*)

$$r_p\,(\text{Å}) = \frac{1}{2}\left(\frac{\pi}{6N}\right)^{1/3}$$

and

$$r_i\,(\text{Å}) = \left[\frac{1}{N}\right]^{1/3}.$$

The field strength caused by these ions in the glass matrices is described through the oxidation numbers and the ionic radii of Na^+ and Ca^{+2} ions (*13*):

$$F = \left[\frac{Z}{r_p^2}\right]$$

Results and Discussion

For purposes of convenience the $Pb(PO_3)_2$-based glasses have been designated as Pb glasses (A → I) describing the chemical compositions of nine glasses. Similarly the $Ba(PO_3)_2$-based glasses have also been abbreviated as Ba glasses (A → I). The chemical compositions of these two categories of glasses are given in the second column of Table I. Table I reports the values of molecular weight (MW), densities (D),

TABLE IV

TOTAL NUMBER OF ATOMS AVAILABLE IN EACH GLASS (n_i), ATOMIC VOLUME (V) REFLECTION LOSSES ($R\%$), MOLAR REFRACTIVITY (R_M), AND THE MOLECULAR POLARIZIBILITIES (α_e) OF $Pb(PO_3)_2$ AND $Ba(PO_3)_2$ GLASSES INCORPORATED WITH DIFFERENT PROPORTIONS OF CaF_2 AND NaF

Glass type	n_i	V (g/cm^3/atom)	$R\%$	R_M (cm^3)	$\alpha_e \times 10^{21}$ (cm^3)
Pb glass					
(A)	900	8.74	7.27	31.68	1.26
(B)	780	8.47	7.26	26.58	1.05
(C)	770	8.48	7.21	26.18	1.04
(D)	760	8.50	7.16	25.81	1.02
(E)	720	8.33	7.18	24.00	0.95
(F)	640	8.24	7.13	21.01	0.89
(G)	620	8.26	6.97	20.17	0.80
(H)	575	8.11	6.91	18.28	0.72
(I)	550	8.19	6.89	17.63	0.70
Ba glass					
(A)	900	8.93	5.19	27.13	1.07
(B)	780	8.59	5.39	23.06	0.91
(C)	770	8.63	5.24	22.55	0.89
(D)	760	8.71	5.22	22.40	0.89
(E)	660	8.44	5.31	19.01	0.75
(F)	640	8.47	5.14	18.21	0.73
(G)	620	8.55	5.08	17.68	0.70
(H)	600	8.38	5.11	16.84	0.67
(I)	575	8.51	5.00	16.19	0.64

refractive indices (n_e), dielectric constants (ε), Abbe number (ϑ_e), and dispersive power ($1/\vartheta_e$) of lead- and barium-based glasses with the mixed alkali and alkaline fluoride contents. Because of the presence of lead the magnitudes of MW, D, ε, and $1/\vartheta_e$ are found to be better with the Pb glasses than with the Ba glasses. However, there are lower values of ϑ_e for lead glasses than for barium glasses as is shown in Table I. None among the Pb glasses (A $\rightarrow$ I) possesses a dispersive power defining factor (ϑ_e) of 50 or more. However, the situation with Ba glasses is different, with the ϑ_e's approaching values of 60 and more. By following the reports made earlier (*1, 2*), it becomes easier to suggest that the Ba glasses are certainly better optical glasses.

On looking at the results given in Table II, it is found that the nonlinearity refractive index parameters (n_2 and γ) of Pb glasses are better by 2 to 3 orders of magnitude than those of the barium-based glasses. According to the observations made by (*1, 2*) we also observe that the Ba glasses are better, with the required smaller values of n_2 and γ, than the Pb glasses. Although the nonlinearity refractive index coefficients are in the required optical efficiency limitations, the values of nonlinearity susceptibilities are found to be 3 to 4 orders of magnitude lower compared to those of the lead-based systems with sufficiently greater N and ω_0 values, as shown in Table II. Thus the different physical properties given in Tables I and II confirm the optical efficiency of the barium-based glasses. Table III reports the electronegativities and the ionic characteristics

TABLE V

CONCENTRATIONS OF ALKALI (Na^+), ALKALINE (Ca^{+2}) CONTENT, IONIC RADII (r_p), INTERIONIC DISTANCES (r_i), AND FIELD STRENGTHS OF THESE IONS IN THE OPTICAL GLASSES PREPARED FROM $Pb(PO_3)_2$ AND $Ba(PO_3)_2$

Glass type	N (ions/cm³) 10^{-18}		r_p (Å)		r_i (Å)		$F \times 10^{-15}$ (cm^{-2})	
	Na^+	Ca^{+2}	Na^+	Ca^{+2}	Na^+	Ca^{+2}	Na^+	Ca^{+2}
Pb glass								
(A)	—	—	—	—	—	—	—	—
(B)	—	0.1825	—	3.2980	—	8.1830	—	1.8388
(C)	0.0923	0.0923	4.1400	4.1400	10.2730	10.2730	0.5834	1.1669
(D)	0.1865	—	3.2750	—	8.1240	—	0.9324	—
(E)	—	0.3012	—	2.7910	—	6.9240	—	2.5675
(F)	—	0.2285	—	3.0600	—	7.5920	—	2.1359
(G)	0.4705	—	2.4050	—	5.9680	—	1.7289	—
(H)	—	0.3231	—	2.7260	—	6.7640	—	2.6907
(I)	0.6689	—	2.1390	—	5.3074	—	2.1853	—
Pb glass								
(A)	—	—	—	—	—	—	—	—
(B)	—	0.1799	—	3.3140	—	8.2220	—	1.8211
(C)	0.0907	0.0907	4.1646	9.1646	10.3325	10.3325	0.5766	1.1532
(D)	0.1823	—	3.2996	—	8.1866	—	0.9185	—
(E)	—	0.4328	—	2.4733	—	6.1364	—	3.2695
(F)	0.2222	0.2222	3.0887	3.0887	7.6630	7.6630	1.0482	2.0964
(G)	0.4547	—	2.4328	—	6.0359	—	1.6896	—
(H)	—	0.5991	—	2.2192	—	5.5060	—	4.0610
(I)	0.3079	0.3079	2.7704	2.7704	6.8735	6.8735	1.3029	2.6059

of the glasses. An examination of this table shows that the $Ba(PO_3)_2$ glasses are much stronger in ionicity compared to the $Pb(PO_3)_2$ glasses. Even among the $Pb(PO_3)_2$ glasses a majority of them [Pb glasses (E $\rightarrow$ I)] also demonstrate the ionic bonding nature. It is interesting to note that the glass with the chemical composition of

$$50\ Ba(PO_3)_2 + 25\ CaF_2 + 25\ NaF$$

has the highest I_c value of any of the glasses, as shown in Table III, and the lowest I_c value has been reported for a Pb glass without CaF_2 and NaF of composition

$$100\ Pb(PO_3)_2.$$

Table IV lists out the determined values of numbers of atoms (both cations and anions) present in each of the glasses (n_i), atomic volumes (V), the reflection losses encountered by the glass surfaces ($R\%$), molar refractivities (R_M), and electronic polarizabilities (α_e) of $Pb(PO_3)_2$ and $Ba(PO_3)_2$ glasses as a function of both the alkali and the alkaline fluorides as the modifiers of physical characteristics. From this table, it is observed that the Ba glasses have lower reflection losses, molar refractivities, and polarizabilities than the Pb glasses. In Table V, yet another important physical property, namely, the ionic field strengths (F) of Na^+ and Ca^{+2} ions, is given for comparison. These field strengths have been computed by the estimation of the ionic radii (r_p) and interionic distances (r) for the Na^+ and Ca^{+2} ions. The results of this table show that the mixed ions could cause significant effects on the Ba glasses with appreciable variations in different physical properties.

When compared with the individual field strengths of Na^+ and Ca^{+2} (Table V), it is found that Ca^{+2} ions could certainly dominate over the Na^+ ions in influencing the surroundings of the glass matrices of the phosphates of lead and barium.

Conclusions

From the measured densities and refractive indices of the $Ba(PO_3)_2$ and $Pb(PO_3)_2$ glass systems other physical properties have been estimated to make a comparison of their optical efficiencies. On the basis of the results listed in Tables I–V, we find that the $Ba(PO_3)_2$ glasses are promising materials with superiority in different nonlinear parameters (ϑ_e, n_2, γ, and $\chi^{e(3)}_{1111}$) and a few supportive physical parameters over the $Pb(PO_3)_2$-based systems. Even among the nine $Ba(PO_3)_2$ glasses, the chemical composition 50 $Ba(PO_3)_2$ + 25 CaF_2 + 25 NaF appears to be an ideal system for further work on laser emission characterization.

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