Intercalation of Alkali Metal−Polyethylene Oxide Polymer Electrolytes in Layered $CdPS_3$

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Polyethylene oxide (PEO) has been inserted into the interlamellar space of $CdPS_3$ pre-intercalated with hydrated alkali cations (Li, Na, K, and Cs). The intercalated compounds have been characterized by X-ray diffraction, vibrational spectroscopy, and conductivity measurements. These materials are interesting since the corresponding alkali metal PEO salts are well known solid polymer electrolytes (SPEs). The lattice expansion on intercalation, $\Delta d \sim 8$ Å, and the ether oxygens to alkali metal ratio of the intercalated polymer electrolyte show only minor change for different alkali cations and are the same irrespective of the molecular weight of PEO. The corresponding polypropylene oxide (PPO) intercalated compounds showed a similar lattice expansion. The projected one-dimensional electron density calculated from the X-ray diffraction shows that the alkali cations in the interlamellar space are displaced by ±1.7 Å from the center of the gap. The mid-IR spectra show features arising from the ($-O-CH_2-CH_2-O-$) moiety of the PEO in both *trans* and *gauche* conformations. A helical conformation for the intercalated PEO may be ruled out. The data suggests that the intercalated PEO adopts a planar zig-zag structure with at least two strands complexing the alkali cation. The ambient temperature conductivity of the intercalated polymer electrolyte is comparable with that of the corresponding SPEs. Conductivity measurements provide evidence for change in the conductivity mechanism with temperature. Below 200 K the conductivities, irrespective of the cation, are small. Above 200 K, the conductivity rises rapidly with temperature. For the K and Cs compounds, the conductivities show an Arrhenius temperature dependence, but for the Li and Na intercalated polymer electrolytes the temperature variation follows the Vogel−Tamann−Fulcher relation characteristic of ionic motion coupled to polymer segmental relaxation modes. The conductivity parameters of the intercalated polymer electrolytes have been compared with those of the corresponding solid polymer electrolytes.

1. Introduction

Insertion of polymers into inorganic low-dimensional materials is a topic of current interest.[1,2] Intercalation of polymers could, in principle, lead to new materials that combine the optical and electrical properties as well as the processability of the guest polymer with the mechanical strength, thermal stability, and electronic properties of the host inorganic lattice and so possess properties that may not be achieved by either component separately. For example, a recent report indicates how plastic-like superconductors can be formed by intercalation of polymers into the layered superconducting $NbSe_2$.[3] In clays, especially mica-type silicates, a variety of polymers, such as polyethylene oxide (PEO), poly(vinyl alcohol), and poly(acrylamide), as well as anionic and cationic polymers have been intercalated.[4]

The intercalation of PEO in Li/Na ion-exchanged layered solids is of particular significance since alkali metal salts dissolved in PEO—solid polymer electrolytes (SPEs)—are well known ionic conductors.[5,6] SPEs have received considerable attention in applications such as batteries and electrochromic devices and are also of fundamental interest for investigating ionic motion in disordered materials since ion transport is known to be is assisted by the local or segmental motion of the polymer.[7] Ruiz-Hitzky and co-workers[8] have reported a detailed investigation of the intercalation of PEO into Na- and Li-exchanged montmorillonite from a methanolic solution of PEO. Giannelis and co-workers[9a] showed that the same reaction could be realized by a more environmentally friendly route from PEO melts.

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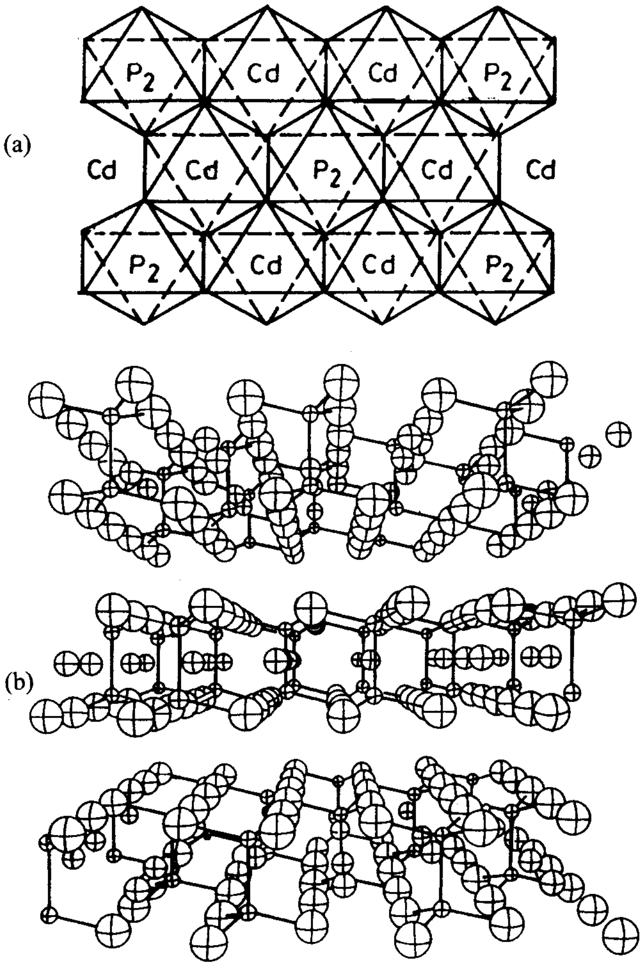

Figure 1. Structure of $CdPS_3$. (a) The in-plane structure in which CdS_6 and P_2S_6 polyhedra are linked to form $CdPS_3$ sheets. The P−P bond is collinear with the trigonal axis of the P_2S_6 polyhedra. (b) Perspective view of the structure viewed along the *b* axis showing the stacking of the $CdPS_3$ layers. The *a* axis is horizontal to the center of the figure. The circles represent P, Cd, and S with increasing size.

Direct intercalation of PEO from solution has also been reported in V_2O_5,[10] MoO_3,[11] and hydrated sodium and potassium intercalates of $MnPS_3$ and $CdPS_3$.[12]

In this paper we report results of a detailed characterization of alkali metal (Li, Na, K, and Cs)−PEO intercalation compounds of the insulating layered cadmium thiophosphate, $CdPS_3$ (Figure 1). We have also synthesized the corresponding alkali metal polypropylene oxide (PPO) intercalation compounds in order to investigate how an additional methyl group affects the structure of the intercalated compound. Insertion of the polymer electrolytes was effected by a two-step ion-exchange solvation shell-exchange reaction. In the first step, hydrated alkali ions from an aqueous solution are inserted into the interlamellar space of $CdPS_3$ with an equivalent loss of cadmium ions from the layer. This reaction unique to the divalent metal thiophosphates[13] leaves immobile cadmium ion vacancies in the layer and proceeds with a lattice dilation which depends on the nature and extent of hydration of the guest alkali cation.[14,15]

$$CdPS_3 + 2xA^+{}_{aq} \rightarrow Cd_{1-x}PS_3A_{2x}(H_2O)_y + xCd^{2+}{}_{aq}$$
$$(A = Li, Na, K, Cs)$$

In the second step, the hydration shell of the intercalated alkali cations are replaced by the ether linkage of PEO/PPO.

$$Cd_{1-x}PS_3A_{2x}(H_2O)_y + PEO \rightarrow Cd_{1-x}PS_3A_{2x}(PEO) + yH_2O$$

The reaction was first reported in $CdPS_3$ for A = K by Clement and co-workers.[12]

In the present study we have investigated the structure and conformation of the intercalated polymer by powder X-ray diffraction and vibrational spectroscopy for A = Li, Na, K, and Cs. We have also measured the conductivity of the intercalated polyethylene oxide electrolytes as a function of temperature for different alkali cations and compared the results with those for conventional PEO-based SPEs.

2. Experimental Section

Preparation. Cadmium thiophosphate was prepared from the elements following the procedure reported in ref 16. Cadmium metal powder, phosphorus, and sulfur, in stoichiometric amounts, were sealed in quartz ampules at 10^{-5} Torr and heated at 650 °C for a period of 2 weeks. The formation of $CdPS_3$ was confirmed by X-ray diffraction (XRD). Single crystals of $CdPS_3$ were grown by chemical vapor transport using excess sulfur as a transporting agent. The charged end of the ampule was maintained at 650 °C while the cooler end at 600 °C. Platelet-like, transparent crystals of hexagonal morphology were obtained with typical size of $7 \times 7 \times 0.1$ mm^3.

Potassium and cesium ion-exchanged intercalation compounds were obtained by stirring $CdPS_3$ powder in aqueous solution of the desired cation along with a complexing agent, EDTA. The pH of the solution was maintained at 10 using a 1 M $K_2CO_3/KHCO_3$ buffer.

$$CdPS_3 + 2xK^+{}_{aq} \rightarrow Cd_{1-x}PS_3K_{2x}(H_2O)_y + xCd^{2+}{}_{aq}$$

Complete ion-exchange intercalation was ascertained by the absence of the host 00*l* reflections and the appearance of new 00*l* reflections with lattice spacing, 9.3 Å. A facile route for the preparation of the corresponding Na and Li ion-exchanged compounds was by ion-exchanging the K ion in $Cd_{1-x}PS_3K_{2x}(H_2O)_y$ for these ions.

$$Cd_{1-x}PS_3K_{2x}(H_2O)_y + 2xLi^+{}_{aq} \rightarrow Cd_{1-x}PS_3Li_{2x}(H_2O)_y + 2x\,K^+{}_{aq}$$

Ion-exchange of the K ion by Na or Li ions causes the lattice spacing to increase from 9.3 to 12.2 Å. Complete ion-exchange as ascertained by XRD took ~60 min. The alkali ion-exchange intercalation was also carried out with crystals of $CdPS_3$. Stirring the reactants was avoided; the intercalated com-

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Table 1. Analytical Data of $CdPS_3$−Polymer Intercalates

intercalate	basal spacing (Å)	analytical data (% w/w) C	H	polymer	O:A ratio
$Cd_{0.75}PS_3Li_{0.5}(CH_2{-}CH_2{-}O)_{1.65}$	15.09	13.66	2.35	PEO (6 × 10^5)	3.3:1
$Cd_{0.75}PS_3Na_{0.5}(CH_2{-}CH_2{-}O)_{1.88}$	14.93	14.57	2.46	PEO (2 × 10^3)	3.8:1
$Cd_{0.75}PS_3Na_{0.5}(CH_2{-}CH_2{-}O)_{2.03}$	15.00	15.70	2.56	PEO (6 × 10^5)	4.1:1
$Cd_{0.74}PS_3K_{0.57}(CH_2{-}CH_2{-}O)_{2.08}$	15.59	15.59	2.36	PEO (6 × 10^5)	3.6:1
$Cd_{0.75}PS_3Cs_{0.5}(CH_2{-}CH_2{-}O)_{1.97}$	16.10	13.05	1.52	PEO (6 × 10^5)	3.9:1
$Cd_{0.75}PS_3Li_{0.5}(OCH(CH_3){-}CH_2)_{1.76}$	15.31	20.15	3.14	PPO (4 × 10^3)	3.5:1

pounds are extremely fragile. Lattice expansion along the interlayer axis was identical to that in the corresponding powders.

The intercalation of PEO was carried out by refluxing the alkali ion-exchanged intercalation compound, $Cd_{0.75}PS_3A_{0.5}(H_2O)_y$ (A = Li, Na, K, Cs), with a methanolic solution of PEO of desired molecular weight at 55 °C for 1 day.

$$Cd_{1-x}PS_3A_{2x}(H_2O)_y + (CH_2{-}CH_2{-}O)_n \xrightarrow{\mathrm{MeOH}} Cd_{1-x}PS_3A_{2x}(CH_2{-}CH_2{-}O)_2$$

The progress of the reaction was monitored by the appearance of a new 00*l* reflection with $d \sim 15$ Å in the powder XRD. Completion of the reaction was ascertained by the absence of the $Cd_{0.75}PS_3A_{0.5}(H_2O)_y$ reflections. The powder was filtered and washed with dry methanol to remove PEO adsorbed on the surface of the crystallites. The intercalation reactions were carried out for PEO of different molecular weights (Aldrich; $M_w = 380$ to 5×10^6) and for different alkali metal cations (Na, K, Cs). The reaction was also carried out with crystals of $Cd_{0.75}PS_3A_{0.5}(H_2O)_y$.

The intercalation of PEO in $Cd_{0.75}PS_3Li_{0.5}(H_2O)_2$ required a slightly different procedure. For short reaction times (<2 h), the intercalation reaction resulted in the formation of a mixture of phases characterized by lattice spacings of 15.1 Å ($\Delta d = 8.56$ Å) and 17.0 Å ($\Delta d = 10.46$ Å). If the reaction was allowed to proceed for longer times (~1 day), only the phase with $d = 17.0$ Å was obtained. In the literature,[11] a phase with $\Delta d = 10.46$ Å for PEO intercalated in layered solids is known and arises when the intercalated PEO is associated with water. The $d = 15.1$ Å phase corresponds to intercalated PEO without associated water. On evacuation, the 17.0 Å phase was found to convert to the phase with lattice spacing $d = 15.1$ Å.

The preparation of the $Cd_{0.75}PS_3Li_{0.5}$(PEO) phase with $d = 15.1$ Å was achieved as follows. After refluxing the $Cd_{0.75}PS_3Li_{0.5}(H_2O)_2$ in methanolic PEO for 2 h, excess methanol was decanted and the product evacuated at 10^{-2} Torr for 1 h. Unreacted PEO was removed by washing the products repeatedly with dry methanol using Schlenk techniques. Fortunately, once prepared, the 15.1 Å phase of $Cd_{0.75}PS_3Li_{0.5}$ (PEO) is stable to the atmosphere, the 17.0 Å phase being formed only when the sample is in contact with methanol. The absence of adsorbed PEO on the surface of the intercalated compounds was ascertained by the absence of the melt endotherm at 338 K in the differential scanning calorimetry (DSC). The melting temperature of pure PEO is 338 K.

Poly(propylene oxide)(PPO)(Aldrich; $M_w = 4000$) was intercalated by the same procedure and took about a day for completion.

$$Cd_{0.75}PS_3A_{0.5}(H_2O)_y + \mathrm{PPO} \xrightarrow{\mathrm{MeOH}} Cd_{0.75}PS_3A_{0.5}(\mathrm{PPO}) + yH_2O$$

Intercalation proceeds with the formation of a phase with $d \sim 15.3$ Å.

Giannelis and co-workers[9] had shown that the intercalation of PEO in mica-type silicates (MTS) could be effected by heating a physical mixture of the MTS and PEO. The same reaction could be carried out with $CdPS_3$. The alkali metal ion-exchanged, $Cd_{0.75}PS_3A_{0.5}(H_2O)_y$ and PEO (40% by weight) were ground thoroughly, pelletized, and heated in a tubular furnace. For A = K and Cs, heating at 80 °C for 4 h was sufficient to give a single phase with XRD identical to that obtained by solution intercalation ($d = 15.4$ Å). However, in the case of the smaller alkali ions, A = Li and Na, the reaction was slower and occurred only at a higher temperature (~200 °C). In the case of melt intercalated compounds, removal of excess PEO required washing with methanol, and consequently the procedure did not offer any additional advantage for characterization studies.

Cadmium and alkali metal stoichiometries were established by atomic absorption spectroscopy (Perkin Elmer 4381) after dissolving a weighed quantity of the intercalated compound in aqua-regia followed by dilution. Phosphorus and sulfur stoichiometries were not estimated but assumed identical to the starting host. The amount of PEO/PPO intercalated was estimated from the carbon and hydrogen content in the intercalated samples by elemental analysis (Carlo Erbo CHN analyzer). The results are given in Table 1. The values for the potassium compound are similar to those reported in ref 12.

In SPEs the stoichiometry is usually characterized by the ether oxygen to alkali metal ratio (O:A). It may be noticed that the O:A ratio of the intercalated polymer electrolytes (Table 1) is close to 4:1, and this ratio seems to be independent of the nature of the alkali metal ion and also the molecular weight of intercalated PEO.

The stoichiometry of the Li−PPO intercalated sample was established in a similar way and is $Cd_{0.75}PS_3Li_{0.5}(OCH(CH_3)CH_2)_{1.7}$ for PPO-4000. The O:Li ratio is 3.4:1.

Measurements. The thermalgravimetric (TG) analysis of the intercalated compounds was recorded in flowing nitrogen gas using a Polymer Laboratories STA 1000 simultaneous TG-DTA thermal analyzer. Differential scanning calorimetry was recorded for powder samples on a Rheometric Scientific DSC plus instrument. Infrared spectra were recorded on a Bruker IFS-66 FT-IR spectrometer in the spectral range 400−4000 cm^{-1}. Powder samples were recorded as KBr pellets. Crystal spectra of thin platelets were recorded directly in the transmission mode.

X-ray diffraction was recorded on a Shimadzu-XD-D1 diffractometer using Cu Kα radiation. 00*l* reflections of the crystals were recorded after being mounted on a glass slide using silicone grease. Attempts to solve the structure of the intercalated compounds by single-crystal diffraction methods were unsuccessful since crystals showed considerable mosaic. Thus the Weissenberg photographs showed spots only for the 00*l* reflections, while other reflections appeared as streaks.

The one-dimensional electron density of the intercalated compounds was calculated from the X-Ray diffraction data.[17] 00*l* reflections up to 12th order were recorded for crystals mounted flat on a glass slide. The slide occupied the same position as the regular sample holder on the goniometer. The integrated intensities of the 00*l* reflections, after correction for Lorentz polarization effects, were used to calculate the structure factor

$$|F_{00l}| = (I_{00l}/\mathrm{Lp})^{1/2} \tag{1}$$

where I_{00l} is the integrated peak intensity and Lp, the Lorentz polarization factor, is $\mathrm{Lp} = (1 + \cos^2 2\theta)/\sin^2\theta \cos\theta$). The

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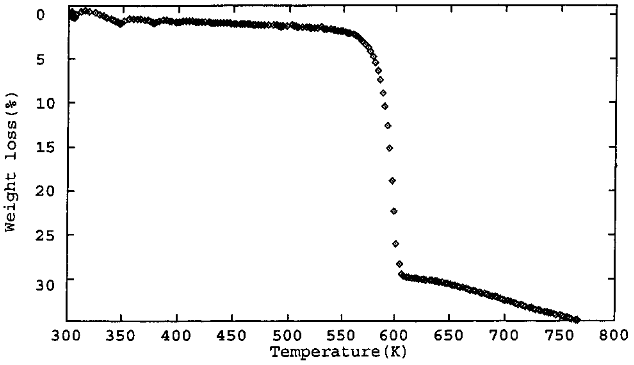

Figure 2. Thermogram of $Cd_{0.75}PS_3Li_{0.5}(PEO)$. The molecular weight of the intercalated PEO is 6×10^5.

projected electron density, $\rho(z)$, was synthesized from $z/L = 0-1$ from the discrete transform.

$$\rho(z) = (1/L)\sum_l F_{00l} \exp(-2\pi i l z/L) \qquad (2)$$

where L is the lattice periodicity. The phase of the structure factors was assumed identical to that of $CdPS_3$. The assumption is not too drastic since the intercalated compounds crystallize in the same space group as $CdPS_3$, $C2/m$, with only the c lattice parameter changing on intercalation. Moreover, the scattering contribution from PEO is relatively small. Spurious features arising from truncation errors were checked by deleting (including) the last few reflections in the transform, eq 2.

dc conductivities were obtained from an ac impedance (admittance) analysis in the frequency range 5 to 10^5 Hz. The electrical measurements were carried out on pellets using platinum electrodes. The area of the electrode was 0.595 cm^2 and the thickness of the pellets, typically, 0.1 cm. The complex admittance, $Y^* = Y' + iY'' = 1/Z^*$, was determined by measuring the in-phase and quadrature voltage drop across the sample in series with a standard resistor using a dual phase Lock-in-Analyzer (PAR 5208).[18] The dc conductivity values (σ_{dc}) were obtained from the intercept on the real axis of the complex admittance plot.[19] The sample temperature could be varied continuously from 10−350 K with ±0.5 K accuracy using a closed cycle cryostat (CTI-Cryogenics). The temperature of the sample was measured using a chromel-constantan thermocouple. The extreme fragility of the intercalated crystals prevented anisotropy conductivity measurements from being made.

3. Results and Discussion

Thermal Analysis. The alkali metal−PEO and −PPO intercalation compounds are stable in air. The TG shows that decomposition occurs by a single-step weight loss close to 600 K which is also the decomposition temperature of the bulk polymer. A typical thermogram is shown in Figure 2. The sample is $Cd_{0.75}PS_3Li_{0.5}(PEO)$ and the decomposition temperature 598 K. The decomposition temperature does not depend on the molecular weight of the intercalated PEO or on the nature of the intercalated alkali cation.

In the temperature range 90−380 K, the DSCs of the intercalated PEO samples were found to be featureless. The absence of the PEO melt endotherm at 338 K confirmed that crystalline PEO adsorbed on the surface of the sample was not present. No signature of a glass transition (T_g) was observed for any of the polymer intercalated compounds. The T_g of PEO is 213 K and that for PPO, 200 K.

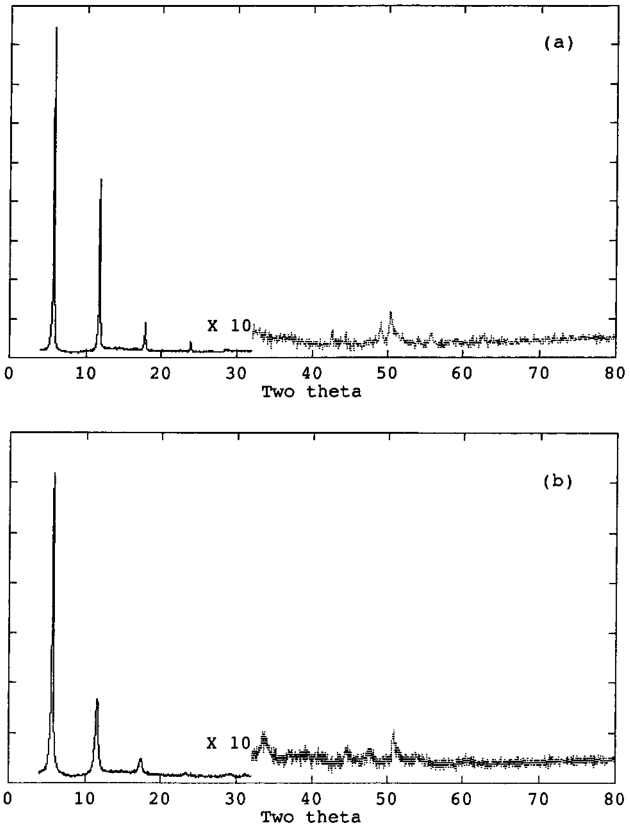

Figure 3. Powder XRD pattern of (a) $Cd_{0.75}PS_3Li_{0.5}(PEO)$ and (b) $Cd_{0.75}PS_3Li_{0.5}(PPO)$.

X-ray Diffraction. The XRD patterns of $Cd_{0.75}PS_3A_{0.5}(CH_2-CH_2-O)_2$(A = Li, Na, K, Cs) could be indexed in the same space group $C2/m$ as that of the host $CdPS_3$. A typical XRD pattern is shown in Figure 3a. The only change from the parent $CdPS_3$ structure being an expansion of the c axis. The a and b lattice parameters, which are defined in the plane of the layers, remain essentially unchanged. The unit cell parameters of the intercalated compounds were calculated from the XRD patterns and are given in Table 2 for different alkali cations. The lattice parameters are independent of the molecular weight of the intercalated PEO. For all intercalated compounds, values of the a, b, and β lattice parameters are almost identical to that of the host $CdPS_3$. The lattice expansion, however, depends on the nature of the cation. This may clearly be seen in Figure 4 where the $00l$ reflections for different alkali cation intercalated compounds are shown.

A typical XRD pattern for $Cd_{0.75}PS_3Li_{0.5}(PPO)$ is shown in Figure 3b. For this compound too, the XRD pattern could be indexed in the $C2/m$ space group with lattice parameters $a = 6.374$ Å, $b = 10.579$ Å, $c = 16.044$ Å, and $\beta = 107.36°$. As in the case of the PEO intercalated samples, only the c parameter showed a cation dependence. The lattice expansion for the different cations are, for Li, $\Delta d = 8.69$ Å; Na, $\Delta d = 8.95$ Å and K, $\Delta d = 9.23$ Å.

Density of Intercalated Polymer. The unit cell volume of the $Cd_2P_2S_6$ ($C2/m$) is 438.1 Å^3. The formation of $Cd_{0.75}PS_3A_{0.5}(PEO)$(A = Li, Na, K, Cs) occurs with a

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Table 2. Unit Cell Parameters of the Alkali Metal−PEO ($M_w = 6 \times 10^5$) Intercalation Compounds of $CdPS_3$[a]

sample	a (Å)	b (Å)	c (Å)	β (°)	Δd (Å)	volume of unit cell (Å^3)	density of PEO g/mL
$CdPS_3$	6.218	10.763	6.867	107.58		438.1	
$Cd_{0.75}PS_3Li_{0.5}$(PEO)	6.596	10.440	15.681	107.24	8.55	1031.3	0.493
$Cd_{0.75}PS_3Na_{0.5}$(PEO)	6.754	10.840	15.525	107.17	8.46	1085.9	0.454
$Cd_{0.74}PS_3K_{0.57}$(PEO)	6.474	10.703	16.605	111.06	9.05	1073.7	0.467
$Cd_{0.75}PS_3Cs_{0.5}$(PEO)	6.537	10.643	17.062	107.35	9.56	1132.9	0.433

[a] The last column is the calculated density of the intercalated PEO.

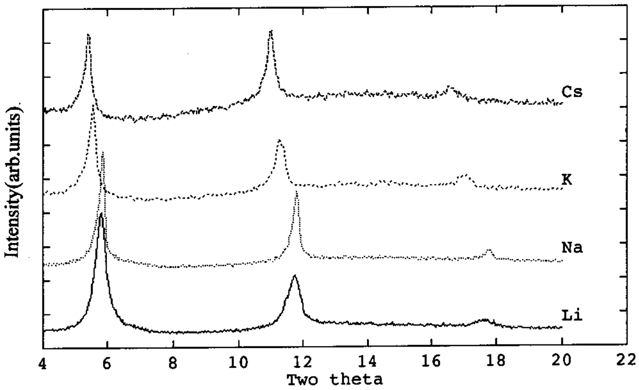

Figure 4. 00l reflections in the powder XRD pattern of $Cd_{0.75}PS_3A_{0.5}$(PEO) (A = Li, Na, K, Cs).

dilation of the lattice (Table 2). The corresponding increase in volume, ΔV, of the unit cell is indicated in Table 2. The volume available for the (CH_2CH_2−O) units in the unit cell may be obtained by subtracting the ionic volume of the corresponding A^+ ion from ΔV. Assuming that the entire volume is available for the (CH_2−CH_2O) units, the density of the intercalated PEO may be calculated and is shown in the last column of Table 2. These values, when compared with that for pure PEO (1.1 g/mL), show that the density of the intercalated polymer is about a half of that of bulk PEO of 80% crystallinity. The calculated density for the intercalated PPO $Cd_{0.75}PS_3Li_{0.5}$(PPO) is 0.65 g/mL, which, too, is less than that of bulk PPO (1.004 g/mL).

Electron Density. In order to locate the position of the alkali metal ions and the possible structure of the polymer chains in the interlamellar space of $Cd_{0.75}PS_3A_{0.5}$(PEO), a one-dimensional Fourier transform of the experimental 00l structure factors of the PEO intercalated compounds, $Cd_{0.75}PS_3A_{0.5}$(PEO)(A = Na, K, Cs), was carried out. The Fourier transform gives the projected electron density along the c axis, i.e., along the layer-stacking axis.

The projected one-dimensional electron density map for $CdPS_3$ is shown in Figure 5a. The peaks at $z/L = 0.248$ and $z/L = 0.760$ are due to sulfur atoms. The Cd−S distance of 1.7 Å agrees with the crystallographic values. The resolution of the present experiment did not allow the phosphorus atom electron densities to be detected, which, according to single-crystal data, should have appeared at 1.17 Å. Figure 5a shows that there is no electron density between 2.48 and 4.24 Å, which corresponds to the van der Waals gap of $CdPS_3$.

The one-dimensional electron density maps for $Cd_{0.75}PS_3A_{0.5}(CH_2{-}CH_2{-}O)_2$ (A = Na, K, Cs) are shown in Figure 5b. On comparison with the electron density map of pure $CdPS_3$, considerable electron density in the gap may be noticed. The peaks at $z/L = 0.09$ and $z/L = 0.91$ are due to sulfur atoms of the $CdPS_3$ layer. A number of peaks may be noticed in the interlayer gap. The main feature are the peaks at $z/L = 0.41$ and $z/L = 0.59$, which grow in intensity with the size of the alkali metal cation, being largest for the Cs sample. These peaks may consequently be assigned to the alkali metal ions. Figure 5b shows that the alkali metal ions do not sit in the center of the gap but are displaced by ±1.7 Å from the center. A number of other peaks are seen at 4.4, 8.3, 10.8, and 12.3 Å. These are probably due to the electron density from the PEO chain. Attempts to model the structure and hence assign the peaks from known C−C and C−O distances and analysis were unsuccessful.

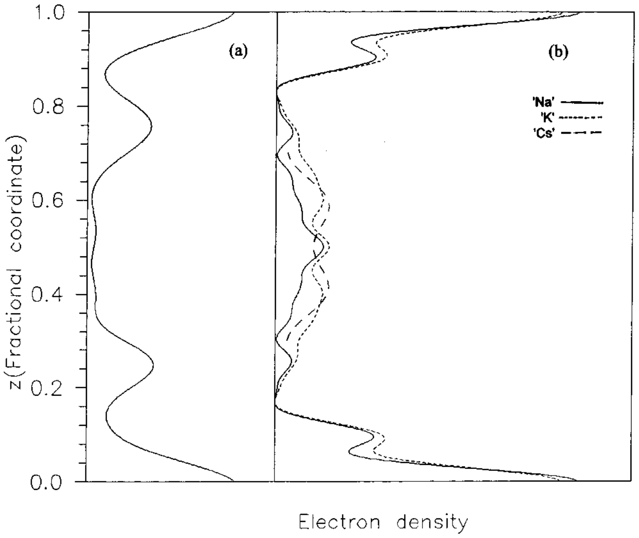

Figure 5. One-dimensional electron density map of (a) $CdPS_3$ and (b) $Cd_{0.75}PS_3A_{0.5}$(PEO) (A = Na, K, Cs).

Infrared Spectra. Infrared spectra were recorded for both powder samples and for crystals ($\vec{E} \perp \vec{c}$). The IR spectra for $Cd_{0.75}PS_3Na_{0.5}(CH_2{-}CH_2{-}O)_2$ ($M_w = 6 \times 10^5$) powder and crystal are shown in Figure 6. The positions of the bands in pure PEO have been marked in Figure 6. The position of the IR bands for the different alkali metal−PEO intercalated samples along with the assignment are given in Table 3. (The assignments are from refs 11 and 20.) The IR spectra of $Cd_{0.75}PS_3Na_{0.5}(CH_2{-}CH_2{-}O)_2$ for different molecular weights of the PEO were recorded and found identical and consequently not shown. There is no substantial difference in either band positions or band intensities between the crystal and powder samples, which suggests that there is no preferred orientation of the intercalated polymer chain with respect to the $CdPS_3$ layer. The bands of the host lattice that appear below 600 cm^{-1} are not discussed.

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(20) Papke, B. L.; Ratner, M. A.; Shriver, D. F. *J. Phys. Chem. Solids* **1981**, *42*, 493.

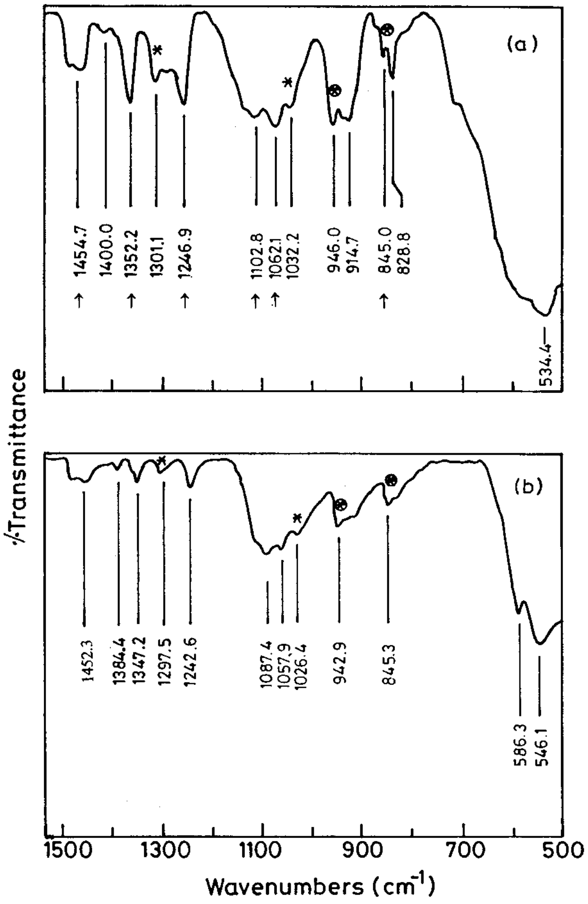

Figure 6. IR spectra of $Cd_{0.75}PS_3Na_{0.5}(PEO)$ ($M_w = 6 \times 10^5$): (a) crystal ($\vec{E} \perp \vec{c}$) and (b) powder. The positions of the bands of pure PEO have been marked with arrows.

Table 3. IR Band Positions (cm^{-1}) for $Cd_{0.75}PS_3A_{0.5}(PEO)[A = Li, Na, K, Cs]$[a]

Li	Na	K	Cs	PEO	assignment	Type I PEO:HgCl$_2$
1468	1452	1463	1466	1467	$\delta(CH_2)_a$	1466
1450			1447		$\delta(CH_2)_a$	1442
	1384	1378				1384
1351	1347	1353	1348	1358	$\omega(CH_2)_s,\nu_{CC}$	1346
1300	1297	1305	1302		$\delta_{CH}(CH_2)$ of *trans* $O-[CH_2]_2-O$	1309
1243	1242	1247	1247	1241	$t(CH_2)_a$	1243
1091	1087	1096	1098	1099	$\nu(COC)_a$	1081
				1147	$\nu_{CC},\nu(COC)_a$	
1065	1062		1061			1046
1035	1032	1035	1036		$r(CH_2)_a + \nu(COC)$ of *trans*	1029
1008			1008		$r(CH_2)_a + \nu(COC)$ of *trans*	1014
946	943	949	951	960	$r(CH_2)_a$	942
850	845	850	850	842	$r(CH_2)_a$	856
608		608	606		host	
590	585	592	590		host	
553	546	553	546		host	
450			452		host	

[a] The assignments are from refs 11 and 20. The band positions observed for Type I PEO:HgCl$_2$ complex (from ref 22) are also shown.

As compared to bulk PEO, the major differences are in the positions of the mid-IR bands of the intercalated PEO. These differences are as follows: (i) new bands at ~1300 and ~1030 cm^{-1} are seen in the intercalated PEO (marked with an asterisk in Figure 6), (ii) there is a shift to lower frequencies of the PEO 1099 cm^{-1} band for the Na and Li intercalated compounds, and (iii) the broad and intense ν_{CH_2} band centered at 2890 cm^{-1} in pure PEO is resolved into three distinct bands in the intercalated compounds.

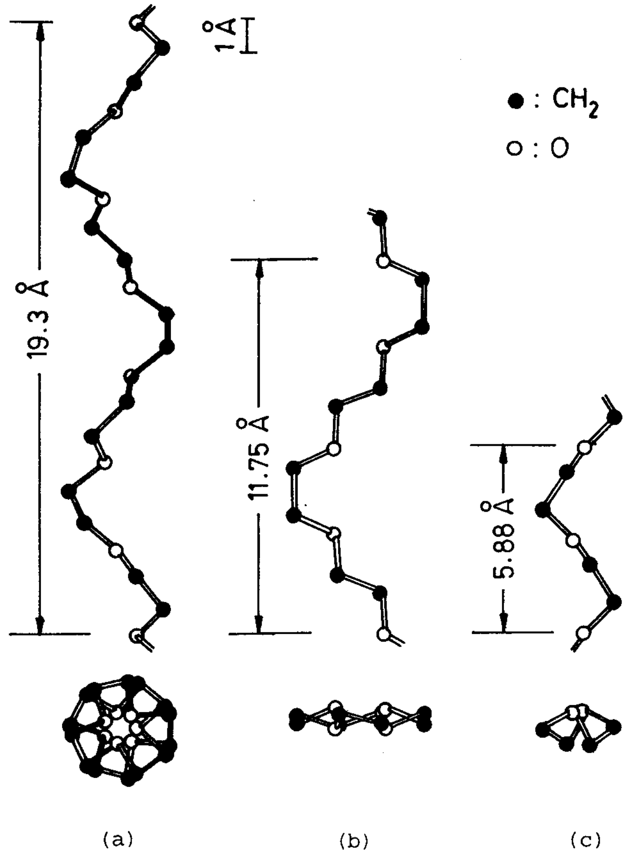

Figure 7. Observed molecular conformations of PEO: (a) helical PEO, $(T_2G)_7$; (b) zig-zag Type-I, $T_5GT_5\textit{G}$; and (c) zig-zag Type-II, $TG_2T\textit{G}_2$.

In the literature[20] IR vibrational spectroscopy has been used extensively to distinguish possible PEO conformations—helical$(TTG)_7$, zig-zag Type I$(T_5GT_5\textit{G})$ and zig-zag Type II$(TG_2T\textit{G}_2)$—in both pure PEO as well as its complexes. (The notation refers to the conformation about CCOC, COCC, and OCCO part of the PEO skeleton, Figure 7.) The helical conformation is the most common. In crystalline PEO as well as in most alkali metal—PEO complexes, the polymer has this structure in which the $O-CH_2-CH_2-O$ moiety has an *all-gauche* conformation.[21] The IR spectra of these materials show characteristic bands at ~950 and 850 cm^{-1} due to CH_2 rocking vibration modes of the $O-CH_2-CH_2-O$ group.[20] In PEO-HgCl$_2$ Type I complex where the $O-CH_2-CH_2-O$ conformation alternates between *trans* and *gauche*, additional strong bands at 1322 and 1012 cm^{-1} are also observed.[22] These have been assigned to $\delta_{CH}(CH_2)$ of a *trans* $O-CH_2-CH_2-O$ while the second to a combination of CH_2 rocking and stretching. Thus the mid-IR(1500−500 cm^{-1}) region of the PEO-based polymer electrolytes provides a "fingerprint" for different possible PEO chain conformations.

The bands observed at ~850 and ~950 cm^{-1} in the intercalated compounds (see Table 3) and marked with a crossed circle in Figure 6 are characteristic of $O-CH_2-CH_2-O$ in the *gauche* conformation and may be assigned to a rocking vibrational mode of the CH_2 group.

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(21) Chatani, Y.; Okamura, S. *Polymer* **1987**, *28*, 1815.
(22) Blumberg, A.; Pollack, S. S. *J. Polym. Sci.: Part A* **1964**, *2*, 2499.

The intercalated compounds show an additional set of bands at 1300 and 1030 cm^{-1}. Bands at these positions have been observed in the Type I PEO-$HgCl_2$ complex[22] (Table 3) and consequently interpreted similarly. The 1300 cm^{-1} band is assigned to a $\delta_{CH}(CH_2)$ of a *trans* $O-CH_2-CH_2-O$ conformation and the 1030 cm^{-1} band to a combination of CH_2 rocking(r_{CH_2}) and stretching mode(ν_{COC}) of *trans* $O-CH_2-CH_2-O$. Thus the IR spectra provides evidence that the $O-CH_2-CH_2-O$ group of the intercalated polymer adopts both *trans* and *gauche* conformations.

The splitting of the 2890 cm^{-1} band in PEO into three components has been observed in other PEO intercalated compounds[8] and had been interpreted as being due to the interaction of the polymer with the layer. The strong band at 1099 cm^{-1} in bulk PEO which is due to combination of symmetric and asymmetric C−O−C stretching modes is known to shift to lower frequencies on complexation with alkali metal cation, e.g., in PEO−NaSCN, it appears at 1085 cm^{-1}.[20] In the intercalated compounds, the lowest frequency is observed for Na followed by Li. In the K and Cs compounds, the position of the band is identical to that in pure PEO. This may be interpreted as suggesting that the PEO−alkali metal interactions in the intercalated compounds are strongest for the Na ion.

Structure and Conformation of the Intercalated PEO—A Possible Model. The results so far do not provide direct evidence for the structure of the intercalated polymer. It is, however, possible to rule out certain possibilities. Any model of the intercalated polymer would have to account for the following:

(i) Lattice expansion is approximately the same irrespective of whether the intercalating polymer is PEO ($\Delta d = \sim 8.5$ Å) or PPO ($\Delta d = \sim 8.7$ Å). The lattice expansion is independent of the molecular weight of the intercalated PEO.

(ii) Lattice expansion depends on the cation. For Li and Na it is approximately identical ($\Delta d \approx 8.5$ Å), but for K ($\Delta d = 9.05$ Å) and Cs ($\Delta d = 9.56$ Å) expansion varies with cation size. This was observed for both PEO and PPO intercalates.

(iii) The mid-IR spectra of $Cd_{0.75}PS_3A_{0.5}$(PEO) has features arising from $O-CH_2-CH_2-O$ in both *trans* and *gauche* conformers.

(iv) The alkali metal ions in the interlamellar van der Waals gap do not sit in the center of the gap but are displaced by ±1.7 Å.

Although a helical PEO conformation (Figure 7a) with alkali ions residing within the helix is the most commonly encountered in crystalline alkali metal−PEO complexes, a helical conformation for the intercalated PEO can be ruled out since the lattice expansion for alkali metal−PEO and alkali metal−PPO intercalation compounds are almost the same. Since PPO has an additional methyl group, a larger lattice expansion would be anticipated if the conformation was indeed helical. Moreover, the IR spectra clearly rules out an *all-gauche* conformation of the $O-CH_2-CH_2-O$ required of a helical structure (Figure 7a).

A model for the intercalated PEO that does not conflict with the experimental results is a conformation similar to that in the PEO−$HgCl_2$ Type I complex (note the similar IR frequencies in Table 3). In this conformation, the $O-CH_2-CH_2-O$ alternates between *trans* and *gauche* conformations. (In the present studies there is evidence for both *trans* and *gauche* conformations but not for an alternation of *trans* and *gauche*!) A schematic drawing showing a zig-zag structure with a TTT TTG conformation for the intercalated PEO is shown in Figure 8. The figure shows a *single* strand of PEO. To maintain the observed O:A ratio of 4:1 as well as the observed lattice expansion, at least two such strands are required. The alkali metal ions sit off-center, complexed by ether linkages from *at least* two different strands. A second strand is not shown in Figure 8. Since the IR spectra of the crystal and powder are identical, it is reasonable to assume that different strands are not oriented with respect to the negatively charged layer.

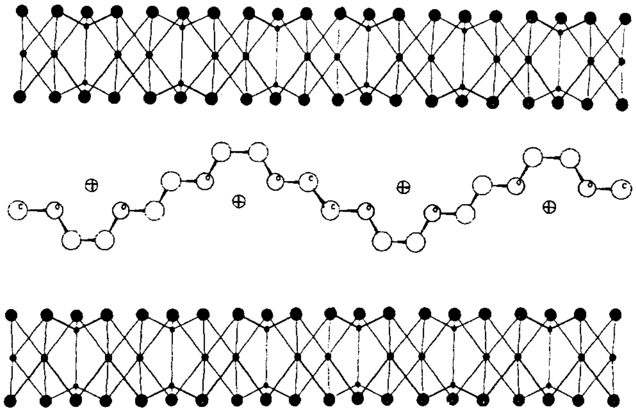

Figure 8. Schematic of a single strand of intercalated PEO (only the polymer skeleton is shown). To maintain the observed stoichiometry and lattice spacing *at least* two such strands are needed. The filled circles are P, Cd, and S with increasing size, and the open circles are O and C. The sodium ions, ⊕, are displaced from the center of the interlamellar gap. Cadmium vacancies are not shown.

dc Conductivity. In parts a−d of Figure 9, the dc conductivity of $Cd_{0.75}PS_3A_{0.5}$(PEO) (A = Li, Na, K, Cs) is plotted as function of inverse temperature. In these compounds the negatively charged $Cd_{0.75}PS_3$ layers are electrically inert[15] and consequently the observed conductivity response (Figure 9) is entirely due to the intercalated alkali cation−PEO in the interlamellar space. The dc conductivity shows two temperature regimes. For $T < 200$ K, the conductivity values are small ($<10^{-10}$ S/cm) and show only a weak temperature dependence, whereas for $T > 200$ K, the conductivity rises sharply, reaching a value between 10^{-5} and 10^{-6} S/cm at 330 K. (For the $Cd_{0.75}PS_3Cs_{0.5}$(PEO) sample it was not possible to obtain σ_{dc} values below 200 K because of the presence of a dielectric relaxation; this aspect of the low-temperature electrical behavior in $Cd_{0.75}PS_3Cs_{0.5}$(PEO) will be presented elsewhere.) The Li−PEO intercalated samples show the highest conductivity at room temperature, while K−PEO intercalated compounds show the lowest. At lower temperatures ($T < 200$ K), it is the potassium compounds that have the highest conductivity. The $Cd_{0.75}PS_3Li_{0.5}$(PEO) compounds show the maximum change in conductivity with temperature, increasing from 5×10^{-13} at 133 K to 8×10^{-5} S/cm at 340 K. Within experimental error, the σ_{dc} values, irrespective of the alkali cation, showed no variation with the molecular weight of the intercalated polymer (Figure 10).

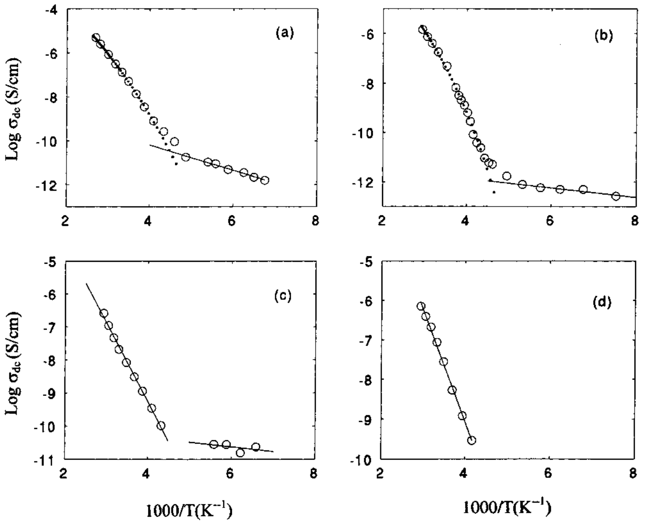

Figure 9. dc conductivity vs inverse temperature for $Cd_{0.75}PS_3A_{0.5}(PEO)$ ($M_w = 6 \times 10^5$): (a) A = Li, (b) A = Na, (c) A = K, and (d) A = Cs. The dotted lines are the fits to the VTF equation, and the solid lines are the fits to the Arrhenius equation.

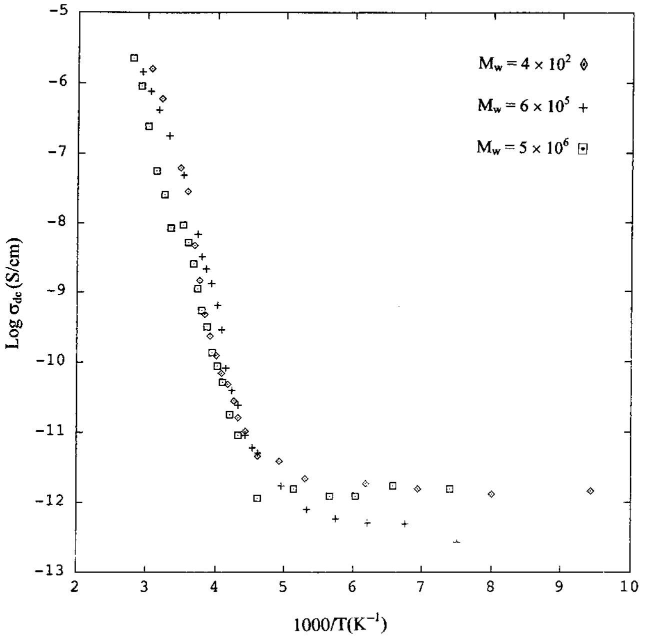

Figure 10. dc conductivity vs inverse temperature of $Cd_{0.75}PS_3Na_{0.5}(PEO)$ for various molecular weights of the intercalated PEO.

The low-temperature ($T < 200$ K) conductivity of the intercalated polymer electrolytes shows an Arrhenius temperature dependence (solid line in Figure 9) with E_a values as shown in Table 4. The description of the conductivity for $T > 200$ K, however, depends on the alkali cation. The temperature variation of the conductivity of $Cd_{0.75}PS_3Li_{0.5}(PEO)$ and $Cd_{0.75}PS_3Na_{0.5}(PEO)$ follow the Vogel−Tamann−Fulcher (VTF) relation, $\sigma_{dc} = \sigma_o \exp(-B/T - T_o)$ (dotted line in Figure 9a,b) while that of $Cd_{0.75}PS_3K_{0.5}(PEO)$ and $Cd_{0.75}PS_3Cs_{0.5}(PEO)$ show an Arrhenius temperature dependence (solid line in Figure 9c,d). The values of the VTF B, the pseudo activation energy, and T_0 that gave the best fit are given in Table 4 along with the Arrhenius activation energies for the potassium and cesium compounds.

Table 4. Fitted Parameters for dc Conductivity of the Alkali Metal−PEO Intercalation Compounds, $Cd_{0.75}PS_3A_{0.5}(PEO)[A = Li, Na, K, Cs]$[a]

	$T > 225$ K					$T < 225$ K	
	VTF parameters			Arrhenius parameters		Arrhenius parameters	
sample	σ_0	B (eV)	T_0 (K)	σ_0	E_a (eV)	σ_0	E_a (eV)
Li	3.477	0.257	90.67			1.3996×10^{-8}	0.115
Na	1.848	0.204	125.6			8.0382×10^{-12}	0.038
K				1.843	0.472	1.7357×10^{-10}	0.028
Cs				161.28	0.559		

[a] The molecular weight of the intercalated PEO is 6×10^5.

In the SPEs VTF behavior is considered characteristic of ionic motion strongly coupled to the polymer segmental relaxation mode[23] with T_o identified as the ideal glass transition temperature below which all segmental motion is frozen. Although in the $Cd_{0.75}PS_3A_{0.5}(PEO)$ compounds no DSC evidence for T_g is observed, it is still reasonable to assume that the enhanced conductivity above $T = 200$ K is associated with polymer segmental motion and the lower values of σ_{dc} below 200 K due to freezing of the segmental motion so that conductivity arises from a classical hopping of ions. (It has been suggested for the SPEs that changes in microviscosity due to local segmental motion are sufficient for enhanced conductivity; changes in viscosity on the length scale of the molecular weight are not a prerequesite.[24])

A possible clue as to why the conductivity for $T > 200$ K of Li− and Na−PEO intercalated compounds follow VTF behavior whereas that of the K and Cs compounds follows Arrhenius behavior is the observation that the lattice expansion for Li− and Na−PEO intercalates are roughly the same, $\Delta d \approx 8.5$ Å, while for K and Cs ions, it is larger and dependent on the size of the ion, $\Delta d = 9.05$ and 9.56 Å, respectively. The IR spectra also suggest that the complexation of Li and Na ions by the ether linkages of PEO are stronger as compared to those for K and Cs. Consequently it may be anticipated that the motion of the smaller ions, Li and Na, are more strongly coupled to polymer segmental motion as compared to that of the larger ions. Since polymer segmental motion follows VTF behavior,[23] the conductivity of ions strongly coupled to this motion also follows the same functional form. For K− and Cs−PEO intercalates, ionic motion is probably decoupled from polymer segmental motion and consequently the Arrhenius conductivity.

It is interesting to compare the conductivity and its temperature dependence of the intercalated polymer electrolytes with those of SPEs of similar O:A ratio. The comparison is not straightforward since, for the SPEs, the nature of counteranions not only affects the magnitude of the conductivity but also affects whether the temperature dependence is VTF or Arrhenius.[25] The quantities that we are interested in comparing are the dc conductivities at ambient temperature and the Arrhenius and VTF parameters. A comparison of the

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(24) Watanabe, M.; Ogata, N. In *Polymer Electrolyte Reviews Vol. 1*; MacCallum, J. R., Vincent, C. A., Eds.; Elsevier: London, 1987.

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conductivity data in Figure 9a,b with data for $LiClO_4-PEO(O:Li = 4:1)$ from ref 26 and $NaClO_4-PEO(O:Na = 4:1)$[27] shows that the room temperature dc conductivities of the intercalated polymer electrolytes are superior to that of the corresponding conventional SPEs. At 300 K the conductivity of the intercalated Li−PEO is 1.3×10^{-7} S/cm whereas that of $LiClO_4-PEO(O:Li = 4:1)$ is 1.1×10^{-8} S/cm. Similarly at 300 K the conductivity of the intercalated Na−PEO, 1.8×10^{-7} S/cm, is higher than that of $NaClO_4-PEO$ (O:Na = 4:1), 1.3×10^{-8} S/cm. Although the conductivity of the conventional PEO-based SPEs are appreciable at higher temperature, there is a sharp drop at ∼330 K due to crystallization of the polymer salt complex.[25] This temperature corresponds to the melting point of the uncomplexed PEO. In PEO-based SPEs, VTF behavior is rarely encountered below this temperature. In the intercalated polymer electrolytes, however, the conductivity shows a smooth variation with temperature down to 200 K.

For $Cd_{0.75}PS_3Li_{0.5}(PEO)$ and $Cd_{0.75}PS_3Na_{0.5}(PEO)$, the value of the VTF T_o is considerably smaller than that for the corresponding SPEs whose conductivity follows the VTF relation, e.g., the T_o value of 90 K for the intercalated Li−PEO is considerably smaller than the T_o value of ∼230 K observed in lithium salt complexes of PEO.[28] The T_o values of the intercalated polymers are, in fact, lower than the T_o value of 163 K for bulk PEO, which may be approximated as $T_g - 50$ K. This result is rather surprising since it is well known that alkali metal salt complexation causes the PEO chains to stiffen and shift T_g (and T_o) to higher temperatures.[29] The results may, however, be understood by considering the density of the intercalated polymer (Table 2), which is about half of that of bulk PEO (1.13 g/mL). Thus the free volume, defined as the difference in the volume available to a molecule and its van der Waals volume, is larger for the PEO confined between the negatively charged $Cd_{0.75}PS_3$ sheets as compared to that for bulk PEO. It is therefore not surprising that T_o, the temperature at which segmental motion is “frozen” is lower for the intercalated polymer electrolytes.

The room temperature (300 K) conductivity of $Cd_{0.75}PS_3K_{0.5}(PEO)$ and $Cd_{0.75}PS_3Cs_{0.5}(PEO)$, 0.2×10^{-7} and 0.7×10^{-7} S/cm, are comparable with conductivity values of the corresponding, K and Cs, PEO-based SPEs. Representative room temperature values for these SPEs are 2×10^{-7} S/cm for $PEO-KCF_3SO_3$ (O:K = 4.5:1)[25] and 4×10^{-7} S/cm for PEO−CsSCN (O:Cs = 8:1).[25] It is interesting to note that for $Cd_{0.75}PS_3K_{0.5}(PEO)$ and $Cd_{0.75}PS_3Cs_{0.5}(PEO)$, the Arrhenius activation energies for $T > 200$ K are comparable to the high-temperature ($T > 330$ K) Arrhenius activation energies of potassium-based SPEs which are typically 0.47 eV.[30] It may be recalled that $T \sim 330$ K corresponds to the congruent melting of the eutectic SPE compositions above which the conducting amorphous phase is formed.

It thus appears as if the ambient temperature dc conductivity behavior of the alkali metal−PEO intercalates is what could have been expected if the high-temperature conductivity behavior of the PEO-based SPEs could be smoothly extrapolated to ambient temperatures. These results suggest that the mechanisms of dc conductivity at ambient temperatures in the intercalated A−PEO (A = Li, Na, K, Cs) are similar to those in the high-temperature amorphous phase of the SPEs.

4. Concluding Remarks

We have prepared $Cd_{0.75}PS_3A_{0.5}(PEO)$ (A = Li, Na, K, and Cs) and characterized the materials by X-ray diffraction, IR spectroscopy, and conductivity measurements. We find that for the intercalated polymer electrolytes the ratio of the ether oxygens to alkali ions, O:A, is roughly 4:1, irrespective of the nature of the cations or the molecular weight of the intercalated PEO, and in fact does not change drastically when the polymer is changed from PEO to PPO. The lattice expansion on intercalation is approximately the same whether the intercalated polymer is PEO or PPO. It does, however, depend on the cation. For the Li− and Na−PEO compounds, it is approximately identical ($\Delta d \approx 8.5$ Å), but for the K ($\Delta d = 9.05$ Å) and Cs ($\Delta d = 9.56$ Å) compounds, the lattice expansion depends on the cation size. The projected one-dimensional electron density calculated from the X-ray intensities shows that alkali metal ions in the interlamellar van der Waals space are displaced from the center of the gap. The density of the intercalated PEO is considerably less than that of bulk PEO, and since the mid-IR spectra are identical for powder and oriented crystals, it is unlikely that the PEO strands have any specific orientation with respect to the layers. The mid-IR spectra of $Cd_{0.75}PS_3A_{0.5}(PEO)$ (A = Li, Na, K, and Cs) have features arising from $O-CH_2-CH_2-O$ in both *trans* and *gauche* conformations. The results rule out a helical conformation for the intercalated PEO and suggest a planar zig-zag conformation with *at least* two strands complexing the alkali cation.

The conductivity behavior of the alkali metal−PEO compounds of $CdPS_3$ are extremely interesting. Perhaps the most significant result is that the room temperature dc conductivity values of the Li− and Na−PEO intercalated compounds are higher than that of the conventional PEO-based SPEs of similar stoichiometry. Unlike the SPEs, the conductivity of the intercalated polymer electrolyte does not show a drastic drop at 330 K due to crystallization. The dc conductivities of the $Cd_{0.75}PS_3A_{0.5}(PEO)$ show two temperature regimes. At temperatures below 200 K, the conductivities are small and show a weak Arrhenius temperature dependence. Above 200 K, the conductivity rises fairly rapidly, and in this regime, the temperature variation depends on the alkali cation. For the K− and Cs−PEO intercalation compounds, the dc conductivity for $T > 200$ K shows an Arrhenius dependence with an activation energy similar in value to that observed for the corresponding SPEs in their high-temperature phase above 330 K. The conductivity of the Li− and Na−PEO intercalation compounds, however, follows the VTF function, characteristic of ionic motion coupled to poly-

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[30] Rietman, E. A.; Kaplan, M. L.; Cava, R. J. *Solid State Ionics* **1987**, *25*, 41.

mer segmental motion. The VTF T_o, the temperature at which segmental motion freezes, is significantly lower for the intercalated polymer electrolyte as compared to values reported for SPEs and, in fact, is lower than that of bulk PEO. This observation is probably a consequence of the lower density of the intercalated PEO in $Cd_{0.75}PS_3A_{0.5}(PEO)$ as compared to that of the bulk polymer.

From an application perspective, the high values of ionic conductivity in $Cd_{0.75}PS_3Li_{0.5}(PEO)$ in conjunction with the fact that there is no contribution to the conductivity from the massive, negatively charged $Cd_{0.75}PS_3$ layer make this material a promising candidate as "solventless-anionless" electrolytes in lithium electrochemical devices. Work on the application of these materials as electrolytes in a lithium rechargeable cell is currently in progress.

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Supporting Information Available: The figure showing the 00*l* reflections for $Cd_{0.75}PS_3A_{0.5}(PEO)$ and tables of *d* spacings and *hkl* reflections (4 pages). Ordering information is given on any current masthead page.

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