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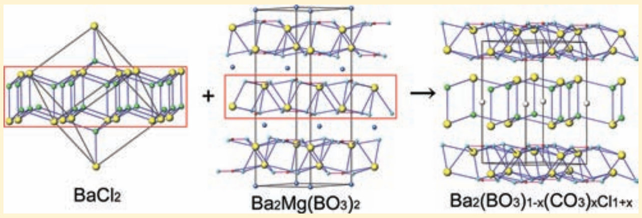
$Ba_2(BO_3)_{1-x}(CO_3)_xCl_{1+x}$: A Mixed Borate and Carbonate Chloride Crystallized from High-Temperature Solution

Jing Zhao[†,‡] and R. K. Li*[,†]

[†]Beijing Center for Crystal Research and Development, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

[‡]Graduate University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

Ⓢ *Supporting Information*



ABSTRACT: A mixed borate and carbonate chloride $Ba_2(BO_3)_{1-x}(CO_3)_xCl_{1+x}$ was obtained by spontaneous crystallization from a high-temperature melt in open air. It crystallizes in the trigonal crystal system with space group of $P3\overline{m}1$ and lattice constants of $a = 5.4708(8)$ Å and $c = 10.640(2)$ Å. The structure can be viewed as an intergrowth of trigonal $Ba_2Mg(BO_3)_2$ (001) slab and (111) slab of the cubic fluorite $BaCl_2$. During Fourier analysis of the single-crystal X-ray diffraction data, additional electron density was found locating at *1b* (0, 0, 1/2) site and attributed to chlorine surplus, which was confirmed by chemical titration. Charge balance of the compound was found, unexpectedly in an acidic borate containing high-temperature melt, by partial CO_3^{2-} group substituting the BO_3^{3-} group. The existence of CO_3^{2-} anion in the crystal was detected by thermogravimetry−mass spectrum analysis and Raman spectrum. The transmittance spectrum shows that the crystal is transparent from ultraviolet to infrared with short-wavelength absorption edge at about 220 nm.

■ INTRODUCTION

Crystal chemistry of borates differs from those of phosphates, silicates, sulfates, nitrates, and carbonate, because the boron atom is capable of coordination to oxygen in either 3- or 4-fold mode. Investigation of the phase diagrams of borate systems has resulted in the synthesis of more than 600 anhydrous borates, borosilicates, and their structure derivatives.[1] This gives great potential for designing and selecting structure types favorable for new functional materials. Many polyfunctional materials with device potential have been reported: new laser medium with double function, laser and nonlinear optical (NLO) materials with high efficiency, and wide UV transparency piezoelectric and acousto-electrics.[1] The ongoing intensive studies on borates involving members of this lab have resulted in the discovery of many good NLO materials, such as β-BaB_2O_4 (β-BBO),[2] LiB_3O_5 (LBO),[3] CsB_3O_5 (CBO),[4] $KBe_2BO_3F_2$ (KBBF),[5] and $CsLiB_6O_{10}$ (CLBO)[6] to name just a few. The relationship between structure and NLO properties of borates has been investigated,[7] and it is now well-known that the BO_3 group is the fundamental unit contributing to the NLO effect. To achieve high efficient NLO materials, the fundamental unit has to be aligned in the structure. Various routes have been proposed to align the anion groups: by hydrogen-bonding, lone pair, and cation−anion interactions.[8] We recently have found that the alignment of BO_3 groups can be controlled by cation-oxygen coordination. By selecting suitable cations, two new fluoroborates with expected NLO effects have been obtained, $BaZnBO_3F$ and $BaMgBO_3F$.[9] During the study of layered cuprate superconductor, it is found that the intergrowth of different structures can lead to many novel structures.[10] In the present work, we tried to combine the two principles to design a new borate structure.

We have chosen Ba as the cation, which is known to align the borate group perfectly in the equatorial coordination plane where the Ba ion is large enough to host three chelating BO_3 groups, such as the Ba-BO_3 coordination in $Ba_2Mg(BO_3)_2$ (It must be pointed out here that although the Ba^{2+} ion can align the equatorial BO_3 groups perfectly, interplane alignment is not guaranteed. In the named compound, the BO_3 groups in neighboring planes are actually antiparallel aligned). Taking the double $[Ba_2(BO_3)_2]^{2-}$ layer in $Ba_2Mg(BO_3)_3$ and using the $[Ba_2Cl_2]^{2-}$ layer in the (111) direction of cubic $BaCl_2$ ($Fm\overline{3}m$) as a spacer with both parts that have a common dimension in the joining plane (~5.4 Å) (Figure 1), we can expect to obtain an intergrowth compound with an ideal composition Ba_2BO_3Cl. Such intergrowth structures by joining the (111) plane of cubic $BaCl_2$ have been realized in many perovskite-related compounds.[11] We tried to introduce such a principle to the trigonal borate structures, and finally, crystals with compositions of $Ba_2(BO_3)_{1-x}(CO_3)_xCl_{1+x}$ were successfully grown from a high-temperature solution. It is a surprising observation that the CO_3 group can exist at a high temperature (as high as 970 °C) in an acidic borate solution. From a survey of the inorganic database,[12] only two anhydrous mixed borate and carbonate compounds have been reported, $Sr_2CuO_2(CO_3)_{0.85}(BO_3)_{0.15}$[13] (a cuprate superconductor, synthesis in CO_2 atmosphere) and $Ca_4Mn_3O_3(BO_3)_3CO_3$[14] (a mineral called gaudefroyite, found in geologic

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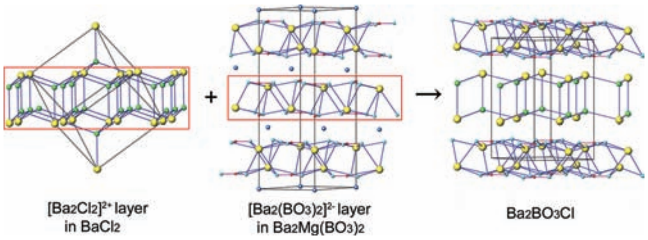

Figure 1. Structure design of $Ba_2(BO_3)_{1-x}(CO_3)_xCl_{1+x}$.

conditions presumably at high pressure and hydrothermal environments). It is known that borate chlorides, like Ca_2BO_3Cl[15] and $Ba_2B_5O_9Cl$,[16] are good luminescent host materials; when doping with Eu^{2+}, Ce^{3+}, Tb^{3+}, and Yb^{3+}, the present compound may also emit fluorescence and play a role in white light-emitting diodes.

EXPERIMENTAL SECTION

All of the chemicals were analytically pure from commercial sources and used without further purification. The $Ba_2(BO_3)_{1-x}(CO_3)_xCl_{1+x}$ crystal was obtained by spontaneous crystallization with $BaCl_2 \cdot 2H_2O$ as self-flux. Raw materials were weighed according to the molar ratio of $BaCl_2 \cdot 2H_2O/BaCO_3/H_3BO_3$ = 3:3:2. The starting materials were thoroughly ground and put in a platinum crucible heated by a temperature programmable electric furnace to 970 °C, held for 24 h for complete melting and homogenizing, then cooled at 5 °C/h to 680 °C, and finally cooled to room temperature (RT) in 24 h. Transparent hexagonal lamellar crystals were obtained and handpicked from the matrices.

The optic transmission spectrum with a crystal in the size of 5 × 5 × 0.5 mm^3 was recorded at RT with a Lambda 900 UV/vis/NIR (Perkin-Elmer) spectrophotometer in the range of 185−3300 nm. The differential thermal analyses (DTA) of the title crystal were carried out with a LABSYS thermal analyzer. A total of 9.3 mg of powder sample ground from transparent single crystal was put in a platinum crucible and heated to 1100 °C with a rate of 10 °C/min in a nitrogen atmosphere and cooled at a rate of 20 °C/min to RT. The thermogravimetry−mass spectrum analysis (TG-MS) was performed by NETZSCH STA 449C and NETZSCH QMS Aêolos 403C instrument, respectively. The single crystal was ground into powder and was put in an alumina crucible and heated from 38 to 1000 °C in a rate of 10 °C/min in a N_2 gas flow of 30 mL/min. A perfect lamellar single crystal with clean surfaces was selected to perform the Raman and attenuated total reflection infrared (ATR-IR) experiments with an inVia-Reflex microzone Raman spectrometer and Excalibur 3100 infrared spectrometer, respectively.

Structure Determination. Single crystal of $Ba_2(BO_3)_{1-x}(CO_3)_xCl_{1+x}$ with approximate dimensions 0.13 × 0.11 × 0.08 mm^3 was selected for single-crystal X-ray diffraction. The diffraction data were collected in flowing low-temperature nitrogen gas at 153.15 K with a Rigaku AFC 10 diffractometer equipped with a Saturn CCD detector and Mo Kα radiation. Numerical absorption corrections were applied with the CrystalClear package.[17] A centrosymmetric space group $P\bar{3}m1$ was proposed by data preparation program of SHELX97 and was selected for the subsequent structure solution.[18] Crystallographic data and structural refinements for the $Ba_2(BO_3)_{1-x}(CO_3)_xCl_{1+x}$ are summarized in Table 1. Atomic coordinates, equivalent isotropic temperature factors, and bond valence sum (BVS) are listed in Table S1 in the Supporting Information. Polycrystalline samples of the title compound were synthesized by solid-state reactions at 800 °C. The X-ray powder diffraction analysis of the polycrystalline samples was conducted at RT on a Bruker D8 diffractometer with Cu Kα radiation in the 2θ range from 7 to 70°, with a scanning step of 0.02° and scanning rate of 1 s/step, as shown in Figure S4 in the Supporting Information.

Table 1. Crystallographic Data for $Ba_2(BO_3)_{0.9}(CO_3)_{0.1}Cl_{1.1}$

formula	$Ba_2(BO_3)_{0.9}(CO_3)_{0.1}Cl_{1.1}$
fw	372.60
temperature	153 K
space group	$P\bar{3}m1$
a (Å)	5.4708(8)
c (Å)	10.640(2)
V	275.78(8)
Z (Å^3)	2
crystal size	0.13 × 0.11 × 0.08 mm^3
D_{calcd} (g/cm^3)	4.487
radiation (Mo Kα)	0.71073
range for data collection (°)	3.83−30.88
index ranges	$-7 \le h \le 7$
	$-7 \le k \le 7$
	$-15 \le l \le 15$
reflections measured	3151
GOOF	1.213
R_1, $wR2$	0.0224, 0.0401
largest diff peak and hole (e/Å^3)	2.15, −1.86

RESULTS AND DISCUSSION

It is found from the transmission spectrum (Figure S1 in the Supporting Information) that the $Ba_2(BO_3)_{1-x}(CO_3)_xCl_{1+x}$ crystal is highly transparent (>80%) in the range above 350 nm with an absorption cutoff edge in the UV range at about 220 nm. Thermal analysis (Figure S2 in the Supporting Information) shows an endothermic peak in the heating curve at 886 °C, indicating the decomposition of $Ba_2(BO_3)_{1-x}(CO_3)_xCl_{1+x}$, and this was confirmed by XRD of samples heated at 920 °C for 3 h and quenched quickly to RT. The powder XRD pattern of the sample quenched from 920 °C is completely different (Figure S3 in the Supporting Information), by referring to a paper published in 2011,[19] and it was identified to be $Ba_5(BO_3)_3Cl$.

At first, we assumed the molecular formula of the title compound as Ba_2BO_3Cl, and reasonable agreement indices of wR_2 = 0.0653 and R_1 = 0.0322 were obtained for the structure solution; however, Fourier analysis of the single-crystal X-ray diffraction data revealed a significant electron density of 10.47 e/Å^3 locating at *1b* (0, 0, 1/2) site. Assigning that electron density to the Cl atom from chlorine surplus (about 10%) dramatically improves both the agreement indices (wR_2 = 0.0405 and R_1 = 0.0225) and the residual electron density (2.15 e/Å^3). The Mohr titration method was adopted to determine the total Cl content. Crystals of second attempted growth were weighed and dissolved in dilute HNO_3 solution. NaCl basic reagent standardized $AgNO_3$ was served as the titrating solution, and K_2CrO_4 acted as an indicator. Three repeated experiments gave the Cl contents of 12.61, 12.18, and 12.72%, respectively, with an average value of 12.50%. The calculated Cl content with the Ba_2BO_3Cl molecular formula is 9.61%; thus, the electron density at the *1b* site was confirmed to be Cl. Therefore, the chemical formula of the title compound based on the titrations should be $Ba_2BO_3Cl_{1+x}$ (x = 0.30). Assuming Cl surplus, structure determination gave a similar formula of $Ba_2BO_3Cl_{1+x}$ (x = 0.10, a different batch of grown crystal from the titration ones).

As we expected, the structure of $Ba_2BO_3Cl_{1+x}$ can be viewed as an intergrowth along the (001) direction of the slab $[Ba_2(BO_3)_2]^{2-}$ in trigonal $Ba_2Mg(BO_3)_2$ and the (111) slab $[Ba_2Cl_2]^{2+}$ of the cubic fluorite $BaCl_2$ structures. In the $[Ba_2(BO_3)_2]^{2-}$ slab, the Ba1 atom is sandwiched by two BO_3

planes and coordinated to nine oxygen atoms from six different BO_3 groups (Figure 2). Three BO_3 groups from the nearest BO_3 plane contribute two O atoms each, chelating the Ba1 atom at the equatorial plane forming six Ba1−O bonds with the distance of 2.818 Å. Same as in the $Ba_2Mg(BO_3)_2$[20] structure, these three equatorial BO_3 groups align perfectly by the Ba−O6 coordination controlling, which is favorable for engineering a structure possessing large NLO effects.[9] However, the Ba1 atom also connects to three other BO_3 groups from a farther BO_3 plane with a Ba1−O bond distance of 2.902 Å. These farther three BO_3 groups align antiparallelly to the equatorial BO_3 ones, canceling their contributions to the NLO effect. There is only one Ba1−Cl1 bond with a distance of 3.251 Å between Ba1 to the fluorite layer.

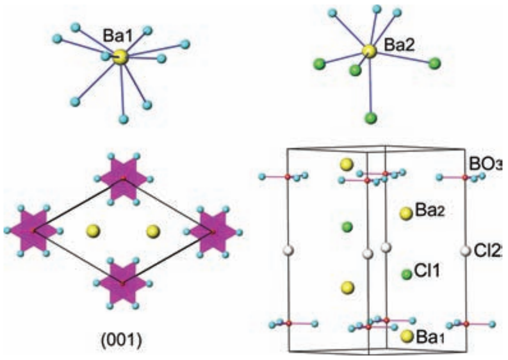

Figure 2. Coordination environment of Ba1 and Ba2, the view of the nearest two Ba1−BO_3 layers from the *c*-axis, and the content of $Ba_2(BO_3)_{1-x}(CO_3)_xCl_{1+x}$ unit cell.

Within the fluorite $[Ba_2Cl_2]^{2+}$ layer, the Cl1 atom sits inside 2 Ba2 layers, and each of them is surrounded by one Ba1 and four Ba2 atoms, forming edge-sharing trigonal-biyramid just like the (111) plane of the cubic fluorite $BaCl_2$ ($Fm\bar{3}m$) structures.[21] The Ba2−Cl1 bond lengths in the ClBa5 trigonal bipyramid are 3.201 and 3.237 Å, respectively, in good agreement to those found in cubic $BaCl_2$ (3.291 Å) and in hexagonal $BaCl_2$ (3.062−3.397 Å). The Ba2 atom, besides coordinating to the intralayer 4 Cl1 atoms, makes three strong Ba2−O bonds (2.598 Å) to the neighboring $[Ba_2(BO_3)_2]^{2-}$ layers. It is these three Ba2−O bonds and the single Ba1−Cl1 bond holding the $[Ba_2(BO_3)_2]^{2-}$ and $[Ba_2Cl_2]^{2+}$ layers together. As aforementioned, within this fluorite $[Ba_2Cl_2]^{2+}$ layer, the additional electron density corresponding to about 20% occupation of the Cl2 atom at the *1b* (0, 0, 1/2) site. This site actually corresponds to the body center site (0.5, 0.5, 0.5) of the cubic $BaCl_2$ structure, which sits in a large void surrounded by six Ba2 atoms at a distance of 3.716 Å and six Cl1 at a distance of 3.395 Å. Bond valence calculations[22] show that Cl2 is only very weakly bonded to Ba2 (with BVS: 0.062 × 6 = 0.372) and also show somewhat Cl2−Cl1 contact (at a distance of 3.395 Å and BVS: 0.022 × 6 = 0.132).

Because the Cl2 atom bonds weakly to the remaining entities of the structure, we first expected that it sits in the lattice as a form of Cl_2 and no charge balance is needed. To check the existence of Cl_2 in the structure, a TG-MS of a freshly grown crystal was conducted in N_2. To our surprise, a large flux of CO_2 gas (2 orders of magnitudes higher than that of Cl_2 or HCl) was actually recorded (Figure 3) at 400−600 °C and above 800 °C with a total weight loss of 1.3% from the TG result, which corresponds to a CO_3 content of 0.114 in the title formula.

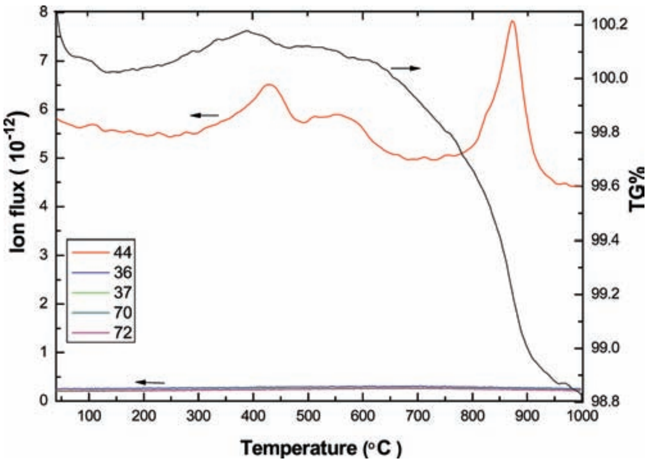

Figure 3. TG curve and mass spectrum of $Ba_2(BO_3)_{1-x}(CO_3)_xCl_{1+x}$; the numbers in the figure represent the mass to charge ratio.

The accommodation of CO_3 in the structure was further proved by a micro-Raman spectroscopy analysis (Figure 4) of freshly grown lamellar single crystals. The peaks of the Raman spectrum at 1063 and 1450 cm^{-1} can be attributed to the symmetrical (ν_1) and antisymmetrical (ν_3) stretching mode of CO_3 group, and the peak at 687 cm^{-1} corresponds to the CO_3 inplane bending (ν_4). The strong peak at 913 cm^{-1} (ν_1) and the weak one at 1180 cm^{-1}(ν_3) are characteristics of BO_3 asymmetric and symmetric stretching vibrations. The bands observed at 573(ν_4), 768, and 787 cm^{-1} (ν_2) can be assigned to the bending modes of triangular BO_3 groups. The peaks observed in this Raman spectrum are well in accordance with other synthetical as well as mineral compounds containing CO_3 and BO_3 groups.[23] It is worth noting that although the powdered sample of the title compound is hygroscopic, there is no indication of H_2O absorption in the freshly prepared crystals as proved by nonobservation of OH vibrations in ATR-IR spectrum (Figure S4 in the Supporting Information).

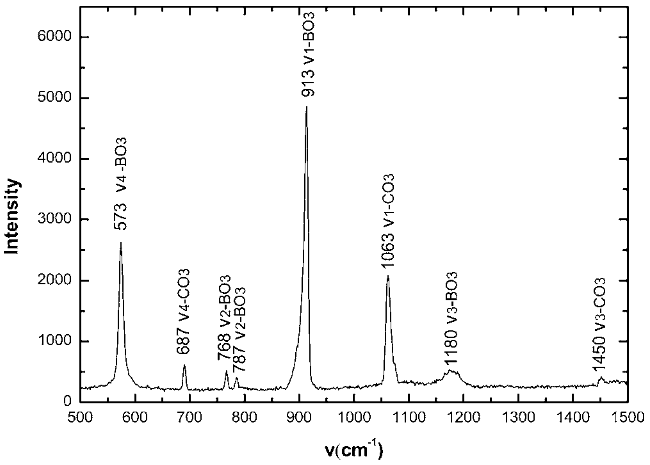

Figure 4. Raman spectrum of $Ba_2(BO_3)_{1-x}(CO_3)_xCl_{1+x}$.

Therefore, the chemical formula of the title compound is actually $Ba_2(BO_3)_{1-x}(CO_3)_xCl_{1+x}$, and the charge balance of the Cl surplus is in fact achieved by simultaneously CO_3^{2-} substituting the BO_3^{3-} group. With the constraint of identical

CO_3^{2-} and Cl^- contents, we reanalyzed the crystal diffraction data, and significant changes of the results were not observed since the difference of scattering powers of B and C are negligible, which gave again $x = 0.1$ and final agreement indices of $wR_2 = 0.0401$ and $R_1 = 0.0224$. Knowing the chemical formula, we also tried to synthesize $Ba_2(BO_3)_{1-x}(CO_3)_xCl_{1+x}$ (with $0 \leq x \leq 0.5$) by solid-state reaction. The results showed that relatively pure samples can be obtained with $x = 0.2$ and $x = 0.3$ (as shown in Figure S5 in the Supporting Information).

■ CONCLUSION

A new mixed borate carbonate chloride $Ba_2(BO_3)_{1-x}(CO_3)_xCl_{1+x}$ has been prepared by spontaneous crystallization with molten fluxes. $Ba_2(BO_3)_{1-x}(CO_3)_xCl_{1+x}$ can be viewed as an intergrowth along the (001) direction with a trigonal $[Ba_2(BO_3)_2]^{2-}$ from $Ba_2Mg(BO_3)_2$ and a (111) $[Ba_2Cl_2]^{2+}$ slab of cubic fluorite $BaCl_2$. About 10% Cl surplus was found occupying the *1b* (0, 0, 1/2) site. Charge balance was achieved by the same amount of CO_3^{2-} substituting for BO_3^{3-}, and this was supported by MS-TG analysis, IR/Raman spectrum, and solid-state synthesis. The transmission spectrum shows that the crystal is transparent from ultraviolet to near-infrared and with a cutoff edge of 220 nm. The DTA and quench experiment verify that it melts incongruently. It is the first observation that the carbonate group can exist in an acidic borate high-temperature melt in open air. Considering the CO_3 group usually accompanied by large anisotropic polarization hence large birefringence and the difficulty in carbonate growth, success growing of CO_3-containing crystals may open new ways to engineer useful functional materials.

■ ASSOCIATED CONTENT

Supporting Information

Electronic files of the crystal structure data (CIF), tables of atomic coordinates, equivalent isotropic temperature factors, transmittance spectrum, DTA, XRD of the quenched sample, ATR-IR spectrum, and powder XRD of the synthesized samples. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: rkli@mail.ipc.ac.cn.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Leonyuk, N. I. *J. Cryst. Growth* **1997**, *174*, 301.

(2) Chen, C. T.; Wu, B. C.; Jiang, A. D.; You, G. M. *Sci. Sin. Ser. B* **1985**, *28*, 235.

(3) Chen, C. T.; Wu, Y. C.; Jiang, A. D.; Wu, B. C.; You, G. M.; Li, R. K.; Lin, S. J. *J. Opt. Soc. Am. B* **1989**, *6*, 616.

(4) Wu, Y. C.; Sasaki, T.; Nakai, S.; Yokotani, A.; Tang, H. G.; Chen, C. T. *Appl. Phys. Lett.* **1993**, *62*, 2614.

(5) Mei, L. F.; Wang, Y. B.; Chen, C. T.; Wu, B. C. *J. Appl. Phys.* **1993**, *74*, 7014.

(6) Mori, Y.; Kuroda, I.; Nakajima, S.; Sasaki, T.; Nakai, S. *Appl. Phys. Lett.* **1995**, *67*, 1818.

(7) Chen, C. T.; Wu, Y. C.; Li, R. K. *Chin. Phys. Lett.* **1985**, *2*, 389.

(8) (a) McMillen, C. D.; Kolis, J. W. *Inorg. Chem.* **2011**, *50*, 6809. (b) Ra, H. S.; Ok, K. M.; Halasyamani, P. S. *J. Am. Chem. Soc.* **2003**, *125*, 7764. (c) Marvel, M. R.; Lesage, J.; Baek, J.; Halasyamani, P. S.; Stern, C. L.; Poeppelmeier, K. R. *J. Am. Chem. Soc.* **2007**, *129*, 13963. (d) Chang, H. Y.; Kim, S. H.; Ok, K. M.; Halasyamani, P. S. *J. Am. Chem. Soc.* **2009**, *131*, 6865.

(9) Li, R. K.; Chen, P. *Inorg. Chem.* **2010**, *49*, 1561.

(10) (a) Tokura, Y.; Arima, T. *Jpn. J. Appl. Phys.* **1990**, *29*, 2388. (b) Li, R. K. *Appl. Phys. Com.* **1992**, *11*, 295.

(11) (a) Wilkens, J.; Müller-Buschbaum, Hk. *J. Less-Common Met.* **1991**, *171*, 255. (b) Neubacher, M.; Müller-Buschbaum, H. *Z. Anorg. Allg. Chem.* **1992**, *609*, 59. (c) Tancret, N.; Roussel, P.; Abraham, F. *J. Solid State Chem.* **2004**, *177*, 806 and references therein.

(12) *Inorganic Crystal Structure Database*; Gmelin Institute: Karlsruhe, Germany, 2011.

(13) Uehara, M.; Nakata, H.; Akimitsu, J. *Phys. C* **1993**, *216*, 453.

(14) (a) Yakubovich, O. V.; Simonov, M. A.; Belov, N. V. *Kristallogr.* **1975**, *20*, 152. (b) Li, R. K.; Greaves, C. *Phys. Rev. B* **2004**, *70*, 132411.

(15) (a) Xiao, F.; Xue, Y. N.; Zhang, Q. Y. *Phys. B* **2009**, *404*, 3743. (b) Yang, Z. P.; Wang, S. L.; Yang, G. W.; Tian, J.; Li, P. L.; Li, X. *Mater. Lett.* **2007**, *61*, 5258.

(16) Meijerink, A.; Blasse, G. *J. Lumin.* **1989**, *43*, 283.

(17) *CrystalClear*; Rigaku Corporation: Tokyo, Japan, 2008.

(18) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

(19) Reckeweg, O.; Schulz, A.; Disalvo, F. J. *Z. Naturforsch.* **2011**, *66b*, 359.

(20) Akella, A.; Keszler, D. A. *Mater. Res. Bull.* **1995**, *30*, 105.

(21) Haase, A.; Brauer, G. *Z. Anorg. Allg. Chem.* **1978**, *441*, 181.

(22) Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, *41*, 244.

(23) (a) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compound*; A Wiley-Interscience Publication: New York, 1997. (b) Farmer, V. C. *The Infrared Spectra of Minerals*; Bartholomew Press: Dorking, Surrey, 1974.