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A barium copper titanate. The synthesis and structural characterization of $Ba_8Cu_2Ti_{22}O_{54}$

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Abstract—The barium copper titanate compound $Ba_8Cu_2Ti_{22}O_{54}$, **1**, was obtained in a crystalline form by heating a mixture of $BaCO_3$, CuO, and TiO_2 at 1380°C for 48 h. Compound **1** was characterized by single crystal X-ray diffraction methods. There are ten independent transition metal sites in the lattice. In nine of these sites the metal ions are surrounded by six oxide ions in octahedral arrangements. The one remaining metal site is surrounded by a square pyramidal arrangement of five oxide ions with a sixth remotely positioned oxide ion. This site contains approximately 39% of the copper contained in the material. The remainder of the copper appears to be disordered uniformly among the octahedral metal sites. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: barium; copper; titanate; crystal structure.

Although alkali and alkaline earth titanates have attracted attention for their use in ion exchange processes [1], in ceramic capacitors [2], in applications as dielectric resonators in microwave oscillators and bandpass filters [2,3] and for various other properties [4], there have been relatively few reports of titanates mixed with copper in the recent literature [5]. Alkali titanates exhibit a range of layered, corrugated layered and tunnel type structures in the solid state [6]. In previous reports, we have found that it is possible to prepare mixed metal titanates formed by replacing one or more of the Ti^{4+} ions in known alkali titanates structures with transition metal ions in lower oxidation states when the alkali ions are replaced with alkaline earth ions [7]. These transition metal containing titanates can exhibit interesting magnetic properties due to the presence of the unpaired electrons on the transition metal ions.

We wish to report that we have now obtained a barium copper titanate compound $Ba_8Cu_2Ti_{22}O_{54}$, **1**, by heating a mixture of $BaCO_3$, CuO, and TiO_2 at 1380°C for 48 h. Compound **1** was characterized by single crystal X-ray diffraction analysis.

EXPERIMENTAL

The reagents $BaCO_3$ (99.98%) and TiO_2 (99.9%) were purchased from Aldrich. CuO (99.8%) was purchased from J. T. Baker. These reagents were used without further purification. The reaction mixture was heated in a Thermolyne Model F46120CM oven in an atmosphere of air. Single crystal diffraction measurements were made on a Rigaku AFC6S automatic diffractometer by using graphite-monochromated Mo-K_α radiation. Scanning electron microscopy measurements were performed on a Hitachi S-2500Δ scanning electron microscope using a Kevex energy dispersion X-ray (EDX) analysis at the University of South Carolina Electron Microscopy laboratory.

Preparation of $Ba_8Cu_2Ti_{22}O_{54}$, **1**

A mixture consisting of 0.987 g (5.00 mmol) of $BaCO_3$, 0.400 g (5.03 mmol) of CuO, and 0.803 g (10.01 mmol) of TiO_2 was ground thoroughly in a mortar, and then transferred to a platinum crucible. The platinum crucible was placed in the oven and heated to 1380°C for 48 h. After this period, the oven was cooled slowly (approx. 1°C/min) to 1000°C and then allowed to cool rapidly to room temperature. The sample was removed from the oven at room temperature. There were only very small amounts of the dark red product $Ba_8Cu_2Ti_{22}O_{54}$, **1** present. Analysis (EDX): relative metal % composition Ba + Ti/Cu % calc 94/6; (% found) 91/9. Due to overlap of emissions it is not possible to analyze the relative amounts of Ba

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and Ti, but their sum relative to Cu can be determined. The principal components of the reaction mixture were identified as $BaTiO_3$ and CuO. Surprisingly, we have not been able to synthesize **1** successfully in good yield by using stoichiometric ratios of these reagents.

Crystallographic analysis

Single crystals of **1** suitable for X-ray diffraction analysis were obtained from the crucibles in which the preparations were carried out. A dark red crystal was cleaved from the bulk sample with a scalpel. The crystal used for the intensity measurements was mounted in thin-walled glass capillary. The unit cell was determined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analysis are listed in Table 1. All data processing was performed on a Silicon Graphics INDIGO2 computer by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Lorentz-polarization (Lp) and an absorption correction (DIFABS) were applied to all data. An extinction correction was applied. Neutral atom scattering factors were calculated by the standard procedures [8a]. Anomalous dispersion corrections were applied to all non-hydrogen atoms [8b]. Crystals of compound **1** belonged to the monoclinic crystal system. The pattern of systematic absences observed in the data is consistent with either of the space groups *C*2/*m*, *C*2 or *Cm*. The centrosymmetric space group, *C*2/*m*, was selected as the starting point and was confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. Full matrix least-squares refinements minimized the function: $\Sigma_{hkl} w(|F_0|-|F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_0^2)/2F_0$, and $\sigma(F_0^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$. All atoms were refined with anisotropic thermal parameters. Atomic coordinates have been deposited with the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

The new mixed metal titanate $Ba_8Cu_2Ti_{22}O_{54}$, **1**, was obtained as dark red crystals when mixtures of $BaCO_3$, CuO, and TiO_2 in a 1 : 1 : 2 ratio were heated to 1380°C for 48 h. Compound **1** was characterized by single crystal X-ray diffraction analysis. A projection of the crystallographic unit cell in the *ac* plane is shown in Fig. 1. Selected interatomic distances are listed in Table 2. The barium ions occupy three independent sites. Two of these are special positions 4*i* which have mirror symmetry; the third occupies a general position. From this the barium ion composition is established as 8. The barium atoms are surrounded by 12 nearest neighboring oxygen atoms in the range 2.707–3.24 Å. The transition metal ions occupy ten independent sites in the lattice. Seven of these sites are special positions; three are general positions. From

Table 1. Crystallographic data for compound **1**

Formula	$Ba_8Cu_2Ti_{22}O_{54}$
Formula weight	3143.50
Crystal system	monoclinic
a (Å)	19.865(4)
b (Å)	11.469(2)
c (Å)	9.940(2)
α (°)	90.0
β (°)	109.02(2)
γ (°)	90.0
V (Å^3)	2141.1(8)
Space group	*C*2/*m* (#12)
Z value	2
ρ_{calc} (g cm^3)	4.88
μ (Mo-K_α) (cm^{-1})	121.64
Temperature (°C)	20
$2\Theta_{max}$ (°)	53.0
No. of obs. ($I > 3\sigma$)	1887
No. of variables	217
Goodness of fit	2.20
Residuals: R; Rw	0.034; 0.037
Absorption correction	DIFABS
Transmission Coeff. (max/min)	1.00/0.61
Largest peak in final diff. map (e Å^3)	2.68

$R = \Sigma_{hkl}(||F_{obs}| - |F_{calc}||/\Sigma_{hkl}|F_{obs}|$, $R_w = [\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\Sigma_{hkl}wF_{obs}{}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; GOF $= [\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|)^2/(n_{obs} - n_{vari})]^{1/2}$

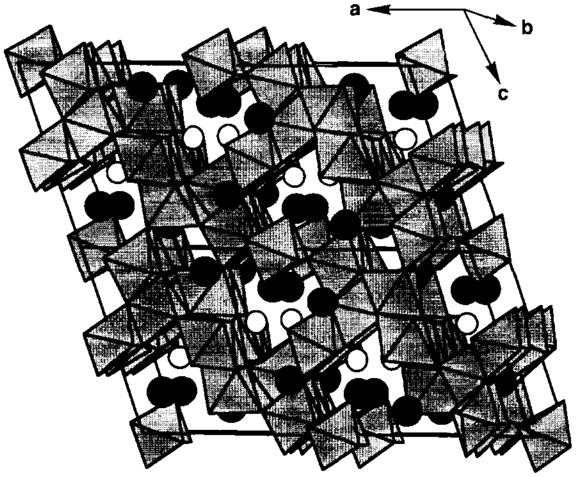

Fig. 1. A plot of two adjacent unit cells of the solid state structure of $Ba_8Cu_2Ti_{22}O_{54}$ projected onto the *ac* lattice plane. The polyhedra show the arrangement about the octahedral sites which contain a mixture of titanium and copper ions. The contacts between the metal ion in the square pyramidal site (open circles) and oxide ions are not represented. The contacts to the barium ions (dark gray circles) and the oxide ions are not represented either.

this total, the metal composition in the formula was established as 24. The oxide composition of the formula was similarly established to be 54. From this the copper and titanium compositions were calculated to be 2 and 22, respectively on the basis of charge balance. Occupancy refinements of the metal composition in the various sites indicate that the copper is disordered throughout all of the metal containing sites, but a high proportion (≈39%) was found in one site M(1). Conversely, the bulk of the titanium lies in the remaining metal sites M(2) through M(10). The titanium and copper was found to be distributed in approximately equal proportions 94.4/5.6 Ti/Cu in each of these sites.

In each of the metal sites M(2) through M(10), the metal ions are surrounded by six oxide ions in octahedral arrangements. The M—O distances all lie within the range 1.85–2.16 Å. The metal site M(1), has only five closely positioned oxide ions which lie in the range 1.94–2.00 Å. These ions are arranged in the form of a square pyramid. There is a sixth oxide ion O(16) in a position that approximates the sixth site of an octahedron, but it lies much farther from the metal ion, 2.620(8) Å. To a first approximation, the M(1) site has only five nearest neighbor oxide ions and thus

Table 2. Selected interatomic distances[a] with Esds for **1**.

Ba(1)—O(3)	2.758(6)	M(3)—O(13)	1.852(6)
Ba(1)—O(9)	2.841(6)	M(4)—M(10)	3.020(2)
Ba(1)—O(10)	2.855(6)	M(4)—O(7)	1.959(8)
Ba(1)—O(13)	2.877(6)	M(4)—O(8)	1.999(6)
Ba(1)—O(14)	3.24(1)	M(5)—O(2)	2.159(6)
Ba(1)—O(16)	2.809(9)	M(5)—O(3)	1.823(6)
Ba(2)—O(1)	2.777(8)	M(5)—O(4)	2.015(5)
Ba(2)—O(3)	2.882(5)	M(5)—O(5)	2.030(6)
Ba(2)—O(6)	2.937(5)	M(5)—O(6)	1.910(6)
Ba(2)—O(10)	3.166(6)	M(5)—O(16)	2.007(5)
Ba(2)—O(11)	3.069(6)	Ba(3)—O(15)	2.913(5)
Ba(2)—O(12)	2.838(6)	M(6)—O(2)	1.947(5)
Ba(2)—O(14)	2.97(1)	M(6)—O(5)	1.986(6)
Ba(3)—O(2)	2.707(6)	M(6)—O(11)	2.013(6)
Ba(3)—O(6)	2.765(6)	M(7)—O(3)	1.946(6)
Ba(3)—O(8)	2.783(5)	M(7)—O(6)	1.857(5)
Ba(3)—O(9)	3.015(6)	M(7)—O(9)	2.150(5)
Ba(3)—O(10)	3.126(6)	M(7)—O(10)	1.884(6)
Ba(3)—O(11)	3.125(6)	M(7)—O(12)	2.041(6)
Ba(3)—O(13)	2.878(6)	M(7)—O(15)	1.979(6)
Ba(3)—O(14)	3.1172(9)	M(7)—O(12)	2.041(6)
M(1)—O(11)	1.997(6)	M(8)—O(15)	1.848(6)
M(1)—O(13)	1.942(6)	M(9)—O(1)	1.969(9)
M(1)—O(14)	1.966(9)	M(9)—O(2)	1.932(6)
M(1)—O(16)	2.620(8)	M(9)—O(11)	2.010(6)
M(2)—O(10)	2.049(6)	M(9)—O(16)	2.082(9)
M(2)—O(14)	1.940(9)	M(10)—O(1)	2.000(6)
M(2)—O(14)	1.940(9)	M(10)—O(5)	1.866(6)
M(3)—O(8)	2.086(6)	M(10)—O(7)	2.143(6)
M(3)—O(9)	1.993(5)	M(10)—O(8)	1.949(5)
M(8)—O(7)	2.130(8)	M(10)—O(9)	1.963(6)
M(8)—O(12)	2.055(6)	M(10)—O(12)	1.899(5)

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

a formal proximate negative charge of -10 (5 O^{2-}). The octahedral sites have six nearest neighbor oxide ions and thus a formal proximate negative charge of -12 (6 O^{2-}). Localized charge balance effects may thus provide a partial explanation for the presence of the greater quantity of titanium $(+4)$ in the octahedral sites and copper $(2+)$ in the square pyramidal site, that is, the titanium ions are attracted to the more highly negatively charged octahedral sites. The copper ions are then relegated to the less negatively charged square pyramidal site M(1). Our EDX compositional analysis indicated that the copper content might be even higher than that indicated by the formula $Ba_8Cu_2Ti_{22}O_{54}$. This could only be possible if there were oxygen deficiencies in some of the oxide sites. However, efforts to refine the structure with increased quantities of copper produced poorer agreement indices and these results were thus discarded.

Unfortunately, the yield of this compound is very low. Attempts to improve the yield were made by heating mixtures of these reagents in the proper stoichiometric ratios. However, under these conditions only the known titanate, $Ba_4Ti_{13}O_{30}$ [9], was obtained. Interestingly, this $Ba_4Ti_{13}O_{30}$ was colored red, suggesting that some copper may have been dispersed into the $Ba_4Ti_{13}O_{30}$ lattice as an impurity.

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