doi:10.1246/cl.2011.524

Synthesis and Crystal Structure of Cubic Perovskite-type $BaMo_xTi_{1-x}O_3$ with $x \approx 0.175$

Kunimitsu Kataoka,*[1,2] Norihito Kijima,[1] Hiroshi Hayakawa,[1] Ken-ichi Ohshima,[2] and Junji Akimoto[1]
[1]*National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565*
[2]*Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573*

(Received February 18, 2011; CL-110141; E-mail: kataoka-kunimitsu@aist.go.jp)

Single crystals of a novel solid-solution compound $BaMo_xTi_{1-x}O_3$ ($x \approx 0.175$) in a $BaTiO_3$ and $BaMoO_3$ system were successfully grown by flux in Ar at 1423 K using the $BaCO_3$–B_2O_3 system flux. The obtained crystals were black and rectangular with a maximum dimension of $0.2 \times 0.2 \times 0.3$ mm^3. The EDX and EPMA analyses confirmed the Mo–Ti solid solution composition. Single-crystal X-ray structure analysis revealed the cubic perovskite structure, space group $Pm\bar{3}m$ and the lattice parameters of $a = 4.0112(6)$ Å and $V = 64.54(3)$ Å^3. The chemical composition and crystal structure were refined by the present structure refinement with the conventional values of $R = 1.69\%$ and $wR = 1.89\%$ using 156 independent observed reflections.

Barium titanium oxide ceramics are important industrial materials. The perovskite $BaTiO_3$ and hexagonal $BaTiO_3$ have been extensively investigated because of their electric properties for use in dielectric and relaxor materials.[1–3] It is well-known that impurity or additive incorporation in $BaTiO_3$ in even quite small proportions may change the dielectric properties appreciably, e.g., Sb-doped $BaTiO_3$[4] and $Ba_{1-x}Na_xTi_{1-y}Nb_yO_3$.[5] On the other hand, perovskite $BaMoO_3$ is reported to be a good electrical conductor with resistivities in the range of 10–100 µΩ cm.[6] However, substitution of titanium by molybdenum in $BaTiO_3$ has, to our knowledge, not been reported. In the present study, single crystals of the solid-solution compound $BaMo_xTi_{1-x}O_3$ with $x \approx 0.175$ were successfully grown by flux, and the crystal structure was refined by single-crystal X-ray diffraction.

Single crystals of $BaMo_xTi_{1-x}O_3$ were synthesized by flux using a $BaCO_3$–B_2O_3 system. The as-prepared $Ba_2Ti_{13}O_{22}$ powder[7] was mixed with $BaCO_3$ (99.9%) and B_2O_3 (99.9%) in order to form a flux material with a nominal mass ratio of $Ba_2Ti_{13}O_{22}$:$BaCO_3$:B_2O_3 = 1:5:5. The mixture was placed in Mo crucibles, heated in Ar at 1423 K for 10 h, and then cooled on standing. The products were easily separated from the frozen flux by rinsing the crucibles in hot water for several hours.

The qualitative chemical composition of the products was investigated by scanning electron microscopy–energy dispersive X-ray analysis (SEM-EDX, JEOL JSM-5400) and electron probe microanalysis (EPMA, JEOL JXA-8100).

Integrated intensity data were collected on a Rigaku AFC-7S four-circle diffractometer at 295 K using selected single-crystal specimens. The electron density distribution was analyzed by the maximum entropy method (MEM) using the present single-crystal X-ray diffraction data with the PRIMA program.[8] The obtained three-dimensional electron density distributions were visualized with the VESTA program.[9]

Black single crystals of $BaMo_xTi_{1-x}O_3$ with a maximum size of $0.2 \times 0.2 \times 0.3$ mm^3 were grown in the frozen flux, as shown in Figure 1. The crystal surfaces were covered with the polycrystalline Ba–B–O flux materials which were hardly removed by washing even using hot water. The good quality of the obtained rectangular crystal was confirmed by single-crystal X-ray diffraction. The EDX (Figure 1) and EPMA analyses revealed that the chemical constituents of the crystals were Ba, Ti, Mo, and O. The accurate atomic ratio of Mo/Ti was determined by the occupancy refinement by the present structure analysis.

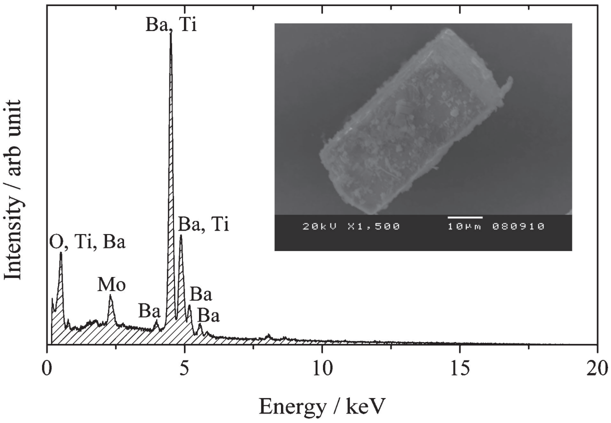

Figure 1. SEM photograph and the EDX spectrum of the $BaMo_xTi_{1-x}O_3$ single crystal. The scale of SEM photograph is 10 µm.

It is considered as a matter of course that the Mo atoms came from the crucible materials at high temperature. In the present synthetic route, we used $Ba_2Ti_{13}O_{22}$ as the starting compound, which is a Ti^{3+}/Ti^{4+} mixed-valence compound.[7] We think that this compound reacts with the Mo crucible at high temperatures at first and then followed by oxidation in the molten Ba–B–O flux.

The lattice parameters, determined by least-squares refinement using 2θ values of 24 strong reflections in the range of 8–30° and Mo Kα radiation ($\lambda = 0.71069$ Å) on the four-circle diffractometer at 295 K, were $a = 4.0112(6)$ Å and $V = 64.54(3)$ Å^3. It should be noted that the present lattice parameter lied on the intermediate between 4.006(2) Å for $BaTiO_3$[10] and 4.0404(3) Å for $BaMoO_3$.[6] This indicates the existence of the solid-solution compound in the system $BaTiO_3$–$BaMoO_3$. The Laue group was determined to be $m3m$ using the intensity data by 2θ-ω scan with a scan rate of 16.0° min^{-1}.

A small cubic crystal, with the dimensions $0.16 \times 0.16 \times 0.16$ mm^3, was used for the structure analysis. The intensity data were collected by 2θ-ω scan with a scan rate of 1.0° min^{-1} at room temperature on the four-circle diffractometer (operating conditions: 50 kV; 40 mA) using graphite monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å). The fluctuations of the intensities, monitored by examining sets of three standard reflection ($(\bar{1}0\bar{1})$, $(\bar{2}00)$, $(\bar{1}1\bar{1})$) obtained after every 150 measurements, were within 0.5%. A total of 1353 reflections was obtained within the limit of $2\theta < 135°$. Absorption correction, estimation of initial structure model, and structure refinement were carried out using the Xtal3.5,[11] superflip,[12] and Jana2006 program,[13] respectively. Structure factors were obtained after averaging the equivalent Bragg intensities, which were corrected for Lorenz and polarization factor, scale factor, absorption and extinction effects. Extinction effect was corrected using Becker–Coppens type 1. Neutral atomic scattering factors for all atoms were applied in the refinement. The crystallographic and experimental data are summarized in Table 1.

In the following structure analysis, the space group of $Pm\bar{3}m$, confirmed by successful refinement, was adopted. The refinement was initiated with three chemical formulae: $BaTiO_3$ (model I), $BaMoO_3$ (model II), and $BaTi_xMo_{1-x}O_3$ (model III). The model I and model II failed in the refinement with $R =$ 4.1% and 8.7%, respectively. Therefore, we selected model III in the present refinement. The chemical composition of particular single-crystal specimen, especially the Mo/Ti content, was determined to be $BaMo_{0.175}Ti_{0.825}O_3$ by the structure refinement. Finally, the crystal structure was refined to be $R = 1.69\%$ and $wR = 1.89\%$ for 151 observed reflections, using anisotropic displacements for all atoms with a shift/error for all 8 parameters of less than 0.001. The final atomic coordinates and displacement parameters are listed in Table 2.

Table 1. Experimental and crystallographic data of $BaMo_{0.175}Ti_{0.825}O_3$

Structure formula	$BaMo_{0.175}Ti_{0.825}O_3$
Temperature/K	295
Crystal system	cubic
Laue group	$m3m$
Space group	$Pm\bar{3}m$
Lattice parameters	
a/Å	4.0112(6)
V/Å^3	65.54 (3)
D_x/g cm^{-3}	6.215
Crystal size/mm^3	0.16 × 0.16 × 0.16
Maximum 2θ/degree	135
Absorption correction	Gaussian integration
Transmission factors: min. and max.	0.0609 and 0.1967
Extinction parameter (g_{iso})	0.015 (4)
Measured reflections	1353
R_{int}/%	2.51
Independent reflections	158
Independent reflections ($>3\sigma$)	156
Number of variables	8
R/wR [$w = 1/\sigma^2F$]/%	1.69/1.89

The average crystal structure of $BaMo_{0.175}Ti_{0.825}O_3$ is shown in Figure 2a. In the present single-crystal study, the dodecahedral Ba–O and octahedral Mo/Ti–O distances were determined to be 2.8363(6) and 2.0056(6) Å, respectively. This Mo/Ti–O distance is considerably longer than that (1.962(2) Å) for the octahedral Ti^{4+}–O distance without the distortion.[14] This fact may be explained by the Mo substitution at the octahedral site. Figure 2b shows the electron density distribution of $BaMo_{0.175}Ti_{0.825}O_3$ obtained by the single-crystal MEM analysis using single-crystal X-ray diffraction data. The reliability factor of the MEM, R_{MEM}, was 2.7%. Strong covalent bonding between the Mo/Ti and O atoms is clearly visible. The electron density heights at the saddle point between the Mo/Ti and O atoms are determined to be 0.74 Å^{-3}. This covalent bond is formed of interaction of d and p orbitals. Therefore, it is thought that the covalent bonding of Mo/Ti–O is due to the Mo-4d/Ti-3d orbitals and O-2p orbital interaction near the Fermi level. On the other hand, no bonding is observed around the Ba atom, as shown in Figure 2b. The isosurface density distribution at 0.7 Å^{-3} is spherical, suggesting the ionic character of the Ba atoms.

In summary, we successfully prepared single crystals of $BaMo_xTi_{1-x}O_3$ with $x \approx 0.175$ by a flux method and determined the crystal structure and electron density distribution of $BaMo_xTi_{1-x}O_3$ using the single-crystal X-ray diffraction data. The chemical composition of a particular single-crystal specimen was determined to be $BaMo_{0.175}Ti_{0.825}O_3$ by the present structure refinement with the final R value of 1.69%. The single-crystal MEM analysis revealed strong covalent bonding between the Mo/Ti and O atoms, while no bonding was observed between the Ba and O atoms.

This research was supported by Research Fellowships from the Japan Society for the Promotion of Science for Young Scientists (No. 21-3933).

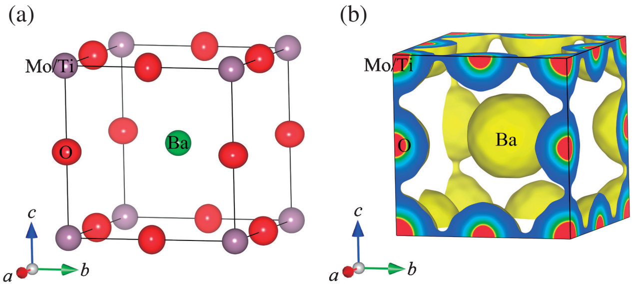

Figure 2. (a) Average crystal structure and (b) electron density distribution of $BaMo_{0.175}Ti_{0.825}O_3$. The isosurface density level is equal to 0.70 Å^{-3}.

Table 2. Atomic coordinates and equivalent isotropic and anisotropic displacement parameters (Å^2) for $BaTi_{0.825}Mo_{0.125}O_3$[a]

Atom	Site	Occ.	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}
Ba1	1b	1.0	0.5	0.5	0.5	0.00781(7)	0.00781(12)	$= U_{11}$	$= U_{11}$
Ti1	1a	0.825(17)	0	0	0	0.0079(1)	0.0079(2)	$= U_{11}$	$= U_{11}$
Mo1	1a	0.175(17)	0	0	0	0.0079(1)	0.0079(2)	$= U_{11}$	$= U_{11}$
O1	3d	1.0	0.5	0	0	0.0096(3)	0.0085(6)	0.0101(4)	$= U_{22}$

[a] Anisotropic parameter conditions; $U_{12} = U_{13} = U_{23} = 0$.

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