

## Magnetic properties of a linear dioxonickelate(II) ion imbedded in apatite-type strontium and barium phosphates

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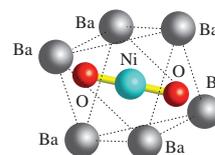
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**Strontium and barium hydroxyapatite phosphates doped with nickel oxide were prepared by a high-temperature solid state synthesis. The compounds contain a linear dioxonickelate(II) anion, which reveals strong easy-plane magnetic anisotropy with a zero-field splitting energy of 57 cm<sup>-1</sup>.**

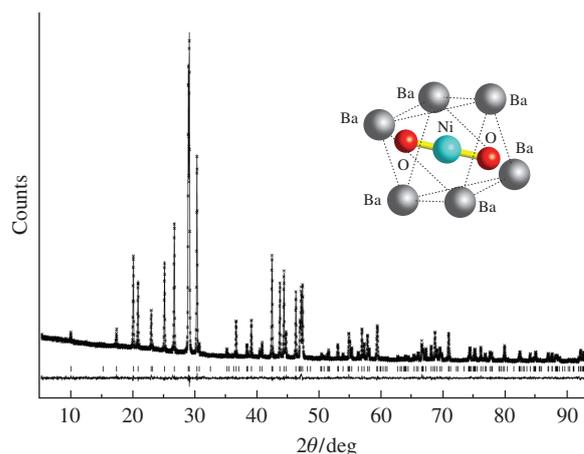


A variety of compounds crystallize in apatite-type structures exemplified by calcium phosphate  $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$ , where X is a small anion such as  $\text{OH}^-$  or a halide ion situated in the apatite channel.<sup>1</sup> The hydroxide groups can be partially replaced by 3d metal–oxygen atomic groups, which form monomeric dioxometallate anions  $[\text{OMO}]_n^-$ , where M = Cu and  $n = 1$ , 3<sup>2–4</sup> or M = Co, Zn, and Ni and  $n = 2$ ;<sup>5,6</sup> Fe and Mn can also be incorporated in the apatite channel.<sup>7</sup> This coordination of open-shell 3d metal ions is very rare for inorganic solids; the majority of such compounds are complexes with bulky organic ligands.<sup>8</sup> A strontium phosphate apatite doped with Cu shows a brilliant blue-violet color, and it is applied as a pigment.<sup>9</sup> Paramagnetic Cu- and Co-loaded alkaline-earth phosphate apatites exhibit high magnetic anisotropy and slow magnetization relaxation being a rare example of inorganic single-molecule magnets.<sup>10–12</sup> Such compounds are very promising materials for ultrahigh density magnetic recording, spintronics, and quantum computing.<sup>13–16</sup> In case of Ni, the strontium apatite  $\text{Sr}_{10}(\text{PO}_4)_6(\text{Ni}_{0.2}\text{OH}_{0.6})_2$  is well known.<sup>5</sup> It contains a linear  $[\text{ONiO}]^{2-}$  anion in the apatite channel and reveals a paramagnetic behavior. It was found that Ni enters into the channels of calcium hydroxyapatite.<sup>7</sup> In this work, we synthesized Ni-doped strontium and barium phosphate apatites and analyzed in detail their magnetic properties.

The samples of  $\text{A}_{10}(\text{PO}_4)_6(\text{Ni}_x\text{OH}_{1-2x})_2$ , where A = Sr,  $x = 0.2$  (**1**),  $x = 0.5$  (**2**); A = Ba,  $x = 0.2$  (**3**),  $x = 0.5$  (**4**), were prepared by a high-temperature solid state reaction in air<sup>5</sup> using  $\text{BaCO}_3$  or  $\text{SrCO}_3$ ,  $(\text{NH}_4)_2\text{HPO}_4$ , and NiO (Sigma-Aldrich,  $\geq 99\%$ ) as starting compounds mixed in a stoichiometric ratio with a 2% excess of an alkaline-earth carbonate. The mixtures were slowly heated to 800 °C for 4 h and annealed at this temperature for 10 h. The products were reground, pressed in pellets, and annealed at 1150 °C for 24 h. The pellets were reground, pelletized again, annealed at 1400 °C for 6 h, and air quenched. Compounds **1** and **2** were light-green and **3** and **4** were green-brown. According to powder X-ray diffraction (XRD) data obtained using a Rigaku D/MAX 2500 diffractometer with  $\text{CuK}\alpha$  radiation, **1** and **3** consisted of a pure apatite phase with Ni fully incorporated into the apatite structure, while **2** and **4** contained both the apatite phase and NiO suggesting the solid solubility of Ni in the apatite

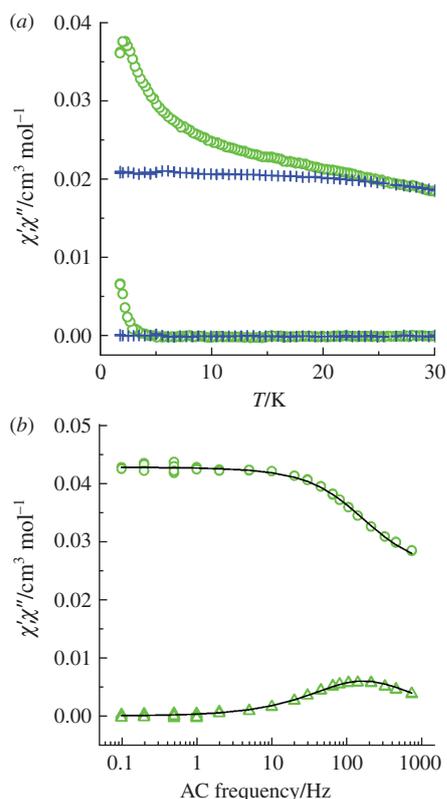
to be limited to  $x < 0.5$ . The Rietveld refinement of **1** showed that Ni was found in the apatite channel in a quantity corresponding to  $x = 0.198(5)$ , which confirms the identity of the compound to that reported earlier.<sup>5</sup>

As barium compound **3** was prepared for the first time, its crystal structure was refined by the Rietveld method using a better quality XRD pattern measured on a STOE STADI-P diffractometer ( $\text{CuK}\alpha_1$  radiation; step, 0.01°). Figure 1 shows that the Ni atom is located at the center of a trigonal channel contacting two intrachannel oxygen atoms in the linear  $[\text{ONiO}]^{2-}$  ion. The Ni site occupancy is  $x = 0.202(8)$ . The value is consistent with a nominal Ni content of 0.2, and it indicates that the Ni ions enter into the apatite channels only so that other cation sites are



**Figure 1** X-ray powder diffraction patterns of **3**: observed (crosses), calculated (solid line), and difference (solid line below) plots. Positions of Bragg reflections are shown as strokes underneath. Inset: a fragment of the crystal structure, dioxonickelate(II) ion in the channel formed by the Ba atoms. Space group  $P6_3/m$ ,  $a = 10.1934(1)$ ,  $c = 7.7315(1)$  Å,  $R_{\text{wp}} = 0.028$ ,  $R_{\text{f-all}} = 0.023$ . Atomic fractional coordinates  $x$ ,  $y$ ,  $z$ , and  $U_{\text{iso}}(\text{Å}^2)$ : Ba(1), 1/3, 2/3,  $-0.0007(5)$ , 0.0157(7); Ba(2), 0.2418(2),  $-0.0193(2)$ , 1/4, 0.0191(7); P(1), 0.3989(7), 0.3661(9), 1/4, 0.009(2); O(1), 0.343(2), 0.488(2), 1/4, 0.017(6); O(2), 0.576(2), 0.461(2), 1/4, 0.017(6); O(3), 0.3432(9), 0.2667(10), 0.0884(11), 0.019(4); O(4), 0, 0, 0.25, 0.06(2); Ni(1), 0, 0, 0, 0.02. Occupancies of O(4) and Ni(1) are 0.69(4) and 0.202(8), respectively.





**Figure 4** In-phase  $\chi'$  (upper curves) and out-of-phase  $\chi''$  (lower curves) AC magnetic susceptibility per mole of Ni (nominal) under a field of 1.5 kOe. (a) Temperature dependence at an AC frequency of 80 Hz; crosses, **2**; circles, **4**. (b) AC frequency dependence at  $T = 2 \text{ K}$  for **4**. Symbols, experimental points; lines, fitting.

ground state acquires  $M_J = 0$  with the first excited magnetic state of  $\sim 140 \text{ cm}^{-1}$  above. Further lowering of the  $d_{z^2}$  orbital energy results in a decrease of the first excited state energy. When  $d_{z^2}$  and  $d_{x^2-y^2,xy}$  become comparable in energy and  $d_{xz,yz}$  being well above the former orbitals (of an order of  $10^4 \text{ cm}^{-1}$ , see Figure 3), the magnetic properties can be well described with the formalism of a zero field split orbitally non-degenerated term with  $S = 1$ . Using the crystal field parameters in Wybourne<sup>23</sup> notation  $B_{20}$  and  $B_{40}$  of  $1 \times 10^4$  and  $-3 \times 10^4 \text{ cm}^{-1}$ , respectively, we obtained electronic structure corresponding to  $D = 57 \text{ cm}^{-1}$  and  $\mu_{\text{eff}} = 3.24 \mu_{\text{B}}$  at  $T = 300 \text{ K}$ . Therefore, the ground electronic multiplet of the linear dioxonickelate(II) anion is most probably an orbital singlet  $^3\Sigma_g^-$ .

Low temperature AC susceptibility data are shown in Figure 4. Strontium compound **2** does not show any hints of slow relaxation of magnetization down to 1.8 K. On the contrary, barium compound **4** reveals the onset of slow relaxation below 4 K [see Figure 4(a), non-zero  $\chi''$  values]. Figure 4(b) shows the frequency dependence of the AC susceptibility of **4** at  $T = 2 \text{ K}$ . The fitting using a generalized Debye model<sup>24</sup> yields a relaxation time of  $9.6(3) \times 10^{-4} \text{ s}$ . A magnitude of the relaxing susceptibility is  $0.0178(2) \text{ cm}^3 \text{ K mol}^{-1}$ , which is comparable with the susceptibility of the paramagnetic admixture estimated by the above fitting of  $\chi T(T)$ . Probably, a small part of Ni in barium compounds is incorporated in the apatite phase in a different oxidation state and/or into a different site, and it may be characterized by a negative  $D$  or unquenched orbital moment, which are important factors for the single-ion magnet properties to arise.

Therefore, the incorporation of Ni in strontium and barium hydroxyapatites results in the formation of the linear  $[\text{ONiO}]^{2-}$  anion in the channel. The anion does not reveal slow relaxation of magnetization and exhibits strong easy-plane magnetic anisotropy, which is very little affected by the crystal environment. This linear dioxonickelate(II) anion in an apatite matrix can be related to the dioxocobaltate(II) anion,<sup>12</sup> which in contrast has a bent geometry, possesses easy axis magnetic anisotropy, and reveals slow relaxation of magnetization. This knowledge can promote a better understanding and more efficient controlling of magnetic anisotropy of transition metal ions, which is a key element in single-molecule magnets prospective for spintronics and quantum electronics.

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