Preparation, characterization, ac conductivity and permittivity studies on vitreous M₄AlCdP₃O₁₂ (M = Li, Na, K) system

C.R. Mariappan, G. Govindaraj, S. Vinoth Rathan, G. Vijaya Prakash

Abstract

Vitreous M₄AlCdP₃O₁₂ (M = Li, Na, K) NASICON-type materials are synthesized, characterized and their electrical properties are reported at different temperatures in the frequency range of 42 Hz to 1 MHz. Ac conductivity and permittivity data are analyzed by using conductivity formalism. The dc conductivity and hopping frequency are thermally activated and their activation energies found to be in the range of 0.79–0.85 eV. The variation of dielectric permittivity with frequency is attributed to ion diffusion and polarization occurring in the NASICON-type vitreous materials. Scaling in conductivity and permittivity shows that the relaxation mechanisms are independent of temperature for the NASICON-type vitreous materials.

1. Introduction

The discovery of Na⁺-superionic conductors (NASICONs) Na₃AlₓZr₂Si₃₋ₓP₃O₁₂ represents an important improvement in solid electrolyte developments because their three-dimensional framework structure with high ionic conductivity comparable to that of two-dimensional networks, such as γ-alumina [1]. Numerous NASICON-related phosphate materials are prepared and their ionic conductivity has been reported [2–11]. The great stability of the tetrahedral oxyanions (PO₄)³⁻ gives phosphates a remarkable structural diversity in the case of monophosphates for which the atomic structure results from the Coulomb attraction between independent cations and oxyanions. The general formula of NASICON materials is MₓBₙP₃O₁₂, where M is an alkali ion and B is one or more ions in tr-, tetra-, or penta-valent state. The NASICON materials is built up of Bₙ(PO₄)₃ units in which two BO₆ octahedra are linked to three PO₄ tetrahedra by shared oxygens. During the past few years, particular attention has been paid to combine titanium and aluminum-based different materials with NASICON structure due to high ionic conductivity. The high conductivity value 0.7 × 10⁻³ S/cm at room temperature is obtained for the Li₁⁺₄ₓAlₓTi₂₋ₓP₃O₁₂ for x = 0.3, and Li₁⁺₄ₓAlₓGeₓ₋₂₋₂₋ₓP₃O₁₂ for x = 0.5 and y = 0.8. These are amongst the highest value reported so far [2,7,12]. However, the applicability as solid electrolyte is limited by a possible Ti⁴⁺/Ti³⁺ reduction in contact with anodes and by large grain boundary contribution. The above drawbacks can be removed (i) by avoiding Ti in the preparation and (ii) the vitrification of NASICON compositions.

Further, it is interesting to know the ability to vitrification for NASICON compounds and to examine the ionic conduction and relaxation mechanism. The primary source of experimental electrical information regarding the relaxation mechanism has been derived from frequency dependent dielectric spectroscopy. Measurement of frequency dependent conductivity and permittivity not only provide for information on the steady state transport, but also reflect at high frequency transient dielectric response resulting from localized displacement of the ions [13,14].
In the present paper, we report the synthesis, characterization and relaxation mechanism in $M_4$AlCdP$_3$O$_{12}$ ($M$ = Li, Na, K) aluminum-based NASICON-type vitreous materials. Ac conductivity and permittivity are analyzed by using conductivity formalism. We also present the time temperature superposition principle (TTSP) of conductivity and permittivity spectra at different temperatures for given NASICON-type sample and for various alkali ions present in NASICON-type vitreous materials at arbitrary temperature.

2. Experiment

The vitreous materials $Li_4$AlCdP$_3$O$_{12}$ (LACP), $Na_4$AlCdP$_3$O$_{12}$ (NACP) and $K_4$AlCdP$_3$O$_{12}$ (KTCP) were prepared by a solid-state reaction from $Li_2CO_3$, $Na_2CO_3$, $K_2CO_3$, Al$_2$O$_3$, CdO, NH$_4$H$_2$PO$_4$. The LACP system was prepared by taking stoichiometric quantities of $Li_2CO_3$, Al$_2$O$_3$, CdO, NH$_4$H$_2$PO$_4$ and these were heated. The overall reaction for the formation of LACP is given by:

$$2Li_2CO_3 + 1Al_2O_3 + CdO + 3NH_4H_2PO_4 \rightarrow \Delta$$

$$Li_4AlCdP_3O_{12} + 2NH_4O + 2CO_2$$

The procedure followed in the synthesis of samples are: (i) the calculated amounts of the starting materials were ground in an agate mortar for 45 min; (ii) the mixture was placed in silica crucible and slowly heated in an electrical furnace up to 523 K and further heated and held at a temperature of 623 K for 6 h in order to ensure the total decomposition of the reagents; (iii) after cooling the sample to room temperature, the mixture was again ground for 45 min in agate mortar and heated in a silica crucible for ~16 h at temperature 973–1073 K without melting the mixtures; (iv) the sample was heated further to temperatures of 1273–1373 K and the sample was melted at these temperature range and stirred 5–10 min to ensure homogeneity; (v) finally, the melt was poured into stainless steel plate and quenched by pressing with another stainless steel plate at room temperature.

X-ray powder diffraction (XRPD) patterns were recorded for all the compounds using the Rigaku miniflex X-ray diffractometer with another stainless steel plate at room temperature. The DSC thermogram was recorded for all the samples up to 523 K and further heated and held at a temperature of 1273–1373 K without melting the mixtures; (iv) the sample was heated further to temperatures of 1273–1373 K and the sample was melted at these temperature range and stirred 5–10 min to ensure homogeneity; (v) finally, the melt was poured into stainless steel plate and quenched by pressing with another stainless steel plate at room temperature.

The vitreous materials were prepared by cutting the prepared vitreous samples ∼10 mm diameter and ~1.5–2.0 mm thickness. Both sides of the samples were ground and polished by using silicon carbide plate and silicon carbide powder (mesh size 1200) with water as free lubricant. Then the samples were washed in flow water. Immediately the washed samples were heated slowly up to 423 K and held at this temperature for 1 h to remove the water on sample surface. Silver paint was pasted on parallel surface of the polished sample. Measurements were performed in vacuum atmosphere. Spring loaded contacts were connected the silver plates of the sample to the input ports of a commercial Hioki 3532-50 LCR HiTester which together with a dedicated computer and software acquired measurements of the parallel conductance ($G$) and capacitance ($\epsilon$) of the material as a function of frequency range of 42 Hz to 1 MHz at different temperatures.

3. Results and discussion

The amorphous nature of the NASICON-type samples was confirmed by XRPD studies and the results are shown in Fig. 1(a). Fig. 1(b) shows the FT-IR absorption spectra observed for the different NASICON-type vitreous materials. The entire region down to 400 cm$^{-1}$ is dominated by the vibrations of the PO$_4$ tetrahedra and these features are same in all samples. Table 1 shows the FT-IR absorption bands and their attribution of NASICON-type vitreous samples are assigned to various vibrational contributions of the basic phosphates [15–20]. Further, FT-IR spectra show the absence of carbonates related IR peaks in the region 1400–1500 cm$^{-1}$, suggesting fully vitrified composition. Density of the samples found by using Archimede’s principle and it is used to calculated the molar volume $V_m = M/\rho$, where $M$ is the corresponding molecular weight of the samples (Table 2).

The DSC thermogram was recorded for all the samples and it is shown in Fig. 1(c) at scan rate of 10 K/min. The endothermic peak and exothermic peaks observed in the DSC are corresponds to the glass transition and crystallization respectively for the present amorphous material. The glass transition ($T_g$) and crystallization temperatures ($T_c$) of all vitreous samples are shown in Table 2. It is to be noted that the sample NACP shows two exothermic peaks related to the crystallization temperatures ($T_{c1}$ and $T_{c2}$). Relatively high glass transition temperatures suggesting thermal durability of the present glasses.

3.1. Ac conductivity studies

The measured parallel conductance ($G$) data were converted with appropriate geometric factor to find the frequency dependent conductivity $\sigma(\omega)$. Ac conductivity for KACP is shown in Fig. 2, as an example. The conductivity ($\sigma(\omega)$) is found to be frequency independent in the lower frequency region ($\omega < \omega_x$), suggesting that the ionic diffusion is random.
Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Harmonics of O–P–O bending</th>
<th>O–P–O asymmetric bending</th>
<th>P–O–P stretching</th>
<th>Ionic group PO$_4$ $^{3-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LACP</td>
<td>413</td>
<td>574</td>
<td>731</td>
<td>949, 1074</td>
</tr>
<tr>
<td>NACP</td>
<td>444</td>
<td>550</td>
<td>719</td>
<td>1069, 1092</td>
</tr>
<tr>
<td>KACP</td>
<td>424</td>
<td>555</td>
<td>729</td>
<td>940, 1057</td>
</tr>
</tbody>
</table>

FT-IR absorption maxima (in cm$^{-1}$).

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho$ (gm/cm$^3$)</th>
<th>$V_m$ (cm$^3$)</th>
<th>$T_g$ (K)</th>
<th>$T_c1$, $T_c2$ (K)</th>
<th>$T_c1 - T_g$ (K)</th>
<th>$n \pm 0.03$</th>
<th>$E_{\sigma}$ (eV) $\pm 0.03$</th>
<th>$E_p$ (eV) $\pm 0.02$</th>
<th>$E_a$ (eV) $\pm 0.02$</th>
<th>$\Delta c$ ($\Delta R^2_{cr}$) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LACP</td>
<td>2.71</td>
<td>166.82</td>
<td>402</td>
<td>435</td>
<td>33</td>
<td>0.63</td>
<td>0.81</td>
<td>0.79</td>
<td>0.30</td>
<td>3.43, 0.99</td>
</tr>
<tr>
<td>NACP</td>
<td>3.12</td>
<td>165.47</td>
<td>388</td>
<td>420, 471</td>
<td>32</td>
<td>0.63</td>
<td>0.85</td>
<td>0.83</td>
<td>0.31</td>
<td>4.36, 1.05</td>
</tr>
<tr>
<td>KACP</td>
<td>2.41</td>
<td>240.95</td>
<td>389</td>
<td>409</td>
<td>20</td>
<td>0.63</td>
<td>0.78</td>
<td>0.79</td>
<td>0.29</td>
<td>3.38, 0.90</td>
</tr>
</tbody>
</table>

Fig. 1. (a) XRPD spectra for Li$_4$AlCdP$_3$O$_{12}$ (LACP), Na$_4$AlCdP$_3$O$_{12}$ (NACP), and K$_4$AlCdP$_3$O$_{12}$ (KACP) samples. (b) FT-IR spectra of NASICON-type samples. (c) DSC thermogram of NASICON-type materials.

les, i.e. the ions perform correlated forward-backward motions [21]. While the frequency exceeds hopping frequency $\omega_p$, $\sigma(\omega)$ increases with frequency following power law dispersion $\sigma(\omega) \propto \omega^n$ (where $n < 1$). The ac conductivity behavior is analyzed by using conductivity formalism i.e. universal power law (UPL) [13,22]:

$$\sigma(\omega) = \sigma_{dc} + A\omega^n = \sigma_{dc} \left[1 + \left(\frac{\omega}{\omega_p}\right)^n\right]$$

(1)

Ac conductivity spectra for different temperatures are fitted to Eq. (1) and the parameters $\sigma_{dc}$, $\omega_p$ and $n$ are extracted from the analysis. Continuous lines in Fig. 2 represent the UPL fit at different temperatures and similar results are obtained for other samples. The frequency exponent 'n' is found to be about 0.63 and is independent of temperature as well as composition. In general $\sigma_{dc}$ and $\omega_p$ parameters show strongly temperature dependent. Such dependence is fitted with the Arrhenius equations

$$\sigma_{dc} T = \sigma_{dc0} \exp\left(-\frac{E_{\sigma}}{kT}\right),$$

(2)

$$\omega_p = \omega_{p0} \exp\left(-\frac{E_p}{kT}\right),$$

(3)

where $\sigma_{dc0}$ is the dc conductivity pre-exponential factor, $k$ the Boltzmann’s constant, $E_{\sigma}$ the dc conductivity activation energy for mobile ions, $\omega_{p0}$ the pre-exponential of hopping frequency, $E_p$, the activation energy for hopping frequency. Fig. 3 (a) and (b) show the Arrhenius plots for $\sigma_{dc}$ and $\omega_p$, respectively. Both of these parameters show strong

Fig. 2. Ac conductivity of KACP at different temperatures. The solid lines are the fits to Eq. (1).
correlation with the temperature with the general trend of LACP > NACP > KACP. These features suggest strong M-site alkali ion radius dependence and possible thermally-activated drift mobility of ions according to hopping mechanism [22]. Activation energies, $E_{\sigma}$ and $E_p$, thus derived from the fitting are shown in Table 2. It is also to be noted that the activation energies, $E_p$ and $E_{\sigma}$ are very close to each other, within the experimental error. This indicates that the charge carrier have to overcome the same energy barrier while conducting as well as relaxing. Further, the ac conductivity activation energy $E_a$ is calculated by using $E_a = (1-n)E_{\sigma}$ and is also tabulated in Table 2. The ac activation energy follows the trend of KACP > LACP and NACP. A similar experimental situation has been reported for alkali ion migration barriers in silicates, M$_2$O–2SiO$_2$ (M = Na, K) and binary NASICON-type glasses M$_3$Fe$_2$P$_3$O$_{12}$, M$_3$Ga$_2$P$_3$O$_{12}$, M$_4$NbP$_3$O$_{12}$ (M = Li, Na, K) [23,24].

We also evaluated the physical parameters, the dielectric loss strengths [25] ($\Delta \varepsilon$) and many-particle crossover lengths [26] ($\langle R^2 \rangle_{cr}$) to give further emphasis to our studies. Both these parameters show lower values for KACP, similar to the trends shown by activation energies (Table 2).

Subsequently, to examined the correlation between the ac and dc conduction, we followed the Barton, Nakajima, and Namikawa (BNN) relation, where the following equation is to be valid for the most of the ion conducting materials [27]

$$\sigma_{dc} = \frac{\varepsilon_0}{\Delta \varepsilon \omega^p},$$

where $p$ is a numerical constant expected to be in the order of 1. Slope of the plot in Fig. 4 is equal to unity, implies that the dc and ac conductions are finely correlated and further suggesting that they follow the same mechanisms for different NASICON-type vitreous materials.

### 3.2. Ac permittivity studies

The imaginary part of the complex dielectric permittivity $\varepsilon''$ is obtained from Eq. (1) as

$$\varepsilon''(\omega) = \frac{\varepsilon_{dc}(\omega) - \varepsilon_{\infty}}{\varepsilon_{0}} \omega^{-(1-n)},$$

while the real part $\varepsilon'$ is given by:

$$\varepsilon'(\omega) = \varepsilon_{\infty} + \left( \frac{A}{\varepsilon_{0}} \right) \tan \left( \frac{\pi n}{2} \right) \omega^{-(1-n)},$$

where $\varepsilon_{\infty}$ is the high frequency value of $\varepsilon'(\omega)$. The measured capacitance (C) data were converted with appropriate geometric factor to find the real part of the dielectric permittivity $\varepsilon'(\omega)$ and the results are shown in Fig. 5 for KACP at different temperatures. We have fitted the $\varepsilon'(\omega)$ data at different temperatures to Eq. (6) using the magnitudes of $n$ and $A = (\sigma_{dc}/\varepsilon_{0})$, obtained from the ac conductivity analysis [23]. In the high frequency region, at low temperatures, the well-known non-Debye behavior $\omega^{-(n-1)}$ is observed [13,28]. However, in the low frequency region, at high temperatures, the sharp increase is due to the contribution from the charge accumulation at the electrode-sample interface. At high fre-
quencies, due to the high periodic reversal of the field at the
terface, the contribution from charge carriers towards the
dielectric constant decreases with increasing frequency [28].
Hence, $\varepsilon'(\omega)$ is found to decrease with increasing frequency.

3.3. Ac conductivity scaling

Ion dynamic process in ion conducting materials has been
the subject of intense scientific interest for the past several
years [29]. The ac conductivity is a direct evidence for the
ion dynamic process in solids and the study of the conduc-
tivity spectra in disordered solids at different temperatures
leads to a scaling law and it is called the time-temperature
superposition principle (TTSP) [29]. This means, for a given
material, the conductivity isotherms can be collapsed into a
single curve with appropriate scaling of the conductivity and
frequency axis. This feature can be expressed by:

$$\frac{\sigma(\omega)}{\sigma_{dc}} = F_1 \left( \frac{\omega}{\omega_c} \right),$$  \hspace{1cm} (7)

where $F_1$ is a temperature-independent function and $\omega_c$ is
a temperature dependent characteristic frequency. Various
workers have considered the dc conductivity $\sigma_{dc}$ as a scal-
ing factor for the ac conductivity axis and the characteristic
frequency $\omega_c$ as a scaling parameter for the frequency axis
[29–31].

We have studied the ac conductivity scaling by choosing
the characteristic frequency $\omega_c = \omega_p$. The scaled conductivity
spectra are shown in Fig. 6 for KACP at different tempera-
tures, where the conductivity axis is scaled by $\sigma_{dc}$, and the
frequency axis by $\omega_p$. The scaled ac conductivity data are
collapsed into a single curve. Obviously, the TTSP is ful-
filled and suggesting the conductivity relaxation mechanism is inde-
pendent of various alkali ions present in the NASICON-type
vitreous samples.

3.4. Permittivity scaling studies

The real part of permittivity increases with decreasing fre-
quency and approaches a limiting value $\varepsilon_s$ at low frequencies
associated with the polarization resulting from alignment of
the dipoles along the direction of the electric field. For ion
conducting glasses the mobile ions and oppositely charged
matrix are assumed as dipoles. In ion conducting glasses po-
larization and conduction process are integrated into a single
and continuous process [25].

Scaling behavior is also investigated for the real part of
permittivity of NASICON-type samples by using the relation,

$$\frac{\varepsilon'(\omega) - \varepsilon_{\infty}}{\Delta\varepsilon} = F_2 \left( \frac{\omega}{\omega_p} \right),$$  \hspace{1cm} (8)

where $\varepsilon_{dc}$ is the dielectric permittivity at high frequency,
$\Delta\varepsilon$ the dielectric loss strength, $F_2$ the temperature indepen-
dent function, and $\omega_p$ the temperature dependent hopping frequency.

The scaled permittivity spectrum is shown in Fig. 8 for KACP at different temperatures, where the ac permittivity is subtracted by dielectric constant, $\varepsilon_\infty$, and then scaled by dielectric loss strength, $\Delta\varepsilon$, and the frequency axis scaled by $\omega_p$. In Fig. 9, frequency axis is scaled by $\omega_p$ for different NASICON-type samples at arbitrary temperature. The scaled ac permittivity data of NASICON-type materials are superimposed into a single curve, except in the lower frequency region where the electrode effects are prominent. This study suggests that the permittivity relaxation mechanism is independent of temperatures and the compositional variation in the NASICON-type vitreous materials.

4. Conclusions

The NASICON-type vitreous materials: $M_4\text{AlCdP}_3\text{O}_{12}$ ($M = \text{Li}, \text{Na}, \text{K}$) are successfully prepared and further characterized by using XRPD, DSC, and FT-IR. Electrical properties of these materials were studied over a wide range of temperature and frequency. Conductivity formalism is used to evaluate various important parameters, namely dc conductivity, the hopping frequency, and dielectric loss strength. Crystallization temperature, dc conductivity and hopping frequency are found to be increasing with the decrease of alkali ionic radius of $M$ site. The BNN relation confirms that the ac and dc conduction mechanism are successfully correlated. Scaling studies of conductivity and the permittivity spectra further appreciates the merit of our systems, and also shows generalized features of other reported ionic crystalline materials and glasses.

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References