IONIC CONDUCTIVITY OF PRUSSIAN BLUE TYPECOMPOUNDS DOPED WITH ALKALI METAL CHLORIDES

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Abstract

Prussian blue type compounds (heavy metal ferro and ferricyanides) doped with alkali metal chlorides are found to exhibit alkali-metal ion conductivity. An unusual property of these systems is that the highest conductivity is obtained for K^+. Ferric ferricyanide doped with KCI under optimum conditions is found to have a room temperature (26^0C) conductivity of 5×10^{-1} ohm cm^{-1}

1. Introduction

The search for and studies on solid electrolytes exhibiting alkali-metal ion conduction have received a great deal of attention, mainly because of the potential applications of these materials in solid state batteries[1-5]. A number of Li^+ and Na^+ ion conductors having room temperature conductivities in the range 10^{-1} - 10^{-2} ohm^{-1} cm^{-1} are documented. However K^+ ion conducting solids with similar conductivities are exceptionally rare and not recorded in literature, at least to the knowledge of the author. The reasons for this are well understood, the ionic radius and to a lesser extent the polarizability are generally the key factors that determine the mobility of an ion in a lattice of given type[4]. As the polarizing effect increases with the decrease in the ionic radius, in few instances, the Na^+ conductivity is found to be higher than the Li^+ ion conductivity in materials of similar structure (e.g., sodium ß-alumina compared to lithium ß-alumina). In this we report our observations on alkali-metal ion transport in several Prussian blue type compounds (ferro-and ferri-cyanides of heavy metals) doped with alkali-metal chlorides, where the conductivity is found to be highest for K^+ and under optimum conditions the room temperature conductivity reaches values as high as 5×10^{-1} $ohm^{-1}cm$.

2. Experimental

The materials used in this investigation were ferric ferricyanide (Berlin green, Fe Fe $(CN)_6$, ferric ferrocyanide (Prussian blue, Fe_4 [FE $(CN)_6]_3$) and cobaltous cobalticyanide $(Co_3[Co(CN)_6]_2)$. Ferric ferricyanide was prepared by adding potassium ferricyanide 0.2M (Analar grade BDH) to an excess of 0.2M ferric chloride acidified with HCl. The solution containing the precipitate was boiled for 30min, filtered and washed until the filtrate is free from K^+ ions (the presence of excess ferric chloride and boiling was necessary to avoid the formation of double salts containing potassium). Ferric ferrocyanide was made by the identical procedure using potassium ferrocyanide instead of potassium ferricyanide[6-7]. Cobaltous cobalticyanide was prepared by adopting the same method using potassium cobalticyanide and cobaltous nitrate.

The materials were doped with alkali-metal chlorides XCI (X = Li, Na, K, Cs) by the following method. Approximately 5g of the compound was mixed with known amounts of XCl, moistened with water and ground into a paste. The paste was dried at 120^0C in a current of nitrogen for 2h to expel moisture and the material ground into a powder was compacted between stainless steel electrodes (pressure ~ 10^6Pa) in a pyrex tube (diameter ~ 0.6cm) when a pellet (length 0.7 cm) is formed. Ends of the tube are sealed with epoxy resin and the A. C. conductivity (80 Hz) of the samples were measured using Philips PW 9527 conductivity meter. D. C. measurements showed rapid polarization and residual electronic conductivity estimated from the I-V plots is several roders of magnitude smaller than the ionic conductivity (Room temperature electronic conductivities of ferric ferricyanide, ferric ferrocyanide and cobaltous cobalticyanide are of the order 10^{-4}, 10^{-5} and 10^{-6} ohm^{-1} cm^{-1} respectively).

3. Results and discussion

Fig. 1 shows the variation of the room temperature (26^0C) ionic conductivities of XCl (x = Li, Na, K, Cs) doped compounds with the mole ratio R = moles of the compound/moles of XCl. In each case there is a criticaldoping level corresponding to maximum conductivity. Measurements at higher temperatures showed the criticaldoping concentration remain nearly independent of the temperature. The tempeture dependence of the conductivity at the critical concentration of XCl is shown in Fig. 2, the maximum room temperature conductivities and the corresponding thermal activation energies are summarized in the Table. 1.
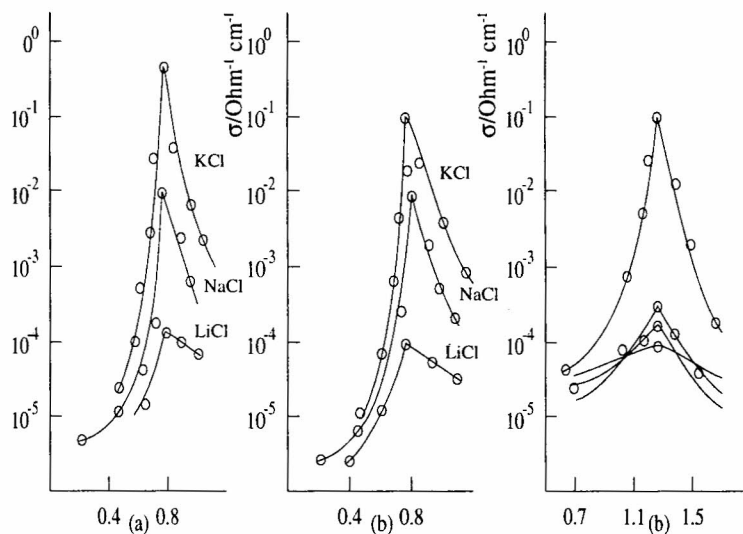
1.   The variation of the roomtemperature (26°C) ionic conductivity with the mole ratio R (moles of compound/mols of XCl) (a) Fe [Fe(CN)$_6$] (b) Fe$_4$[Fe(CN)$_6$] (c) Co$_3$[Co(CN$_6$]$_2$

System	R	(260C) ohm-1 cm-1	E (ev)
Fe [Fe(CN)$_6$]KC1	0.74	$5,0 \times 10^{-1}$	0.62
Fe [Fe(CN)$_6$]NaC1	0.75	1.0×10^{-2}	0.53
Fe [Fe(CN)$_6$]LiC1	0.74	2.5×10^{-4}	-----
Fe$_4$ [Fe(CN)$_6$]$_3$KC1	0.75	9.9×10^{-2}	0.62
Fe$_4$ [Fe(CN)$_6$]$_3$NaC1	0.75	6.0×10^{-3}	0.56
Fe$_4$ [Fe(CN)$_6$]$_3$LiC1	0.74	7.5×10^{-5}	0.48
Co$_3$[Fe(CN)$_6$]$_2$/KC1	1.27	1.0×10^{-1}	0.39
Co$_3$[Fe(CN)$_6$]$_2$/NaC1	1.23	5.2×10^{-4}	0.28
Co$_3$[Fe(CN)$_6$]$_2$/LiC1	1.21	3.0×10^{-4}	0.25
Co$_3$[Fe(CN)$_6$]$_2$/CsC1	1.20	1.5×10^{-4}	0.24

Table 1.   Romm temperature conductivity, critical mole rations and corresponding activation energies of different systems.

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The crystal structure of Prussian type compounds are well studied [6-10]. All these materials have metallic cations arranged on a face-centered cubic lattice of unit cell length ~ 10 A. Cyanide ions li along the edges of the cubes coordinated to metallic ions on either side. The presence of large interstitial cavities is a peculier property of this structure. Interstices can accommodage ions, atoms or molecules, Undoubtedly the ionic conductivity we have observed arise from the presence of large interstitial cavities. Perhaps the salt the enters the cavities are ionized by the lattic efield and ions
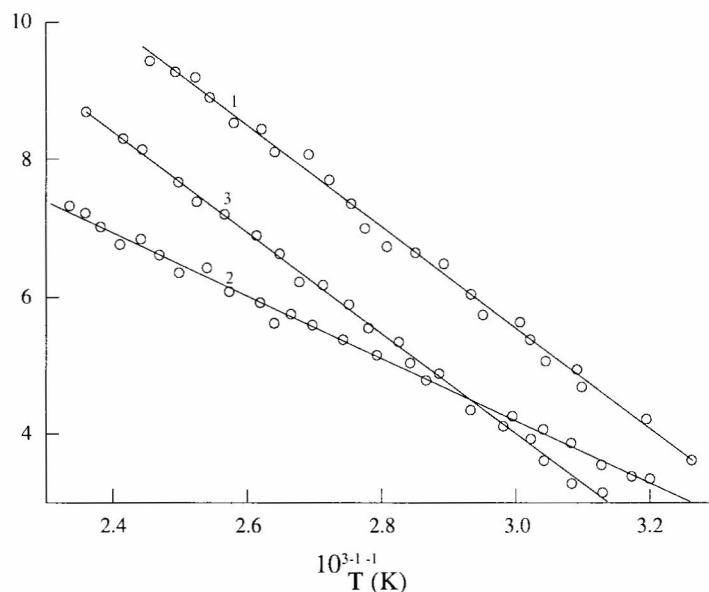
2. The temperature variation (in $ohm^{-1} cm^{-1}$) of the conductivity of (1) $Fe[Fe(CN)_6]/KCl$ (2) $Fe_4[Fe(CN)6]_3/KCl$ (3) $Co3[Co(CN)_6]_2/KCl$ at the mole R (Moles of the compound/moles of XCl) corresponding to maximum conductivity.

become mobile. The mobility depends on ionic radius, ionic polarizability, nature of the lattice field and geometry and volume of the interstitial cavity. A simple calculation (based on lattice constants, ionic radii of ions in the lattice to estimate the free interstitial volume per unit cell) shows that the cavities get filled with KCl (density assumed to be same as that of KCl crystals) when R = 0.21. As expected this value is smaller than the value of R corresponding to maximum conductivity indicating that maximum conductivity occurs when KCl concentration within the interstices is well below the saturation level. We are unable explain why the highest peak conductivity is obtained with ferric ferricyanide. The chloride ion mobility in these systems is oabsent r negligible. This is supported by the following observa-

tion. When large d. c currents are passed through thin discs of the KC1 doped compound there is no evidence of electrolysis with chlorine liberation. At KC1 doping levels below or around the critical value, the X-ray diffraction spectra does not show lines corresponding to KC1 crystals, suggesting that the mixture is more like a solid solution. The transport of alkali metal ions through the substrata depends on inonc size and the polarization field. An optimum is observed fro potassium probably as a compromise of the two effects. A decrease in the ionic radius and the polarization field both favour high conductivity. However, the decrease of ionic size increases the
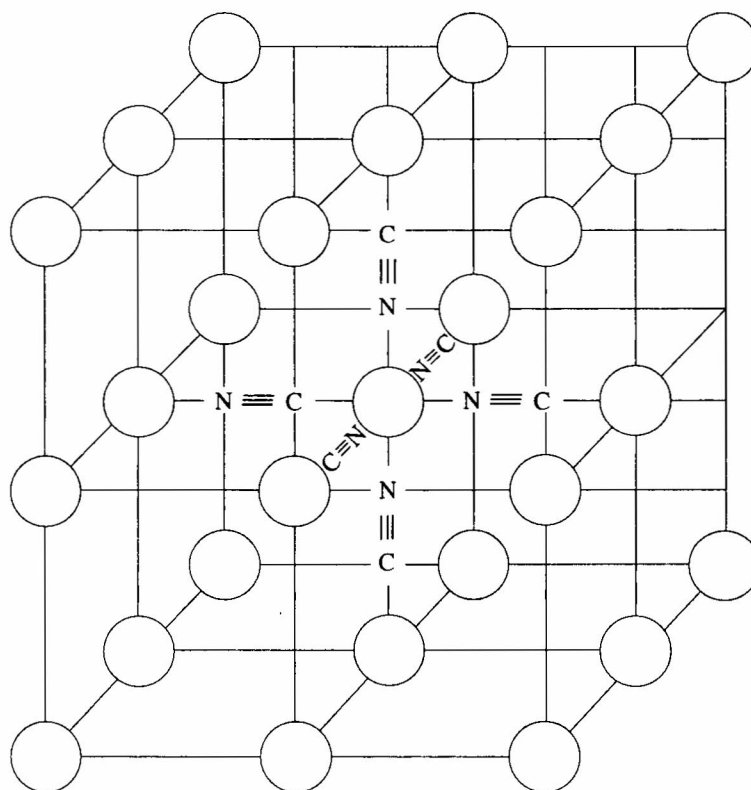
3.   Crystal structure of Prussian bule type compounds. The circls correspond to positions of metal cations.

polarization field. Composite systems are known to have high ionic conductivities and the mechanisms involved are reasonably well understood[11]. Although the large interstitial cavities of the Prussian blue is a key factor, the exact mechanism involved here remains uncertain. Another important observation we have made is the effect of trace quantities of water. Samples are tested above are not 100% free of water. If the samples are dried several hours in vaccum at 150^0C conductivity is reduced by a factor ~ 8. The estimated water loss is less than ~ 0.5%. In Prussian blue type compounds interstitial water was found increase the dielectric constant. An increase in the dielectric constant could enhance the ionic conductivity. Another possibility is association of the water molecules with the alkali metal halide resulting dissociation into ions.

4. References

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