Study of Dielectric Relaxation Phenomena of Na$_2$ZnP$_2$O$_7$ Diphosphate Glass Doped with Cobalt (II) By Impedance Spectroscopy

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Abstract — Na$_2$ZnP$_2$O$_7$ diphosphate glass doped with Co(II) have been studied by dielectric measurement spectroscopy. The imaginary part of the permittivity is explained by using a model which is based on the existence of a distribution function of the interaction energies between the sodium ions and the glassy framework, taking into account the existence of three sites involved in the glass structure. The parameters of the global distribution function determined from the fitting of the experimental data, show that it is possible to obtain specific information concerning the structure of this material, such as the activation energy of the ion hosting sites and their distribution.

Keywords — Complex Impedance Spectroscopy, Dielectric Relaxation, Polarisation, Conductivity, Phosphate Glass.

I. INTRODUCTION

Double phosphate A$_2$BP$_2$O$_7$ containing simultaneously an alkaline ion A$^+$ and a divalent cation B$^{2+}$ form a large family of materials [1]. The crystalline structure of these phosphates which has been the object of various investigations is diverse, and it is difficult to classify these materials as a function of fundamental parameters such the cation sizes and the coordination number of the chemical bonding. Alkali metal phosphates (ABP$_2$O$_7$ or A$_2$BP$_2$O$_7$) have potential applications in X-ray and gamma radiation scintillators [2], catalysts and ion conductors [3], solid state lasers [4]. The layer structure of A$_2$BP$_2$O$_7$ is characterised by BO$_4$ tetrahedral sharing corners with four different [P2O$_7$] groups. The hosting sites of the cation A are in the interlayers space [5]. Although the cation B is known to be relatively fixed inside the structure, the interlayer position of the cation A makes possible its displacement from site to site via a classical thermally activated hopping process. This displacement is therefore assumed to be responsible for the ionic conductivity which can be investigated by mean of dielectric relaxation spectroscopy (DRS).

In the present work, we investigate the dielectrical properties of the Na$_2$ZnP$_2$O$_7$ (NZPO) compound doped with different concentrations of cobalt (II) as a function of frequency and temperature.

We thus aim at gaining some insights into the local mobility of the cation A and, hence, about its hosting sites.

II. MATERIALS AND METHODS

A. Synthesis

Pure NZPO compounds are synthesized by the conventional solid state phase reaction method. Stoichiometric mixture of high purity (> 99.9 %) NH$_4$H$_2$PO$_4$, Na$_2$CO$_3$ and ZnO powders are carefully ground together and progressively heated in a platinum crucible up to 633 K to allow ammonia and water to evacuate. After grinding, the so-obtained powders are heated at 993 K and maintained at this temperature during two days in order to complete the reaction, i.e. departure of CO$_2$. The products are then melted at 1093 K.

Doped precursor powders were prepared in a similar manner. The only difference is the addition of the adequate amount of cobalt nitrate Co(NO$_3$)$_2$ to the solid state reactions using the following scheme:

$$(1-x)ZnO + Na_2CO_3 + 2NH_4H_2PO_4 + xCo(NO_3)_2 \rightarrow Na_2Zn(1-x)Co_xP_2O_7 + (2x + 2)NO_3^+ + 6H_2O^1 + CO_2^1 + (x - 7)/2 O_2^1$$

B. Electrical proprieties

The electrical properties are determined by DRS [11], using a Novocontrol Broad-band Dielectric Spectrometer (BDS 4000). The frequency range is $10^{-2}$ to $10^6$ Hz, over the thermal interval 273-473K in several temperature cycles. For each temperature measurement, the sample is maintained for 30 min in order to reach thermal equilibrium.

The pellets used for DRS measurements are obtained by crushing the glass from the chemical synthesises, and then by compaction, up to 5 tons. The pellets are then placed in the spectrometer sample holder and isolated from the metallic plates by two insulating barriers, i.e. 10 μm thin films of PTFE (PolyTetraFluoroEthylene).
III. DIELECTRIC STUDY

When the applied electric field is alternative, with a pulsation \( \omega \), the imaginary part of the permittivity can be written, if considering a single type of dipoles having all the same relaxation time \( \tau \):

\[
\varepsilon'' = A(T) \frac{\omega \tau}{1 + \omega^2 \tau^2}
\]  

Where \( A(T) \) is an experimental factor related to the temperature \( T \) and the polarisability of the considered dipoles. In a real system, it can be assumed that all the dipoles are not similar and hence that the dielectric response results from a distribution of the relaxation time \( G(\tau) \). Hence it is possible to write:

\[
\varepsilon''(\omega) = \int_{0}^{\tau} G(\tau) \frac{\omega \tau}{1 + \omega^2 \tau^2} \, d\tau
\]  

Eq.2 can be transformed to as a discrete series to enable numerical calculations. It is possible to write, regrouping all the independent terms of \( \tau \) within the factor \( B(T) \).

\[
\varepsilon''(\omega) = B(T) \sum_{j} G(\tau_{j}) \frac{\omega \tau_{j}}{1 + \omega^2 \tau_{j}^2}
\]

Applied to ionic conducting solids, DRS allows us to assess the characteristic parameters of dielectric relaxation response considering that the dielectric relaxation can be regarded as resulting from an ionic hopping process between two neighbouring crystallographic positions[6,7,8].

The ion hop is characterised by the relaxation time \( \tau_j \), which is related to the potential barrier \( \Delta G_j \), to be overcome by the ion and therefore to the hopping probability. The relaxation time is thermally activated and can be expressed by:

\[
\tau_j = \tau_{0} \exp^\frac{-\Delta G_j}{kT}
\]

In this expression \( \Delta G_j = \Delta H_j - T \Delta S_j \) where \( \Delta S_j \) is the variation of entropy due to the number of possible configurations for this hopping process \( j \), \( k \) is the Boltzmann constant, and \( \nu_{0} = \frac{1}{\tau_{0}} \) is the attempt vibration frequency of the ion in its site, i.e. \( \nu_{0} \approx 10^{-13} \, s^{-1} \) Thus it is possible to relate the relaxation time to the enthalpy and entropy of the hopping process:

\[
\tau_j = \tau_{0} \exp^\frac{-\Delta S_j}{kT} \exp^\frac{\Delta H_j}{kT}
\]

Considering that the distribution of \( \Delta S_j \) is much narrower than that of \( \Delta H_j \), the expression of the imaginary part of the permittivity can be related to a distribution of enthalpy, i.e. the \( G(\Delta H_j) \) [9].

This distribution function accounts for thermals fluctuations, lattice vibrations or for the different local geometry and chemical environment around a given mobile ion. In a first approximation, it can be assumed, the energy levels \( \Delta H_j \) are distributed according to a Gaussian function [10]. Thus, if we refer to a statically distribution of the charge carriers and to a non-interacting ion-ion system, we can assume that \( G(\Delta H_j) \) corresponds to the contribution of different Gaussian functions, each of them arising from the contribution of different ion hosting sites, \( G(H_j) = g_1(H_j)+g_2(H_j) + \ldots \) where:

\[
g(H_j) = A \exp\left(-\frac{(H_j-H_{0})^{2}}{\gamma^{2}}\right)
\]

The central value \( H_{0} \) corresponds to the most probable energy level and the width \( \gamma \) reflects the dispersion in energy. \( A \) is the proportionality coefficient assigned to each Gaussian function and therefore represents the statistical weight of each cation hosting site.

The determination of \( G(\Delta H_j) \), which characterizes the studied system, is obtained by adjusting the experimental data with Eqs 3 and 4.

IV. DISCUSSION

Figures 1 illustrates the evolution of the dielectric loss at various temperatures as a function of frequency in the case of NPZO glass doped with 2 and 5 weight % of cobalt (II) respectively.

Fig. 2a shows the experimental and calculated spectra using the distribution function reported in fig.2b. It can then be seen that the energy distribution function \( G(\Delta H) \) results from the superposition of three Gaussian functions.

According to the initial assumption, i.e. the dielectric dipole corresponds to the reorientational motions of ions between two neighbouring sites, these three Gaussian contributions can be related to three different types of ionic hops. The distributions obtained here are significant and clearly emphasizes that the sodium cation environment changes throughout the glassy structure. If we refer to similar investigations carried out on sodium crystalline aluminosilicates such as, zeolites [12], or on sodium oxide glasses [13] it can be supposed that these different types of cationic sites differ by the strength of the global negative charge and the number of the oxygen atoms, i.e. the site coordination, which constitutes the hosting site.
Fig. 1 Variation of dielectric loss with angular frequency at different temperatures for NZPO glass sample doped with 2% (a) and 5% (b) of cobalt using insulating barriers.
It is also possible to follow each Gaussian contribution as a function of the measurement temperature. These evolutions are reported in Fig.3. We can thus see that, when the temperature increases the energy in each site slightly decreases. This decrease can be explained by the softening of the glassy structure upon increasing temperature and by concomitant lowering of the cation/network interaction.

Last but not least, comparison of figs.2a and b shows that the increase of Co(II) doping yields a decrease of the potential wells in which Na$^+$ are trapped.

V. CONCLUSION

This work presents an analysis of the dielectric loss measured on a sodium zinc diphosphate glass doped with 2 and 5% weight of cobalt. In these solids, the sodium is assumed to hop from a given site to a neighbour one above a potential barrier $\Delta H$. Because of the thermal fluctuations and of the structure complexity, it is possible to characterise the glass by a function of distribution $G(\Delta H)$.

The results reported here shown that it is possible to obtain specific information on the structure of these materials: the energy of the cation hosting sites and its distribution. It is thus emphasised that the activation energy for localized ion hopping slightly decreases with the temperature and it also decreases with the increase of Co doping.

REFERENCES