

Zn(C₃H₃N₂)₂: a novel diamagnetic insulator

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Abstract

We have prepared polycrystalline samples of Zn(C₃H₃N₂)₂ by a liquid-mix technique. Characterization of the obtained samples has been performed with the aid of elemental, thermogravimetric, infrared spectra and X-ray powder diffraction analysis. We have measured electric permittivity (ϵ' , ϵ''), ac-conductivity (σ_{ac}), magnetic susceptibility (χ) and specific heat (C_p). The obtained data indicate that this material is a new diamagnetic insulator. A maximum around 4.5 K is found in $C_p T^{-3}$, and it is suggested that in addition to the Debye lattice contribution, there exists a low-frequency mode assigned as an Einstein mode contribution to the total specific heat. As a main result of the study, we found ϵ' to be constant in a wide temperature range and to have a small value of 2.3 at room temperature. This feature in combination with other properties like crystallization, good thermal stability (up to 400°C), weak moisture sensitivity and simple synthesis makes Zn(C₃H₃N₂)₂ to be a promising candidate for good insulating material in various applications.

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1. Introduction

Properties of transition metal complexes containing *p*-electron ligands are interesting from the point of view of their electronic transport and magnetic properties because of a synergy of conductivity and magnetism. The conductivity realized in these complexes is owing to the mobile electrons, i.e., π -electrons of conducting networks, while the magnetism is resulted from strong magnetic interactions between the *d*-electrons of central ions. Many complexes of such kind were synthesized and characterized in the last decade. A lot of them display various interesting phenomena, such as superconductivity, coexistence of superconductivity and antiferromagnetism and colossal magnetoresistance [1–9]. As demonstrated by different researches [5,9–11], the coupling between π - and *d*-electrons has to impart to a variety of anomalous phenomena mentioned above. However, the knowledge about the role of the π -*d* interactions is still scarce. For instance, it is of big

mystery how these interactions influence the bi-functional conducting and magnetic properties of the complexes. It seems that one of the routes providing to better understanding the role of these interactions is a comparative study of magnetic and electric behavior exhibited by different complexes. With this aim a series of compounds $M(Im)_2$ and $M(HIm)_2 \cdot CO_3 \cdot (H_2O)_2$, where M = transition metal and $Im = C_3H_3N_2^-$ has been chosen by us for investigations. The existence of the complexes $M(Im)_2$ and $M(HIm)_2 \cdot CO_3 \cdot (H_2O)_2$ dates from the middle of 1960s [12–14], but to our knowledge, except for well-documented crystallographic [15–18], spectroscopic data [18–20], and a little information about magnetic properties [13,19], neither dielectric nor magnetic and thermodynamic measurements at low temperatures have been done so far. We have undertaken systematic investigations of physical properties of these complexes, and a paper on $Co(HIm)_2 \cdot CO_3 \cdot (H_2O)_2$ has recently been published [21]. The original aim of this work was to characterize Zn(*Im*)₂ being a reference for other complexes of $M(Im)_2$. From the point of view of zero magnetic moment of Zn^{2+} ions, as a consequence of complete filling of the 3-*d* band,

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nothing more interesting is expected in this compound, except for a diamagnetism connected with the diamagnetic core, and an insulating ground state, resulting from the non-polar character of the imidazole ring. Indeed, we have observed the diamagnetic and insulating properties in $\text{Zn}(\text{Im})_2$, but we have found, most unexpectedly, that this material exhibits a very small electric permittivity of 2.3 at room temperature, i.e., significantly smaller than that of SiO_2 (= 3.9) [22]. In terms of the demand for materials to replace SiO_2 [23],¹ the observation of low electric permittivity in $\text{Zn}(\text{Im})_2$ had motivated us to pay more attention to characterize this compound as a potential material for applications. Therefore, in the present study, in addition to measurements of infrared spectra, electric permittivity, magnetic susceptibility and heat capacity of $\text{Zn}(\text{Im})_2$, we have characterized the sample with respect to the thermal stability and moisture sensitivity. The obtained data are compared to those of SiO_2 and polytetrafluoroethylene (PTFE). The latter material is known by the DuPont trade name Teflon.

2. Experimental

2.1. Material and characterization

The bisimidazole-zinc $\text{Zn}(\text{C}_3\text{H}_3\text{N}_2)_2$ compound was synthesized for the first time by Von Lehnert and Seel [17], by a low-temperature melting method. Vecchio-Sadus [19] had synthesized this compound using an electrochemical method. In this study we have used samples, which were chemically prepared, starting from a mixture of imidazole (6.1236 g, 0.09 mol), NaHCO_3 (20.1624 g, 0.24 mol) and ZnCl_2 (4.0911 g, 0.03 mol). The latter component was gradually added and the reaction mixture was refluxed for about 30 min. A white precipitate of chemical formula $\text{Zn}(\text{C}_3\text{H}_3\text{N}_2)_2$ was filtered off by gravity, and washed with cold water and alcohol $\text{C}_2\text{H}_5\text{OH}$. The polycrystalline samples were dried in air at 110°C for 5 h. Elemental analyzes, carried out using a Perkin-Elmer analyzer 2400 yield a satisfied agreement between calculated and found contents (Anal. Calcd: C, 36.62, H, 2.97, N, 28.05 Found: C, 36.12; H, 3.03 and N, 28.08). The purity of the prepared $\text{Zn}(\text{Im})_2$ samples was examined by X-ray powder diffraction (XRD) method using a Siemens D5000 diffractometer with monochromatized $\text{CuK}\alpha$ radiation. The observed XRD patterns at room temperature are characteristic of a tetragonal structure (space group $I4_1cd$). Analyses of the patterns indicate that the major phase crystallizing in the tetragonal structure with lattice parameters:

$a = 22.875(3)$ and $c = 12.855(7)$ Å. The obtained parameters by means of a least-squares fitting, do not differ so much with those reported previously by Von Lehnert and Seel [17]. Additional small traces of secondary phases with three not indexed reflections at $2\theta = 16.90, 19.99$ and 26.26 , are estimated to be less than 3% weight.

2.2. Measurements

TG-DTA measurements were performed on a Derivatograph Q-1500 D. The $\text{Zn}(\text{Im})_2$ sample was heated in air at a rate of 5°C/min in the temperature range 20–800°C. Infrared spectra were recorded on a Bruker IFS 113v spectrometer using KBr pellet. Electric permittivity (ϵ) was obtained from impedance (ωZ^*) measurements in the frequencies, f , up to 1000 kHz, using a Hewlett-Packard 4284A LCR meter, and in the frequencies up 1 GHz using a Hewlett-Packard 4191 RF impedance analyzer. The measurements were carried out on several samples of a typical diameter of 8 mm and changing thickness from 1 to 2 mm. The surfaces were coated with a silver paint or Cu foil. The samples were placed between two Be–Cu sheets and were connected to the autobridge by four coaxial cables. The error in the absolute value of complex permittivity was less than 0.1. The measurements were performed on a heating run from 100 to 420 K using a rate of 0.5 K/min. The thermocouple Cu-Constantan, calibrated with a standard cernox resistor, was kept near the sample, and was used to control the temperature within the experimental error of 0.5 K. The complex permittivity were calculated after proper calibration using a standard teflon and single-crystal KBr sample, using the following equation:

$$\epsilon^*(T, \omega) = \frac{1}{j\omega Z^*(T, \omega) C_0}, \quad (1)$$

where C_0 is the geometrical capacitance and $\omega = 2\pi f$ is the angular frequency. The real part of complex conductivity is computed from the relation

$$\sigma'(\omega) = \epsilon_0 \omega \text{Im}(\epsilon^*), \quad (2)$$

where ϵ_0 is the permittivity of vacuum. Magnetic susceptibility (χ) and magnetization (M) measurements were performed using a Quantum Design MPMS-5 SQUID magnetometer and magnetic fields up to 5 T were applied. The background contribution of a plastic straw was separately measured. The diamagnetic core contribution was not subtracted. Specific heat (C_p) was measured on a sample of 20 mg in the form of pressed pellet, using a quasi-adiabatic method. The sample was mounted on sample holder using a small amount of Apiezon-N grease.

¹ Semiconductor Industry Association. International Technology Roadmap for Semiconductors, 1998, (<http://www.itrs.net/ntrs/publntrs.nsf>).

3. Results

3.1. TG–DTA data

TG and DTA curves of the thermal degradation of $\text{Zn}(\text{Im})_2$ are shown in Fig. 1. The thermal stability limit of the $\text{Zn}(\text{Im})_2$ sample is located at 400°C . Above this temperature, a gradual loss of weight and irregular heat flux was observed. This behavior is due to the oxidative degradation of sample. Note that over the temperature range $25\text{--}400^\circ\text{C}$ the weight loss was 5%. Considering the temperature dependence of the weight loss reveals a small loss of $\sim 1\%$ near 100°C . This would correspond to the evaporating of water absorbed in the sample.

3.2. IR spectra

The IR spectra of $\text{Zn}(\text{Im})_2$ are plotted in Fig. 2. The most significant spectral evidence for the complex feature is the presence of the strong peak at wavenumber 310 cm^{-1} . This band corresponds to the stretching frequency $\nu(\text{Zn-N})$. The bands found in the region $1600\text{--}600\text{ cm}^{-1}$ are attributed to the vibrations of the

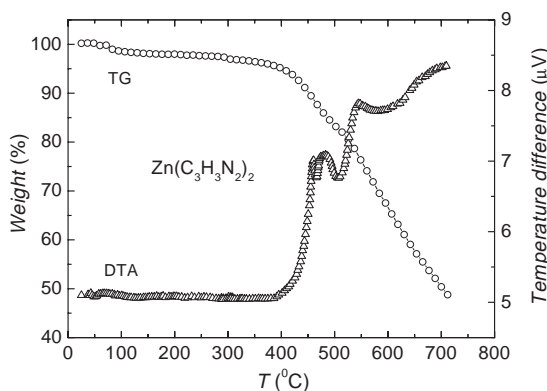


Fig. 1. Thermogravimetric curve of $\text{Zn}(\text{C}_3\text{H}_3\text{N}_2)_2$.

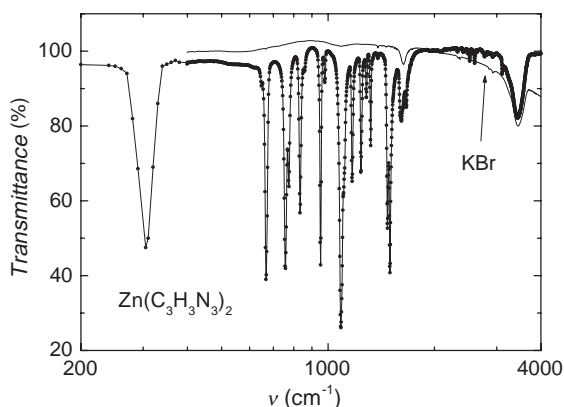


Fig. 2. Room temperature IR spectra of $\text{Zn}(\text{C}_3\text{H}_3\text{N}_2)_2$. Typical spectra of KBr as a function of wavenumber, showing the OH stretching around 3400 cm^{-1} .

imidazole rings. Thus, the spectra of $\text{Zn}(\text{Im})_2$ and those of $\text{Cu}(\text{Im})_2$ [18] and $\text{Co}(\text{Im})_2$ [19,20] complexes in this frequency range are similar to each other.

3.3. Electric permittivity and conductivity

In Fig. 3 we show the temperature dependence of the real part (ϵ') of the electric permittivity of $\text{Zn}(\text{Im})_2$ at a frequency of 1 kHz. The permittivity of $\text{Zn}(\text{Im})_2$ is found to be independent of both thickness of the samples and surface coats. The observed ϵ' -values are quite reproducible within 5%, in different runs. The outstanding feature of our data is a low electric permittivity found in $\text{Zn}(\text{Im})_2$. At 300 K, the absolute value of ϵ' amounts to 2.3 only, i.e., it is comparable to that of Teflon ($= 2.1$) [24,25] and thus, significantly smaller than that of SiO_2 ($= 3.9$) [22]. Furthermore, we observe that in the temperature range $120\text{--}320\text{ K}$, ϵ' is nearly temperature-independent. At higher temperatures, ϵ' little decreases and levels off to a value of 2.1 at 420 K. It is worth to note that the dielectric loss tangent, $\tan \delta$, (not shown here) is found to be reasonably constant over the temperature range investigated with the value of the order of 10^{-3} .

Frequency dependence of the electric permittivity at several temperatures is shown in Fig. 4, where one observes that ϵ' slowly decreases with increasing frequency. Based on a small change in $\epsilon'(f)$ for the high-frequency range $200\text{--}1000\text{ MHz}$ (Fig. 4b) only, either dispersion or absorption cannot be concluded. We have concerned the moisture sensitivity of the sample by determining the permittivity for different samples kept in different conditions. The obtained data on the samples kept at room temperature and in the normal humid condition for a long period, (shown in Figs. 3 and 4), allow us to expect that the moisture does not give observed effect on ϵ' . In fact we have observed an increase in the electric permittivity of about 10% on the samples, which were kept in a high humid condition for

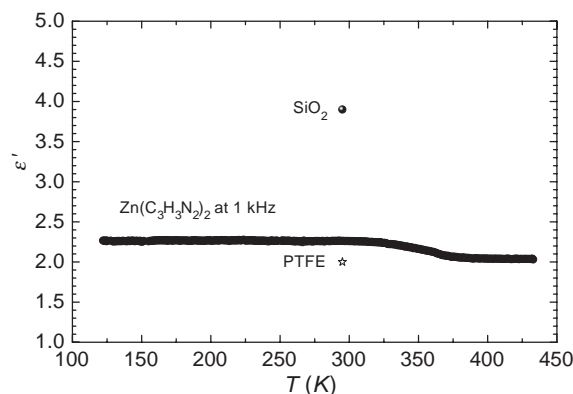


Fig. 3. Temperature dependence of the real part of the electric permittivity of $\text{Zn}(\text{C}_3\text{H}_3\text{N}_2)_2$. For a comparison, the electric permittivity of SiO_2 and PTFE at room temperature is shown.

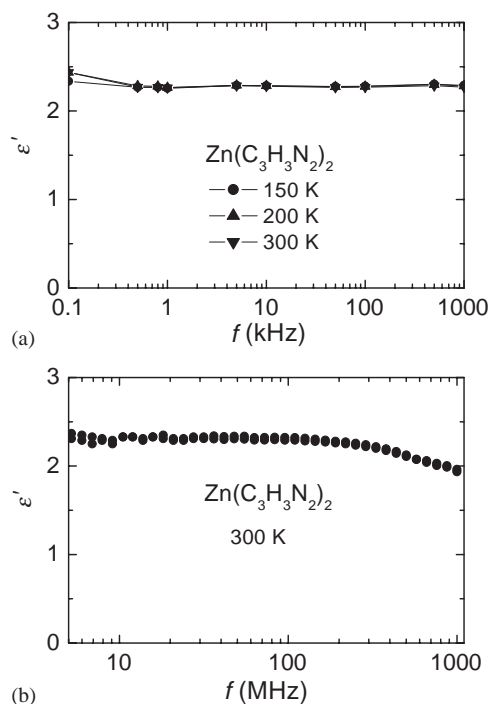


Fig. 4. (a) The electric permittivity of $\text{Zn}(\text{C}_3\text{H}_3\text{N}_2)_2$ as a function of frequencies up to 1000 kHz, (b) up to 1000 MHz.

3 days. However, the total elimination of the moisture can be achieved after drying at 110°C .

In Fig. 5 we plot the frequency dependence of the real part of the conductivity of $\text{Zn}(\text{Im})_2$ collected at several fixed temperatures. It can be seen that the frequency dependence of $\text{Zn}(\text{Im})_2$ can be the sum of two independent contributions [26,27]:

$$\sigma = \sigma_{dc} + \sigma_{ac}, \quad (3)$$

where σ_{dc} is dc conductivity, independent of the frequencies, while σ_{ac} is ac conductivity, which strongly depends on frequencies. Our measurements indicate that the values of dc conductivity in our sample are of the order 10^{-10} S/m, and they seem to increase with increasing temperature. However, these values should be taken with a caution, because due to the presence of a few percents of contaminations, we are not certain whether the observed σ_{dc} -values are intrinsic or not? In the case of the ac conductivity, it is expected that the general behavior of σ_{ac} can be described by [26,27]

$$\sigma_{ac} = A\omega^s, \quad (4)$$

where A is a temperature-dependent constant. The exponent s is also temperature dependent, but usually attains a value less than unity [28].

The behavior of $\text{Zn}(\text{Im})_2$ in the frequency range 1–10,000 kHz, however, does no longer match up to $s < 1$. When applying Eq. (4) to the data presented in Fig. 5, s is found to mount to ~ 1.2 . In fact, one has to keep in mind that the evaluation of s in the radio frequency

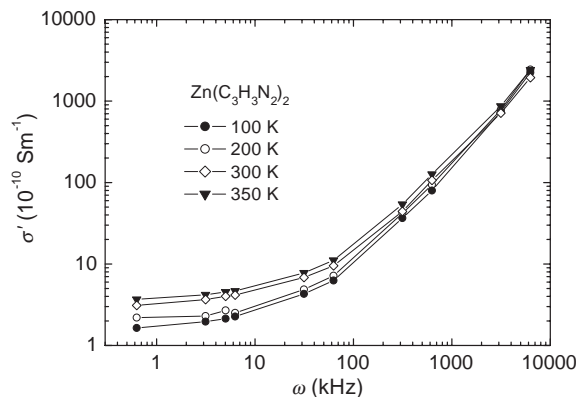


Fig. 5. Frequency dependence of the real part of the conductivity of $\text{Zn}(\text{C}_3\text{H}_3\text{N}_2)_2$.

range is less accurate compared to that in higher frequencies. Moreover, the influence of contaminations on σ' is not known. Therefore, one may deduce only that further experiments and performed on samples of better quality should give the final answer for s value.

3.4. Magnetic susceptibility and magnetization

The temperature dependence of the magnetic susceptibility of $\text{Zn}(\text{Im})_2$ is displayed in Fig. 6. Basically, $\text{Zn}(\text{Im})_2$ behaves as a diamagnet. $\chi(T)$ of this compound at room temperature is on the order of -0.5×10^{-9} m³/mol. We may note, however, that at low temperatures a paramagnetic contribution starts to show up. Thus, as illustrated in the inset to Fig. 6, in fields up to 5 T, magnetization shows positive response. At present, we attribute this contribution to some paramagnetic impurities.

3.5. Specific heat

The results of the specific heat measurements of $\text{Zn}(\text{Im})_2$ are shown in Fig. 7 as a plot of C_p/T^3 vs T . Since $\text{Zn}(\text{Im})_2$ is a non-magnetic insulator, the specific heat must be composed of the lattice contribution only. Consequently, if C_p of $\text{Zn}(\text{Im})_2$ follows the Debye lattice model, the C_p/T^3 quantity should be independent of temperature at $T \ll \Theta_D$. Clearly visible is a maximum in $C_p(T)/T^3$ at ≈ 4.5 K, indicating that a T^3 approximation is not sufficient to describe the $C_p(T)$ behavior at low temperatures. Similar phonon anomalies have been known to exist in various systems, from a glass SiO_2 [29], semicrystalline polymers (PTFE [30]), through superconductors (TaC, [31] $\text{Yb}_2\text{Cu}_3\text{O}_{7-x}$, [32]) to perovskites [33]. For these materials the additional term of the heat capacity mode was attributed to a low-frequency Einstein mode contribution. In an intuitive way we may assign the observed anomaly in $\text{Zn}(\text{Im})_2$ to an Einstein mode contribution too. Applying the

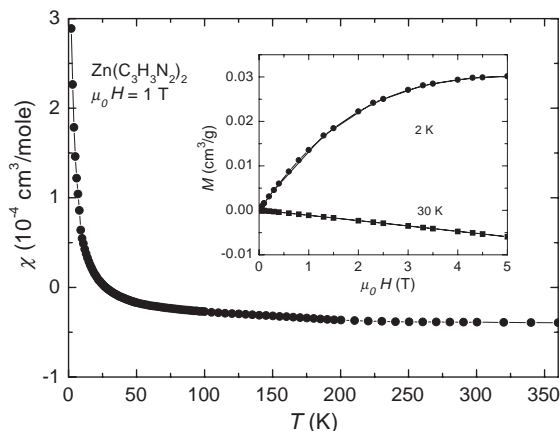


Fig. 6. Temperature dependence of the magnetic susceptibility $\text{Zn}(\text{C}_3\text{H}_3\text{N}_2)_2$. The inset shows the magnetization measured at 2 and 30 K.

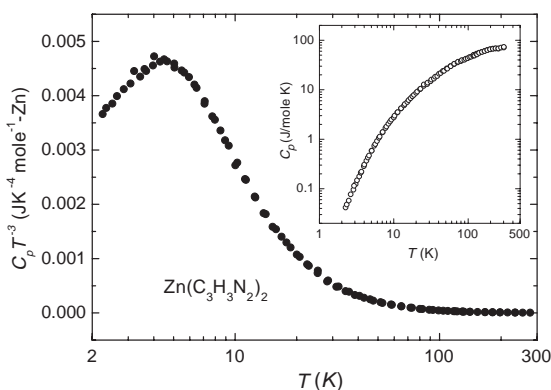


Fig. 7. Temperature dependence of the heat capacity of $\text{Zn}(\text{C}_3\text{H}_3\text{N}_2)_2$ divided by T^3 . The inset shows the heat capacity as a function of temperature.

Einstein's model

$$C_p(T) = 3rR \left(\frac{\Theta_E}{2T} \right)^2 \text{csch}^2 \left(\frac{\Theta_E}{2T} \right) \quad (5)$$

to the C_p -data of $\text{Zn}(\text{Im})_2$ reveals the Einstein's temperature Θ_E of 21 K and the number of vibrators r of 0.3. The latter value is of typical found in perovskites [33].

4. Discussion

From the experimental results presented above it becomes clear that $\text{Zn}(\text{C}_3\text{H}_3\text{N}_2)_2$ is a new diamagnetic insulator. This behavior is being understandable if we are able to look at its electronic structure. Unfortunately, these data are not available for $\text{Zn}(\text{Im})_2$ yet. Nevertheless, considering atomic bonding of $\text{Zn}(\text{Im})_2$ in comparison to that of the wide-band gap semiconductor ZnO reveals some similarities, i.e., both the compounds

possess the same s , p and d orbitals, originating from the respective pair Zn/O and Zn/N, and intuitively, in the both compounds there are similar electronic configurations associated with the Zn^{2+} ions. Therefore, the electronic structure of ZnO is worthwhile to mention here. In accordance to band structure calculations based on the local-density approximation, density-functional theory, Hartree–Fock approximation and full-potential muffin-tin orbital method [34–36], the valence band in ZnO, consisting mainly of hybridized p – d band, resides very low in energy below the Fermi level. There is a transferred charge from $4s$ of Zn to $2p$ of O. As a result, the p -like bonding states are pushed down, while the s -like antibonding states are pushed up in energy. This means that the energy gap in ZnO results from a bonding and antibonding interactions between $4s$ and hybridized p – d states. Since in $\text{Zn}(\text{Im})_2$ the Zn–N bond is most probably of a valence type possessing the p – d character, one may suspect the insulating gap in $\text{Zn}(\text{Im})_2$ could be of charge-transfer nature like in ZnO. However, contrary to ZnO, $\text{Zn}(\text{Im})_2$ contains the imidazole molecules which yields a molecular character to the material. So, the application of a simple model mentioned above to the case of $\text{Zn}(\text{Im})_2$ should take with some caution.

A main result of this study is the finding of a low value of the electric permittivity in $\text{Zn}(\text{Im})_2$. In fact, the material possesses several features favorable for a low electric permittivity, like symmetrical structure, symmetrical and small atoms (C, H, N). We think that the non-polar character of the imidazole ring and a low density (1.5 g/cm^3) are additional reasons leading to a low value of ϵ . From the physical point of view, we can consider the observed permittivity to be a sum of several contributions: atomic, electronic, ionic, dipolar and of space charge. The latter contribution mainly comes from impurity or defects, and for the frequencies above 1 kHz, it practically does not influence on the total value of the electric permittivity. Inspection of the practically frequency independent (Fig. 4) reveals that the eventual contribution of the charge space is negligible. In such a circumstance also the ionic contribution does not play any role. Furthermore, the lacking of any relaxation phenomena suggests that the dipolar contribution may be negligible as well. The atomic and electronic contributions always exist. Therefore, we suspect that these polarizations are the main mechanism giving rise to the observed ϵ -value in $\text{Zn}(\text{Im})_2$. To get more information of the role of ligand, we plan to measure electric permittivity for other Zn^{2+} -based complex, notably $\text{Zn}(\text{pyrazole})_2$.

Finally, let us compare the physical properties of $\text{Zn}(\text{Im})_2$ to those of known insulators like PTFE and SiO_2 . The latter material is conventionally used as one of core components in the silicon industry. For higher performance of semiconductor devices, the thickness of

SiO₂ is required to be thinner [23]. However, in such case the charge leakage arising from electron tunnelling through the electric becomes a real problem [37]. It is obvious that low- ϵ materials are keys for realizing of low leakage currents. It is clear that, our observation of the low- ϵ in Zn(Im)₂ meets an essential criterion of the demand for new materials to replace SiO₂. From the viewpoint of compatibility with fabrication process, thermal stability of about 400°C is demanded. The characterization by means of TG-DTA measurements has indicated that the heat stability of Zn(Im)₂ provides a sufficient heat resistance for technology process. Naturally one could suspect that PTFE with the lowest and the smallest electric loss tangent among the dielectric materials known so far could be the best insulator for such applications. Unfortunately, the use of PTFE in microelectronics is still a technologically subject of investigations because of difficulties in the preparation and micromachining of thin PTFE films. In comparison with PTFE, Zn(Im)₂ has an advantage with the crystallization and good thermal stability properties. Additionally, a simple synthesis of Zn(Im)₂ indicates that the production technology of this compound compared to PTFE should be more simpler than that for PTFE.

In summary, we have characterized a tetragonal Zn(Im)₂ compound by means of X-ray, TG-DTA, IR spectroscopic, dielectric, magnetic and thermodynamic properties measurements. We have compared the dielectric properties of this compound with those of PTFE and SiO₂. The low permittivity along with the good thermal stability of the material and the ease of synthesizing pushes Zn(C₃H₃N₂)₂ to the group of compounds contending for applications as an insulator.

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