

New quaternary alkali metal, rare earth (3+) thiophosphate, $K_2SmP_2S_7$ with both $[P_2S_6]^{4-}$ and $[PS_4]^{3-}$ anions

V. Manríquez*, A. Galdámez, D. Guzmán-Águila

Departamento de Química, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile

Received 29 January 2007; received in revised form 12 July 2007; accepted 17 July 2007

Available online 22 July 2007

Abstract

A new quaternary alkali metal, rare earth thiophosphate was synthesized by the ceramic method and characterized by single crystal X-ray diffraction: $K_2SmP_2S_7$ crystallizes in the monoclinic space group $C2$ (no. 5) with the unit cell parameters $a = 22.746(5) \text{ \AA}$, $b = 6.7362(13) \text{ \AA}$, $c = 8.9004(18) \text{ \AA}$, $\beta = 99.68(3)^\circ$, $V = 1344.3(5) \text{ \AA}^3$ and $Z = 2$. The phase $K_2SmP_2S_7$ can be better described as $K_4Sm_2[PS_4]_2[P_2S_6]$ because it contains in the crystal structure both discrete anions $[PS_4]^{3-}$ and $[P_2S_6]^{4-}$. The crystal structure consists of infinite chains of ${}^1_\infty[SmPS_4]$ that are linked together through the ethane-like $[P_2S_6]^{4-}$ anions to form two-dimensional layers. The packing of $K_2SmP_2S_7$ is formed by layers of ${}^2_\infty[Sm_2[PS_4]_2[P_2S_6]]^{4-}$ separated by K^+ cations. $K_2SmP_2S_7$ was characterized by Raman and Fourier transform infrared (FTIR) spectroscopy and SEM-EDX microprobe analyses. The optical band gap of $K_2SmP_2S_7$ was determined by UV–vis diffuse reflectance measurements to be 2.59 eV.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: B. Chemical synthesis; C. X-ray diffraction; D. Optical properties

1. Introduction

The chalcophosphates of the type $AM_xP_yQ_z$ ($A =$ alkali metal, $M =$ transition metal and $Q = S, Se$) present anions $P_yQ_z^{n-}$ that are coordinated to the metals A and M through chalcogen atoms Q . The study of chalcophosphates is of strong interest due to their anisotropic physical properties such as thermoelectric properties and nonlinear optic behaviour [1–5]. Moreover, these phases present a great variety of structures in the solid state. A possible structural representation is to consider them as a salt formed by the ions A^+M^{m+} and $P_yQ_z^{n-}$. They possess structural anionic units $P_yQ_z^{n-}$, with chalcogen–phosphorus bonds and the metal ions compensate the negative charge of these anionic fragments. These materials possess different packing arrangements, which are a product of the different possibilities of bonding between the anionic structural fragments and the metal cations and give rise to structures with mono-dimensional (1D), two-dimensional (2D) and three-dimensional character (3D).

The investigations on chalcophosphate compounds have focused on the synthesis of quaternary phases to form salts, which take advantage of the flexibility and stability of the anions $P_yQ_z^{n-}$ ($Q = S, Se$) and their ability to form compounds with cations in several oxidation states. The quaternary phases present, in certain cases, a laminar 2D structure, as happens in the phases $CdFeP_2S_6$, $Mn_{1-x}Cu_{2x}P_2S_6$ and $Mn_{1-x}Ag_{2x}P_2S_6$ [6,7]. In other cases, the structure suffers important structural change from a 2D structure to a 1D structure in the phase $K_2FeP_2S_6$ [8]

* Corresponding author. Tel.: +56 2 9787388; fax: +56 2 2713888.

E-mail address: vmanriqu@uchile.cl (V. Manríquez).

and to 3D structure in β -Bi₂(P₂Se₆)₃ [9]. Another interesting structural arrangement is present in the phase KNiPS₄ [10], where the cations Ni²⁺ are surrounding by four sulfur atoms in a square planar coordination. The NiS₄ units are joined by tetrahedral groups [PS₄]³⁻, forming chains [-PS₄³⁻-Ni²⁺-PS₄³⁻]. The phases Rb₃M₃[PS₄]₄ (M = Pr, Er) have three crystallographic types of cations (3+) [11]. The phases APd[PS₄] (A = Na, Rb) contain chains ¹_∞[Pd PS₄]⁻ formed by alternate cations Pd²⁺ in square planar coordination and tetrahedral anions PS₄³⁻ [12]. The metal atoms, in the above thiophosphates, are linked together through thiophosphate anions [P₂S₆]⁴⁻ or [PS₄]³⁻.

Stable thiophosphate phases containing the anions P_YS_Zⁿ⁻ can be formed by the ceramic method at high temperatures (solid–solid reactions) [13]. Typically, these phases are synthesized by direct combination of the elements at temperatures between 500 and 800 °C; under these conditions, complex equilibria between anions such as: [P₂S₆]⁴⁻; [P₂S₆]²⁻; [P₂S₇]⁴⁻; [PS₄]³⁻ have been observed [14].

Many quaternary rare earth metal thiophosphate have been prepared and structurally characterized. Examples include phases such as: K₃CeP₂S₈ [15]; K₃CeP₂S₈ [16]; Na(RE)P₂S₆ (RE = Y, Sm) and KSmP₂S₇ [17]; K₂NdP₂S₇ [18]; KErP₂S₇, NaErP₂S₆ and Cs₃Er₅(PS₄)₆ [19] and Cs₄Pr₂(PS₄)₂P₂S₆ [20].

In the course of our work on quaternary heterocharged metal thiophosphates, we have previously reported the crystal structures of the layered phases KMP₂S₆ (M = Bi, Sb) [21,22] and the α - and β -phases of NaSbP₂S₆ [23]. In these phases, the layers are formed by ethane-like anions [P₂S₆]⁴⁻ bridging the M³⁺ metal atoms, which are held together by layers of alkali cations. Our investigation of quaternary systems containing alkali metal, rare earth (3+), phosphorus and sulfur has yielded a new samarium thiophosphate: K₂SmP₂S₇, which contains in its crystal structure two anionic units, [P₂S₆]⁴⁻ and [PS₄]³⁻. We report here the synthesis, crystal structure, spectroscopic characterization and optical properties of this new quaternary samarium thiophosphate compound.

2. Experimental

2.1. Synthesis

The preparation of the phase K₂SmP₂S₇ was carried out by direct combination, in stoichiometric amounts, of powders of the corresponding high purity elements (99.99%), supplied by Aldrich. The reaction mixture was sealed in evacuated quartz ampoules and placed in a programmable furnace. All manipulations were carried out under Ar atmosphere. The reaction mixture was heated to 800 °C at 50 °C/h. After 5 days, the reacted matter was slowly cooled to room temperature at a rate of 6 °C/h. The ampoule was opened to reveal a yellow crystalline reaction product. The product appeared to be air- and moisture-stable over several weeks.

The reaction led to the formation of pale-yellow crystals. Elemental analysis confirming the chemical composition of the crystals was obtained from energy dispersive spectroscopy on a JOEL 6400 scanning electron microscope system equipped with an Oxford LinK ISIS microanalyzer.

2.2. Characterization

Pale-yellow plate-like crystals of K₂SmP₂S₇ with dimensions 0.2 mm × 0.1 mm × 0.05 mm were mounted on glass fibers with the long axis of the crystals oriented roughly parallel to the length of the fiber. Single-crystal X-ray diffraction data were obtained with the use of graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) at 293 K on a Bruker AXS SMART CCD area detector diffractometer. The collection of intensity data was carried out with the program SMART [24]. Cell refinement and data reduction were carried out with the program SAINT [24]. The observed Laue symmetry and systematic extinctions clearly pointed to the space group C2. The empirical absorption correction was done using SADABS [24]. The structures were solved by direct methods allowing the unambiguous space group assignments and refined in full-matrix least-squares using the SHELXL package of crystallographic programs [25]. The final cycle of refinement included all anisotropic displacement parameters to obtain final *R*₁ and *wR*₂ values 0.0974 and 0.2195. The maximum and minimum peaks on the final difference Fourier map corresponded to 4.892 eÅ⁻³ and 2.302 eÅ⁻³. The crystal data are summarized in Table 1. The fractional atomic coordinates and equivalent isotropic thermal parameters are listed in Table 2. Selected interatomic distances with their estimated standard deviation (E.S.D.s) are given in Table 3.

The infrared spectra were obtained in the frequency range 200–650 cm⁻¹ for samples pressed into polyethylene disks, with a Perkin-Elmer FTIR spectrophotometer system 2000. The Raman spectra were recorded in the frequency

Table 1
Crystal data and structure refinement for $K_2SmP_2S_7$

Compound	$K_2SmP_2S_7$
Color and habit	Pale-yellow block
Crystal size	0.2 mm × 0.1 mm × 0.05 mm
Space group, Z	$C2, 2$
a (Å)	22.746(5)
b (Å)	6.7362(13)
c (Å)	8.9004(18)
β	99.68(3)°
V (Å ³)	1344.3(5)
μ (mm ⁻¹)	2.895 mm ⁻¹
$2\theta_{max}$	27.56°
$N(h\ k\ l)_{measured}$	3554 [$R_{int} = 0.0807$]
$N(h\ k\ l)_{unique}$	2195
$I_{obs} > 2\sigma(I_{obs})$	1744
$N(param)_{refined}$	111
Goof (S) ^a	0.991
$R1^b$	0.0974
$wR2^c$	0.2195

$$^a \text{Goof} = \sqrt{\frac{\sum [w(F_o^2 - F_c^2)]^2}{n - p}}$$

$$^b R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^c wR2 = \sqrt{\frac{\sum (w(F_o^2 - F_c^2))^2}{\sum w(F_o^2)^2}}$$

Table 2
Fractional atomic coordinates and isotropic thermal parameter of $K_2SmP_2S_7$

Atom	x	y	z	U_{eq}^a
Sm	0.83707(6)	0.8749(6)	0.46705(19)	0.0190(5)
K1	0.6771(4)	0.859(3)	0.1083(11)	0.052(3)
K2	0.9402(3)	0.377(3)	0.2838(11)	0.054(3)
P1	0.7295(3)	0.876(3)	0.7084(10)	0.0273(19)
P2	0.9863(3)	0.861(2)	0.6122(10)	0.0175(18)
S1	0.8095(9)	1.123(2)	0.2123(19)	0.041(5)
S2	0.8185(3)	0.874(3)	0.7708(9)	0.0270(18)
S3	0.7129(4)	0.7966(12)	0.4745(11)	0.024(2)
S4	0.8080(7)	0.6073(19)	0.213(2)	0.044(5)
S5	0.9366(4)	0.8445(18)	0.2408(12)	0.030(3)
S6	0.9362(5)	1.1155(17)	0.6133(13)	0.013(3)
S7	0.9319(8)	0.6280(18)	0.612(3)	0.060(6)

^a Equivalent isotropic U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

range 200–700 cm⁻¹ using a micro-Raman Renishaw system 1000, laser line 514.5 nm and laser power 1 mW. The diffuse reflectance UV–vis spectra were recorded using a UV-2450 Shimadzu UV–visible spectrophotometer. BaSO₄ powder was used as reference at all energies (100% reflectance). Reflectance measurements were converted to absorption spectra using the Kubelka–Munk function.

3. Results and discussion

The phase $K_2SmP_2S_7$ has a two-dimensional layered structure as shown in Fig. 1a. The layers are stacked perpendicularly to the ab -plane and are separated by the van der Waals gaps. Each layer has the thickness of two opposed PS₄ units (Fig. 1b).

Table 3
Selected bond distances (Å) and bond angles (°)

Environment of Sm			
Sm–S1	2.801(14)	S1–Sm–S4	75.3(3)
Sm–S2	2.806(8)	S4–Sm–S6	139.5(4)
Sm–S3	2.884(9)	S4–Sm–S3	130.9(4)
Sm–S4	2.882(18)	S7–Sm–S6	69.6(2)
Sm–S5	3.280(10)	S1–Sm–S3	92.3(4)
Sm–S6	2.901(12)	S1–Sm–S2	137.1(5)
Sm–S7	2.853(18)	S6–Sm–S3	72.3(3)
		S6–Sm–S5	75.3(3)
		S2–Sm–S4	134.7(5)
Tetrahedral environment of P1			
P1–S1	2.10(3)	S1–P1–S3	96.3(9)
P1–S2	2.006(9)	S2–P1–S3	106.0(5)
P1–S3	2.120(14)	S4–P1–S2	112.7(11)
P1–S4	1.96(2)	S4–P1–S3	122.3(8)
P2–P2 ethane-like environment			
P2–P2	2.190(16)	S5–P2–S6	117.8(8)
P2–S5	2.007(12)	S7–P2–S5	115.5(10)
P2–S6	2.059(19)	S7–P2–S6	108.1(4)
P2–S7	2.00(2)		

The layered structure contains Sm^{3+} ions coordinated to eight sulfur atoms in a distorted dodecahedral geometry. The Sm^{3+} ions are coordinated by three $[\text{PS}_4]^{3-}$ and one $[\text{P}_2\text{S}_6]^{4-}$ groups. Fig. 2 shows the coordination around the samarium atom, where the two types of thiophosphate anions, $[\text{PS}_4]^{3-}$ and $[\text{P}_2\text{S}_6]^{4-}$ can easily be distinguished. These SmS_8 dodecahedra are linked together to form layers, in the *ab*-plane, via the two different types of thiophosphate ligands $[\text{PS}_4]^{3-}$ and $[\text{P}_2\text{S}_6]^{4-}$. The Sm–S bond distances range from 2.801(14) to 3.280(10) Å with an average distance of 2.944 Å. The closest Sm···Sm distance within the layers is 5.307 Å.

Fig. 3 shows a polyhedral view of the structure showing the layers in the *ab*-plane. All $[\text{PS}_4]^{3-}$ tetrahedra are tetra-coordinated to three Sm centers. This arrangement results in ${}^1_{\infty}[\text{SmPS}_4]$ chains with two PS_4 tetrahedra oriented in opposed sense. In this way $[\text{SmPS}_4]$ can be regarded as a building block. The chains run along the crystallographic *b*-axis. The neighboring chains are further bridged by ethane-like $[\text{P}_2\text{S}_6]^{4-}$ units to form layers in the *ab*-plane (Fig. 3). This connectivity creates channels that run along the *c* direction through each layer. These channels have dimensions 7.3 Å × 6.7 Å.

Table 4
IR and raman spectroscopic data for $\text{K}_2\text{SmP}_2\text{S}_7$ in cm^{-1}

IR	Raman
627 m	620 w
546 vw	581 m
437 w	570 m
305 m	554 sh
268 m	487 vw
250 m	441 m
	430 vs
	393 vs
	341 w
	303 vw
	287 m
	273 w
	254 m
	232 w

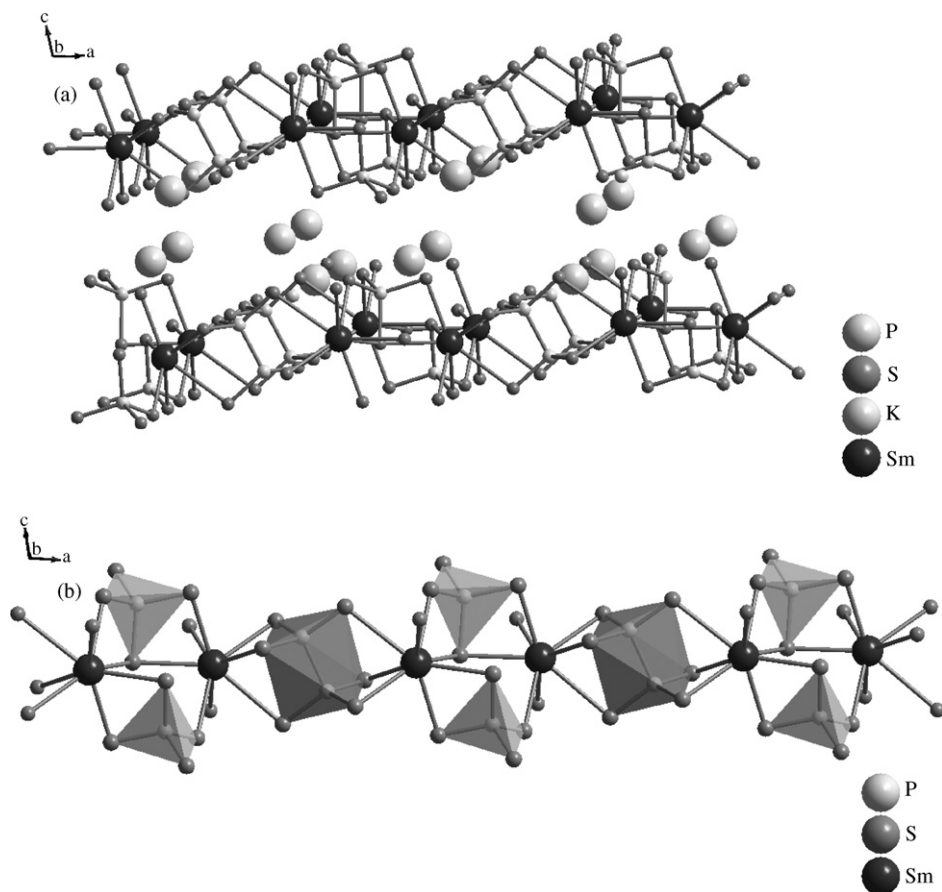


Fig. 1. Crystal structure of $K_2SmP_2S_7$ viewed down the a -axis: (a) view of the stacking of ${}^2_{\infty}\{Sm_2[PS_4]_2[P_2S_6]\}^{4-}$ layers; (b) view of a single ${}^1_{\infty}\{Sm[PS_4][P_2S_6]\}$ chain, with the two different thiophosphate polyhedra.

The $[PS_4]^{3-}$ anions consists of phosphorus atom surrounded by four sulfur atoms in a distorted tetrahedral geometry. The smaller angle for P is $96.3(9)^\circ$. The P–S bond distances range from 1.96(2) to 2.120(14) Å with an average distance of 2.047 Å. The ethane-like $[P_2S_6]^{4-}$ ligands chelate to two Sm^{3+} cations; the bond lengths P–P are 2.190(16) Å, and the bond lengths P–S range from 2.00(2) to 2.059(19) Å (Table 3). The bond lengths P–P and P–S, in

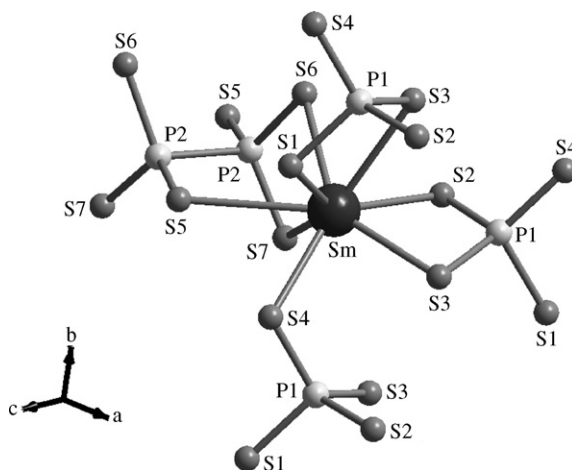


Fig. 2. The coordination around Sm^{3+} cations showing atom labelling.

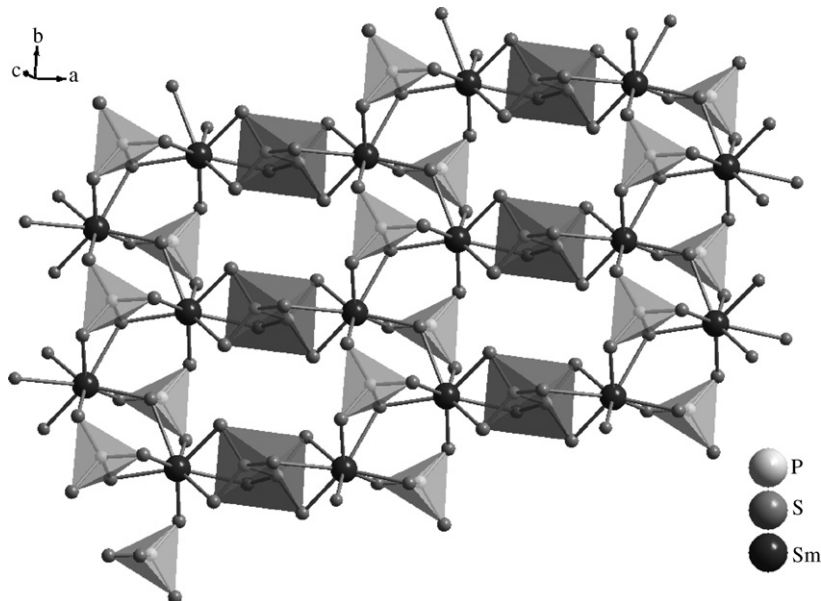


Fig. 3. View down the c -axis of one layer of $K_2SmP_2S_7$, showing the large parallel channels present. The plot shows polyhedra of $[PS_4]$ and $[P_2S_6]$ and Samarium atoms are dark circles.

both anions, are consistent with typical thiophosphate bond distances [17,21,26,27]. These thiophosphate coordinate the Sm^{3+} cations, as shown in Fig. 2.

The packing of $K_2SmP_2S_7$ is formed by layers of ${}^2_{\infty}[Sm_2[PS_4]_2[P_2S_6]]^{4-}$ separated by K^+ cations (Fig. 1a). There are two crystallographically different K^+ cations in this structure, all of which are coordinated to S atoms. K1 and K2 atoms are coordinated by seven and eight S atoms, respectively. The average $K \cdots S$ distance is 3.371 Å. The potassium atoms K1 lie between the layers, though they are not located in the middle of the interlayer space. The potassium atoms K2 lay within the channels, described above; they are symmetrically situated with respect to the centers of the channels.

The far-IR and Raman spectra are summarized in Table 4. The far-IR spectra display absorptions at 627 and 546 cm^{-1} , that are consistent with the presence of the PS_4 and P_2S_6 ligands. The absorption at 437 cm^{-1} may be assigned to the P–P stretching vibration by analogy to $Sr_2P_2S_6$ [28]. The sharp absorption at 400 cm^{-1} represents the

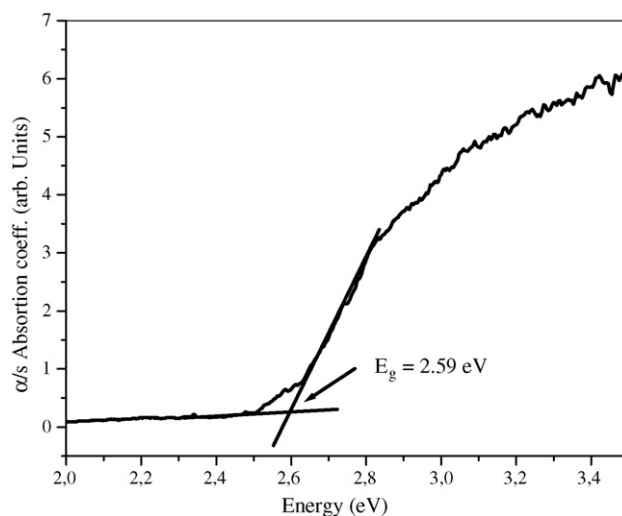


Fig. 4. The optical absorption spectrum of $K_2SmP_2S_7$.

characteristic P–S–P stretching vibrations. The remaining absorptions can be tentatively assigned to the –PS₂ stretching vibrations by analogy to KAuP₂S₇ [29] and K₂CuP₂S₇ [30]. The Raman spectra display absorptions in the 200–700 cm⁻¹ range; the general features of the Raman spectra comprise low-energy peaks indicative of the PS₄ and P₂S₆ units. The spectrum is dominated by the symmetric stretch at 430 cm⁻¹, which indicate the presence of PS₄ tetrahedral units [12]. The sharp absorption at 393 cm⁻¹ is assigned to the –PS₃ stretching vibration by analogy to K₂AuPS₄ and KAuP₂S₇ [29]. The absorptions above 340 cm⁻¹ are tentatively assigned to P–S or P–P vibrations.

Band gap analysis using UV–vis diffuse reflectance spectroscopy indicates that K₂SmP₂S₇ has a band gap energy of 2.59 eV (Fig. 4). This value is typical of that expected for yellow compounds. By comparison, the corresponding band gap of NaSmP₂S₆ is 2.54 eV [17] and α-NaSbP₂S₆ and β-NaSbP₂S₆ [23] are 2.17 and 2.25 eV, respectively.

Acknowledgements

This work was supported by FONDECYT through operating grant no. 1061116. The authors thank the FONDAP no. 11980002 for the Bruker SMART CCD single crystal diffractometer.

References

- [1] H.J. Moller, Semiconductor for solar cell, Artech House, Boston, 1993.
- [2] K. Borkowski, J. Pyzyluski, Mater. Res. Bull. 22 (1987) 381.
- [3] P.M. Bridenbaugh, Mater. Res. Bull. 8 (1973) 1055.
- [4] C.D. Carpentier, R. Nitsche, Mater. Res. Bull. 9 (1974) 1097.
- [5] E. Arnaudova, E. Sviridov, E. Rogach, E. Savchenko, A. Grekov, Integr. Ferroelectr. 1 (1992) 117.
- [6] B. Bhowmick, S. Bal, M. Ganduly, M.L. Bhattacharya, Kundu, J. Phys. Chem. Solids 53 (1992) 1279.
- [7] Y. Mathey, R. Clément, J.P. Auduere, O. Poizat, C. Sourisseau, Solids State Ionics 9/10 (1983) 459.
- [8] W. Carrillo-Cabrera, J. Sassmannshausen, H.G. von Schnering, Z. Kristallogr. 202 (1992) 150.
- [9] B.E. Taylor, J. Steger, A. Wold, J. Solid State Chem. 7 (1973) 461.
- [10] S.H. Elder, A. Van der Lee, R. Brec, E. Canadell, J. Solid State Chem. 116 (1995) 107.
- [11] Th. Komm, Th. Schleid, J. Solid State Chem. 178 (2005) 454.
- [12] S. Coste, H. Jason, M. Bujoli-Doeuff, G. Louarn, M. Evain, R. Brec, B. Alonso, S. Jobic, M.G. Kanatzidis, J. Solid State Chem. 175 (2003) 133.
- [13] J.A. Cody, M.F. Mansuetto, S. Chien, J.A. Ibers, Mater. Sci. Forum 35 (1994) 152.
- [14] F. Menzel, L. Ohse, W. Brockner, Heteroat. Chem. 1 (5) (1990) 357.
- [15] K. Chondroudis, T.J. McCarthy, M.G. Kanatzidis, Inorg. Chem. 35 (1996) 840.
- [16] G. Gauthier, S. Jobic, R. Brec, J. Rouxel, Inorg. Chem. 37 (1998) 2332.
- [17] E.-Y. Goh, E.-J. Kim, S.-J. Kim, J. Solid State Chem. 160 (2001) 195.
- [18] T. Schleid, I. Hartenbach, T. Komm, Z. Anorg. Allg. Chem. 628 (2002) 7.
- [19] T. Komm, T. Schleid, Z. Anorg. Allg. Chem. 632 (2006) 42.
- [20] Th. Schleid, Th. Komm, Z. Kristallogr. Suppl. 20 (2003) 152.
- [21] V. Manríquez, A. Galdámez, D. Ruiz-León, M.T. Garland, Z. Kristallogr. NCS 218 (2003) 403.
- [22] V. Manríquez, A. Galdámez, D. Ruiz-León, M.T. Garland, M. Jiménez, Z. Kristallogr. NCS 218 (2003) 1.
- [23] V. Manríquez, A. Galdámez, D. Ruiz-León, Mater. Res. Bull. 41 (2006) 1337.
- [24] SMART, SAINTPLUS V6.02, SHELXTL V6.10 and SADABS; Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 2000.
- [25] G.M. Sheldrick, SHELXL-97. Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
- [26] T. McCarthy, M.G. Kanatzidis, J. Alloys Compd. 236 (1996) 70.
- [27] W. Klingen, G. Eulenberger, H. Hahn, Z. Anorg. Allg. Chem. 401 (1973) 97.
- [28] Y. Mathey, R. Clément, C. Sourisseau, G. Lucazeau, Inorg. Chem. 19 (1980) 2773.
- [29] K. Chondroudis, J.A. Hanco, M.G. Kanatzidis, Inorg. Chem. 36 (1997) 2623.
- [30] J.A. Hanco, J. Sayettat, S. Jobic, R. Brec, M.G. Kanatzidis, Chem. Mater. 10 (1998) 3040.