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# Studies on electrical and optical properties of vanadium-incorporated ion-deficient perovskites

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Partial substitution of $V^{5+}$ for $Ti^{4+}$ in $SrTiO_3$ has been carried out and the effect of the cation vacancies so created on the polarity of the bonds in the substrate has been investigated. With this end in view compounds with the general formula $Sr_{(1-x/2)}\square_{x/2}Ti^{4+}_{(1-x)}V^{5+}_xO_3$, where $x \leqslant 0.5$, have been prepared, and their optical and electrical properties studied. A comparison of the results with those obtained for a similar perovskite having all the cation vacancies filled up by potassium ions suggested an increase in covalency of the B–O bond in the peroskite due to the incorporation of $V^{5+}$.

## 1. Introduction

One of the most important aspects of oxide chemistry that has been recognized as a dominant factor in controlling the electrical, optical and catalytic properties of oxides, is the role of ion-vacancies [1]. Lattice defects in $V_2O_5$ [2] and in $FeMoO_4$ [3] have been established as solely responsible for their catalytic activities. More recently, for many oxidation reactions ternary oxides with the scheelite structure, $AMO_4$, have been found to be catalytically active only when a sizeable number of A sites happened to be vacant [4, 5]. The effect of cation vacancies in oxide catalysts on their catalytic activities has been demonstrated by Voorhoeve *et al.* [6] through a study of oxides crystallizing in a perovskite lattice. Oxides with the perovskite structure have the generic formula $ABO_3$, where A is a large cation and B is a small cation. In one of the several manifestations of the lattice, an A ion occupies the centre of the cube with a B ion at each cube-corner and oxide ion at each edge-centre. B ions and oxide ions are in octahedral coordination whilst A ions are in dodecahedral coordination. Detailed physico-chemical studies of vacancy-studded perovskites have not been carried out, though partial substitution of B ions of a perovskite by higher valent ions have often been undertaken for tailoring the dielectric properties of a ceramic [7, 8]. The present paper is the consequence of an effort to study the effect of systematic substitution of $V^{5+}$ for $Ti^{4+}$ in $SrTiO_3$ on electrical conductivity, optical spectra and electron paramagnetic spectra of the substrate. This particular substitution has not so far been attempted, presumably because $V^{5+}$ is known to have ambiguous preference for tetrahedral and octahedral sites in any lattice [9]. The present investigation is aimed at preparing $Sr_{(1-x/2)}\square_{x/2}Ti^{4+}_{(1-x)}V^{5+}_xO_3$, where $x \leqslant 0.5$, and studying a few of their electrical and optical properties. In order to highlight the differences, if any, between the above ion-deficient perovskites on the one hand, and the corresponding stoichiometric perovskites on the other, it was proposed that the following two compounds were prepared and characterized (labelled as KV-20 and KV-50, respectively): $Sr_{0.8}K_{0.2}Ti_{0.8}V_{0.2}O_3$ and $Sr_{0.5}K_{0.5}Ti_{0.5}V_{0.5}O_3$.

## 2. Experimental procedure

Strontium titanate was prepared by the co-precipitation of strontium titanyl oxalate and subsequent calcination of the oxalate at 800° C.

Vanadium-incorporated strontium titanates were prepared by the total impregnation method. A stoichiometric amount of $TiO_2$ was added to an aqueous solution containing the required quantities of $Sr(NO_3)_2$ and $NH_4VO_3$. The solution was evaporated to dryness with constant stirring; the

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TABLE I

| Sample code | Formula | at % vanadium ($V^{5+}$) (cationic %) | Percentage of B sites occupied by vanadium ($V^{5+}$) |
|---|---|---|---|
| STV-10 | $Sr_{0.91}\ {}_{0.09}Ti_{0.81}V_{0.19}O_3$ | 10 | 19 |
| STV-20 | $Sr_{0.82}\ {}_{0.18}Ti_{0.63}V_{0.37}O_3$ | 20 | 37 |
| STV-25 | $Sr_{0.78}\ {}_{0.22}Ti_{0.55}V_{0.45}O_3$ | 25 | 45 |
| STV-29 | $Sr_{0.75}\ {}_{0.25}Ti_{0.5}V_{0.5}O_3$ | 29 | 50 |

dried mass ground well and calcined at 500° C for 8 h; followed by firing at 850° C for 48 h in a muffle furnace. The products were labelled STV-10, STV-20, STV-25 and STV-29. The numerical figures at the end of the symbols indicate the cation percentages of vanadium in the samples. The percentage of B sites occupied by vanadium is not the same as the cation percentage of vanadium. For instance, in STV-29 the cation percentage of vanadium is 29 whilst the percentage of B sites occupied by vanadium is 50. In other words, $x = 0.5$ for STV-29 in the general formula given in Table I.

Any attempt to prepare samples containing more than 30 at % of vanadium was not successful due to the formation of a fused, hard, unbreakable mass. Two compositions with potassium ions in the vacant sites of STV-20 and STV-29 were prepared by working stoichiometric quantities of potassium hydroxide into the mixture of the starting materials.

The densities of the samples were determined by the pyknometric method using carbon tetrachloride as the liquid. X-ray diffraction patterns of the powdered samples were obtained using a Dron-1 unit, Cu*Kα* radiation with a nickel filter.

Electron spin resonance (ESR) spectra of powdered samples were recorded at room temperature (and at liquid nitrogen temperature as well for $SrTiO_3$) using an X-band transmission type spectrophotometer. A magnetic field of around 3200 G, microwave frequency of 9.70 GHz and microwave power of 10 MW were employed. The small pip on each trace corresponded to a $g$ value of 2.0027 (marker was TCNE). $g$ values were calculated following the procedure of Hecht and Johnstone [10]. An independent estimate of the $g$ value was also arrived at from optical spectra recorded for this purpose. A method suggested by Ballhausen *et al.* [11] was used for this calculation.

Optical spectra of $SrTiO_3$, STV-20, STV-25, STV-29 and KV-20 were recorded in a Cary-17 D spectrophotometer using a pure quartz cell and pure magnesium oxide as the reference reflector. The spectrum for STV-10 was not recorded as the compound was practically white in colour.

Electrical conductivity measurements were made with silver painted pellets of the samples using a two-probe method. Resistance was measured with a vacuum tube voltmeter (Toshniwal) or an AVC megohm-meter depending on the range of conductivities measured. The readings from 150 to 500° C were considered for plotting $\log \rho$ against $10^3/T$.

## 3. Results

XRD patterns of strontium titanate and the potassium-containing compositions were identical with the $d$-spacings given in the ASTM powder diffraction file for $SrTiO_3$. The patterns for STV-10, STV-20 and STV-25 could all be indexed to a tetragonal lattice using a Hull–Davey chart. The lattice parameters are given in Table II. STV-29 was found to be cubic with a lattice parameter equal to that of $SrTiO_3$. This suggests that titanium and vanadium ions are in a disordered arrangement. Comparison of densities calculated from lattice parameters with those determined experimentally points to the presence of vacancies in STV materials and the absence of oxygen interstitials [12]. The fact that no phase other than that of the perovskite was present in the samples coupled with the situation that the relative amounts of the starting materials were such as to fill in all the B sites in

TABLE II

| Sample code | $c$ (nm) | $a$ (nm) | $c/a$ |
|---|---|---|---|
| STV-10 | 0.781 | 0.773 | 1.008 |
| STV-20 | 0.814 | 0.773 | 1.011 |
| STV-25 | 0.821 | 0.770 | 1.066 |
| STV-29 | 0.390 | 0.390 | 1.000 |
| $SrTiO_3$ | 0.390 | 0.390 | 1.000 |

TABLE III

| Sample code Room temp./ Low temp. | $g$ factor | | | hfs (cm$^{-1}$) | |
|---|---|---|---|---|---|
| | $g_\parallel$ | $g_\perp$ | $g_0$ | $A_\parallel$ | $A_\perp$ |
| $SrTiO_3$ (RT) | – | – | 1.999 | No hfs | |
| $SrTiO_3$ (LT) | 2.011 | 1.998 | 2.002 | 19.52 | 22.46 |
| STV-10 (RT) | 2.004 | 1.995 | 1.998 | 70.34 | 31.02 |
| STV-20 (RT) | 1.993 | 1.995 | 1.968 | 159.6 | 26.77 |
| STV-25 (RT) | 2.019 | 1.926 | 1.957 | 166.5 | 49.58 |
| STV-29 (RT) | 1.957 | 2.022 | 2.000 | 163.2 | 38.05 |
| KV-20 (RT) | | | A mixture of noise and signal | | |

the perovskite with titanium and vanadium showed that the vacancies in these perovskites were in the A sites.

ESR parameters of the samples are given in Table III. A representative ESR spectrum of the STV material is given in Fig. 1. Strontium titanate has an ESR signal which is isotropic at room temperature and anisotropic at 113 K. Anisotropy at the lower temperature may be due to the crystal field splitting and to the interaction of the nuclear spin of titanium with the electron spin. At room temperature spin-lattice relaxation vitiates the spectrum.

All the STV samples exhibited sharp signals with well-defined hyperfine splittings. Absence of spin–spin broadening in these signals clearly suggests that the paramagnetic species, namely $V^{4+}$, is present in extremely low concentrations. This may be considered as pointing to the presence of vanadium almost wholly as $V^{5+}$. The ESR spectra of $V_2O_4$ (which contains only $V^{4+}$) and $V_2O_5$ (which contains an appreciable percentage of $V^{4+}$ due to a defective structure) give ESR signals with broad spin–spin broadening. Thus in the samples under consideration, $V^{4+}$ must be present only in traces.

One of the KV compounds, (KV-20) which was subjected to ESR analysis showed a mixture of noise and signal. The hyperfine structure (hfs) consisted of a greater number of lines than the octet characteristic of the vanadium nuclei.

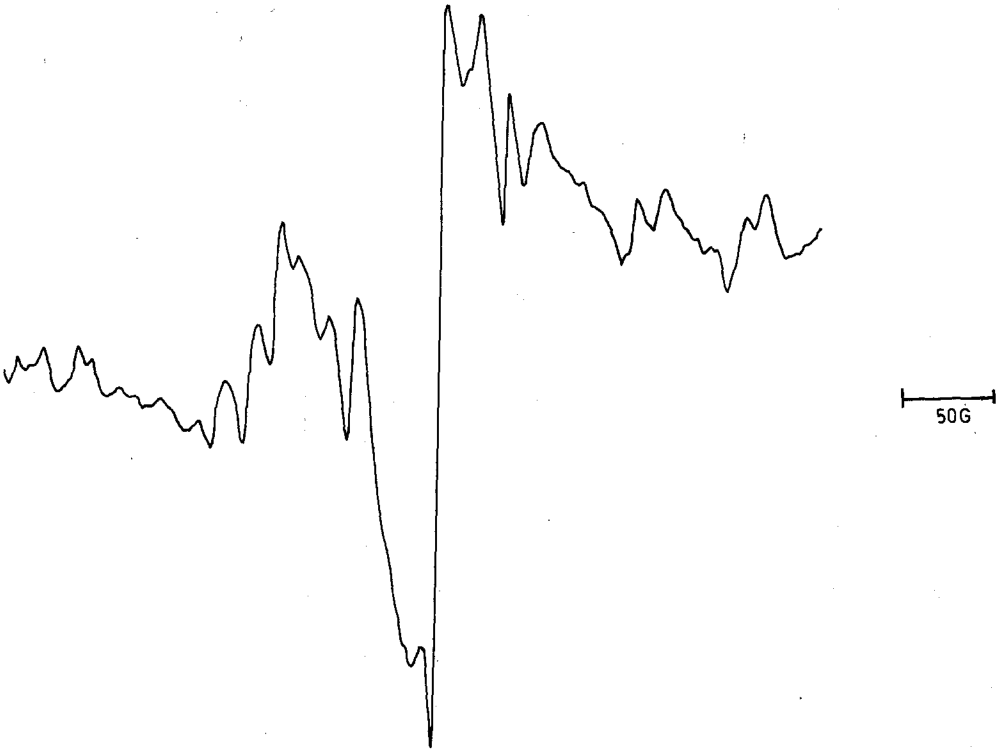

*Figure 1* A representative ESR spectrum for STV material.

TABLE IV

| Sample code | Electrical conductivity at 325° C (ohm$^{-1}$ cm$^{-1}$) | Energy of activation for conduction (eV) |
|---|---|---|
| SrTiO$_3$ | $1.995 \times 10^{-8}$ | 1.037 |
| STV-10 | $2.884 \times 10^{-9}$ | 0.345, 1.41* |
| STV-20 | $3.63 \times 10^{-8}$ | 0.967 |
| STV-25 | $5.01 \times 10^{-8}$ | 0.932 |
| STV-29 | $1.202 \times 10^{-8}$ | 0.994 |
| KV-20 | $3.52 \times 10^{-8}$ | 1.45 |

*Slope changes

Electrical conductivities of the samples at 325° C (temperature at which most of the catalytic vapour phase oxidation reactions are carried out) and activation energies for conduction of the substances under investigation are given in Table IV. The Arrhenius plots are given in Fig. 2. The energies of activation for conduction of the STV materials are significantly lower than that of strontium titanate.

The absorption maximum occurs at the near UV region (Fig. 3) for SrTiO$_3$, STV-20, STV-25 and STV-29. As these partly intrude into the visible, the samples are yellow in colour. The KV-20 sample, which is brown in colour, has a maximum at 383 nm.

## 4. Discussion

Values of $g$ indicate the field seen by an unpaired electron. Interaction of the electron spin with the orbital moment is reflected in the value of $g$. A free spin with no orbital influence has a $g$ value of 2.0023. A positive spin-orbit coupling results in a $g$ value less than the free spin value. Paramagnetic transition metal ions generally have $g$ values less than 2. Instances where the $g$ values are equal to or slightly greater than the free spin value may arise

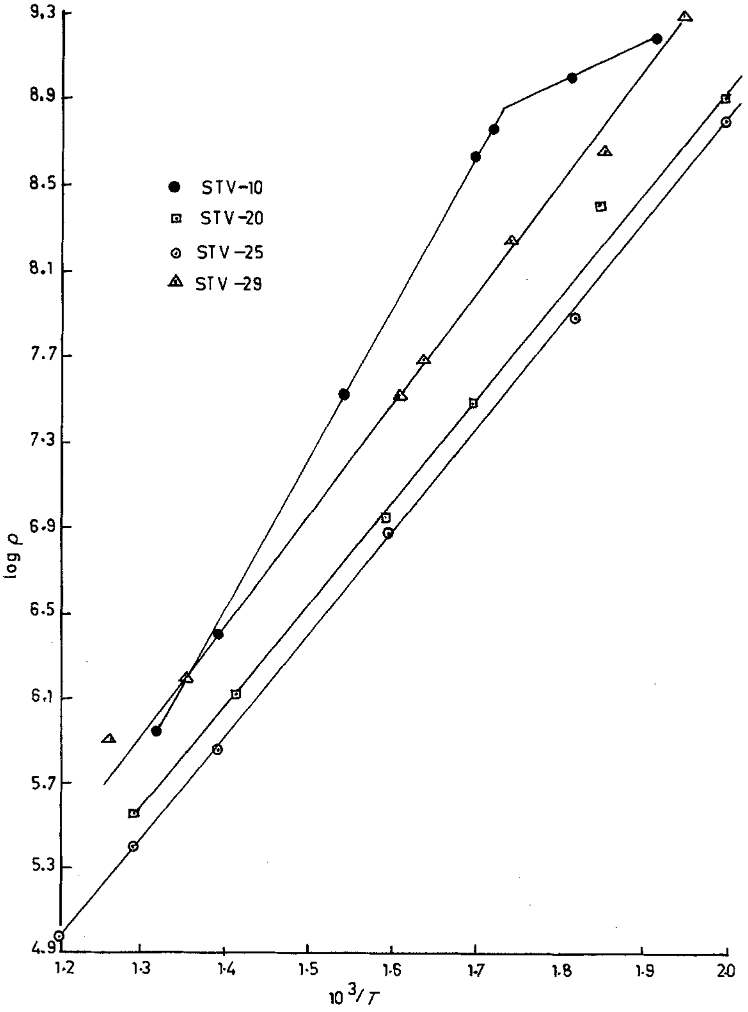

*Figure 2* Arrhenius plots for STV materials.

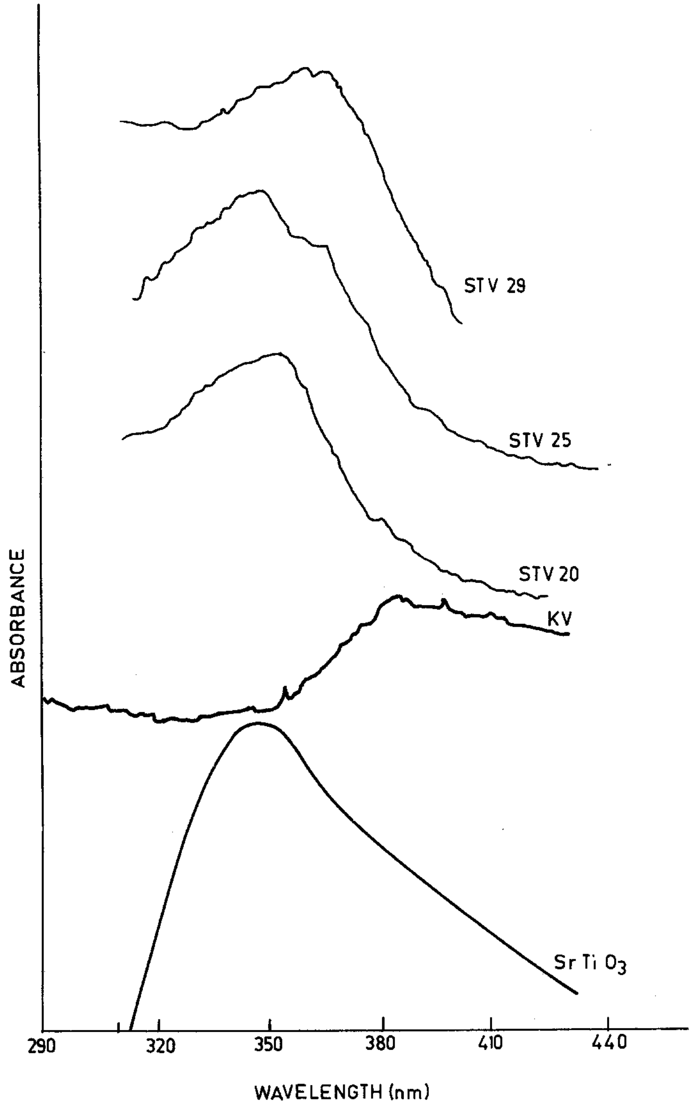

*Figure 3* Plots of absorbance against wavelength.

due to the presence or interplay of the following factors: (a) the free radical nature of the paramagnetic species [13]; (b) F-centres, i.e. lattice vacancies housing electrons; (c) adsorbed ionic oxygen species such as $O^-$, $O_2^-$, which have anisotropic $g$ values in the range 2.001 to 2.08 [14, 15] and (d) a high degree of covalency. A few of the $g$ values in the present work very nearly equal the free spin value. A paramagnetic ion cannot be a free radical and hence the first of the above factors cannot be responsible for the observed free spin value. F-centres do not occur in the STV samples because the latter contain only cation vacancies which cannot accommodate electrons. The second factor is thus ruled out. Comparison of the ESR spectra obtained in the present work with those professedly obtained for ionosorbed oxygen species [6] revealed that charged oxygen species do not exist on the surface of the perovskites. The only feature likely to have given rise to the free spin $g$ component is predominant covalency [17]. In the case of $SrTiO_3$ alone there is a possibility for the existence of colour centres because oxygen vacancies have been identified earlier in this compound [18].

Hyperfine structure in ESR spectra of vanadium compounds is caused by the nuclear magnetic moment of the $^{51}V$ isotope of vanadium which has a nuclear moment of 7/2 and which accounts for more than 99% of the natural abundance of the element. If $I$ is the nuclear moment, there must be $(2 \times I) + 1$ lines in the hfs of the ESR spectrum. Thus an octet is the expected hyperfine structure of the vanadium spectrum. However, anisotropies of both the *g* factor and the hyperfine structure complicate the spectrum. Still, all the ESR traces obtained in the present work showed hfs consistent with theoretical predictions [19]. Values of the parallel and perpendicular components of hyperfine tensors broadly agree with the values observed for quadrivalent vanadium-doped crystals of a number of compounds by earlier workers [20]. These authors explained the axially symmetric spectra on the basis of the existence of vanadyl ion rather than that of $V^{4+}$ ion. If a similar $VO^{2+}$ moiety exists in the STV samples, the V–O bond must be covalent. Though it seems strange to expect $VO^{2+}$ to be present in a perovskite, the presence of titanium certainly affects the polarity of the V–O bond.

Optical spectral findings also attest to the polarity of the V–O bond having been affected by the lattice environment. Bands in the near UV region correspond to charge transfer, i.e. transfer of an electron from the ligand (oxide ion) to the metal ion and vice versa. Such charge transfer spectra in permanganate and dichromate ions have been identified as features solely responsible for the colours of these ions. Likewise, the colours of STV and KV series of the present work may be ascribed to the charge transfer phenomenon because these compounds contain $V^{5+}$ with a $d^0$ configuration in the same way as $MnO_4^-$ and $Cr_2O_7^{2-}$ which contain the metal ions in their highest oxidation states (i.e. $d^0$ configuration). The intensity of any of the bands obtained with STV and KV compounds (Fig. 3) is low, revealing the very low concentration of defects arising from such transfer. In other words, the oxidation state of vanadium in these materials is mainly $V^{5+}$. However, even the mere occurrence of charge transfer denotes the presence of covalency. Between STV-20 and KV-20 there is a difference in the wavelength of absorption. Besides explaining the different colours of the two compounds (STV-20 is yellow whilst KV-20 is brown), this also points to the possibility that bond polarity is modified by the presence of $K^+$ in place of vacancies in the A sites.

Electrical conductivity measurements (Table IV) have helped in confirming the covalent nature of the B–O bond. The finding that the energies of activation for conduction are very high for all the materials studied shows that charge-carriers, namely unpaired electrons, are very few. This conclusion is found by the following reasoning: Conduction occurs through electronic defects caused by valency changes in titanium or vanadium ions, ionic conduction being impossible in the temperature range under study. The high activation energy indicates that the $Ti^{4+}$ or $V^{5+}$ states are relatively stable. This relative stability leads one to expect a low concentration of charge carriers.

Electrical conduction in $SrTiO_3$ and STV materials can only be due to the presence of $Ti^{3+}$ and $V^{4+}$ ions, respectively. The lower $E_a$ for conduction of STV compositions compared with that of $SrTiO_3$ suggests that the unpaired electron on $V^{4+}$ can be more easily delocalised than the one on $Ti^{3+}$ ion. In other words, the $V^{4+}$ bond with oxygen is more covalent than the $Ti^{3+}$ bond with oxygen. This is in consonance with the ESR finding that the V–O bond is more covalent in the STV materials than the Ti–O bond in $SrTiO_3$. $E_a$ for conduction is lower for STV-20 than that for KV-20. Based on the theoretical premise that covalent bonding (partial delocalization) is intermediate between ionic bonding (complete localization) and metallic bonding (complete delocaization), the above experimental fact can be explained by the suggestion that the B–O bond in the perovskite STV-20 (vacancy perovskite) is more covalent than that in the perovskite KV-20 (stoichiometric perovskite).

For any perovskite oxide the radius of the oxide ion can be independently calculated from the spherical cation radii of the A and B cations and the lattice parameter of the perovskite [21]. From the extent of the departure of the value of the oxygen radius from the spherical value (non-polarization oxygen) an idea of the polarity of the metal–oxygen bond can be obtained. A corollary of this calculation is that for a given A ion in a perovskite, the polarities of the A–O and the B–O bonds are inversely related. Thus the more covalent nature of the B–O bond in STV-20 compared with that in KV-20 established by experiment means that the A–O bond is more polar in the ion-deficient perovskite.

In perovskites the lattice parameters are functions of both ionic radii and ionic charges. Hence the distortion of the strontium titanate lattice by the presence of the vanadium ions (most of which are the $V^{5+}$ type with its size incompatibility in this lattice) is partly offset by the polarity of the A–O bond. The latter is a function of the extent of vacancies in the A sites of the perovskites because an A–O bond contiguous to another A–O bond cannot be expected to possess the same polarity as an A–O bond contiguous to a □–O arrangement. However, it has to be admitted that in the present work a linear relation between vacancy concentration and polarity has not been obtained. This may be due to the scattering of the vacancies.

In the STV series STV-10 appears as an exception. Both the conductivity and the $E_a$ for conduction fail to conform to the pattern observed for the other members of the series. This may be due to the matrix isolation of the vanadium ions in this compound.

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