Journal of Alloys and Compounds 522 (2012) 141–143

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Synthesis, crystal structure and magnetic properties of $Sr_5(CrO_4)_3(Cu_{0.586}O)$ with apatite-like structure

A.P. Tyutyunnik [a], G.V. Bazuev [a,b,*]

[a] Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, 620990 Ekaterinburg, GSP, Russia
[b] Ural Federal University, 620002 Ekaterinburg, GSP, Russia

ARTICLE INFO

Article history:
Received 24 November 2011
Received in revised form 19 January 2012
Accepted 23 January 2012
Available online 2 February 2012

Keywords:
Chromates
Synthesis
Apatite-like structure
Magnetic properties

ABSTRACT

The crystal structure of apatite $Sr_5(CrO_4)_3(Cu_{0.586}O)$ was solved using X-ray diffraction data with GSAS program in the space group $P6_3/m$ with hexagonal unit cell parameters: $a = 10.0292(1)$, $c = 7.4623(1)$ Å, $V = 650.033(8)$ Å^3, and $Z = 2$. This compound is stable up to 1473 K in air. It was found that copper in the form of Cu^+ cations is located in infinite linear $(CuO)^{-1}$ chains inserted into the tunnels parallel to the hexagonal c axis. The chains contain about 40% vacancies in copper positions. The experimental value of the effective magnetic moment (μ_{eff}) for the 1 Cr atom in formula $Sr_5(CrO_4)_3(Cu_{0.586(4)}O)$ (1.671 μ_B) is slightly smaller than the theoretical moment (1.732 μ_B) calculated in the assumption that all chromium is present as Cr^{5+} cations and copper as Cu^+.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Four stable ternary oxides, $SrCr^{6+}O_4$, $Sr_2Cr^{4+}O_4$, $SrCr_2{}^{3+}O_4$, and $Sr_3Cr_2{}^{5+}O_8$, have been identified in the Sr—Cr—O system under usual synthesis conditions and a temperature of 1250 K [1]. According to EDX analysis, the former three oxides are stoichiometric compounds. The composition of the latter oxide differs from the stoichiometric one ($Sr_{2.86}Cr_2O_8$), and chromium in this compound has a mixed valence state of +5.2 derived from XANES spectroscopy data. This system is of interest since complex chromium and strontium oxides stable in oxidizing media at high temperatures can be possibly used in electrochemical devices.

The compound $Sr_4Cr_3O_9$ [2] with mixed chromium valance (+3.33) was obtained in an argon atmosphere. Its trigonal crystal structure is related to the structures of $Sr_4Ni_3O_9$, Ca_3AMnO_6, and $Sr_4AMn_2O_9$ ($A = $ Cu, Ni, Co) oxides. A distinguishing feature of the structures of these compounds is the presence of infinite chains consisting of face-shared MnO_6 octahedra and AO_6 trigonal prisms. These structural units lie along the hexagonal *c* axis and are surrounded by six chains made of Ca(Sr) antiprims [3–5]. The compounds belong to the family of quasi-one-dimensional oxides $A_{3n+3m}A'_nB_{3m+n}O_{9m+6n}$, where $B = $ Mn, metals of the Pt group, etc. Trying to obtain complex oxides Sr_3ACrO_6 and $Sr_4ACr_2O_9$ in air at high temperatures, we registered the formation of new hexagonal compounds with Sr/Cr = 5/3. Since no ternary compound of this composition [1] was present in the Sr—Cr—O system under these thermal treatment conditions, we suggested that Cu, Ni, and Co should have a stabilizing effect on their formation. In order to revise the composition and structure of the new compounds, we used the structural data for the strontium chromate fluoride $Sr_{10}(CrO_4)_6F_2$ with apatite-like structure and the hexagonal cell parameters $a = 9.956(1)$, $c = 7.437(1)$ Å, and $V = 638.4$ Å^3. This compound was reported [6] to be synthesized from $SrCO_3$, SrF_2, and Cr_2O_3 at 1400 K in a corundum crucible. To avoid hydrolysis reactions, $Sr_{10}(CrO_4)_6F_2$ was synthesized in dry N_2.

Apatite-structure compounds of the general composition $A_5(MO_4)_3X$ are widely used in chemistry as natural, biological, and synthetic objects [7]. A defining structural feature of apatite (sp. gr. $P6_3/m$) is the presence of tetrahedral groups MO_4 and two non-equivalent positions for large-size cations *A*. The tetrahedra contain highly charged cations *M* having a small size (P, As, V, etc.). Cations *A*(1) occupy 4*f* positions and are coordinated with 9 oxygen anions. Cations *A*(2) are in 6*h* positions with 7-fold coordination of 6 O^{2-} anions and $1X^-$ anion and form hexagonal tunnels stretching along the hexagonal axis. X^- ions are located in these spacious hexagonal tunnels and occupy 2a positions with $z = 1/4$.

According to [7], many compounds with apatite-like structure are nonstoichiometric. Nonstoichiometry of these compounds is due to the circumstance that the 2*a* structural positions can be partially occupied by anions or be completely vacant. Phosphate $Pb_4K(PO_4)_3$ [8] can be cited as an example of compounds with completely vacant 2*a* positions. Note also that besides F, Cl^-, OH^-, and O^{2-}, more complex groups such as $MO_2{}^{2-}$ ($M = $ Cu, Ni, Co [9]),

---

* Corresponding author. Tel.: +7 343 374 4943; fax: +7 343 374 4495.
E-mail address: bazuev@ihim.uran.ru (G.V. Bazuev).

0925-8388/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2012.01.138

BO_2^- [10], etc. can be located in hexagonal tunnels as 2*a* position anions. Along with phosphate $Sr_5(PO_4)_3(CuO_2)_{1/3}$ [11], these apatites include also compounds based on transition metals, in particular, $Sr_5(VO_4)_3(CuO)$ [12]. Cu atoms in these compounds occupy (0, 0, 0) positions, are coordinated with two O4 anions, and form infinite linear chains $[CuO]^{1-}$ along the *c* axis. In [12] was also mentioned compound $(Sr_{0.9}Ca_{0.1})_5(CrO_4)_3(CuO)$ without any details of synthesis and properties.

In this work we report the results of synthesis and structural analysis, as well as magnetic properties of the apatite-like compound–strontium chromate cuprate $Sr_5(CrO_4)_3(Cu_xO)$.

2. Experimental

The sample of $Sr_5(CrO_4)_3(CuO)_x$ was prepared from mixtures of stoichiometric amounts of $SrCO_3$, Cr_2O_3, and CuO by means of the solid-phase reaction at 1423 K in air for 36 h. The sample was reground after 12 and 24 h annealing. The powder X-ray diffraction pattern measurements were performed at room temperature using a STADI P (STOE) diffractometer in transmission geometry with a linear mini-PSD detector with $CuK\alpha_1$ radiation over range of $2 \leq 2\theta \leq 120^\circ$ with a step size of 0.02°. Polycrystalline silicon (*a* = 5.43075(5) Å) was used as an external standard. The refinement of the crystal structure of $Sr_5(CrO_4)_3(Cu_{0.586(4)}O)$ was carried out with the GSAS program [13]. The peak profiles were fitted with a pseudo-Voigt function, $I(2\theta) + x^*L(2\theta) + (1-x)^*G(2\theta)$ (where *L* and *G* are the Lorentzian and Gaussian part, respectively). The angular dependence of the peak width was described by the relation $(FWHM)^2 = Utg^2\theta + Vtg\theta + W$, where *FWHM* is the full line width at half maximum. The background level was described by a combination of thirty-six-order Chebyshev polynomials.

The magnetic susceptibility measurements were performed on a MPMS-5-XL SQUID magnetometer on powdered samples in the 4–300 K temperature range. The applied magnetic field was 5 kOe. The molar magnetic susceptibility value was revised with allowance for diamagnetism of Sr^{2+}, Cr^{5+}, Cu^+, and O^{2-} ions [14].

3. Results and discussion

To determine the actual composition of the compound with the apatite structure, we first performed structural analysis of the products of synthesis of the phase $Sr_4CuCr_2O_9$. Along with the apatite-like compound, the sample was found to contain strontium chromate $Sr_3Cr_2O_8$ and $SrCuO_2$. By refining the crystal structure of the apatite-like phase, we found its composition: $Sr_5(CrO_4)_3(Cu_{0.62}O)$. Later on, a complex oxide of the same composition was synthesized under the same conditions (1423 K, 36 h, in air). According to structural refinement, the synthesized compound was $Sr_5(CrO_4)_3(Cu_{0.586(4)}O)$. Analysis of the powder XRD pattern showed that in addition to this compound there is trace amount (~0.5 mass%) of CuO. Complex oxide $Sr_5(CrO_4)_3(Cu_{0.586(4)}O)$ have a dark green color and is stable in air up to 1473 K. At higher temperatures, it decomposes with the formation of $Sr_3Cr_2O_8$ и $SrCuO_2$.

The XRD pattern of $Sr_5(CrO_4)_3(Cu_{0.586}O)$ was indexed with a hexagonal unit cell with parameters: *a* = 10.0292(1) Å, *c* = 7.4623(1) Å, and V = 650.033(8) Å^3. Fig. 1 presents experimental (crosses), calculated (solid line), and difference (bottom line) X-ray diffraction patterns for $Sr_5(CrO_4)_3(Cu_{0.586}O)$. Series of tick marks correspond to the Bragg reflection. The crystallographic data and displacement parameters are given in Table 1; selected interatomic distances are listed in Table 2.

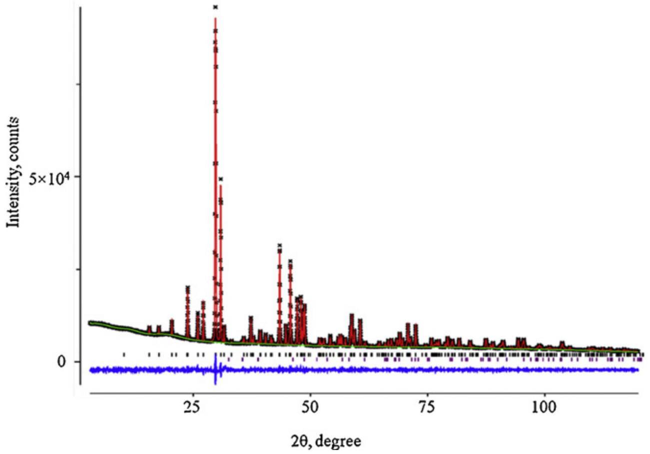

Fig. 1. Observed (crosses), calculated (solid line) and difference (bottom line) X-ray powder diffraction pattern of $Sr_5(CrO_4)_3(Cu_{0.586}O)$. Lower vertical lines indicate the reflections of impurity phase CuO.

Table 1
Atomic coordinates and isotropic displacement parameters ($U_{iso} \times 100$, Å^2) for $Sr_5(CrO_4)_3(Cu_{0.586(4)}O)$.

Atom		*x*/*a*	*y*/*b*	*z*/*c*	Fraction	$U_{iso} \times 100$
Sr(1)	4*f*	1/3	2/3	0.5013(3)	1.0	2.90(3)
Sr(2)	6*h*	0.0115(2)	0.2528(1)	1/4	1.0	2.79(2)
Cr	6*h*	0.6302(2)	0.0321(2)	1/4	1.0	2.46(5)
Cu	2b	0	0	0	0.586(4)	3.0(2)
O(1)	6*h*	0.5150(7)	0.8386(7)	1/4	1.0	3.3(2)
O(2)	6*h*	0.5307(7)	0.1272(8)	1/4	1.0	2.5(2)
O(3)	12*i*	0.3479(4)	0.2519(4)	0.0681(5)	1.0	2.8(1)
O(4)	2*a*	0	0	1/4	1.0	3.0(3)

wRp = 2.13%, Rp = 1.55%, $R(F^2)$ = 2.58%.

$Sr_5(CrO_4)_3(Cu_{0.586}O)$ is isostructural to $Sr_5(VO_4)_3(CuO)$ [12] and $Sr_5(PO_4)_3(CuO_2)_{1/3}$ [11] which were shown to be derivatives of the apatite structure $Ca_5(PO_4)_3OH$ [15,16]. The crystal structure contains isolated tetrahedral $[CrO_4]^{3-}$ anions and infinite linear $[CuO]^{1-}$ chains inserted into the tunnels parallel to the hexagonal *c* axis (Fig. 2). The chains are formed by Cu and O(4) placed at special sites 2*b* (0,0,0) and 2*a* (0, 0, 1/4), respectively. Copper atoms are bonded to two O(4) atoms with average Cu—O distance 1.8656(0) Å. Chromium atoms are in the centers of slightly distorted oxygen tetrahedrons with the mean Cr—O distance 1.696 Å. Two types of Sr^{2+} cations occupy two kinds of cavities formed by oxygen atoms of $[CrO_4]^{3-}$ and $[CuO]^{1-}$ anions. Sr(1) has the coordination number 9 and is centered at a twisted tricapped trigonal prism (red polyhedron in Fig. 2) with the mean Sr—O distance 2.701 Å. Sr(2) (CN7) occupies a pentagonal bipyramide (blue polyhedron in Fig. 2) with an oxygen atom (O4) of the Cu—O chain at one apical position and mean Sr—O distance 2.605 Å. The O(4) atoms occupy the position of F^- in the classical apatites, while Cu atoms lie near the H^+ positions of hydroxyapatites.

Table 2
Selectic interatomic distances *d* (Å) and angles (°) for $Sr_5(CrO_4)_3(Cu_{0.586(4)}O)$.

Interatomic distances		Interatomic distances	
Sr(1)—O(1)	2.582(4) 3×	Sr(2)—O(2)	2.514(6)
Sr(1)—O(2)	2.600(5) 3×	Sr(2)—O(3)	2.541(4) 2×
Sr(1)—O(3)	2.920(4) 3×	Sr(2)—O(4)	2.4798(9)
Average	**2.701**	Sr(2)—O(3)	2.672(4) 2×
Expected[a]	*2.69*	Sr(2)—O(1)	2.816(4)
		Average	**2.605**
Cr—O(1)	1.691(7)	*Expected*[a]	*2.59*
Cr—O(2)	1.690(6)		
Cr—O(3)	1.701(4) 2×	Cu—O(4)	1.8656(0) 2×
Average	**1.696**	*Expected*[a]	*1.85*
Expected[a]	*1.713*	Cu—O(3)	3.162(3) 6×
Angles		Angles	
O(1)—Cr—O(2)	113.0(4)	O(1)—Cr—O(3) 2×	112.3(2)
O(3)—Cr—O(3)	105.9(3)	O(2)—Cr—O(3) 2×	106.4(2)

[a] The sum of the crystal radii were calculated according to [Shannon R.D. Acta Cryst. A 32 (1976) 751]: Sr^{2+} IX – 1.45 Å, Sr^{2+} VII – 1.35 Å, Cr^{5+} IV – 0.485 Å, Cr^{6+} IV – 0.40 Å, Cu^{1+} II – 0.60 Å, O^{2-} IV–1.24 Å, O^{2-} VI – 1.26 Å, and general formula $Sr_5^{2+}(Cr_{2.586}{}^{5+}Cr_{0.414}{}^{6+}O_4{}^{2-})_3\,(Cu_{0.586}{}^{1+}O^{2-})$.

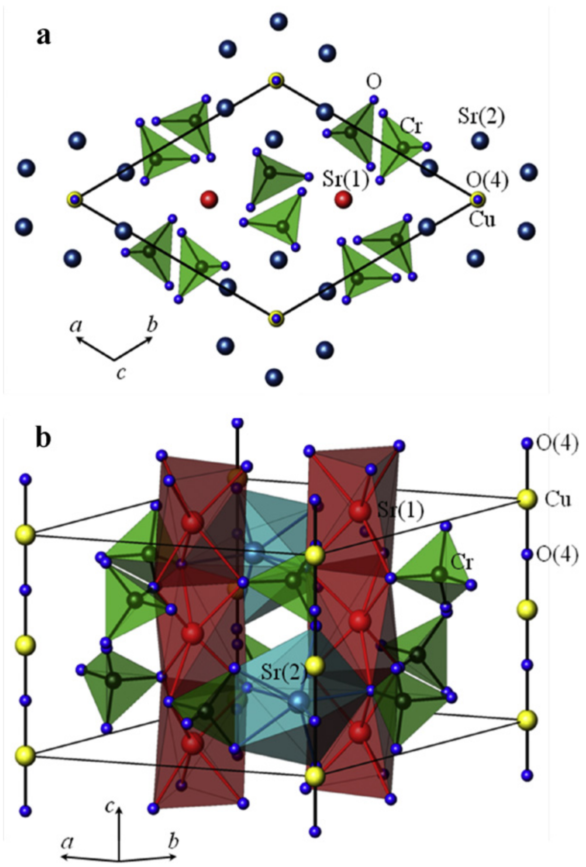

Fig. 2. Crystal structure of $Sr_5(CrO_4)_3(Cu_{0.586}O)$: (a) projection along the *c*-axis, (b) side view showing the infinite $[CuO]^{1-}$ chains and the coordination polyhedra of the Cr and Sr atoms.

The mean Cr—O distance in the tetrahedra (1.696 Å, Table 2) closely corresponds to that found in the structure of $Sr_{10}(CrO_4)_6F_2$ (1.695 Å [6]). The small distortion of the polyhedron is due to the Jahn-Teller nature of Cr^{5+} cations (d^1 configuration). The interatomic Cu—O bond length in the linear chains (1.8656 Å) suggests that copper in this compound should be in the form of Cu^+ cations [12].

Magnetization measurements show that in the temperature range from 4 to 300 K the complex oxide $Sr_5(CrO_4)_3(Cu_{0.586}O)$ is paramagnetic with magnetic susceptibility obeying the Curie law (Fig. 3)

$\chi = C/T$, where χ is molar susceptibility (emu/mol), C is the Curie constant (1.048 cm^3 K/mol). The experimental value of the effective magnetic moment (μ_{eff}) for the 1 Cr atom in formula $Sr_5(CrO_4)_3(Cu_{0.586}O)$ (1.671 μ_B) is somewhat smaller than the theoretical moment (1.732 μ_B) calculated in the assumption that all chromium is present as Cr^{5+} cations and cupper as Cu^+ cations. Thus, the magnetic measurements performed confirm the results of structural studies showing that cations Cu^+ are located in the linear chains. Therefore, it is worth noting that according to X-ray photoelectron spectroscopy data copper in apatites $A_{10}(PO_4)_6Cu_xO_y(H)_z$ (A = Ca, Sr) [17] is mainly in the divalent state. The presence of a small amount of Cu^{3+} cations was also noticed. At the same time the existence of Cu as Cu^+ is found at $Sr_5(PO_4)_3(CuO_2)_{1/3}$ obtained at high temperatures [11]. After annealing the sample at lower temperature part of copper is oxidized to Cu^{2+}. The OH^- hydroxyl groups are formed in the lattice in these conditions.

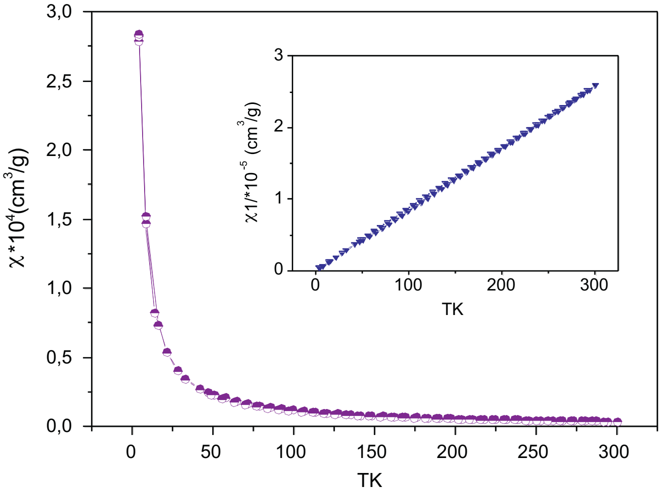

Fig. 3. Temperature dependence of magnetic susceptibility χ for $Sr_5(CrO_4)_3(Cu_{0.586}O)$ (H = 5 kOe). The inset shows the dependence of $1/\chi = f(T)$.

A smaller effective magnetic moment in $Sr_5(CrO_4)_3(Cu_{0.586}O)$ as compared with the theoretical value evidently indicates that some chromium in this compound, like in $Sr_3Cr_{2.86}O_8$ [1], is in the form of Cr^{6+} cations.

4. Conclusion

In summary, the apatite-like strontium chromate $Sr_5(CrO_4)_3(Cu_{0.586}O)$ have been successfully synthesized by the solid state reaction method at usual conditions. The crystal structure of $Sr_5(CrO_4)_3(Cu_{0.586}O)$ has been determined from the XRD date. According to cation–anion bond distances and magnetic measurements the valence states of Cr and Cu may be mainly +5 and +1, respectively.

Acknowledgments

This work was supported by grant of Presidium of the Russion Academy of Sciences.

References

[1] K.T. Jacob, K.P. Abragam, J. Phase Equilib. 21 (2000) 46.
[2] R. Cuno, H. Muller-Buschbaum, Z. Anorg. Allg. Chem. 572 (1989) 175.
[3] F. Abraham, S. Minaud, C. Renard. J. Mater. Chem. 4 (1994) 1763.
[4] G.V. Bazuev, V.G. Zubkov, V.N. Krasil'nikov, K.N. Mikhalev, T.I Arbuzova, Doklady akademii nauk. 363 (1998) 634.
[5] G.V. Bazuev, Russ. Chem. Rev. 75 (2006) 749.
[6] E. Herdtweck, Acta Cryst. C47 (1991) 1711.
[7] T.J. White, ZhiLi. Dong, Acta Cryst. B59 (2003) 1.
[8] M. Mathem, W.E. Brown, M. Austin, T. Negas, J. Solid State Chem. 35 (1980) 69.
[9] P.E. Kazin, O.R. Gazizova, A.S. Karpov, M. Jansen, Yu.D. Tretyakov, Solid State Sci. 9 (2007) 82.
[10] C. Calvo, R. Faggiani, N. Krishnamachari, Acta Crystallogr. B31 (1975) 188.
[11] P.E. Kazin, A.S. Karpov, M. Jansen, J. Nussc, Y.D. Tretyakov, Z. Anorg. Allg. Chem. 629 (2003) 344.
[12] W. Carrillo-Cabrera, H.G.Z. von Schnering, Anorg. Allg. Chem. 625 (1999) 183.
[13] A.C. Larson, R.B. Von Dreele, GSAS, LANSCE, MS-H805, Los Alamos National Laboratory, Los Alamos, NM 87545.
[14] P.W. Selwood. Magnetochemistry, 2 ed., NY, London, 1956.
[15] M.I. Kay, R.A. Young, A.S. Posner, Nature 204 (1964) 1050.
[16] J.M. Hughes, M. Cameron, K.D. Crowley, Am. Min. 74 (1989) 870.
[17] T. Baikie, G.M.H. Ng, S. Madhavi, S.S. Pramana, K. Blake, M. Elcombe, T.J. White, Dalton Trans. (2009) 6722.