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Comment on "A Study on Structural, Optical, mechanical and Ferroelectric Properties of Tri-glycine barium nitrate Single Crystals"

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Abstract

We argue that the "tri-glycine barium nitrate" crystal reported by R. Ezhil Vizhi and D. Rajan Babu, *Ferroeclectrics Letters Section* **40**, 1–10 (2013) is not a new ferroelectric but a dubious crystal.

Keywords glycine; barium nitrate; tri-glycine barium nitrate; ferroelectric crystal

Comment

Ezhil Vizhi and Rajan Babu [1] claim on obtaining of a new crystal "tri-glycine barium nitrate" (TGBN), moreover, on discovering of a new ferroelectric. According to the authors, the crystal was prepared by the slow evaporation method from an aqueous solution containing glycine and barium nitrate $Ba(NO_3)_2$ in 3:1 mole ratio. The authors claim to have characterized "tri-glycine barium nitrate" with the aid of single crystal and powder X-ray diffraction, infrared and UV-visible spectra. Although the authors state '*The structure of the grown crystal was solved by single crystal XRD analysis by direct method and by the full matrix-least-squares technique using SHELXL program*' only unit cell parameters are reported. In a case study of NLO crystals of salts of amino acids Fleck and Petrosyan [2] have shown that formulating new materials based only on unit cell data is not reliable. According to [1] the crystal "tri-glycine barium nitrate" is orthorhombic with a=5.6840 Å, b=5.6965 Å, c=8.1222 Å and cell volume V=262.9821 Å^3. We opine that these data cannot be correct. The

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volume of glycine molecule is equal to *ca*. 78 Å^3 based on structures of α, β, γ-forms of glycine [3-5], while for cubic centrosymmetric $Ba(NO_3)_2$ (space group *P*a3, a=8.1184(2) Å, Z=4) it is *ca*. 134 Å^3 [6]. So, even for Z=1, one may expect for "tri-glycine barium nitrate" a cell volume V=368 Å^3. Actually for orthorhombic symmetry one can expect Z=4. In addition, it should be noted that the indexed X-ray powder pattern shown in [1] is not compatible with indicated cell parameters. Indeed, taking 2θ=18.92° for reflection (200), 2θ=20.00° for reflection (002) and 2θ=35.42° for reflection (320) the following cell parameters *a*=9.381 Å, *b*=8.655 Å, *c*=8.879 Å can be obtained for orthorhombic symmetry.

More definite results may be obtained by an analysis of the infrared (IR) spectrum of "tri-glycine barium nitrate" shown in [1]. A scrutiny of the spectrum allows one to unambiguously conclude that the crystal does not contain glycine molecules [7]. So, it was natural to compare the spectrum with the known IR spectra of anhydrous barium nitrate and several hydrated barium nitrates, reported in the literature [8, 9]. This comparison reveals that the IR spectrum reported in [1] corresponds well to the spectrum of anhydrous barium nitrate $Ba(NO_3)_2$. The strong signal at ~3433 cm^{-1} [1] is probably due to the hygroscopic nature of KBr. All other bands, whose assignments are given in [8, 9] perfectly match with the reported spectra. Thus, the IR spectrum of "tri-glycine barium nitrate" shows that the crystal actually is anhydrous barium nitrate. However, powder XRD pattern does not correspond to that of barium nitrate [10], which indicates that XRD data and the IR spectrum do not belong to the same sample. In view of contradictory XRD and IR data, TGBN can at best be declared as a dubious crystal and not a new ferroelectric. We believe that the authors formulated the title crystal based on an incorrect assumption that by use of glycine and $Ba(NO_3)_2$ in 3:1 mole ratio in aqueous medium, they can grow TGBN crystal. In a recently published paper [11] the authors claim to obtain another crystal "glycine barium nitrate". However, the infrared spectrum of "glycine barium nitrate" also exactly corresponds to the spectrum of anhydrous barium nitrate. An earlier reported "glycine barium nitrate potassium nitrate" crystal, has been proved to be γ-glycine [12]. A recent paper reports on the growth of γ-glycine by dissolving glycine and $Ba(NO_3)_2$ in 2:1 ratio [13].

The hysteresis loop presented in [1] is not a ferroelectric loop, because such a graph can also be attributed for nonlinear dielectric loss from crystal imperfection. The authors make no mention of the measured direction and temperature changes of "polarization" and "coercive field". As ferroelectric domain cannot be seen by AFM we are not in agreement with such a

claim. It is worth mentioning that the authors of [1] had earlier claimed to have obtained a new ferroelectric crystal "N-acetylglycine phosphite", which was proved to be the well-known glycinium phosphite crystal [14].

In summary, we have shown that the so called tri-glycine barium nitrate" (TGBN) crystal is not a new ferroelectric material but instead a dubious crystal.

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