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OF Al (PO3)3 - CONTAINING FLUOROPHOSPHATE
GLASSES

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OPTICAL AND OTHER PHYSICAL PROPERTIES OF Al(PO$_3$)$_3$ - CONTAINING FLUOROPHOSPHATE GLASSES

J. Yasi, J. Pueong and G. Fuxi

Shanghai Institute of Optics and Fine Mechanics, Academia Sinica, Shanghai, China

Abstract.- In this paper, the optical and some other physical properties of fluorophosphate glasses in binary systems containing Al(PO$_3$)$_3$ and the influence of various fluorides on the properties of glass with low Al(PO$_3$)$_3$ content have been studied. The positions of low Al(PO$_3$)$_3$ content glasses in $n_d$-$v$ diagram have been plotted and the partial properties of fluorides in glass have been calculated.

Fluorophosphate glass is a glass with special optical properties such as high Abbe value, transmittance in near UV and IR regions and low nonlinear refractive index ($n_2$), it is now under development. Comparing the properties of various glassy metaphosphate, it shows that Al(PO$_3$)$_3$ possesses a higher refractive index, a greater Abbe value$^{[1]}$ as well as better physical and chemical properties. Therefore Al(PO$_3$)$_3$ has been introduced into many fluorophosphate glasses. The authors have already studied the formation and structure of Al(PO$_3$)$_3$ - containing fluorophosphate glasses$^{[2]}$, and in the present work, the optical and some other physical properties of those glasses are investigated with the emphasis placed on the low Al(PO$_3$)$_3$ content glasses.

The following glass systems were selected for the investigation

1) (100-X) Al(PO$_3$)$_3$.X RF$_n$ ( R = Li, Na, Ba, Sr, Al ).

2) (10 Al(PO$_3$)$_3$.20 AlF$_3$.50 SrF$_2$.20 LiF) + 5 RF$_n$ ( R = Li, Na, K, Be, Mg, Ca, Sr, Ba, Zn, Cd, Pb, Al, Gd ).

3) (5 Al(PO$_3$)$_3$.28 AlF$_3$.30 SrF$_2$.27 CaF$_2$.10 LiF) + 3 RF$_n$ ( R = Li, Na, K, Mg, Ca, Sr, Ba, Zn, Al, Ga ).

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Aluminium metaphosphate and fluorides were used as starting materials. Glasses with high \( \text{Al}(\text{PO}_3)_3 \) content were melted in sintered alumina crucibles, and others in platinum crucibles. Different melting conditions were selected according to different glass systems.

The refractive indices \((n_d, n_F, n_c, n_g)\), the thermal expansion coefficients \(\alpha\), the moduli of elasticity \(E\), and the densities of the glasses were determined, the molecular volumes of glasses, the average atomic volumes of fluorine and oxygen \(V_{OF}\), and the partial refractive indices and Abbe values of various fluorides in glasses were calculated.

1) In the previous work\(^2\), on the basis of experimental results of glass formation, devitrification and structure study, we pointed out that the network of the glasses with low \(\text{Al}(\text{PO}_3)_3\) content is greatly destroyed. Therefore the property variation of these glasses should be similar to that of the oxide glasses in the destroyed region. In general, the refractive index and dispersion increase with increasing ionic radius \(r\), while \(\alpha\) and \(E\) vary with the electrostatic force \(Z/a^2\) between cations and fluorine ions (Fig.1 and 2).

![Fig.1](image1.png) ![Fig.2](image2.png)

Fig.1 \(n_d vs r(A)\) in the system with 10 mol\% \(\text{Al}(\text{PO}_3)_3\)

Fig.2 \(\alpha_{30-T_g} vs Z/a^2\) in the system with 10 mol\% \(\text{Al}(\text{PO}_3)_3\)

2) In the region with low \(\text{Al}(\text{PO}_3)_3\) content, some fluorides such as \(\text{LiF}, \text{MgF}_2\) and \(\text{AlF}_3\) could reconnect the disrupted glass network\(^2\). This is also reflected in the variation of the physical properties of glass. In \(\text{Al}(\text{PO}_3)_3 - \text{RF}_n\) systems, those containing \(\text{LiF}\) or \(\text{AlF}_3\) possess smaller \(V_{OF}\) (Fig.3), and with the increase in the \(\text{RF}_n\) content, the increase in \(V_{OF}\) is relatively slow. The \(\text{LiF}, \text{MgF}_2, \text{AlF}_3\)-containing glasses all have higher \(E\) and lower \(V_{OF}\) (Fig.4,5), it can be considered as the increase in compactness of glass structure.

3) In the glasses with very low \(\text{Al}(\text{PO}_3)_3\) content, besides the particular role of
LiF, MgF₂, AlF₃ mentioned above, other cations filling in the interspace between structural chains can also enhance the glass structure to some extent due to the electrostatic attraction. Generally speaking, \( V_{OF} \) depends on the related ionic radii. However, for the glasses with low \( \text{Al}(PO₃)₃ \) content, from the diagram of \( V_{OF} \) vs \( Z/\alpha^2 \) (Fig.5), it can be obviously seen that \( V_{OF} \) decreases with increasing \( Z/\alpha^2 \).

Combining this and the variations in \( \alpha \) as well as \( E \), it can be considered that electrostatic force has relatively great influence on the properties of glass when the glass network is heavily destroyed.

4) Fig.6 shows the position of the studied glasses containing 5%, 10% \( \text{Al}(PO₃)₃ \) in \( n_d-n_v \) diagram with the addition of various fluorides. Using the optical constants of all the glasses studied in this work, the partial refractive indices and Abbe values of some fluorides introduced have been calculated, and the results obtained are listed in Table 1 together with some data from literature. From Table 1, we can see that there is great deviations among the data from different sources. Nevertheless, we can also see that with the increase in the metaphosphate content, the partial refractive index increases, while the \( v \) decreases and the influence of fluorides on the properties of glass lessens. Hence, the partial properties of fluorides can only be suitable for calculating physical properties of glasses in a certain region.
Fig. 6 Positions of glasses with addition of fluorides on \( n_d - \nu \) diagram.

a. \( \text{Al}(\text{PO}_3)_3 = 5 \text{ mol}\% \)

b. \( \text{Al}(\text{PO}_3)_3 = 10 \text{ mol}\% \)

Table 1. The Partial Properties of Some Fluorides

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<tr>
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<tr>
<td>Fluoride</td>
<td>( \text{Al}(\text{PO}_3)_3&lt;10 )</td>
<td>( \text{Al}(\text{PO}_3)_3&gt;30 )</td>
<td>( \text{Al}(\text{PO}_3)_3&lt;15 )</td>
<td>( \text{Al}(\text{PO}_3)_3&gt;30 )</td>
</tr>
<tr>
<td>LiF</td>
<td>( n_d )</td>
<td>( \nu )</td>
<td>( n_d )</td>
<td>( \nu )</td>
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<tr>
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References

