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Conductivity and Raman Spectroscopy of New Indium(I) and Thallium(I) Ionic Conductors. In_4CdI_6, In_2ZnI_4, and Tl_2ZnI_4, and the Related Compound Tl_4CdI_6

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The new compound Tl_2ZnI_4 has been prepared and characterized by Raman spectroscopy, powder X-ray diffraction, elemental analyses, and a partial binary phase diagram. The compounds In_4CdI_6, Tl_4CdI_6, and In_2ZnI_4, for which phase diagrams are available in the literature, were characterized by Raman spectroscopy and their identities were confirmed by elemental analyses and X-ray powder diffraction. Each of these materials, except Tl_4CdI_6, undergoes a sharp order–disorder phase transition at elevated temperatures that can be detected by the measurement of Raman spectra as a function of temperature. Conductivity measurements as a function of temperature, using both reversible and blocking electrodes, reveal a high ionic conductivity in the disordered, high-temperature phase. This work suggests that indium(I) and thallium(I) ionic conductors may exist, analogous to some well-known double salt conductors based on simple silver(I) and copper(I) halides. In addition, the present study demonstrates the usefulness of Raman spectroscopy in the characterization of heavy-metal ionic conductors.

Introduction

Many Ag(I) and Cu(I) iodide systems exhibit abnormally large values of ionic conductivity, while metal halide compounds containing less polarizable and more highly charged cations possess much lower conductivities. On this basis, it has been argued that highly polarizable, monopositive ions which are stable in both 4-coordinated (tetrahedral) and 3-coordinated configurations will have the highest mobility among the various metal halide systems (*1*, *2*). The present work was designed to test the application of this postulate to the polarizable, monopositive cations In(I) and Tl(I), which have been found to be relatively poor ionic conductors in all but one of the systems studied to date (*3*). The low coordination number of In(I) in its anionic halide complexes (*4*, *5*) makes it particularly promising as a highly mobile cation. The present study also provided a further test of Raman spectroscopic line broadening as a tool for screening and characterizing potential ionic conductors (*6*).

The compounds In_2ZnI_4 and In_4CdI_6 have been chosen for study since their published phase diagrams (*7*, *8*) indicate the existence of a polymorphic phase transition, analogous to those found for ionic conductors such as

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Ag_2HgI_4 (*9, 10*), Cu_2HgI_4 (*10*) and the silver halide chalcogenides and their derivatives (*11*). We also report our findings on the compound Tl_4CdI_6 (*12*), which does not undergo a polymorphic phase transition, and on the previously unreported Tl_2ZnI_4.

Experimental

Synthesis

High-purity metals, resublimed iodine, and reagent grade chemicals were used for all syntheses. Hygroscopic and oxygen-sensitive solids were handled in a nitrogen-filled dry box.

Indium metal, cadmium iodide, and iodine were used to prepare In_4CdI_6, while the analogous thallium compound, Tl_4CdI_6, was prepared from thallium iodide and cadmium iodide. The compound In_2ZnI_4 was prepared from indium, zinc, and iodine and by the direct combination of indium(I) iodide and zinc iodide. These metal iodides were prepared from the respective metals and iodine in the manner described below, characterized by Raman spectroscopy, and used without further purification. Thallium(I) iodide, zinc, and iodine were used to prepare Tl_2ZnI_4.

Stoichiometric amounts of the appropriate starting materials were placed in a 12-mm-o.d. Pyrex tube, flushed with dry N_2, and sealed under vacuum. In all cases except In_2ZnI_4, the tubes were placed vertically in a tube furnace, heated above the melting point of the highest melting component, maintained at that temperature for 48 hr, and then slowly cooled to room temperature. In the case of In_2ZnI_4, the melt was heated for 100 hr just above the melting point to avoid formation of an In(III) species.

Analyses

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee, and Schwarzkopf Microanalytical Laboratories, Woodside, New York. The results are summarized in Table I.

TABLE I

Compound	Element	% Calculated	% Found
In_4CdI_6	In	34.45	34.86
	I	57.11	57.16
Tl_4CdI_6	Tl	48.33	48.53
	I	45.02	44.88
In_2ZnI_4	In	28.61	29.06
	I	63.24	62.88
Tl_2ZnI_4	Tl	41.64	41.93
	I	51.70	51.97

Characterization

Powder X-ray diffraction patterns were taken with a 114.6-mm-diameter Debye–Scherrer camera using Ni-filtered Cu$K\alpha$ radiation.

Differential thermal analyses (DTA) were performed on a DuPont 990 Thermal Analyzer. Scans were made over the range 150 to 350°C at rates of 10 and 20°C/min with the sample maintained under a N_2 atmosphere.

The Raman spectra were recorded with a Spex 0.85 m-double monochromator using backscattering sample illumination, a variable temperature setup, and a digital data acquisition system which has been described previously (*13*). Peak positions relative to the exciting line were determined digitally and these results were checked by visual inspection or strip-chart recordings. The monochromator bandpass was 1–2 cm^{-1} and the laser power was typically between 10 and 30 mW. The 488.0- and 514.5-nm lines of an argon ion laser and the 632.8-nm line of a He–Ne laser were used as exciting lines. The samples, in sealed reaction tubes, were analyzed at several points along their axes to determine their degree of homogeneity. The temperature was monitored with the aid of an iron–constantan thermocouple placed in close proximity to the sample, and a potentiometer. Spectra were recorded during both heating and cooling cycles, verifying the reversibility of the phase transitions.

Conductivity Measurements

Electrical conductivity measurements were made on polycrystalline samples of the materials in the form of pressed pellets, $\frac{1}{2}$ in. in diameter and roughly 2 mm thick. The $\frac{1}{2}$-in. diameter pellets were prepared at room temperature under a pressure of 6000 psi. Measurements were made under dry nitrogen in a tube furnace, using an iron–constantan thermocouple and potentiometer to monitor the temperature. Aluminum disks, coated with either indium or a thin film of thallium–mercury amalgam (~10% Tl), were used as reversible electrodes for the indium and thallium compounds. The sample pellets were sandwiched between the electrodes and the voltage and the current was measured at various temperatures at a frequency of 1 kHz using an ac bridge.

An additional set of measurements was made using a standard ac impedance bridge (Wayne–Kerr Universal Bridge 221 A or General Radio Bridge 1608-A) and an external oscillator (General Radio 1310). The frequency dependance was measured using graphite electrodes (Ultra Carbon 883804 (U626-R), UF4S, LOT 7192) and total DC conductivity was measured using platinum-blocking electrodes. These measurements were made under a purified argon atmosphere with the temperature controlled within +0.3°C.

Results and Discussion

Identity of Compounds

The previously reported compounds In_4CdI_6 (*8*), Tl_4CdI_6 (*12*), and In_2ZnI_4 (*7*) were characterized by Raman spectroscopy and their identities were confirmed by elemental analyses and X-ray powder diffraction patterns. Both In_4CdI_6, a dark brown compound, and Tl_4CdI_6, a dark gray compound, were found to be homogeneous by examining the reaction product at several points along the reaction tube by means of Raman spectroscopy. The Raman spectra are summarized in Table II.

Comparison of these spectra with those given in Table III for InI, TlI, and CdI_2 indicates that the ternary materials are new compounds and not simply mixtures of the component iodides. The significance of some of the Raman bands in terms of the structure of the compounds will be discussed below.

Satisfactory elemental analyses were obtained for both In_4CdI_6 and Tl_4CdI_6 (Table I). The X-ray diffraction patterns obtained agree well with those reported previously for the indium (*8*) and thallium (*12*) compounds.

The pale yellow compound, In_2ZnI_4, has been found to be a homogenous compound, as judged by Raman spectroscopy. The Raman spectrum (Table II) is clearly that of a new compound and not merely a mixture of InI and ZnI_2 (Table III). The major impurity in these preparations is the In(III) species, InI_4^-, which

TABLE II

Raman shift (cm^{-1})	Relative intensity	Raman shift (cm^{-1})	Relative intensity
In_4CdI_6		Tl_4CdI_6	
112.6	2700	114.9	20 300
79.1	1200	76.0	5000
65.9	1300	62.7	9300
40.2	3600	47.1	7200
24.7	1600	33.0	21 500
—	—	19.1	11 500
In_2ZnI_4		Tl_2ZnI_4	
177.4	950	177.5	750
127.9	11 500	127.9	7100
77.2	5100	80.6	3600
57.3	5400	58.3	3500
48.8	5600	49.0	2600
42.2	7200	—	—
30.9	21 000	29.0	14 400

TABLE III

RAMAN SHIFTS AND RELATIVE INTENSITIES OF MAJOR BANDS IN COMPONENT METAL HALIDES

InI[a]	TlI[b]	CdI_2[c]	ZnI_2[d]
39 cm^{-1} (mw)	22 cm^{-1} (vs)	43.5 cm^{-1} (m)	42 cm^{-1} (w)
78 cm^{-1} (vs)	29 cm^{-1} (vs)	112.5 cm^{-1} (vs)	47 cm^{-1} (m)
105 cm^{-1} (mw)	37 cm^{-1} (m)		58 cm^{-1} (m)
135 cm^{-1} (w)	56 cm^{-1} (w)		63 cm^{-1} (w)
211 cm^{-1} (s)	69 cm^{-1} (w)		71 cm^{-1} (w)
			78 cm^{-1} (w)
			120 cm^{-1} (vs)

[a] See Ref. 5. vs = very strong, s = strong, m = moderate, w = weak.

[b] Values from our own spectra, agree well with the literature; see O. Brafman *et al.*, *Solid State Commun.* 7, 449 (1969).

[c] See Ref. (*14*)

[d] Values from our own spectra.

is characterized by a strong, distinct band in the Raman spectrum at 139 cm^{-1} (*5*). This impurity can be avoided by using a stoichiometric excess of In and heating the sample for 100 hr during preparation, or by preparing indium(I) iodide and zinc iodide separately and melting together stoichiometric amounts of these two iodides. The results of the elemental analysis are satisfactory for pure In_2ZnI_4 (Table I). The X-ray powder pattern agrees well with that reported previously (*7*).

The compound Tl_2ZnI_4 has not been previously reported in the literature. It was prepared as described under Experimental and was characterized as described below. The results of elemental analyses demonstrate a bulk composition which agrees with the proposed formula of the compound. An X-ray diffraction pattern has been obtained for this compound which showed no indication of free thallium iodide or zinc iodide (Table IV).

The Raman spectrum of this light gray, nearly white, product is summarized in Table II. Comparison with the spectra of TlI and ZnI_2 suggests that Tl_2ZnI_4 is indeed a new compound containing no free TlI or ZnI_2 (Table III). Raman analysis of the product at several points along the axis of the reaction tube in which it was prepared demonstrates that the product is homogenous. Figure 1 shows that the Raman spectrum of this compound is remarkably similar to that of In_2ZnI_4, suggesting that the compounds may possess closely related structures. Details of the spectrum are discussed below.

To determine whether Tl_2ZnI_4 is a congruently melting compound and to obtain some idea of the phase diagram of the TlI–ZnI_2 system, differential thermal analysis (DTA) measurements were performed on samples containing 60–75 mole% of TlI (40–25 mole% of ZnI_2). These samples were made up with the

TABLE IV

POWDER PATTERN FOR Tl_2ZnI_4[a]

d (Å)	Intensity	*d* (Å)	Intensity
5.2	m	2.14	vw
3.95	m	2.08	m
3.40	s	2.03	w
3.12	s	1.99	s
3.00	s	1.91	w
2.82	w	1.83	m
2.64	w	1.78	m
2.49	w	1.71	s
2.43	m	1.65	m
2.34	w	1.61	w
2.26	w	1.54	w
2.21	w		

[a] vw = very weak, w = weak, m = moderate, s = strong, vs = very strong.

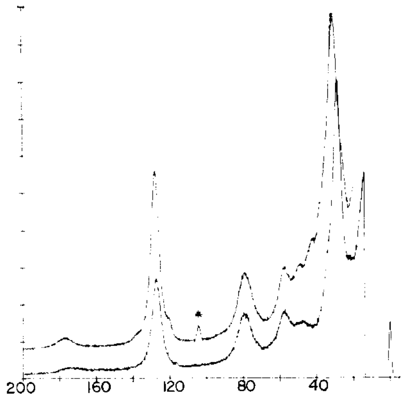

FIG. 1. Raman spectra of In_2ZnI_4 (upper spectrum) and Tl_2ZnI_4 (lower spectrum) (* denotes laser plasma line).

appropriate mole percent of each component, melted, crushed, and run as powdered samples. The results of this study are summarized in Fig. 2, in which it is seen that a material having the composition Tl_2ZnI_4 (66.7% TlI–33.3% ZnI_2) melts congruently at 297°C and undergoes a polymorphic phase transition at 250°C. The eutectics, formed between the ternary compound and one of the simple (binary) salts, i.e., one of the components of the system, occur at 288°C on the ZnI_2-rich side and 279°C on the TlI-rich side. Raman spectra were recorded at room temperature for previously melted products of gross compositions 63% TlI–37% ZnI_2 (excess ZnI_2) and 72% TlI–28% ZnI_2 (excess TlI). The spectra were a combination of those for Tl_2ZnI_4 and the excess component; no evidence of any new species was found. Accordingly, it appears that Tl_2ZnI_4 is the only compound which is stable in this system at room temperature.

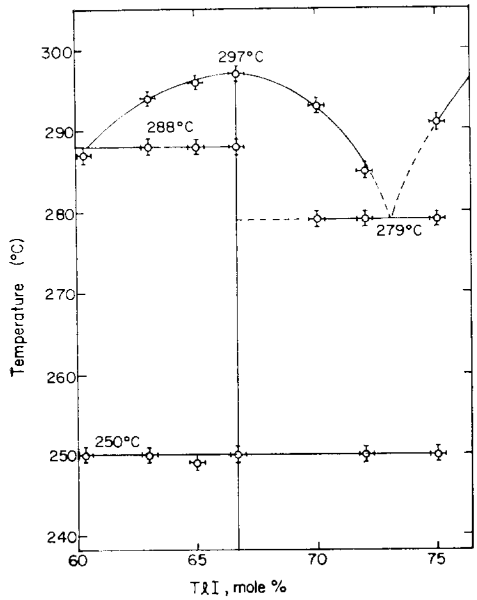

FIG. 2. The TlI–ZnI_2 system between 60 and 75 mole% TlI.

The detailed structures of these compounds are still unknown. However, certain structural features can be inferred from the Raman spectral data. The Raman spectrum of In_4CdI_6 is characterized by an intense band at 112.6 cm^{-1}, and a band of similar intensity if found at 114.9 cm^{-1} for Tl_4CdI_4. For comparison, the Raman spectrum of cadmium iodide, in which the cadmium atom is surrounded by an octahedral arrangement of six iodine atoms, has a prominent band at 112.4 cm^{-1} (*14*). This band was identified as an $A_{1}g$ mode (point group $D_{3}d$) by single-crystal vibrational studies (*15*, *16*). By contrast, the Raman spectra of several tetraalkylammonium salts of the tetraiodocadmate ion display a strong band at a significantly higher frequency, 120 cm^{-1}, attributed to the symmetric CdI_4 stretch of a nearly tetrahedral complex (*17*). This comparison suggests that the bands observed for In_4CdI_6 and Tl_4CdI_6 represent the breathing vibration for an octahedral or nearly octahedral CdI_6 moiety. Indeed, the decrease in stretching frequency with increased coordination number, upon which the above conclusion is based, is a well-known phenomenon for many metal halide systems (*18*, *19*).

The similarity of the Raman spectra of In_2ZnI_4 and Tl_2ZnI_4, which was noted above, presumably results from a similarity of structure for these materials. The Raman spectrum of ZnI_4^{2-} in aqueous solution has been recorded and consists of four bands (*20*). Using the Raman spectrum of Cs_2ZnI_4, vibrational assignments have been made for the species ZnI_4^{2-} (*21*) based on the presumption that it is nearly tetrahedral, as are $ZnCl_4^{2-}$ (*22*) and $ZnBr_4^{2-}$ (*23*) in their respective Cs salts. The Raman spectrum of Cs_2ZnI_4, with vibrational

TABLE V

ZnI_4^{2-} (soln)[a]	Cs_2ZnI_4[b]	In_2ZnI_4	Tl_2ZnI_4
44	60 ν_2 (E)	57.3	58.3
62	70 ν_4 (F_2)	79.2	80.6
122	130 ν_1 (A)	127.9	127.9
172	172 ν_3 (F_2)	177.4	177.5

[a] See Ref. (*20*).
[b] See Ref. (*21*).

assignments, is listed in Table V, along with what appear to be the corresponding bands in Zn_4^{2-} (aq), In_2ZnI_4, and Tl_2ZnI_4. It might be argued that the band at 79.2 cm^{-1} in the spectrum of In_2ZnI_4 corresponds to the very strong band at 78 cm^{-1} in indium(I) iodide (*5*). However, the excellent correspondence of this band with the 80.6 cm^{-1} band in Tl_2ZnI_4 and the absence of other InI bands support the assignment given in Table V. Thus, it seems clear that the species ZnI_4^{2-} exists in both the indium and thallium compounds.

Temperature-Dependent Raman Scattering Experiments

A common feature of many good ionic conductors is the presence of a transition from a low-temperature, poorly conducting, ordered phase, to a higher-temperature, disordered phase, exhibiting abnormally high ionic conduction, a classic example being Ag_2HgI_4 (*9*, *10*). A technique sensitive to the onset of such disorder is potentially useful in screening new materials for fast ionic transport. It has been suggested that broadening of the Rayleigh scattering line in Raman spectroscopy, which has been observed for the disordered phase of AgI, may be a means for detecting such phase transitions (*24*). The observation of line broadening of certain vibration modes in disordered systems has led to the use of vibrational spectroscopy in the investigation of these systems (*6*, *25–27*). For example, a large broadening of certain vibrational modes in the compounds Ag_2HgI_4 and Cu_2HgI_4 is coincident with their transition to a high-temperature, conducting phase, but no such broadening has been observed for Tl_2HgI_4 which is a poor conductor at all temperatures up to its melting point (*6*).

Several origins are possible for the broadening of certain vibrational modes in disordered phases. These include the loss of rigorous selection rules owing to the loss of translational symmetry in the disordered system, and the occurrence of new decay channels for the lifetime broadening of optical transitions (*28*, *29*). Another potential source of broadening in the disordered solid is the creation of a range of new atomic groupings (on an instantaneous or vibrational time scale) producing a more complex spectrum consisting of a series of overlapping bands which give the appearance of simple line broadening. Fortunately, details of the broadening mechanism are not important for the use of the phenomenon as a tool for screening potential ionic conductors.

Raman spectra of the present compounds were studied at various temperatures in order to uncover evidence for disorder. The compound Tl_4CdI_6, which has not been reported to undergo a polymorphic transition, shows only slight broadening of its vibrational modes up to 215°C. The degree of broadening observed for this material is readily attributed to thermal effects and not to structural disorder By contrast, in all of the other materials studied, definite indications were obtained from the Raman spectra for the existence of high-temperature disordered phases. As the temperature of In_4CdI_6 is raised several peaks broaden, and on reaching 175°C the peak at 79 cm^{-1} has broadened completely into the Rayleigh line. Upon raising the temperature above the reported polymorphic transition point (208°C), the peaks at 66 and 112 cm^{-1} disappear completely and the peak at 40 cm^{-1} loses intensity (Fig. 3).

The Raman spectrum of In_2ZnI_4 loses intensity and several peaks broaden dramatically above the polymorphic transition temperature (210°C) (Fig. 4). This phenomenon is particularly clear for the peaks at 30 and 78 cm^{-1}. The band at 127 cm^{-1} due to ZnI_4^{2-} (*20*, *21*) is also seen to broaden, but the appearance

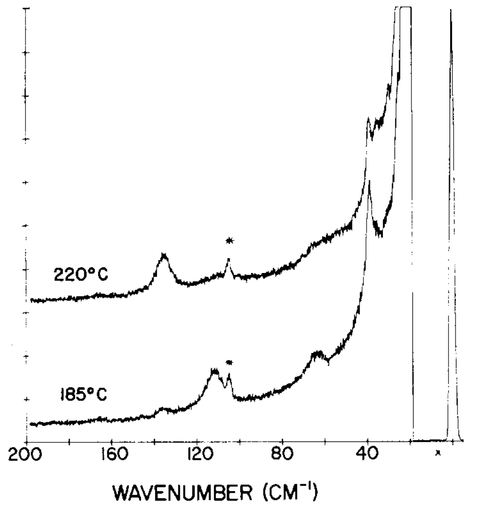

FIG. 3. Variable-temperature Raman spectra of In_4CdI_6 (* denotes exciting and plasma lines).

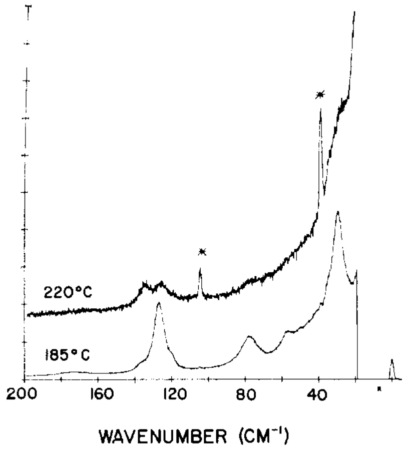

FIG. 4. Variable temperature Raman spectra of In_2ZnI_4 (* denotes exciting and plasma lines).

of a band at 135 cm^{-1} suggests the formation of InI_4^- in the higher-temperature phases (*5*).

The Raman spectra of the compound Tl_2ZnI_4 change dramatically between 239 and 257°C, with only the peak at 125 cm^{-1} remaining distinct; broad features can be seen at 25 and 77 cm^{-1} (Fig. 5); however, this agrees with the DTA results which indicate that Tl_2ZnI_4 undergoes a polymorphic transition at 250°C. These results demonstrate that the compounds In_4CdI_6, In_2ZnI_4, and Tl_2ZnI_4 all exhibit high-temperature disordered phases

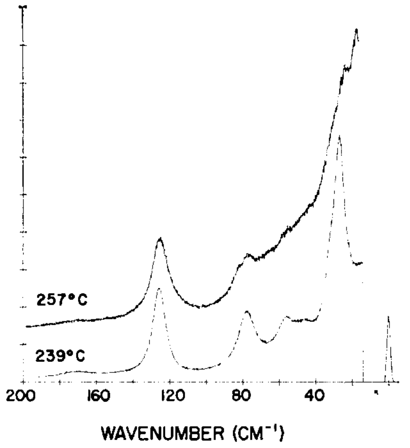

FIG. 5 Variable-temperature Raman spectra of Tl_2ZnI_4 (* denotes exciting line).

which may be accompanied by high ionic conductivity.

Conductivity Measurements

Even though conductivity data obtained from single crystals is preferred over conductivity data derived from polycrystalline samples, nevertheless data obtained using pressed pellets of several ionic conductors based on AgI have been found to agree well with measured conductivity values derived from single-crystal samples of the same material (*30, 31*).

Measurements on Tl_4CdI_6 using reversible electrodes indicate that the conductivity is essentially constant from room temperature to 250°C and extremely low, $\sigma \simeq 10^{-8}\ \Omega\ cm^{-1}$. This apparent lack of dependence of the conductivity on temperature and the small value of the conductivity suggest that capacitance effects are being observed. However, there is no evidence for a polymorphic transition to a conducting phase, in agreement with previous phase studies and variable-temperature Raman results.

The conductivity of In_4CdI_6 was observed to rise abruptly at 210°C when the conductivity was measured as a function of temperature (Fig. 6). Presumably, this change is associated with the phase transition reported to occur at 210°C. The change in conductivity was found to be reversible when the sample was cooled to 195°C. The conductivity did show a fre-

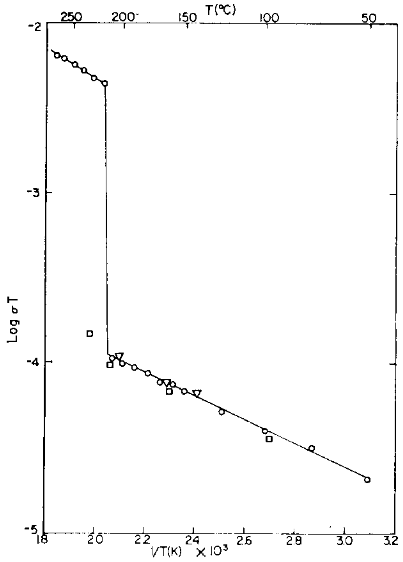

FIG. 6. Temperature-dependent conductivity data for In_4CdI_6 (○, heating; △, cooling; □, electronic).

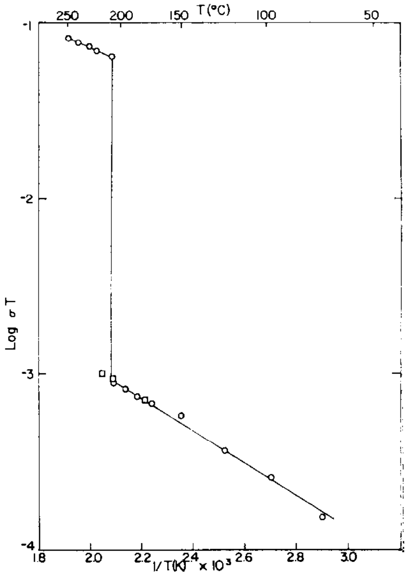

FIG. 7. Temperature-dependent conductivity data for In_2ZnI_4 (○, total; □, electronic).

quency dependance at lower temperatures; however, this frequency dependence decreased and finally disappeared as the temperature was raised above 190°C. Measurements with blocking electrodes indicate that the ionic component of conductivity is 1.5 orders of magnitude greater than the electronic component above the transition temperature. At temperatures below the transition temperature, the conductivity appears to be almost totally electronic, similar to the findings reported for Ag_2HgI_4 (*32*).

There is a sharp rise in the conductivity of In_2ZnI_4 at 210°C when the conductivity is measured as a function of temperature (Fig. 7). As in the case of In_4CdI_6, this change appears to be related to a polymorphic phase transition. The conductivity again showed a frequency dependence at lower temperatures which decreased and finally disappeared altogether at about 140°C. Blocking electrode measurements indicate that above the transition temperature the ionic component of conductivity is 1.5 orders of magnitude greater than the electronic component. Below the transition temperature, the conductivity appears to be almost totally electronic, which again is similar to the behavior observed for Ag_2HgI_4 (*32*).

Temperature-dependent conductivity measurements on Tl_2ZnI_4 indicate a sharp increase in conductivity at 250°C (Fig. 8). This observation agrees with the results of DTA and temperature-dependent Raman studies, all of which suggest that Tl_2ZnI_4 undergoes an order–disorder transition at 250°C. The conductivity is frequency dependent through-

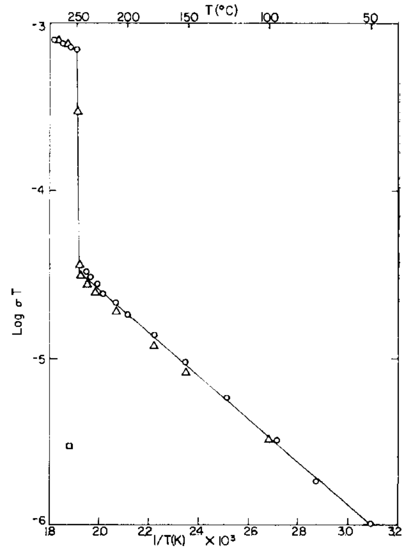

FIG. 8. Temperature-dependent conductivity data for Tl_2ZnI_4 (○, heating, △, cooling, □, electronic).

out the temperature range studied, although the dependence does decrease above the transition temperature. Measurements with blocking electrodes indicate that the electronic component of conductivity is negligible above the transition temperature and not even significant below the transition temperature, where the electronic conductivity is 1.5 orders of magnitude less than the total conductivity.

Summary

The compounds In_4CdI_6, In_2ZnI_4, and Tl_2ZnI_4, all of which undergo polymorphic phase transitions, have been shown to be ionic conductors in their disordered phase; in contrast Tl_4CdI_6, which does not undergo such a transition, is not an ionic conductor. Although these compounds are not exceptionally good conductors, they demonstrate that In(I) and Tl(I) ions may be the conducting species in some materials. The results of Raman measurements conducted as a function of temperature on these compounds demonstrate its usefulness as a screening tool for ionic conductors, through the detection of the onset of a disordered phase on heating the sample.

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