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Stuffed Tridymite Structures: Synthesis, Structure, Second Harmonic Generation, Optical, and Multiferroic Properties

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Abstract: The stuffed tridymite structure $\text{Ba}(\text{Zn}/\text{Co})_{1-x}\text{Si}_{1-x}\text{M}_{2x}\text{O}_4$ ($\text{M} = \text{Al}^{3+}$ and Fe^{3+}) is explored for the possible multiferroic behavior and to develop new inorganic colored materials. The compounds were synthesized by employing conventional solid-state chemistry methods in the temperature range 1100–1175 °C for 24 h. The powder X-ray diffraction (PXRD) and Rietveld refinement studies indicate that the compounds stabilize in the $P6_3$ space group (no. 173). The refinement results were also rationalized by employing Raman spectroscopic studies. The compounds were

found to be second harmonic generation (SHG) active and show weak ferroelectric behavior. The co-substitution of Co^{2+} and Fe^{3+} in the structure gives rise to a weak ferromagnetic behavior to the compound, $\text{BaCo}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$, making it a multiferroic material. The optical studies on the prepared compounds exhibited blue color (Co^{2+} in T_d geometry), purple color (Ni^{2+} in T_d geometry), and simultaneous substitution of Co^{2+} and Fe^{3+} gives rise to blue-green color owing to metal-to-metal charge transfer (MMCT) effect.

Introduction

The structure–property correlation has been the mainstay of research in solid-state chemistry.^[1] The majority of the known compounds, generally, crystallize in symmetrical structures to have the lowest electrostatic potential. It is known that the size of the ions, the bonding as well as the electronic structure of the ions play a significant role in determining the outcome of a particular structure.^[2] Thus, in addition to the symmetrical structures, one finds many compounds stabilized in noncentrosymmetric and polar structures.

Compounds stabilized in noncentrosymmetric space groups are important for their many symmetry-dependent properties. Such compounds find use as pyro/piezoelectric, ferroelectric, and second-order non-linear optical (NLO) materials. There have been attempts to relate crystallography and the physical properties in these classes of compounds.^[3]

The earliest known polar structure is due to the hydrogen bonding in Rochelle salt, $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$.^[4] Over the years, many compounds have been prepared and examined for non-centrosymmetric behavior, especially ferroelectric behavior. Ferroelectricity is normally associated with d^0 electrons (second-order Jahn–Teller effect) and s^2 lone pair of electrons. The classic example of such observation is in BaTiO_3 (d^0 cation)^[5] and $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ ($6s^2$ lone pair).^[6]

The scientific interest in examining ferroelectric materials has been consistent over the years as they are being employed in many useful devices such as capacitors, transducers, and actuators.^[7] Another equally important aspect of materials chemistry is to investigate magnetic behavior in compounds. Magnetism in compounds, generally, requires partially filled d

or f orbitals. Hard magnetic materials such as SmCo_5 , $\text{Nd}_2\text{Fe}_{14}\text{B}$, $\text{BaFe}_{12}\text{O}_{19}$, etc., have been employed in important applications, notably in motors, actuators, power generators, etc.^[8]

In recent years, considerable effort has been expended to combine the properties of polar structures (ferroelectricity) with those of magnetism within the same compound. Such compounds are known as multiferroic materials and have immense potential for efficient memory devices and other applications of technological interest.^[9] Combining ferroelectricity and magnetism in the same material, however, poses considerable challenges in terms of crystal chemistry and symmetry requirements.^[10] To observe multiferroic behavior, the compound needs to be crystallized in one of the ten known polar point groups (1, 2, m , $mm2$, 4, $4mm$, 3, $3m$, 6, and $6mm$).^[11] The area of multiferroics has been recently reviewed, which brings out the subtle relationships between magnetism and ferroelectricity.^[12]

Persistent research over the years has given rise to a number of compounds stabilized in the polar space groups.^[13] One of the well-established compounds is silica and its analogs.^[14] The stuffed derivatives of silica structures have also been explored.^[15] The stuffed tridymite, $\text{A}[\text{BC}]\text{O}_4$, (space group $P6_3$) is a good example of a polar structure where A is an alkali or alkaline earth metal ions and B and C are tetrahedrally coordinated ions.^[16] The common polymorph of tridymite is β -tridymite and the stuffed variant is generated by substituting Si^{4+} by di- and trivalent cations. The charge-compensating large divalent cations occupy channels that are perpendicular to the SiO_4 sheets (Figure 1). Thus, the stuffed tridymite has elements present in different coordination environments, which were exploited to prepare new analogs.^[17] The compounds stabilized in the stuffed tridymite structure have been investigated for luminescence, magnetic, dielectric, ferroelectric, and other properties useful in diverse technology over the years.^[18]

We have been interested in the study of the stuffed tridymite structure, BaZnSiO_4 ,^[19] as it occurred to us that related compounds can be prepared by suitably modifying the composition. As part of this study, we explored replacing Zn^{2+} and Si^{4+} ions with trivalent ions (Al^{3+} , Ga^{3+} , Fe^{3+}) as they have comparable ionic radii [$(\text{Zn}_{0.5}\text{Si}_{0.5})^{3+} = 0.43 \text{ \AA}$, $\text{Al}^{3+} = 0.39 \text{ \AA}$, $\text{Ga}^{3+} = 0.47 \text{ \AA}$, and $\text{Fe}^{3+} = 0.49 \text{ \AA}$]^[20a] and bonding preferences.^[20b] Compounds containing iron with a polar structure (BiFeO_3 , $\text{Zn}_2\text{FeTaO}_6$, GaFeO_3 , etc.) have been of interest for the

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Figure 1. Crystal structure of BaZnSiO₄.

study of magnetism as well as multiferroic behavior.^[21] In this paper, we report the synthesis, structure, SHG, ferroelectric, and magnetic (multiferroic) studies of the new members of the stuffed tridymite structure.

Results and Discussion

Synthesis and structural characterization

The stuffed tridymite structure, BaZnSiO₄, [ABCO₄], has the Ba²⁺ in nine-fold coordination; the Zn²⁺ and Si⁴⁺ have tetrahedral coordination. As part of the study, we have attempted substitutions at the B and C positions employing different elements. We considered the coordination preference (tetrahedral) of the metal ions occupying the B and C positions in the structure. Thus, we have made attempts to substitute Al³⁺, Fe³⁺, Co²⁺, Ni²⁺, and Cu²⁺ ions within the stuffed tridymite structure.^[20a] We have been successful in making the compounds with the stuffed tridymite structure by substituting Al³⁺, Fe³⁺, and Co²⁺. The attempts to prepare compounds with the stuffed tridymite structure was not successful when we attempted simultaneous substitutions of Al³⁺/Fe³⁺ (trivalent) ions along with the divalent Ni²⁺ and Cu²⁺ ions. The list of prepared compounds along with the synthesis conditions is listed in Table S1 (in the Supporting Information).

BaZn_{1-x}M_xSiO₄ (M = Co, Ni, and Cu)

The initial characterization of the synthesized samples was carried out by powder X-ray diffraction (PXRD), which indicated the formation of crystalline single-phase compounds. The compounds were found to be isostructural to the parent PXRD pattern simulated based on the BaZnSiO₄ structure.^[17a] Thus, BaZn_{1-x}Co_xSiO₄ (0 < x ≤ 1.0), BaZn_{1-x}Ni_xSiO₄ (0 < x ≤ 0.25), and BaZn_{1-x}Cu_xSiO₄ (0 < x ≤ 0.1) have been synthesized (Figure 2, Figure S1 in the Supporting Information).

A Rietveld refinement of the structure, from the PXRD data, was carried out for the prepared compounds: BaCoSiO₄ (Figure 3 and Table 1); Ba(Zn_{0.75}Ni_{0.25})SiO₄ (Figure S2 and Table S2 in the Supporting Information); Ba(Zn_{0.9}Cu_{0.1})SiO₄ (Fig-

Figure 2. PXRD patterns of different BaZn_{1-x}M_xSiO₄ (M = Co, Ni, and Cu) samples. Figure 3. Rietveld refinement of BaCoSiO₄ from the PXRD data. The observed (O), calculated (red line), and difference (bottom blue line) profiles are shown. The vertical bars (|) indicate Bragg reflections.Table 1. Crystallographic parameters for BaCoSiO₄ obtained from Rietveld refinement of the PXRD data.

Atom	Site	x	y	z	U _{iso} [Å ²]	Occupancy
Ba1	2a	0.0	0.0	0.25	0.002(2)	1.0
Ba2	2b	0.333	0.667	0.219(1)	0.014(3)	1.0
Ba3	2b	0.667	0.333	0.218(1)	0.013(5)	1.0
Si	6c	0.658(2)	-0.012(1)	0.430(3)	0.017(1)	1.0
Co	6c	0.682(2)	0.671(1)	0.532(2)	0.005(4)	1.0
O1	6c	0.763(4)	0.913(2)	0.521(9)	0.009(7)	1.0
O2	6c	0.464(7)	0.905(8)	0.488(8)	0.021(2)	1.0
O3	6c	0.761(5)	0.195(6)	0.445(3)	0.007(2)	1.0
O4	6c	0.722(8)	0.653(9)	0.752(7)	0.034(3)	1.0

Space group *P*6₃: *a* = 9.126(2) Å, *c* = 8.683(1) Å, α = β = 90°, γ = 120°; Reliability factors: *R*_p = 2.43%, *R*_{wp} = 4.04%, χ² = 3.90; Bond lengths (Å): Co–O = 1.957(2), Si–O = 1.627(1), Ba1–O = 2.888(1), Ba2–O = 2.912(1), Ba3–O = 2.725(3).

ure S3 and Table S3 in the Supporting Information). As expected, the crystal structure contains six-membered rings of corner-shared SiO₄ and the relatively larger CoO₄. The crystal structure consists of alternating six-membered rings of MO₄

($M = \text{Zn/Co}$, Zn/Ni , and Zn/Cu) tetrahedra wherein the Ba^{2+} ions occupy the voids (stuffed in the structure, Figure 1 and Figure S4 in the Supporting Information). There are three crystallographically distinct Ba^{2+} ions and these are located on the three-fold axes and possess different coordination environments.^[17]

$\text{BaZn}_{1-x}\text{Si}_{1-x}\text{M}_{2x}\text{O}_4$ ($M = \text{Al}^{3+}$, Ga^{3+} , Fe^{3+})

As part of this study, we attempted substitution of trivalent ions in the stuffed tridymite structure that contains both di- and tetravalent ions. Thus, $\text{BaZn}_{1-x}\text{Si}_{1-x}\text{Al}_{2x}\text{O}_4$ ($0 < x \leq 1.0$), $\text{BaZn}_{1-x}\text{Si}_{1-x}\text{Ga}_{2x}\text{O}_4$ ($0 < x \leq 0.5$), and $\text{BaZn}_{1-x}\text{Si}_{1-x}\text{Fe}_{2x}\text{O}_4$ ($0 < x \leq 0.25$) with Ga^{3+} and Fe^{3+} ions have been synthesized. The observed PXRD patterns indicated the formation of the desired compounds in pure form (Figure S5 in the Supporting Information). Furthermore, we have also made attempts to substitute divalent Zn^{2+} ions with transition metal elements such as Co^{2+} , Ni^{2+} , Cu^{2+} . The PXRD studies indicated the formation of $\text{BaCo}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, $\text{BaCo}_{0.5}\text{Si}_{0.5}\text{GaO}_4$, and $\text{BaCo}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$ (Figure 4). The single-phase compound with the stuffed tridymite structure was not successful when we attempted simultaneous substitutions of $\text{Al}^{3+}/\text{Fe}^{3+}$ (trivalent) ions along with the divalent Ni^{2+} and Cu^{2+} ions. The relevant Rietveld refinement details for the compounds are provided in the Supporting Information (Figures S6–S11 and Tables S4–S9). The summary of the crystal structure data is given in Table S10 (in the Supporting Information).

Figure 4. PXRD patterns of different $\text{BaZn}_{1-x}\text{Si}_{1-x}\text{M}_{2x}\text{O}_4$ ($M = \text{Al}^{3+}$, Ga^{3+} , Fe^{3+}) samples.

Raman spectroscopic studies

Raman spectroscopic measurements were carried out on all the compounds at room temperature in the range 50–1000 cm^{-1} (Figure 5). For BaZnSiO_4 , the strong Raman bands at approximately 81 cm^{-1} , 399 cm^{-1} , and 864 cm^{-1} arise from the vibrations of BaO_9 , ZnO_4 , and SiO_4 bending modes, respectively.^[22,18e] The substitution of Co^{2+} ions in place of Zn^{2+} gave rise to two strong bands at approximately 197 cm^{-1} and 517 cm^{-1} ,

Figure 5. The Raman spectra of $\text{Ba}(\text{Zn/Co})_{1-x}\text{Si}_{1-x}\text{M}_{2x}\text{O}_4$ ($M = \text{Al}^{3+}$ and Fe^{3+}) members at room temperature.

which may be due to the CoO_4 of BaCoSiO_4 . These bands are known for Co^{2+} ions in tetrahedral coordination.^[23] Al^{3+} ion substitution in BaZnSiO_4 ($\text{BaZn}_{0.5}\text{Si}_{0.5}\text{AlO}_4$) gives a strong and broad band at approximately 82 cm^{-1} , which could be due to the association of BaO_9 and AlO_4 tetrahedra.^[22] A broad band observed at about 410 cm^{-1} could be due to the Zn/AlO_4 tetrahedra. On substituting Co^{2+} ions, in the compound $\text{BaCo}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, two strong bands at approximately 203 cm^{-1} and 526 cm^{-1} were observed. These bands are due to the Co/AlO_4 tetrahedra, similar to that observed for BaCoSiO_4 . On substituting Fe^{3+} ions in BaZnSiO_4 ($\text{BaZn}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$), two bands at approximately 179 cm^{-1} and 512 cm^{-1} were observed, which may be due to the FeO_4 tetrahedra.^[24] A broad band observed at about 405 cm^{-1} , could be due to the Zn/FeO_4 tetrahedra. Furthermore, on substituting Co^{2+} ions in place of Zn^{2+} ions, we observed the same broad bands at approximately 204 cm^{-1} and 527 cm^{-1} , which may be due to the Fe/CoO_4 tetrahedra. In all the compounds, we observed a consistent blueshift of Fe/Al/Zn/CoO_4 bands and a redshift of Fe/Al/SiO_4 bands in our studies (Figure 5). This behavior can be understood by considering the relationship between bond strength (k), the reduced mass (μ), and the Raman frequency (ν), [Eq. (1)]:

$$\nu = \frac{1}{2\pi} \sqrt{k/\mu} \quad (1)$$

The ionic radii of Al^{3+} and Fe^{3+} (0.39 and 49 Å, coordination number, $\text{CN}=4$) is smaller than that of Zn^{2+} and Co^{2+} (0.60 and 0.58 Å, $\text{CN}=4$). The change in the size of the ions would result in changes in both the bond length and in the bond strength. In addition, the reduced mass of Al (26.98) and Fe (55.84) is smaller than that of Zn (65.39) and Co (58.93). Thus, the substitution of Fe/Al/Zn/CoO_4 in the stuffed tridymite structure would lead to band shifts to a higher frequency (blueshift). On the other hand, the Fe/Al/SiO_4 band shifts to a lower frequency (redshift) compared with SiO_4 bands owing to the increase in the ionic radii of Al and Fe compared with Si. The Raman spectroscopic studies appear to agree with the

structure refinement employing Rietveld analysis of the observed PXRD patterns. It is clear that $\text{Al}^{3+}/\text{Fe}^{3+}$ ions substitute simultaneously at $\text{Zn}^{2+}/\text{Co}^{2+}(6c)$ as well as $\text{Si}^{4+}(6c)$. Similarly, $\text{Zn}^{2+}/\text{Co}^{2+}$ and Si^{4+} goes to $\text{Al}(1)/\text{Fe}(1)$ ($6c$) and $\text{Al}(2)/\text{Fe}(2)$ ($6c$) positions, respectively, in the structure.

Second harmonic generation (SHG) studies

The compounds crystallize in the noncentrosymmetric space group $P6_3$ (no. 173), which is one of the ten polar point groups (6)^[11] and, satisfies the Kleinman symmetry^[25] for observing second harmonic generation (SHG). SHG measurements (298 K) were performed with the powdered samples. The observed SHG signal intensities for the prepared compounds were compared with that of potassium dihydrogen phosphate (KDP). The observed SHG values range from $0.5 \times \text{KDP}$ to $2.6 \times \text{KDP}$ (Table S11 in the Supporting Information). We have also examined the variation of particle size of the compounds and its effect on the SHG values, which suggested that the materials are type I phase matchable (Figure 6). It may be noted that the transition metal (TM) substituted compounds exhibited a reduced SHG signal compared with the non-TM

Figure 6. Phase-matching data for strong phase-matchable SHG-active stuffed tridymite compounds. The solid curves are drawn to guide the eye and are not a fit to the data.

substituted compounds. The reduced SHG signals could be due to the strong absorption of the TM-substituted compounds in the $\lambda = 500\text{--}650$ nm region, which results in a weak SHG response.^[26] The compound BaZnSiO_4 exhibits a strong SHG signal (2.6 times that of KDP) and similar behavior has been observed before.^[27]

Dielectric and ferroelectric studies

We have also explored the dielectric behavior of the prepared compounds. The frequency dependence of the dielectric constant and dielectric loss of the compounds was measured at room temperature (Figure S12 in the Supporting Information). All the compounds exhibit a large value for the dielectric constant in the low-frequency region, which decreases with an increase of the frequency. The lower dielectric constant with higher frequency could be due to the relaxation of the dipoles. The dipoles in a compound, generally, have different response times as a function of the applied field and the total polarization (dielectric constant) is frequency-dependent. Generally, at lower frequencies, the different polarizations (interfacial, dipolar, ionic polarizations) respond to the applied field. When the applied frequency increases, the different polarizations are relaxed out, leading to the overall decrease in the value of the dielectric constant. This behavior is commonly known in many ceramic compounds.^[28] The stuffed tridymite compounds investigated in the present study exhibit low dielectric loss and may find use in ceramic dielectric resonator technology and could be useful in wireless communications.^[29]

We have also investigated the temperature dependence of the dielectric constant as well as the dielectric loss in the temperature region $25\text{--}350^\circ\text{C}$ by using frequencies in the range of 25 kHz to 1 MHz (Figure 7, Figure S13 in the Supporting Information). The ϵ' - T studies indicate a maximum at approximately 150°C , which would correspond to a structural phase transition (Figure 7, Figure S13 in the Supporting Information). The ϵ' - T studies indicate the frequency independence of the dielectric constant, which suggests a normal ferroelectric behavior.^[30] The measured dielectric constant of the prepared compounds is approximately 14 at 25°C . Similar dielectric constant values have been reported for BaAl_2O_4 (≈ 10.24).^[31] It may be noted that the observed dielectric constant values are smaller than

Figure 7. Temperature dependence of (a) dielectric constant and (b) dielectric loss for BaZnSiO_4 .

that of classical ferroelectric materials, such as BaTiO_3 .^[5] It is likely that the lower values could be due to the different and lower coordination numbers of Ba (CN=9) and Al (CN=4),^[31] as proposed by Rignanes and co-workers.^[32]

The observed dielectric behavior above and below the Curie temperature was fitted by employing the Curie–Weiss law, [Eq. (2)]

$$\epsilon' = C/T - T_0 \quad (2)$$

where C is the Curie constant and T_0 is the Curie–Weiss temperature. It is known that when, $T_0 < T_c$ the transition would be first-order, and when $T_0 = T_c$ it would be a second-order transition. The plot of the reciprocal of the dielectric constant versus temperature above (C) and below (C') T_c reflects the nature of the Curie constant. Generally, when $C/C' > 4$, it would indicate a first-order ferroelectric transition, whereas $C/C' < 4$ would suggest a second-order ferroelectric transition.^[33] The Curie–Weiss fittings of the dielectric constant above and below

T_c is shown in Figure 8, the C/C' values were found to be in the range 0.48–0.63. This indicates a second-order ferroelectric transition for all the compounds. To understand this and confirm the nature of the phase transition, we carried out differential scanning calorimetry (DSC) measurements from 25 to 480 °C. The DSC studies did not indicate any endothermic or exothermic transitions both during heating and cooling cycles (Figure 9). This suggests that the transition observed at about 150 °C could be a second-order transition only. Similar behavior has been observed before.^[34]

We have carried out the polarization as a function of applied field (P – E) hysteresis measurements in the voltage range up to 80 kV cm^{-1} with a step size of 10 kV cm^{-1} at room temperature. A hysteresis loop was observed with a saturation polarization (P_s) value in the range of 0.48 to 0.76 $\mu\text{C cm}^{-2}$, a remanent polarization (P_r) value in the range of 0.17 to 0.25 $\mu\text{C cm}^{-2}$, and a coercive field (E_c) in the range of 19 to 23.1 kV cm^{-1} (Figure S14, Table S12 in the Supporting Information). We have carried out (positive-up, negative-down) PUND measurements to

Figure 8. Curie–Weiss fitting of dielectric constant (ϵ') above and below T_c for (a) BaZnSiO_4 , (b) BaCoSiO_4 , (c) $\text{BaZn}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, (d) $\text{BaCo}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, (e) $\text{BaZn}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$ and (f) $\text{BaCo}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$.

Figure 9. DSC curves for (a) BaZnSiO_4 , (b) BaCoSiO_4 , (c) $\text{BaZn}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, (d) $\text{BaCo}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, (e) $\text{BaZn}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$ and (f) $\text{BaCo}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$ during the heating and cooling cycles.

eliminate the extrinsic factors and obtain the intrinsic remanent polarization (Figure S15 in the Supporting Information). The intrinsic saturated remanent polarization values for BaZnSiO_4 , BaCoSiO_4 , and $\text{BaCo}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$ compounds are 0.058, 0.046, and $0.037 \mu\text{C cm}^{-2}$, respectively. These results are comparable to the earlier reported stuffed tridymite compounds.^[35,18e] These values, however, are lower than those for BaTiO_3 or KNbO_3 ^[36] and indicate a weak ferroelectric behavior. The weak ferroelectric response could be due to the coordination of the B and C sites (tetrahedral), and their contribution to the macroscopic polarity, which would be limited.^[37] In tetrahedral geometry, the physical displacement of MO_4 polyhedra is energetically unfavorable, which would restrict the reversal of the dipole moment in the material.^[37] In the well-known ferroelectric materials (BaTiO_3 , KNbO_3 , etc.), the ferroelectric behavior arises owing to the polarization reversal involving the displacement of the octahedrally coordinated metal species (Ti^{4+} in BaTiO_3 and Nb^{5+} in KNbO_3).^[38]

Optical absorption studies of $\text{BaZn}_{1-x}\text{M}_x\text{SiO}_4$ ($\text{M} = \text{Co, Ni, and Cu}$)

We also explored the transition metal substituted members of the stuffed tridymite derived structures for their optical behavior as they were colored.

$\text{BaZn}_{1-x}\text{Co}_x\text{SiO}_4$ ($0 < x \leq 1.0$)

BaZnSiO_4 is white in color with band gaps (E_g) of approximately 4.00 eV. On substitution of Co^{2+} ions in place of Zn^{2+} ions, the color of the compounds changes from white to intense blue. It is well established that tetrahedral cobalt (Co^{2+} ions), generally, exhibits a deep-blue color, established as Thenard's Blue (CoAl_2O_4) in 1802.^[39] The intensity of the blue color in $\text{BaZn}_{1-x}\text{Co}_x\text{SiO}_4$ increases progressively from sky blue to intense blue ($0 < x \leq 1.0$) with increasing values of x (Figure S16 in the Supporting Information). The optical absorption spectra (Fig-

ure S17 in the Supporting Information) of $\text{BaZn}_{1-x}\text{Co}_x\text{SiO}_4$ ($0 < x \leq 1.0$) exhibits a broad triplet absorption band in the range 1.75–2.70 eV, with the maximum at 2.00 eV. It is known that Co^{2+} ions in tetrahedral symmetry exhibit three spin-allowed transitions: (i) ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_2(\text{F})$ (IR region), (ii) ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$ (IR region), and (iii) ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$ (visible region).^[40] The triplet band around 2.00 eV for the tetrahedral Co^{2+} ions has the $[{}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})]$ transition. Considering a possible application as an inorganic pigment, we explored the color stabilities of the compounds by treating the samples in 4 N HNO_3 for 24 h at room temperature. The compounds were filtered, dried, and examined for their color and structure, which indicated that the samples did not show any appreciable changes to their colors, PXRD patterns, and optical absorption spectra (Figures S18–S20 in the Supporting Information).

$\text{BaZn}_{1-x}\text{Ni}_x\text{SiO}_4$ ($0 < x \leq 0.25$)

The substitution of Ni^{2+} in BaZnSiO_4 leads to a change from white ($x=0$) to bright purple color under daylight ($x=0.25$; Figure S21 in the Supporting Information). In the optical absorption spectra of $\text{BaZn}_{1-x}\text{Ni}_x\text{SiO}_4$ ($0 < x \leq 0.25$; Figure S22 in the Supporting Information), we observed a doublet absorption in the range 1.60–2.75 eV with two maxima at 1.92 and 2.27 eV. In addition, we also observed a small hump at 1.55 eV. The two absorption maxima correspond to the orange and the green regions, which would result in a complementary color of blue and red. Thus, the nickel compounds exhibit a bright purple color. Although three spin-allowed transitions are known for Ni^{2+} in tetrahedral coordination, only one transition $[{}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})]$, which is spin-allowed and observed in the visible region. The doublet absorption observed at approximately 1.95 and 2.30 eV in $\text{BaZn}_{1-x}\text{Ni}_x\text{SiO}_4$ ($0 < x \leq 0.25$) may be due to the ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$ transition within the tetrahedral symmetry.^[40d] The small shoulder at 1.55 eV could be due to the spin-orbit coupling, which is known for d^8 ions such as Ni^{2+} in the tetrahedral symmetry.^[40] Normally, Ni-containing compounds do not exhibit bright purple color and the observation of such a color in our present compounds for a tetrahedral Ni^{2+} is interesting. Similar purplish (magenta) color has been seen in Ni-doped $\alpha\text{-LiZnBO}_3$,^[41] $\text{Ba}_3\text{TeGa}_2\text{NiSi}_2\text{O}_{14}$.^[40d]

$\text{BaZn}_{1-x}\text{Cu}_x\text{SiO}_4$ ($0 < x \leq 0.1$)

Our efforts at the substitution of Cu^{2+} ions in BaZnSiO_4 were not successful and we were able to substitute only a small amount (up to 10%) in place of Zn, $\text{BaZn}_{1-x}\text{Cu}_x\text{SiO}_4$ ($0 < x \leq 0.1$). The compounds also did not exhibit any distinct color. Many Cu^{2+} -containing compounds and minerals absorb in the near-IR region, which overlaps into the visible region.^[42] Our optical absorption studies also did not exhibit any bands in the visible region (Figure S23 in the Supporting Information).

$\text{BaZn}_{0.5-x}\text{Co}_x\text{Si}_{0.5}(\text{Al/Ga})\text{O}_4$ ($0 < x \leq 0.5$)

Similar to the Co^{2+} substitution in BaZnSiO_4 , our attempts at substituting Co^{2+} ions in $\text{BaZn}_{0.5-x}\text{Co}_x\text{Si}_{0.5}(\text{Al/Ga})\text{O}_4$ ($0 < x \leq 0.5$)

also resulted in intense blue color (Figures S24, S26 in the Supporting Information). The observed optical absorption spectra (Figures S25, S27 in the Supporting Information) of $\text{BaZn}_{0.5-x}\text{Co}_x\text{Si}_{0.5}(\text{Al/Ga})\text{O}_4$ ($0 < x \leq 0.5$) also exhibited similar features as that of $\text{BaZn}_{1-x}\text{Co}_x\text{SiO}_4$ ($0 < x \leq 1.0$) members.

$\text{BaZn}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$

It is known that Fe^{3+} ions can be stabilized in tetrahedral coordination and we have prepared a $\text{BaZn}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$ sample. Then, as prepared, the sample exhibits an intense yellow color (Figure S28 in the Supporting Information). We have also replaced the Zn^{2+} ions in this compound with Co^{2+} ions, which resulted in a greenish blue-colored compound (Figure S28 in the Supporting Information). The optical absorption spectra (Figure S29 in the Supporting Information) of the $\text{BaZn}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$ sample exhibit rather broad absorption with one maxima at approximately 2.6 eV and another at about 3.7 eV. The absorption band at approximately 2.6 eV could be due to the ${}^6\text{A}_1(\text{S}) \rightarrow {}^4\text{T}_1(\text{G})/{}^4\text{T}_2(\text{G})$ transition. Similar absorption has been observed before.^[41] Another band observed at approximately 3.7 eV could be due to the ligand-to-metal charge transfer.^[40,41]

The optical absorption spectra (Figure S29 in the Supporting Information) of $\text{BaCo}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$ exhibits a broad triplet absorption band in the region of 1.75 to 2.30 eV. These bands could be due to the Co^{2+} in tetrahedral coordination. The large redshift in the absorption band could be due to the possible electronic interactions between Co^{2+} ($3d^7$) and Fe^{3+} ($3d^5$) ions involving metal-to-metal charge transfer (MMCT). Similar MMCT has been observed in CoFe_2O_4 and in sapphire where Fe^{2+} ions transfer the charge to Ti^{4+} ions, which is a MMCT transition involving 3d–3d orbitals giving rise to intense blue color.^[43] The experimental band gap ($E_g \approx 2.00$ eV) of the compound $\text{BaCo}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$ agrees well with the theoretically calculated band gap of the compound (Figure 11). The material may find use as a catalyst for visible light photocatalysis.

We determined the CIE 1931 chromaticity coordinates for all the compounds (Figure 10, Table 2). The color coordinates (L^* , a^* , and b^* parameters) for BaCoSiO_4 was compared with other

Figure 10. CIE chromaticity diagram for the prepared compounds.

Table 2. Color coordinates for $\text{BaZn}_{1-x}\text{M}_x\text{SiO}_4$ ($\text{M} = \text{Co}, \text{Ni}$) and $\text{BaZn}_{0.75-x}\text{Co}_x\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$ ($0 < x \leq 0.75$) members.		
Compound	x	y
$\text{BaZn}_{0.9}\text{Co}_{0.1}\text{SiO}_4$	0.12	0.22
$\text{BaZn}_{0.75}\text{Co}_{0.25}\text{SiO}_4$	0.13	0.15
$\text{BaZn}_{0.5}\text{Co}_{0.5}\text{SiO}_4$	0.15	0.10
$\text{BaZn}_{0.25}\text{Co}_{0.75}\text{SiO}_4$	0.15	0.07
BaCoSiO_4	0.15	0.04
$\text{BaCo}_{0.5}\text{Si}_{0.5}\text{AlO}_4$	0.13	0.08
$\text{BaCo}_{0.5}\text{Si}_{0.5}\text{GaO}_4$	0.14	0.07
$\text{BaZn}_{0.75}\text{Ni}_{0.25}\text{SiO}_4$	0.33	0.16
$\text{BaZn}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$	0.48	0.41
$\text{BaCo}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$	0.13	0.57

Table 3. Color coordinates for BaCoSiO_4 , CoAl_2O_4 , $\text{Ca}_3\text{Sb}_2\text{Ga}_2\text{CoO}_{12}$, $\text{LiZn}_{0.5}\text{Co}_{0.5}\text{BO}_3$, and $\text{YIn}_{0.9}\text{Mn}_{0.1}\text{O}_3$.			
Compound	L^*	a^*	b^*
BaCoSiO_4	12.54	1.27	−60.13
CoAl_2O_4 [a]	81.99	−3.9	−15.62
$\text{Ca}_3\text{Sb}_2\text{Ga}_2\text{CoO}_{12}$ [a]	32.46	11.30	−53.24
$\text{LiZn}_{0.5}\text{Co}_{0.5}\text{BO}_3$ [a]	29.87	32.10	−62.67
$\text{YIn}_{0.9}\text{Mn}_{0.1}\text{O}_3$ [a]	39.71	−5.78	−22.28

[a] Data for the reported compounds were taken from Refs. [39c, 40d, 41, 44].

known blue-colored compounds: CoAl_2O_4 ,^[39c] $\text{LiZn}_{0.5}\text{Co}_{0.5}\text{BO}_3$,^[41] $\text{Ca}_3\text{Sb}_2\text{Ga}_2\text{CoO}_{12}$,^[40d] and $\text{YIn}_{0.9}\text{Mn}_{0.1}\text{O}_3$,^[44] (Table 3). The color coordinates of BaCoSiO_4 compares favorably with the reported blue-colored compounds.

NIR reflectance spectra

The NIR reflectance behavior of the compounds was explored as they are important for the development of 'cool pigments'.^[45] The NIR spectrum of BaZnSiO_4 , $\text{BaZn}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, and $\text{BaZn}_{0.5}\text{Si}_{0.5}\text{GaO}_4$ exhibits approximately 85% NIR reflectivity, which is comparable to that observed for TiO_2 ($\approx 70\%$; Figure S30 in the Supporting Information). The TM-substituted compounds, on the other hand, exhibit a NIR reflectivity in the range of 65 to 75%. Thus, the present compounds possess in-

teresting colors and also exhibit good near IR reflectivity, which makes them suitable candidates to develop new 'cool pigment' materials.

Electronic band structure calculations and rationalizing the SHG behavior

First-principles density functional theory (DFT) calculations were carried out to understand the participating electrons near to the Fermi level. We computed the atom resolved density of states (DOS) for the compounds (Figure 11). The compound, BaZnSiO_4 , has O 2p and Zn 3d orbitals forming the top of the valence band. This appears to be a characteristic of Zn-containing compounds.^[27]

The transition metal-substituted compounds have the 3d states occupying near the bottom of the conduction band. This appears to reduce the band gap and consequently re-

Figure 11. Partial density of states for (a) BaZnSiO_4 , (b) BaCoSiO_4 , (c) $\text{BaZn}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$, (d) $\text{BaCo}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$. The Fermi level is set to 0 eV (broken black line).

duces the SHG signal (Figure 6). It has been shown that the change in the parity of the dominant orbitals near the Fermi level would lead to a reduction in the SHG response.^[26] In our studies, we find that in BaZnSiO₄ and TM-substituted analogs there are changes in the parity of the orbitals at the Fermi level, which would also account for the reduced SHG response for the TM-substituted compounds.

Magnetic studies

BaCoSiO₄

Many of the prepared compounds contain transition metal elements substituted fully or partially within the stuffed tridymite structure. We have investigated the magnetic behavior of the compounds to understand the nature of magnetic interactions between the unpaired electrons of the transition elements. Thus, the magnetic susceptibility measurement for BaCoSiO₄ was carried out in the temperature range 2–300 K in an applied magnetic field of 1000 Oe (Figure S31 in the Supporting Information). The molar magnetic susceptibility (χ_m) was found to be 0.0077 emu mol⁻¹ at room temperature, which did not exhibit any appreciable change up to 50 K. The χ_m value starts to increase sharply upon cooling further to reach a value of 0.26 emu mol⁻¹ at 2 K. The thermal dependence of $1/\chi_m$ is shown as an inset in Figure S31 (in the Supporting Information). The observed magnetic behavior was fitted in the temperature range 50–300 K for the Curie–Weiss behavior (Figure S31, inset in the Supporting Information). The values of the Curie constant and Weiss constant obtained by the Curie–Weiss fit were found to be $C=2.46$ emu K mol⁻¹ and $\theta_p=-20.3$ K, respectively. The negative value for the θ_p suggests an overall weak antiferromagnetic interaction between the Co²⁺ centers. The observed effective magnetic moment value (4.30 μ_B) appears to be higher than the expected spin-only value (3.87 μ_B), corresponding to Co²⁺ (3d⁷) with high-spin configuration and $S=3/2$. This suggests an orbital contribution to the effective magnetic moment. Cobalt-containing compounds, generally, exhibit large orbital contributions in their magnetic moments.^[46] We have also carried out M – H studies on this compound at 2 K, which indicates the typical behavior expected for compounds possessing weak anti-ferromagnetic interactions (Figure S31 in the Supporting Information). We ob-

served a maximum saturation magnetization value of 1.64 emu mol⁻¹ at 5 T.

BaCo_{0.5}Si_{0.5}AlO₄

The magnetic susceptibility measurements on BaCo_{0.5}Si_{0.5}AlO₄ indicate a behavior that is comparable to BaCoSiO₄, with similar molar magnetic susceptibility (χ_m) of 0.007 emu mol⁻¹ at room temperature (Figure S32 in the Supporting Information). The χ_m value starts to increase sharply around 50 K to reach a value of 0.11 emu mol⁻¹ at 2 K (Figure S32 in the Supporting Information). The Curie–Weiss fit (50–300 K) gave the values of $C=1.13$ emu K mol⁻¹ and $\theta_p=-18.2$ K, respectively (Figure S32, inset in the Supporting Information). As expected, the calculated effective magnetic moment (2.89 μ_B) is marginally higher than the expected spin-only value (2.74 μ_B), corresponding to half Co²⁺ (3d⁷). The M – H studies at 2 K exhibit a gradual increase with the applied field to reach a value of 0.69 emu mol⁻¹ at 5 T.

BaZn_{0.75}Si_{0.75}Fe_{0.5}O₄

The temperature dependence of the magnetic susceptibility for BaZn_{0.75}Si_{0.75}Fe_{0.5}O₄ is shown in Figure 12. The room-temperature molar magnetic susceptibility (χ_m) was found to be 0.0057 emu mol⁻¹, which reaches a value of 0.16 emu mol⁻¹ at 2 K (Figure 12). The Curie–Weiss fit in the temperature range 100–300 K gave a value of $C=2.12$ emu K mol⁻¹ and $\theta_p=-68.7$ K, respectively. The observed magnetic moment of 3.69 μ_B compares well with the calculated value of 4.18 μ_B corresponding to Fe³⁺ (3d⁵), high spin ($S=5/2$). The experimental magnetic moment value is consistent with those observed for Fe³⁺ in a tetrahedral coordination environment.^[47] For example, magnetic moment values of approximately 3.93 μ_B have been observed for antiferromagnetic Ba₄KFe₃O₉.^[47] Similarly, the reported magnetic moments for tetrahedral Fe³⁺ in BaFe₄O₇ and K_{0.22}Ba_{0.89}Fe₄O₇ are 3.8 μ_B and 4.4 μ_B , respectively,^[48] which compare well with that observed for the present compound.

Figure 12. (a) χ_m vs. T plot for BaZn_{0.75}Si_{0.75}Fe_{0.5}O₄. Inset shows the $1/\chi_m$ vs. T plot. (b) M vs. H plot for BaZn_{0.75}Si_{0.75}Fe_{0.5}O₄.

Figure 13. (a) χ_m vs. T plot for $\text{BaCo}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$. (b) M vs. H plot for $\text{BaCo}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$.

$\text{BaCo}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$

The variation of magnetic susceptibility as a function of temperature for $\text{BaCo}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$ is shown in Figure 13. The room-temperature molar magnetic susceptibility (χ_m) is $0.013 \text{ emu mol}^{-1}$. As can be noted, the magnetic susceptibility is significantly enhanced for $\text{BaCo}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$ in comparison with the $\text{BaZn}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$ compound. The effective magnetic moment was found to be $5.58 \mu_B$, which agrees reasonably well with the expected value ($5.36 \mu_B$), corresponding to Co^{2+} ($3d^7$) and Fe^{3+} ($3d^5$), both existing in high-spin configuration ($S=3/2$ and $5/2$). The $M-H$ studies at 2 K exhibit a hysteresis with a saturation magnetization (M_s) value of $0.6 \mu_B$, a remanent polarization (M_r) value of $0.44 \mu_B$, and a coercive field (E_c) of approximately 3 kOe (Figure 11 b). The $M-H$ curve indicates weak ferromagnetic (FM) behavior. The FM interactions could likely be due to the $\text{Fe}^{3+}/\text{Co}^{2+}$ coupling in the structure via super-exchange interactions.^[49]

Conclusion

New members of the stuffed tridymite structure, BaMSiO_4 (Zn, Co, Ni, Fe), have been synthesized and characterized. The compounds crystallize in the polar space group $P6_3$. The compounds were SHG active and the SHG response was understood and rationalized with the help of band structure calculations. The compounds exhibit moderate ferroelectric behavior. The Curie–Weiss fitting of the dielectric behavior and the DSC studies indicate a second-order ferroelectric phase transition in these compounds. Magnetic measurements on the transition metal ions substituted compounds indicated antiferromagnetic behavior. When both the Co^{2+} and Fe^{3+} ions are co-substituted in $\text{BaCo}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$, a weak ferromagnetic behavior was observed. Thus, this compound exhibits both ferroelectric and ferromagnetic behavior. The various observed properties such as SHG, band gap, dielectric constant, and magnetic behavior of the present compounds are summarized in Table 4. The optical absorption spectra were interpreted based on the ligand field transitions, and the distorted tetrahedral geometry within the $\text{Al}/\text{Fe}/\text{MO}_4$ chromophores. The blue-green color observed for the Co^{2+} and Fe^{3+} co-substituted compounds was attributed to the metal-to-metal charge transfer (MMCT). Many of the prepared compounds could be useful candidates for visible

Table 4. Summary of important properties of the stuffed tridymite compounds.

Compound	SHG at 1064 nm ($\times$ KDP)	Band gap [eV]	Dielectric Constant (ϵ')	Magnetic behavior
BaZnSiO_4	2.6	4.06	14	–
BaCoSiO_4	0.8	2.78	12	antiferromagnetic
$\text{BaZn}_{0.5}\text{Si}_{0.5}\text{AlO}_4$	1.4	3.98	11	–
$\text{BaCo}_{0.5}\text{Si}_{0.5}\text{AlO}_4$	0.9	3.62	13	antiferromagnetic
$\text{BaZn}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$	1.2	2.85	13	antiferromagnetic
$\text{BaCo}_{0.75}\text{Si}_{0.75}\text{Fe}_{0.5}\text{O}_4$	0.6	2.07	12	ferromagnetic

light photocatalysis and photovoltaic applications. Thus, the present study clearly demonstrated the versatility of the stuffed tridymite structure.

Experimental Section

Reagents

The chemicals, BaCO_3 , PbO , Ga_2O_3 , ZnO (Sigma–Aldrich, 99.9%), Fe_2O_3 , $\text{NH}_4\text{H}_2\text{PO}_4$ (SD Fine, India), TeO_2 , Al_2O_3 , GeO_2 , SiO_2 , Sb_2O_5 , $\text{MC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ($M = \text{Co}, \text{Ni}$) (Alfa Aesar, 99%), were used as received.

Synthesis

Synthesis of the compounds was carried out by a conventional solid-state chemistry approach. Stoichiometric mixtures of the binary oxides were heated in air at 1100°C to 1175°C for 24 h with several intermittent grindings to obtain single-phase compounds.

Characterization

All the prepared compounds were characterized by PXRD, scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX). PXRD patterns were recorded by using a Philips X'pert Diffractometer (Ni-filtered $\text{Cu}_{K\alpha}$ radiation, $\lambda = 1.5418 \text{ \AA}$). PXRD data for the Rietveld refinement of the structures were collected at room temperature in the 2θ range $5\text{--}120^\circ$ with a step size of 0.02° and step duration 50 s. The PXRD patterns were refined by using the program GSAS-EXPGUI.^[50] Various parameters such as the lattice parameters, scale factors, background (Fourier polynomial background function), pseudo-Voigt (U , V , W , and X), and isothermal temperature factors (U_{iso}) were refined. Thermal parameters

were kept the same for different atoms occupying the same sites. The theoretical PXRD patterns were simulated with the help of the program POWDERCELL.^[51] The NIR reflectance for all the powdered samples was recorded by using a PerkinElmer Lambda 950 UV/Vis double-beam spectrometer over the spectral region of 200–2500 nm. The reflectance data were converted to the Kubelka–Munk^[52] function by using the equation [Eq. (3)],

$$F(R) = (1-R)^2/2R = \alpha/S \quad (3)$$

in which R is the reflectance, α is absorptivity, and S is the scattering factor. The optical band gaps were calculated from the Tauc plots, using the relation, $ah\nu = A(h\nu - E_g)^n$ where α is the absorption coefficient, A is a constant called the band tailing parameter, n is the power factor of the transition mode.^[53] The plot of $(ah\nu)^{(1/n)}$ versus the photon energy ($h\nu$) gave a straight line. The intercept on the $(h\nu)$ -axis on extrapolation provided the value of the optical band gap (E_g). For pigment quality of the synthesized samples, the CIE 1931 chromaticity coordinates at room temperature in the $\lambda = 380$ –750 nm range and NIR reflectance in the $\lambda = 500$ –2500 nm range were collected by using the same instrument. The CIE 1931 chromaticity coordinates were determined by using the gocie.exe program,^[54] from <https://code.google.com/archive/p/jtchem/downloads>. SEM images and EDX data were recorded with an FEI ESEM Quanta 200 scanning electron microscope. Raman spectroscopy data were recorded by using a LabRam Horiba micro Raman spectrometer with a 180° backscattering geometry equipped with a 532 nm excitation from a Nd:YAG solid-state four-level laser. Differential scanning calorimetry (DSC) measurements were carried out with a simultaneous thermal analyzer (STA) 8000 module with a ramp rate of 5 °C min⁻¹ under an N₂ atmosphere between 25 and 480 °C.

Second-order NLO measurements

The SHG behavior was measured on powder samples by using the Kurtz–Perry method with Q-switched Nd:YAG lasers at 1064 nm.^[3d,55] The synthesized polycrystalline samples and the standard KDP were ground and sieved into distinct particle size ranges (20–45, 45–63, 63–75, 75–90, 90–125, 125–140 μm). The samples were placed in 1 mm-thick fused silica tubes and irradiated by a Q-switched Nd:YAG solid-state laser. The intensity of the frequency-doubled radiation from the samples was measured by using a photomultiplier tube.

Dielectric and ferroelectric measurements

Dielectric measurements were carried out by using a Novocontrol impedance analyzer (Alpha-A) in the frequency range 0.1 Hz to 1 MHz. The ferroelectric characterization (polarization-electric field) and positive-up, negative-down (PUND) measurement of the compounds was carried out by employing a ferroelectric workstation (Radiant Technologies Inc.).

Magnetic measurement

Magnetic studies were carried out in the temperature range 2–300 K by using a SQUID magnetometer (Quantum Design, USA).

Electronic structure calculations

The electronic band structure calculations were carried out by using the density functional theory (DFT) implemented in the plane-wave pseudopotential method CASTEP.^[56,57] The following or-

bital electrons were considered as valence electrons: Ba 5s²5p⁶6s², Al 3s²3p¹, Fe 3d⁶4s², Si 3s²3p², Zn 3d¹⁰4s², Co 3d⁷4s², O 2s²2p⁴.^[58] The exchange-correlation interaction was treated by the Generalized Gradient Approximation (GGA)^[59,60] with the Perdew–Burke–Ernzerhof (PBE) functional.^[60,61] Energy convergence was achieved by having the plane-wave basis set energy cutoff set at 620 eV. The Monkhorst–Pack scheme k-point grid sampling was given by 3 × 3 × 6 in the Brillouin zone. The other calculation parameters and convergent criteria were the default values of the CASTEP code.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: inorganic pigments • multiferroic materials • optical properties • second harmonic generation (SHG) • structure elucidation • stuffed tridymite • tetrahedral geometry

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