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Tuning the magnetic properties of a new family of hybrid mixed metal oxalates having 1D magnetic chains and layers of *J* aggregates of [$DAMS^+$] producing superior SHG

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ABSTRACT

Hybrid mixed metal oxalates of general formula $[M^{III}_2M^{II}(C_2O_4)_6][DAMS]_4 \cdot 2DAMBA \cdot 2H_2O$, where M^{III} = Rh, Fe, Cr; M^{II} = Mn, Zn; DAMBA = *para*-dimethylaminobenzaldehyde and [$DAMS^+$] = *trans*-4-(4-dimethylaminostyryl)-1-methylpyridinium, belong to a new family of multifunctional materials displaying both very high second harmonic generation (SHG) efficiency and tunable magnetic properties. Here we report on the preparation and magnetic characterization of the new Ni^{II} members of this family. Such new hybrid mixed metal oxalates are isostructural with the previously investigated containing Zn^{II} and Mn^{II}, thus preserving the very high NLO efficiency but allowing further significant tuning of the magnetic properties. In particular the delocalization of Ni^{II} magnetic orbitals along the inorganic "stripes" of the crystalline network produces strong next-nearest-neighbor magnetic interactions, otherwise absent in the chains of compounds containing the Mn^{II} ions. Such interactions, when in the presence of magnetic M^{III} ions such as Cr^{III} or Fe^{III}, give rise to an interesting and complex magnetic behavior possibly due to an almost perfect compensation between nearest-neighbor and next-nearest-neighbor interactions along the chain.

1. Introduction

In the last years, inorganic–organic hybrid crystalline materials with interesting electrical, magnetic and non-linear optical (NLO) properties have attracted the attention of the material science community [1–3]. Particular interest was focused on the appealing polyfunctional hybrids [4], whose macroscopic functionalities can be due to cooperative effects between the two moieties (organic and inorganic). The main purpose of the current research is finding the proper synergy between the two subsystems, each of which should contribute to modulate the other's property in an extended crystalline framework.

Within this wide new field, the coupling of magnetic and non-linear optical properties seems to be quite attractive [5], and yet largely unexplored. In particular, although some magnetic materials displaying efficient second harmonic generation (SHG) properties have been reported [6], systems in which the magnetic properties can be easily and rationally tuned, without affecting the SHG efficiency, are still rare. In most multifunctional hybrid materials the provider of the magnetic properties is the inorganic part, while a large second-order NLO response is more frequently originated from the organic counterpart. Anyway changing the inorganic framework often leads to severe structural changes of the whole crystal structure and this induces non-obvious variations of the SHG efficiency of the hybrid material. Layered hybrid materials thus seem particularly well suited, as structural distortions induced by the substitution of the magnetic ion into the inorganic framework can be easily absorbed without significantly altering the whole crystalline framework and therefore the SHG efficiency.

The *trans*-4-(4-dimethylaminostyryl)-1-methylpyridinium cation, [$DAMS^+$], is a well-known second-order NLO chromophore, especially in crystalline systems where [$DAMS^+$] molecules are organized as *J* aggregates in properly oriented layers [7]. As for the magnetic properties, it is known that mixed metal oxalates form a variety of frameworks, including layers, that allow several types of magnetic couplings [8].

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Thus, building hybrid crystalline structures with metal oxalates in conjunction with [DAMS$^+$] chromophores provides unique opportunities to create hybrid magnetic materials with significant SHG activity.

For instance, we have recently reported [9] the synthesis as well as the structural, magnetic and photophysical characterization of a new promising family of magnetic and second-order NLO isostructural layered hybrid materials of general formula $[M^{III}_2M^{II}(C_2O_4)_6][DAMS]_4 \cdot 2DAMBA \cdot 2H_2O$, where M^{III} = Rh, Fe, Cr; M^{II} = Mn, Zn and DAMBA is *para*-dimethylaminobenzaldehyde. This class of materials possesses some important features: it segregates layers of *J*-aggregated [DAMS$^+$] chromophores and of mixed metal oxalate stripes of M^{III} and M^{II} cations which can be properly chosen to produce specific magnetic behaviors. The variety of magnetic properties which arises from different M^{III}/M^{II} pairs, does not influence the very high SHG efficiency.

In view of this tunability of the magnetic properties and of the particular structural arrangement, we decided to extend our investigation studying the Ni^{II} members of this class of hybrid mixed oxalates. Indeed, based on the structures of the Mn^{II} and Zn^{II} compounds of this class, the oxalates should form a cubic anti-prism coordination sphere around Ni^{II} that only very rarely affords octa-coordination with traditional organic ligands. In addition, the magnetic behavior of Ni^{II} chains is particularly interesting as the magnetic orbitals of this metal are usually very delocalized along the chains [10], producing unexpectedly strong magnetic interactions. Finally Ni^{II} chains constitute a perfect experimental background for spin 1 chains, which, based on the so-called Haldane conjecture [11], posses a gapped energy spectrum. In the present study, we will thus analyze the structural, second-order NLO and magnetic properties of the Ni^{II} derivatives of the above described class of multifunctional hybrid mixed metal oxalates [9].

2. Synthesis

The most common classes of hybrid inorganic–organic materials with superior second-order NLO properties are those where the inorganic and organic components are easily segregated. Two examples are the layered materials corresponding to the stoichiometry $[DAMS][M_5I_6]$ (with M = Cu or Ag) [7] and the intercalated materials obtained by ionic exchange of [DAMS$^+$] into the layered structure of MPS_3 (M = Mn, Zn, Cd) [12–14]. In all these compounds the large second-order NLO response is originated by a specific ordered arrangement of the [DAMS$^+$] chromophore between the inorganic layers. The formation of *J* aggregates [15], seems to be particularly important for the second-order NLO high efficiency of these hybrid materials. These layered systems suggest that ample tuning of the magnetic properties is possible, as segregated structures can possibly accommodate subtle changes in the inorganic framework without completely altering the crystal structure. As stated in the introduction, we have already confirmed the validity of such approach, by obtaining a new family of materials with a layered structure in which the [DAMS$^+$] chromophores are efficiently organized into *J* aggregates and the contemporary presence of several substitutable magnetic centers ensures the tunability of the magnetic properties [9]. Here we report that isostructural materials containing Ni^{II} ions can also be obtained, thanks to the flexibility of the layered structure characterizing these hybrid mixed oxalates.

The best general synthetic way to obtain compounds of the family of mixed oxalates of formula $[M^{III}_2M^{II}(C_2O_4)_6][DAMS]_4 \cdot 2DAMBA \cdot 2H_2O$ (M^{III} = Rh, Fe, Cr; M^{II} = Mn, Zn) consists in a two step procedure [9]. We have thus applied the same strategy to obtain the M^{II} = Ni analogous compounds. The first step leads to the formation of the intermediated phase $\alpha_{MIII/NiII}$, by mixing in water $K_3[M(C_2O_4)_3] \cdot nH_2O$ (M = Rh, Fe, Cr), $NiCl_2$and [DAMS]I:

$$K_3[M(C_2O_4)_3] \cdot 4.5H_2O + NiCl_2 \cdot 6H_2O + [DAMS]I \xrightarrow[1.5\,h]{H_2O/MeOH(1:1)} \alpha_{MIII/NiII} \quad (1)$$

In the second step phase $\alpha_{MIII/NiII}$ is dissolved in H_2O and added with DAMBA:

$$\alpha_{MIII/NiII} + DAMBA \xrightarrow[reflux,1.5\,h]{H_2O} [M_2Ni(C_2O_4)_6][DAMS]_4 \cdot 2DAMBA \cdot 2H_2O \text{ (as } \mathbf{1},\ \mathbf{2} \text{ or } \mathbf{3}) \quad (2)$$

It was not possible, as previously reported [9], to grow single crystals of any of the $\alpha_{MIII/NiII}$ phases. XRPD revealed a well-characterized XRPD pattern, mainly controlled by the inorganic layer, and speaking of isomorphous relationship with the previously characterized $\alpha_{MIII/MII}$ species. Kurtz–Perry measurements showed a SHG of the same order of magnitude of [DAMS][*p*-toluenesulfonate] (*i.e.* 1000 times that of urea), when working at 1907 nm incident wavelength [16].

Well-grown single crystals of the final hybrid compounds $[M_2Ni(C_2O_4)_6][DAMS]_4 \cdot 2DAMBA \cdot 2H_2O$, **1** (M = Rh), **2** (M = Cr), **3** (M = Fe), were obtained in high yields and after reasonable waiting times. By the Kurtz–Perry method, working with a non-resonant wavelength of 1907 nm, **1**, **2** and **3** were found to be characterized by the same extremely high SHG (same order of magnitude of [DAMS][*p*-toluenesulfonate] at the same wavelength [16]). Therefore this synthetic route is a general high-yield method for the synthesis of compounds of this family thus producing isostructural hybrid materials with varying M^{III} and M^{II} centers.

3. Structural characterization

All the compounds of general formula $[M^{III}_2M^{II}(C_2O_4)_6][DAMS]_4 \cdot 2DAMBA \cdot 2H_2O$ that we have so far characterized (M^{III} = Cr, Fe, Rh; M^{II} = Mn, Ni, Zn) crystallized in the polar acentric *Fdd*2 space group (for some of them we have evidence only from XRPD analysis). The large asymmetric unit (for example, see compound **3** containing Fe^{III} and Ni^{II} reported in Table 1, or the $M^{III}Mn^{II}$ ones previously investigated [9]) contains two independent [DAMS$^+$] ions, one DAMBA, one water molecule, three oxalate anions, one M^{III} center in a general position and one M^{II} in a twofold special position.

Table 1
Crystallographic data for $[Fe_2Ni(C_2O_4)_6]$ $[DAMS]_4 \cdot 2DAMBA \cdot 2H_2O$ (**3**)

Compound empirical formula	$C_{94}H_{102}Fe_2N_{10}NiO_{28}$
Formula weight	2080.62
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system, space group	orthorhombic, *Fdd*2
Unit cell dimensions	
a (Å)	39.306(9)
b (Å)	48.70(1)
c (Å)	9.505(2)
Volume (Å^3)	18194(12)
Z	8
D_{calc} (Mg/m^3)	1.450
Absorption coefficient (mm^{-1})	0.61
F(000)	8288
Crystal size (mm)	0.15 × 0.10 × 0.02
θ Range for data collection (°)	2.23–26.4
Reflections collected/unique	35983/9307
R_{int}	0.118
R_σ	0.125
Data/restraints/parameters	9307/1/609
Goodness-of-fit on F^2	1.009
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0841, wR_2 = 0.1979
R indices (all data)	R_1 = 0.1626, wR_2 = 0.2397

$R_{int} = \sum|F_o^2 - F_{mean}^2|/\sum F_o^2$; $R_\sigma = \sum \sigma(F_o^2)/\sum F_o^2$; $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = (\sum(F_o^2 - F_c^2)^2/\sum wF_o^4)^{1/2}$.