

Preparation and properties of organic-inorganic perovskite-like $(\text{C}_3\text{N}_2\text{H}_5)[\text{Mg}(\text{HCOO})_3]$ of high phase transition temperature

ZHAO Dong-mei, HOU Ya-fei, LI Wei-ping*

(Faculty of Science, Ningbo University, Ningbo 315211, China)

Abstract: In order to seek high phase transformation materials, a novel material $(\text{C}_3\text{N}_2\text{H}_5)[\text{Mg}(\text{HCOO})_3]$ (ImMg) is successfully prepared using conventional solution method. It is found that the phase transition temperature of ImMg is up to 480.5 K, which has been the highest phase transition temperature for ABX_3 (A=cation, imidazole, B=Metal ions, X=formate) so far. In addition, an obvious dielectric anomaly is observed, and the structure of ImMg turns out to be similar to that of ImMn. The octahedral metal ions (Mg^{2+}) are linked by formate $[(\text{HCOO})_3]^-$ ligands to form cube-like cavities, which are occupied by imidazole cation $(\text{C}_3\text{N}_2\text{H}_5)^+$ through extensive hydrogen bonds in the framework. Owing to the existence of large amount of hydrogen bonds, the phase transition temperature and thermal stability of ImMg are greatly improved.

Key words: MOFs materials; phase transition; dielectric relaxation; thermal stability

CLC number: O437

Document code: A

Article ID: 1001-5132 (2018) 05-0091-05

1 Introduction

In recent years, a large amount of researches have been carried out on metal-organic frameworks (MOFs) consisting of metal ions bridged by organic linkers because of the unusual physical properties and potential applications in many fields, such as photoluminescence, gas storage, nonlinear optics, catalysis and so on^[1-7]. Among various MOFs, metal organic formate frameworks with perovskite ABX_3 architecture have drawn much attention due to the appearance of multiferroic behavior and magnetoelectric coupling in some of these structures, such as $[(\text{CH}_3)_2\text{NH}_2] \cdot [\text{M}(\text{HCOO})_3]$, $[(\text{CH}_3)_2\text{ND}_2] \cdot [\text{M}(\text{HCOO})_3]$ (M=Ni, Mn, Co)^[2,8-11]. According to the previous reports, the above-mentioned materials have the same structure

that B linked by X to form the BX_3 skeleton, and A is located in the cavities. Moreover, the performance of the perovskite ABX_3 architectures will be of great difference when the A, B, X sites are different^[9,12-15].

Up to now, scientists are still obsessed with this kind of material, including the phase transition and dielectric properties. The ligands of organic-inorganic hybrid phase transition materials have been reported mostly to be the linear or short I^- , CN^- , HCOO^- and N^{3-} ions^[9], leading to very low phase transition temperature, most of which are below room temperature, such as $[\text{NH}_4][\text{Mg}(\text{HCOO})_3]$ ($T_c=255\text{K}$)^[1], $[(\text{CH}_3)_2\text{NH}_2] \cdot [\text{Mg}(\text{HCOO})_3]$ ($T_c=270\text{K}$)^[12], and $[\text{NH}_2\text{NH}_3] \cdot [\text{Mg}(\text{HCOO})_3]$ ($T_c=348\text{K}$)^[3]. Although many kinds of ABX_3 materials with phase transition temperature lower than or on the verge of room temperature have been investigated, the lower phase

收稿日期: 2018-03-23.

宁波大学学报(理工版)网址: <http://journalg.nbu.edu.cn/>

基金项目: 国家自然科学基金(11574168); 浙江省自然科学基金(LY14E030001).

第一作者: 赵冬梅(1991-), 女, 安徽阜阳人, 在读硕士研究生, 主要研究方向: 有机-无机杂化钙钛矿特性. E-mail: 1796961178@qq.com

*通信作者: 李伟平(1977-), 男, 浙江缙云人, 教授, 主要研究方向: 能源材料与器件. E-mail: liweiping@nbu.edu.cn

transition temperature greatly limits these ABX_3 materials applications. Therefore, it's very important to look for new materials from the perspective of application, whose phase transition temperature is higher than room temperature. Along this line, Fu et al^[16] have reported a perovskite-like dielectric material, $(C_3N_2H_5)[Mn(HCOO)_3]$ (ImMn) in 2015, which exhibits a high phase transition temperature (438 K) and dielectric anomaly. In spite of some ABX_3 materials with high phase transition temperature been reported, the investigation on the high temperature phase change materials is still scarce, and more works still need to be done.

In this study, a new material $(C_3N_2H_5)[Mg(HCOO)_3]$ (ImMg) is synthesized, whose phase transition temperature is up to 480.5 K below its melting point. The phase transition at 480.5 K of ImMg in our study is the highest phase transition temperature for ABX_3 (A=cation, imidazole, B=Metal ions, X=formate) so far. Moreover, the decomposition temperature of ImMg is about 500 K, which is much higher than that of ImMn, indicating ImMg is more stable than ImMn.

2 Experiment

2.1 Reagent

$Mn(ClO_4)_2 \cdot 6H_2O$ (99%, Aldrich), imidazole (99.5%, Aldrich), and Methanol (Panreac) formic acid (98%, Aldrich) can be used directly without any purification.

2.2 Synthetic method

Compound ImMg was prepared through conventional nature precipitation 6.4 mmol imidazole and 9.6 mmol formic acid were firstly placed at the bottom of a glass tube, 6 ml methanol was added then. For this solution, 2 mL of methanol was slowly dropwise added, followed by layering 4 mL of methanol solution containing 0.80 mmol $Mg(ClO_4)_2 \cdot 6H_2O$. Subsequently, the tube was kept undisturbed for 2 d. Therewith, whiteness and block-shaped crystals were obtained. They were collected, washed with ethanol and dried at room temperature.

2.3 Measurements

The X-ray diffraction (XRD) experiments were performed for phase structure using Cu $K\alpha$ radiation on an XRD apparatus (Bruker D8). Thermal gravimetric analysis (TGA) was performed with a heating rate of $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$ under nitrogen atmosphere from 30 up to 500 $^\circ\text{C}$. The complex dielectric constant and loss were measured as a function of frequency and temperature on the Agilent 4294A precision impedance analyzer. The differential scanning calorimetry (DSC) measurement was performed on a PYRIS Sapphire DSC instrument at a rate of $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$ under a nitrogen atmosphere.

3 Results and discussion

3.1 Crystal structure

The structure mode of ImMn was used for the refinement of ImMg, due to the absence of structure mode for ImMg analogue^[16]. The XRD patterns of ImMn and ImMg compound measured at room temperature are shown in Fig. 1. It can be seen from Fig. 1 that the XRD pattern of ImMg matches very well with that of ImMn at room temperature if the diffraction angles of ImMg shift 0.4° to a lower angel, thus these two crystals have the similar crystal structure. In addition, the detailed crystal data are present in Table 1 after curve-fitting.

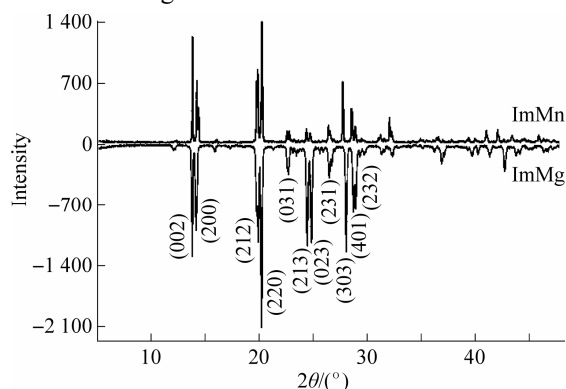


Fig. 1 The XRD pattern of ImMn and ImMg

All crystal indices of reflection peaks were got by Bragg's law diffraction theory calculation and marked in Fig. 1. Three strongest diffraction peaks at 13.7° , 20° , 27.7° , correspond to the diffraction of (002), (220) and

Table 1 Crystal data of ImMg at room temperature

empirical formula	formula weight	crystal system	space group	<i>a</i> /nm	<i>b</i> /nm	<i>c</i> /nm	$\beta/(^{\circ})$	volume/nm ³
C ₆ H ₈ MgN ₂ O ₆	228.31	monoclinic	P2 ₁ /c	1.241 35	1.209 22	1.310 85	84.980 2	1.960 13

(303), respectively. Moreover, ImMg has the structure that the divalent metal cations (Mg^{2+}) is linked by formate groups (HCOO^-) to form the BX_3 skeleton, and the imidazole cations ($\text{C}_3\text{N}_2\text{H}_5^+$) is located in the cavities through extensive hydrogen bonds, which is similar to that of ImMn.

3.2 Decomposition mechanism

As shown in Fig. 2, the TGA curve of ImMg shows a two-step weight loss in the temperature range from 500 to 760 K. The first mass loss process of ImMg occurs at the temperature range from 500 to 561 K, which is corresponding to the loss of one imidazolium and one formic acid per formula unit (found 50.3%, calculated 50.2%), leaving the formation of $\text{Mg}(\text{HCOO})_2$. The second mass loss process of ImMg occurs in the temperature range from 650 to 725 K, which is attributed to the decomposition of $\text{Mg}(\text{HCOO})_2$ and leaving residue of MgO (found 18.3%, calculated 17.7%). Additionally, the DSC curve corresponds with the TGA curve very well, showing two endothermic peaks in the decomposition process of ImMg. Moreover, the decomposition temperature of ImMg is about 500 K in Fig. 2, which is much higher than that of ImMn, indicating ImMg is more stable than ImMn.

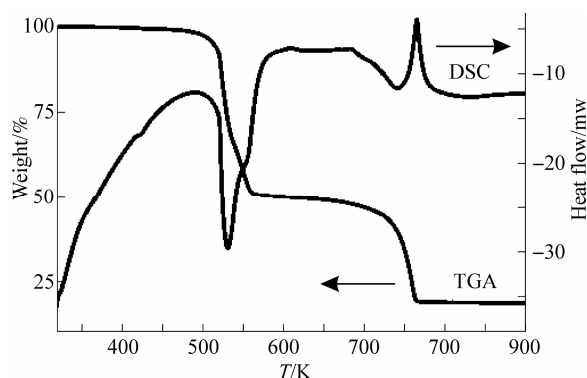


Fig. 2 TGA and DSC curves of ImMg

3.3 Dielectric properties

The temperature dependence of dielectric constant (ϵ') and dielectric loss ($\tan\delta$) for ImMg measured at fixed frequency (10 kHz, 100 kHz and 1 MHz) are

shown in Fig. 3(a) and 3(b), respectively.

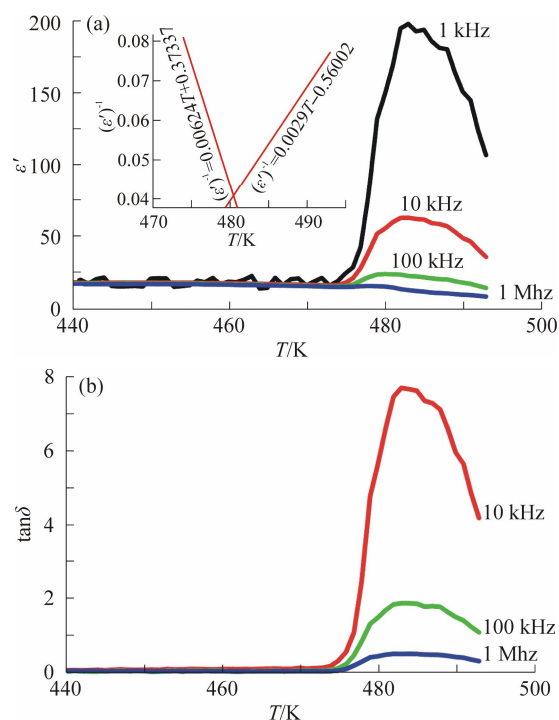


Fig. 3 (a) Real parts ϵ' of the dielectric permittivities of ImMg. Inset: plot of $1/\epsilon'$ vs. temperature (frequency fixed at 100 kHz). (b) Dielectric loss as the function of temperature

It can be observed from Fig. 3(a) that the dielectric constant at 1 MHz shows gradual increase with the increasing of temperature and has a rise step at 477.95 K ($\epsilon' = 12.8$), then slow down and finally leveled off. As the frequency decreases, the temperature of maximum dielectric constant for ImMg gradually increases. Moreover, the $\tan \delta$ in Fig. 3(b) also shows gradual increase with the increasing of temperature and exhibits an obvious peak at a certain temperature. An obvious dielectric anomaly can be seen in the Fig. 3 within the scope of measuring temperature. The data inserted in Fig. 3(a) are fitted with Curie-Weiss law,

$$1/\varepsilon' \approx (T - T_0)/C,$$

where ε' , C , T and T_0 are real part of the dielectric constant, Curie constant, temperature and Curie-Weiss temperature, respectively.

The values of C_1 and C_2 are calculated to be 160 and 345 respectively according to the two equations of $1/\varepsilon' = -0.00624T + 0.37337$ and $1/\varepsilon' = 0.0029T - 0.56002$ that are fitted with Curie-Weiss law. The ratio of C_2/C_1 is approximated to 2.1 that is less than 4. So the phase transition of ImMg at 480.5 K from the inset figure is a second-order phase transition. What's more, the dielectric constant and phase transition temperature of ImMg are higher than those of ImMn, while the dielectric loss of ImMg would be smaller than that of ImMn at the same frequency.

3.4 Phase transition

To further prove the phase transition temperature of ImMg is 480.5 K, more accurate DSC was measured. The variation of heat flow with temperature increasing and decreasing respectively for ImMg is shown in Fig. 4. From Fig. 4, an endothermic peak of ImMg is clearly visible at 480.5 K during the heating process, which is far below its melting point, and an exothermic peak is observed at 470 K during the cooling process. In other words, a small thermal hysteresis of about 9.5 K appears during heating/cooling process, suggesting that the phase transition at 480.5 K of ImMg is close to a second-order one.

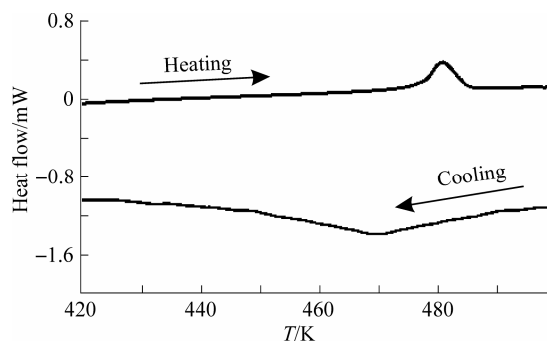


Fig. 4 DSC curves of ImMg

In addition, the enthalpy change (ΔH) was estimated at $4.6 \text{ J} \cdot \text{g}^{-1}$ and the entropy change (ΔS) was estimated at $9.5 \times 10^{-3} \text{ J} \cdot (\text{g} \cdot \text{K})^{-1}$ or $2.1689 \text{ J} \cdot (\text{mol} \cdot \text{K})^{-1}$. According to the Boltzmann equation,

$$\Delta S = R \ln(N),$$

where R is the gas constant and N is the ratio of the numbers of respective distinguishable states of different phases.

N was calculated to be 1.30 in our study, representing the phase transition at 480.5 K of ImMg is not a typical ordered-disordered phase transition. This result matches well with that of Curie-Weiss law. Moreover, the phase transition temperature at 480.5 K of ImMg in our study is the highest temperature for ABX_3 (A =cation, imidazole, B =Metal ions, X =formate) so far, which is much higher than that of perovskite-like previously reported^[1].

4 Conclusions

In summary, ImMg was synthesized for the suitable candidates for high temperature phase conversion materials. The phase transition of ImMg is a second-order one, and the transition temperature is up to 480.5 K, which is the highest phase transition temperature for ABX_3 (A =cation, imidazole, B =Metal ions, C =formate) so far. The octahedral metal ions (Mg^{2+}) were linked by formate (HCOO^-) ligands. The imidazole cation ($\text{C}_3\text{N}_2\text{H}_5^+$) were located within the cube-like cavities of the framework and formed extensive hydrogen bonds with the framework, resulting in a big improvement of thermal stability.

References:

- [1] Maczka M, Pietraszko A, Macalik B, et al. Structure, phonon properties and order-disorder transition in the metal formate framework of $[\text{NH}_4][\text{Mg}(\text{HCOO})_3]$ [J]. *Inorganic Chemistry*, 2014, 53(2):787-794.
- [2] Tian Y, Stroppa A, Chai Y, et al. Cross coupling between electric and magnetic orders in a multiferroic metal-organic framework[J]. *Scientific Reports*, 2014, 4(1):60-62.
- [3] Chen S, Shang R, Hu K L, et al. $[\text{NH}_2\text{NH}_3][\text{M}(\text{HCOO})_3]$ ($M=\text{Mn}^{2+}$, Zn^{2+} , Co^{2+} and Mg^{2+}): Structural phase transitions, prominent dielectric anomalies and negative thermal expansion, and magnetic ordering[J]. *Inorganic Chemistry Frontiers*, 2014, 1(1):83-98.
- [4] Wang B Q, Yan H B, Huang Z Q, et al. Reversible high-temperature phase transition of a manganese(II) formate framework with imidazolium cations[J]. *Acta Crystallographica*, 2013, 69(6):616-619.
- [5] Carnésánchez A, Imaz I, Stylianou K C, et al. Metal-

- organic frameworks: From molecules/metal ions to crystals to superstructures[J]. Chemistry, 2014, 20(18):5192-5201.
- [6] Ying T J, Shi P S, Yi S C, et al. Electric control of magnetism in a multiferroic metal-organic framework[J]. Physica Status Solidi, 2014, 8(1):91-94.
- [7] Maekawa T, Kurosaki K, Yamanaka S. Thermal and mechanical properties of perovskite-type barium hafnate [J]. Journal of Alloys and Compounds, 2006, 407(12):44-48.
- [8] Gómezaguirre L C, Patodoldán B, Mira J, et al. Magnetic ordering-induced multiferroic behavior in $[\text{CH}_3\text{NH}_3][\text{Co}(\text{HCOO})_3]$ metal-organic framework[J]. Journal of the American Chemical Society, 2016, 138(4):1122-1125.
- [9] Sánchezandújar M, Presedo S, Yáñezvilar S, et al. Characterization of the order-disorder dielectric transition in the hybrid organic-inorganic perovskite-like formate $\text{Mn}(\text{HCOO})_3[(\text{CH}_3)_2\text{NH}_2]$ [J]. Inorganic Chemistry, 2010, 49(4):1510-1516.
- [10] Wang W, Yan L Q, Cong J Z, et al. Magnetoelectric coupling in the paramagnetic state of a metal-organic framework[J]. Scientific Reports, 2013, 3(6):2024-2043.
- [11] Fan F R, Wu H, Nabok D, et al. Electric-magneto-optical Kerr effect in a hybrid organic-inorganic perovskite[J]. Journal of the American Chemical Society, 2017, 139(37): 12883-12886.
- [12] Szymborska-Małek K, Trzebiatowska-Gusowska M, Mączka M, et al. Temperature-dependent IR and Raman studies of metal-organic frameworks $[(\text{CH}_3)_2\text{NH}_2][\text{M}(\text{HCOO})_3]$, $\text{M}=\text{Mg}$ and Cd [J]. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2016, 159(15):35-41.
- [13] Gomez-Aguirre L C, Pato-Doldan B, Stroppa A, et al. Room-temperature polar order in $[\text{NH}_4][\text{Cd}(\text{HCOO})_3]$ - a hybrid inorganic-organic compound with a unique perovskite architecture[J]. Inorganic Chemistry, 2015, 54 (5):2109-2116.
- [14] Pato-Doldán B, Gómez-Aguirre L C, Bermúdez-García J M, et al. Coexistence of magnetic and electrical order in the new perovskite-like $(\text{C}_3\text{N}_2\text{H}_5)[\text{Mn}(\text{HCOO})_3]$ formate [J]. RSC Advances, 2013, 3(44):22404-22411.
- [15] Di S D, Stroppa A, Jain P, et al. Tuning the ferroelectric polarization in a multiferroic metal-organic framework[J]. American Chemical Society, 2013, 135(48):18126-18130.
- [16] Fu D W, Wang F F, Chen C, et al. A prominent dielectric material with extremely high-temperature and reversible phase transition in the high thermally stable perovskite-like architecture[J]. Journal of Materials Chemistry C, 2015, 3(24):6350-6358.

高相变温度的有机-无机类钙钛矿 $(\text{C}_3\text{N}_2\text{H}_5)[\text{Mg}(\text{HCOO})_3]$ 的制备及性能研究

赵冬梅, 侯亚飞, 李伟平*

(宁波大学 理学院, 浙江 宁波 315211)

摘要: 运用自然蒸发静置的方式制备出一种新型的有机-无机杂化类钙钛矿晶体 $(\text{C}_3\text{N}_2\text{H}_5)[\text{Mg}(\text{HCOO})_3]$ (ImMg)。这类材料的相变温度高达 480.5 K, 并且低于其熔点。ImMg 的相变温度高于之前报道过的甲酸类钙钛矿的相变温度并且有明显的介电异常。ImMg 属于 ABX_3 型有机-无机杂化框架结构, B 位的 Mg 原子和 X 位的 HCOOH 分子配位形成正八面体结构, A 位的咪唑分子占据了 $[\text{Mg}(\text{HCOO})_3]$ 八面体框架形成的空隙位置。并且在晶体结构中, A 位的咪唑分子与 X 位的 HCOOH 分子形成氢键, 这之前所报道的 ImMn 结构类似。由于大量氢键的存在, ImMg 的相转换温度和热稳定性显著提高。

关键词: MOFs 材料; 相变; 介电弛豫; 热稳定性

(责任编辑 韩 超)