XANES analyses on minor elements and X-ray single crystal structure analyses of Ce- and Nb-perovskite

Ginga KITAHARA*, Akira YOSHIASA*, Makoto TOKUDA*, Tsubasa TOBASE* and Kazumasa SUGIYAMA**

*Graduate School of Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan

**Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Structural analysis of Ce- and Nb-perovskites containing Fe, Zr, Nb, and rare earth elements (REEs) in CaTiO_3 perovskite was performed using single-crystal X-ray diffraction and X-ray absorption near-edge structure (XANES) analyses. Based on chemical analysis results, XANES measurements and the site-occupation of elements at A- and B-sites showed the chemical formula: $(\text{Ca}_{0.817}^{2+}\text{REE}_{0.087}^{3+}\text{Na}_{0.081}^{+}\text{Sr}_{0.005}^{2+}\text{Th}_{0.003}^{4+})_{0.993}^{1.998+}(\text{Ti}_{0.941}^{4+}\text{Nb}_{0.017}^{5+}\text{Fe}_{0.013}^{3+}\text{V}_{0.010}^{5+}\text{Fe}_{0.007}^{2+}\text{Sc}_{0.006}^{3+}\text{Zn}_{0.005}^{2+}\text{Al}_{0.002}^{3+}\text{Ge}_{0.001}^{4+}\text{W}_{0.001}^{6+})_{1.005}^{3.996+}\text{O}_3$ for Ce-perovskite and $(\text{Ca}_{0.937}^{2+}\text{Ce}_{0.021}^{3+}\text{Na}_{0.020}^{+}\text{La}_{0.015}^{3+}\text{Sr}_{0.003}^{2+})_{0.996}^{2.008+}(\text{Ti}_{0.730}^{4+}\text{Nb}_{0.122}^{5+}\text{Fe}_{0.108}^{3+}\text{Al}_{0.020}^{3+}\text{Zr}_{0.009}^{4+}\text{V}_{0.008}^{5+})_{0.997}^{3.990+}\text{O}_3$ for Nb-perovskite. In Ce- and Nb-perovskites, the total charges at the A- and B-sites achieved near-ideal divalent and tetravalent states such as $\text{Ca}^{2+}\text{Ti}^{4+}\text{O}_3$, respectively, due to complex elemental substitutions. Local distortions around Ti in the perovskite solid solutions were greater, and the pre-edge features of the Ti atoms in Ce- and Nb-perovskites were different from those in pure CaTiO_3 . The valence states and local structures of Fe in Ce- and Nb-perovskites were significantly different. The existence of divalent Fe^{2+} at the B-site in Ce-perovskite was confirmed. It is presumed that the displacement ellipsoids of all atoms and local irregularities in Ce-perovskite increase owing to the radiative decay of the actinoid element Th. We reconfirmed that the composition and three-dimensional structure of perovskite-type structures were flexible and caused various electrical, structural changes.

Keywords: Ce-perovskite, Nb-perovskite, Charge balance, XANES, Valence state of iron

INTRODUCTION

Compounds with perovskite-type structures have the chemical formula of ABX_3 . Various cations with different valences and ionic sizes occupy the A- and B-sites. Perovskite compounds exhibit various physical properties such as piezoelectricity, ferroelectricity, paraelectricity, ferromagnetism, electron conductivity, superionic conductivity, and mixed conductivity (Nakatani et al., 2016; Yoshiasa et al., 2016, 2018). These properties make them attractive for applications in solar cell devices (Noorden, 2014). The deformation of the BX_6 octahedra framework and the coordination environment around the cation sites in perovskite-type structures change depending on the solid solution chemical composition and various physical conditions (Sasaki et al., 1983). Distorted charge balance processes and structural relaxation mechanisms in forming solid solutions substituted by heterovalent ions, such as trivalent Ce at A-site and

pentavalent Nb at B-site, are interesting research themes.

Silicate perovskites, such as MgSiO_3 and CaSiO_3 solid solutions, are the dominant phases in the mineral assemblages of the Earth's lower mantle. The $\text{Mg} \leftrightarrow \text{Ca}$ substitution at the A-site hardly occurs in MgSiO_3 and CaSiO_3 . It has been reported that radioactive Th dissolves at the A-site of perovskite-type CaSiO_3 (Greaux et al., 2012). In particular, CaSiO_3 is a host phase for trace elements such as Th and REE, although their contents are low in the lower mantle (Wang et al., 2000). Experimental reports are available on cation substitution in MgSiO_3 solid solutions, where Fe^{3+} is preferably substituted over Fe^{2+} , as represented by the chemical reaction of $3\text{Fe}^{2+} \rightarrow 2\text{Fe}^{3+} + \text{Fe}_{\text{metal}}^0$ (Nishio-Hamane et al., 2005; Hummer and Fei, 2012; Fujino et al., 2013). The oxidation state of Fe in CaSiO_3 is reported to be trivalent (Washington, 1900; Hu et al., 1992; Chakhmouradian, 1998; Mitchell et al., 1998, 2000).

Natural perovskite (CaTiO_3), a low-pressure analog of MgSiO_3 and CaSiO_3 , can be present in a wide range of solid solutions and form under a wide variety of geological settings such as alkaline intrusions, carbonatites,

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G. Kitahara, galaxy.kitahara@gmail.com Corresponding author
A. Yoshiasa, yoshiasa@kumamoto-u.ac.jp

kimberlites, contact metamorphic, and metasomatic rocks (Hu et al., 1992; Schmitt et al. 2019). It has been reported that natural perovskite (CaTiO_3) contains various radioactive elements, REEs such as La and Ce, and heavy metals such as Zr and Nb. (Washington, 1900; Hu et al., 1992; Chakhmouradian, 1998). However, there are few detailed reports on the crystal structure, valence state, and local structure of trace elements in perovskite solid solutions. Research on the valence state and local structure of guest and trace elements in natural perovskite-type solid solution minerals are needed to understand structural stability, element substitution mechanism, and element partitioning with coexisting phases. Elucidating the element substitution mechanism of radioactive elements provides an understanding of the heat source inside the Earth. In this study, we have compared the crystal structure and local structure of Ce-perovskite and Nb-perovskite, in which REEs (mainly Ce) and Nb substitute for Ca and Ti, respectively, in perovskite (CaTiO_3). We report the valence state of Fe, charge balance within the structure, variations in the local structure of minor elements, and irregularities associated with the metamictization of radioactive elements. We also confirmed that local structures found in the perovskite solid solution are substantially different.

EXPERIMENTAL

Specimens and chemical analyses

The naturally large octahedral perovskite crystals used in the measurements are from the Africanda Complex on the Kola Peninsula, Russia (Ce-perovskite) (Chakhmouradian, 1998) and the Perovskite Hill at Magnet Cove, Arkansas, USA (Nb-perovskite) (Washington, 1900). The chemical composition of the specimens was determined using a JEOL scanning electron microscope (JSM-7001F operated at 15 kV, 0.5 nA) equipped with an Oxford energy dispersive X-ray spectrometer (INCA SYSTEM). Based on the initial estimation of the chemical formula, the oxidation state of Fe was Fe^{3+} , and the total number of oxygen atoms was 3.0. Tables 1 and 2 show the average values of the chemical compositions of 15 points for Ce-perovskite and 20 points for Nb-perovskite. In the Ce-perovskite specimens, slight inhomogeneities in composition and chemical zoning were observed in the compositional and secondary electron images. However, the compositional differences in the same grain were not as remarkable as the distribution range of the compositions shown in Table 1.

X-ray absorption near-edge structure measurements

The XANES spectra near the Ti, Fe, Zr, and Nb *K*-edges

and Th L_{III} -edge were measured in transmission and fluorescent modes using the beamlines of BL-9C PF and NW10A AR, KEK in Tsukuba, Japan. During the measurement of Ti *K*-edge XANES spectra in transmission mode, appropriate amounts of fine powder samples and boron nitride powder were mixed and pressed into pellets with a thickness of <0.2 mm and a diameter of 10.0 mm. The fine powder samples were weighed to have an edge jump of $\Delta\mu d = 0.70$, in which μ is the linear absorption coefficient, and d is the thickness. The Fe, Zr, Nb, and Th spectra were measured in fluorescence mode. For comparison, pure synthetic CaTiO_3 , FeOOH , Fe_3O_4 , and Fe_{1-d}O were measured for each element in the same mode. Synchrotron radiation was monochromated by a Si(111) or Si(311) double-crystal monochromator. X-ray energy calibration was performed by setting the copper metal pre-edge absorption peak to 8978.8 eV. Mirrors were used to eliminate higher harmonics. Measurements were performed using normal energy resolution to obtain sufficient X-ray flux to compare with the published results. Measurement details are available in the literature (Okudera et al., 2012; Tobase et al., 2018). The analysis of XAFS data was performed using the XAFS93 and Athena programs. (Yoshiasa et al., 1997; Ravel and Newville, 2005).

Single crystal X-ray diffraction experiments

We carefully selected single crystals suitable for single-crystal structural analysis and were able to find untwinned crystals for each perovskite specimen. Single crystal X-ray diffraction measurements for the Ce-perovskite and Nb-perovskite were performed using a Rigaku SuperNova, offset/far single light source, HyPix3000 diffractometer. Evidence of lower symmetry was not detected, and systematic extinction were consistent with the space group of *Pbnm*. The intensity of reflection was measured using monochromatized $\text{MoK}\alpha$ (0.71073 Å) radiation. The data were corrected for Lorentz and polarization factors and absorption coefficients. Absorption correction was performed using an integration method based on the observed arbitrary shape of the specimens. Independent reflections with $|F_o| > 2\sigma|F_o|$ were used for refinement by the full-matrix least-squares method. Refinement calculations were performed using the program SHELXL97 (Sheldrick, 1997). During the least-squares refinements, a correction for isotropic extinction was applied. Site occupancy was first analyzed based on a model in which A-sites are only occupied by Ca and Ce, and B-sites are occupied by Ti and Nb. After several refinement cycles, displacement parameters were converted from isotropic to anisotropic. In the final stage, the site occupancy was refined using the atomic scattering factors of Ca, Na, and Ce at the A-sites and Ti, Fe,

Table 1. Chemical compositions of Ce- and Nb-perovskites and elemental composition per formula unit

Components	Ce-perovskite		Nb-perovskite		Cations per 3 oxygens		
	wt%	Range	wt%	Range			
Na ₂ O	1.74	1.58-2.02	0.40	0.24-0.53	Na	0.0812	0.0204
CaO	31.63	31.05-32.01	36.10	35.59-36.90	Ca	0.8174	0.9374
SrO	0.33	0.00-0.63	0.22	0.13-0.33	Sr	0.0047	0.0031
LREE ₂ O ₃	9.88	8.96-11.49	4.05	3.54-4.62	LREE	0.0868	0.0361
ThO ₂	0.47	0.00-0.80	n.d.		Th	0.0026	n.d.
Al ₂ O ₃	0.08	0.00-0.17	0.71	0.58-0.80	ΣA	0.9927	0.9970
Sc ₂ O ₃	0.26	0.20-0.34	n.d.		Al	0.0024	0.0202
TiO ₂	51.86	51.46-52.59	40.02	38.80-41.47	Sc	0.0055	n.d.
V ₂ O ₅	0.60	0.37-0.94	0.49	0.05-0.66	Ti	0.9407	0.7298
Fe ₂ O ₃	1.10	0.83-1.30	5.91	5.59-6.14	V	0.0095	0.0079
ZnO	0.26	0.00-0.67	n.d.		Fe ³⁺	0.0199	0.1078
GeO ₂	0.10	0.00-1.12	n.d.		Zn	0.0046	n.d.
ZrO ₂	0.03	0.00-0.21	0.76	0.37-1.33	Ge	0.0014	n.d.
Nb ₂ O ₅	1.52	1.24-1.97	11.16	10.08-12.26	Zr	0.0004	0.0090
Ta ₂ O ₅	0.10	0.00-0.36	n.d.		Nb	0.0166	0.1223
WO ₃	0.19	0.00-0.55	n.d.		Ta	0.0006	n.d.
Total	100.15		99.82		W	0.0012	n.d.
					ΣB	1.0028	0.9970

n.d., not detected.

Table 2. Chemical compositions of Ce- and Nb-perovskites and details of LREEs

Components	Ce-perovskite		Nb-perovskite	
	wt%	Range	wt%	Range
La ₂ O ₃	2.00	1.50-2.63	1.66	1.27-1.99
Ce ₂ O ₃	5.39	4.72-6.20	2.39	2.08-2.73
Pr ₂ O ₃	0.66	0.00-1.06	n.d.	
Nd ₂ O ₃	1.59	1.29-2.03	n.d.	
Sm ₂ O ₃	0.12	0.00-0.57	n.d.	
Eu ₂ O ₃	0.07	0.00-0.38	n.d.	
Gd ₂ O ₃	0.05	0.00-0.49	n.d.	
Total	9.88		4.05	
Cations per 3 oxygens				
La	0.0178		0.0149	
Ce	0.0476		0.0212	
Pr	0.0058		n.d.	
Nd	0.0137		n.d.	
Sm	0.0010		n.d.	
Eu	0.0005		n.d.	
Gd	0.0004		n.d.	
ΣLREE	0.0868		0.0361	

n.d., not detected.

and Nb for the B-sites. In this situation, as a constraint, the overall content of the three elements was 100% for each site.

For example, the occupancy of Na in Ce-perovskite at the A-site was fixed at 0.08. The site occupancy was subsequently refined using a model in which the remaining

92% of the A-site was occupied by Ca and Ce. The occupancy of Ce in Nb-perovskite at the A-site was fixed at 0.04. The site occupancies of Fe in Ce-perovskite and Nb in Nb-perovskite at the B-site were fixed at 0.02 and 0.13, respectively. The R1 indices ($=\Sigma||Fo|-|Fc||/\Sigma|Fo|$) of Ce- and Nb-perovskites converged to 0.0406 and 0.0228, respectively, using anisotropic displacement parameters. The crystal structure was illustrated using VESTA (Momma and Izumi, 2011). The structural refinement data, refined atomic coordinates, anisotropic displacement parameters, and selected geometric parameters are given in Tables 3, 4, and 5.

RESULTS AND DISCUSSION

Comparison of chemical compositions

The specimens include several guest and minor elements as substituents for Ca at the A-site and Ti at the B-site (Table 1). Compared to Nb-perovskite, Ce-perovskite contains higher amounts of minor elements such as light rare earth elements (LREEs), Th, Sc, Zn, Ge, Ta, and W. In particular, the total weight percent of LREEs was nearly 10% at the A-site in Ce-perovskite, and multiple REEs were detected (Table 2). Among LREEs, Ce is higher than La, and Ce is the third richest element after Ca and Na. On the other hand, La and Ce were the only REEs in Nb-perovskite. Nb occupies over 10% of the B-site instead of Ti in Nb-perovskite. Both perovskites

Table 3. Crystal data and structure refinement details of Ce- and Nb-perovskites

	Ce-perovskite	Nb-perovskite
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Pbnm</i>	<i>Pbnm</i>
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
Wavelength (Å)	0.71073	0.71073
Diffractometer	Rigaku XtaLAB Super Nova	Rigaku XtaLAB Super Nova
Unit cell dimensions		
a (Å)	5.4158(3)	5.4030(2)
b (Å)	5.4838(3)	5.4723(2)
c (Å)	7.7039(5)	7.6781(3)
Cell volume (Å ³)	228.80(2)	227.017(15)
c/ $\sqrt{2}$ a	1.0058	1.0049
c/ $\sqrt{2}$ b	0.9934	0.9921
Average	0.9996	0.9985
Crystal size (μ m)	72×57×24	83×58×42
2 θ range (°)	≤ 89.91	≤ 90.16
Range of h,k,l	-10 ≤ h ≤ 10 -10 ≤ k ≤ 10 -15 ≤ l ≤ 13	-10 ≤ h ≤ 10 -10 ≤ k ≤ 10 -15 ≤ l ≤ 14
Number of measured reflections	4023	5124
Number of independent reflections	662	876
Rint	0.0377	0.0286
R1 ($I \geq 2.0 \sigma(I)$)	0.0406	0.0228
wR ($I \geq 2.0 \sigma(I)$)	0.1015	0.0663
Goodness of fit, S	1.104	1.106
Largest diff. peak and hole e/Å ³	1.314/-1.658	0.864/-1.286

have more Nb than Zr. The elements such as Cr, Mn, Co, and Ni were present in low quantities although V was widely detected.

Local structure and valence state of Fe in solid solutions

Figure 1 shows the Fe *K*-edge XANES spectra of Ce-perovskite, Nb-perovskite, and reference Fe compounds. As reference samples for the valence state of Fe, trivalent Fe goethite (FeOOH), divalent and trivalent Fe mixture magnetite (Fe₃O₄), and predominantly divalent Fe wüstite (Fe_{1-d}O) were used. The chemical shift of the threshold energy at the absorption edge occurs in response to changes in the valence state. The threshold energy shifts to a higher energy state due to an increase in the cation oxidation number (Okudera et al., 2012). The XANES spectrum of Ce-perovskite tends to be similar to that of Fe₃O₄. Comparing the first derivative of the XANES spectrum (Fig. 1b), the three peaks of Fe in Ce-perovskite are at the same position as those in Fe₃O₄. Their shapes are also similar to those in Fe₃O₄ and different from those of

FeOOH. The peak located at about 7.126 keV in Figure 1b is mainly derived from Fe³⁺. This peak is low in Fe_{1-d}O, which has low Fe³⁺ content and is clearly different in height from the peak of Ce-perovskite. We estimated that the valence state of Fe in Ce-perovskite is the same as that in Fe₃O₄, and Fe²⁺ and Fe³⁺ exist in a ratio of approximately 1:2. The existence of divalent Fe is clear.

Conversely, the first derivative curve of the XANES spectrum of Nb-perovskite and its threshold energy is similar to FeOOH, and we determined that Fe in Nb-perovskite is trivalent. This result is consistent with previous reports (Mitchell et al., 1998, 2000) suggesting that Fe in the CaTiO₃ solid solution is trivalent. The valence states and local structures of Fe in Ce-perovskite and Nb-perovskite are significantly different. Although ferric ions tend to be substituted more favorably than ferrous ions, divalent Fe, Fe²⁺, certainly exists at the B-site in Ce-perovskite.

Site occupancy and charge balance in Ce- and Nb-perovskite

Based on the chemical analysis results (Table 1), the site

Table 4. Atomic coordinates, site occupancies, and anisotropic displacement parameters ($\text{\AA}^2$)

		Occ	x	y	z	U_{eq}
Ce-perovskite	A site	$\text{Ca}_{0.83(1)} + \text{Ce}_{0.09(1)} + \text{Na}_{0.08}$	-0.00622(8)	0.03317(11)	0.25	0.01380(12)
	B site	$\text{Ti}_{0.96(1)} + \text{Fe}_{0.02} + \text{Nb}_{0.02(1)}$	0	0.5	0	0.01013(11)
	O1		0.42730(4)	-0.01740(5)	0.25	0.0161(4)
	O2		0.2100(3)	0.2100(3)	-0.0384(2)	0.0153(3)
Nb-perovskite	A site	$\text{Ca}_{0.94(1)} + \text{Ce}_{0.04} + \text{Na}_{0.02(1)}$	-0.00667(4)	0.03579(6)	0.25	0.00994(6)
	B site	$\text{Ti}_{0.76(1)} + \text{Fe}_{0.11(1)} + \text{Nb}_{0.13}$	0	0.5	0	0.00631(6)
	O1		0.42660(19)	-0.01776(18)	0.25	0.00886(16)
	O2		0.20975(12)	0.21041(12)	-0.0350(10)	0.00876(11)
CaTiO ₃ (Beran and Libowitzky, 1996)	A site	Ca	-0.00648(8)	0.0356(1)	0.25	0.00813
	B site	Ti	0	0.5	0	0.00520
	O1		0.4289(3)	-0.0161(3)	0.25	0.00710
	O2		0.2103(2)	0.2112(2)	-0.0373(2)	0.00733

		U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ce-perovskite	A site	0.01318(19)	0.0155(2)	0.01277(19)	0	0	-0.00195(16)
	B site	0.01006(18)	0.01065(19)	0.00968(18)	0.00089(12)	-0.00003(12)	0.00011(14)
	O1	0.0177(9)	0.0192(11)	0.0113(7)	0	0	-0.0020(8)
	O2	0.0140(5)	0.0136(6)	0.0181(6)	-0.0012(6)	-0.0006(5)	0.0034(5)
Nb-perovskite	A site	0.00917(10)	0.01087(10)	0.00979(11)	0	0	-0.00168(6)
	B site	0.00648(9)	0.00693(9)	0.00553(9)	0.00038(5)	0.00009(5)	0.00000(4)
	O1	0.0100(3)	0.0114(4)	0.0051(3)	0	0	-0.0011(3)
	O2	0.0080(2)	0.0080(2)	0.0102(2)	-0.0010(2)	-0.0007(2)	0.00210(19)
CaTiO ₃ (Beran and Libowitzky, 1996)	Ca site	0.0082(2)	0.0083(2)	0.0079(2)	0	0	-0.0016(2)
	Ti site	0.0059(2)	0.0052(2)	0.0045(2)	0.00025(9)	0.0000(1)	0.0000(1)
	O1	0.0082(6)	0.0086(7)	0.0045(5)	0	0	-0.0002(5)
	O2	0.0065(4)	0.0060(4)	0.0095(4)	-0.0010(3)	0.0008(3)	-0.0020(4)

Table 5. Selected interatomic distances ($\text{\AA}$), bond angles ($^\circ$), observed tolerance factors of Ce- and Nb-perovskites

		Ce - perovskite		Nb - perovskite	
Space group		<i>Pbnm</i>	<i>Pbnm</i>		
A -	O1	$\times 1$	2.364(3)	2.3592(11)	
	O1	$\times 1$	2.501(3)	2.4811(11)	
	O1	$\times 1$	3.049(3)	3.0599(11)	
	O1	$\times 1$	3.080(3)	3.0760(11)	
	O2	$\times 2$	2.3777(17)	2.3783(8)	
	O2	$\times 2$	2.6463(17)	2.6294(8)	
	O2	$\times 2$	2.6922(17)	2.6809(8)	
	O2	$\times 2$	3.2636(17)	3.2636(8)	
Mean (8 coordination)			2.537	2.527	
Mean (12 coordination)			2.746	2.740	
B -	O1	$\times 2$	1.9681(5)	1.9625(3)	
	O2	$\times 2$	1.9699(17)	1.9679(7)	
	O2	$\times 2$	1.9774(17)	1.9705(7)	
Mean			1.9718	1.9670	
$\angle \text{B} - \text{O1} - \text{B}$			155.00(10)	155.00(5)	
$\angle \text{B} - \text{O2} - \text{B}$			156.24(13)	155.98(6)	
V (TiO ₆)			10.2195	10.1446	
			Observed tolerance factor*		
AO(8)/ $\sqrt{2}$ BO			0.9100	0.9084	
AO(12)/ $\sqrt{2}$ BO			0.9847	0.9850	

* Sasaki et al., 1983.

Figure 1. (a) Fe *K*-edge XANES spectra of Ce-perovskite, Nb-perovskite, and reference iron compounds. The spectrum intensity of the samples in a way that the intensity at threshold energy is 1.0. (b) First derivatives of the Fe *K*-edge XANES spectra of Ce-perovskite, Nb-perovskite, and reference iron compounds.

preference of each cation in terms of ionic radius, site occupancy refinements by diffraction experiments (Table 3), and XANES analysis (Fig. 1), the structural formula of Ce- and Nb-perovskites are shown below:

where the estimated total valence at each site is shown on the right shoulder.

The valence state of Fe occupying the octahedral B-site is similar to that of magnetite, as seen from the XANES analysis. The ionic radius of $^{\text{VIII}}\text{Ca}^{2+}$ is 1.00 Å, which has the smallest size among the A-site cations (Shannon, 1976). Other cations occupying the A-site have a larger ionic radius than Ca (Table 1). The ionic radius of $^{\text{VI}}\text{Ti}^{4+}$ is 0.605 Å, which is the primary ion of the B-site. Similar to A-site, as the second most abundant cation in the B-site, Nb has a larger ionic radius ($^{\text{VI}}\text{Nb}^{5+} = 0.64$) than Ti, and the B-site in the perovskite solid solutions also tends to attract large cations. The ionic radii of $^{\text{VI}}\text{Fe}^{2+}$ and $^{\text{VI}}\text{Fe}^{3+}$ are 0.78 and 0.645 Å, respectively. The ionic radius of $^{\text{VIII}}\text{Fe}^{2+}$ is expected to increase to 0.92 Å as the coordination number increases, but Fe^{2+} seems to prioritize the B-site over the A-site.

In the Ce- and Nb-perovskites, the total valences are 2.00 and 2.01 at the A-site and 4.00 and 3.99 at the B-site, respectively. These are almost the ideal values of divalent and tetravalent ions. Surprisingly, elements with different valence states were present at both sites to obtain ideal valences. Divalent zinc and ferrous ions with lower valences than tetravalent ions are substituted in the B-site of Ce-perovskite. The total charge balance of 4.00 at the B-site is maintained by several ions with higher valences than tetravalent ions.

Crystal structures and degree of average distortion of Ce- and Nb-perovskite

The lattice constants a_o , b_o , and c_o of the orthorhombic perovskite structure ($Pbnm$) have the following relationship with those of the pseudo-cubic structure: $a_o = \sqrt{2}a_c$, $b_o = \sqrt{2}a_c$, and $c_o = 2a_c$. The degree of deviation from the cubic structure can be compared using the following relationship: $c_o/\sqrt{2}a_o$ and $c_o/\sqrt{2}b_o$. In Figure 2, we compared the axial ratio of lattice constants ($c/\sqrt{2}a$, $c/\sqrt{2}b$, and the average of both) as an index of deviation from cubic perovskite. The horizontal axis represents the amount of substitution of different elements for Ca at the A-site. The axial ratios of the synthetic orthorhombic perovskite ($\text{Ca}_{1-x}\text{Sr}_x\text{TiO}_3$) solid solution (Yamanaka et al., 2002)

Figure 2. The axial ratios ($c/\sqrt{2}a$, $c/\sqrt{2}b$, and their average) versus the substitutional amounts in the A-site of orthorhombic Ce-perovskite, Nb-perovskite, and synthetic $\text{Ca}_{1-x}\text{Sr}_x\text{TiO}_3$ solid-solutions (Yamanaka et al., 2002). Differences from the ideal cubic perovskite were compared to the c -axis. Distortions in the directions of the a - and b -axes and their average are shown.

were plotted together for comparison. The additional effect of substituting the B-site atom can also be verified by comparing it with the (Ca,Sr)TiO₃ solid solution. The axial ratios of Ce- and Nb-perovskites deviate from the ideal value of 1.0 for cubic perovskite. Deviations on the a - and b -axes are less than 1%. The average axial ratios of $c/\sqrt{2}a$ and $c/\sqrt{2}b$ are close to the ideal value of 1.0. The a -axis is shorter, and the b -axis is longer than the $c/\sqrt{2}$ axis. Substitution at the A-site increases the axial ratio, and substitution at the B-site increases the difference between the a - and b -directions. In Ce- and Nb-perovskites, $c/\sqrt{2}b$ is 1.0 or greater than $c/\sqrt{2}a$, showing that the deviation is significant in the direction of the b -axis.

The degree of distortion of the perovskite structure is indicated by the observed tolerance factor $t_{obs} = \langle \text{A-O} \rangle / \sqrt{2} \langle \text{B-O} \rangle$, where $\langle \text{A-O} \rangle$ and $\langle \text{B-O} \rangle$ are the mean interatomic distances of 12 coordinates at the A-site and six coordinates at the B-site, respectively (Sasaki et al., 1983). For pure CaTiO_3 , $t_{obs} = 0.9856$, (Sasaki et al., 1987). The observed tolerance factors, t_{obs} , for Nb-perovskite and Ce-perovskite are 0.9850 and 0.9848, respectively (Table 5). In the orthorhombic perovskite structure, the angle reduction of $\angle \text{B-O1-B}$ and $\angle \text{B-O2-B}$ from 180° is used as an indicator of the tilting and rotation angles of the BO₆ octahedron in the BO₃ framework (Sasaki et al., 1983, 1987). Both bond angles are 180° in the cubic perovskite structure and decrease as the degree of distortion of the BO₃ framework increases. The angles of $\angle \text{B-O1-B}$ and $\angle \text{B-O2-B}$ are 155.00(10)° and 156.24(13)° for Ce-perovskite and 155.00(5)° and 155.98(6)° for Nb-perovskite, respectively. The angles for both solid solutions are smaller than those for pure perovskite ($\angle \text{B-O1-B} = 156.3^\circ$ and $\angle \text{B-O2-B} = 158.7^\circ$; Sasaki et al., 1987). From the tolerance factor and the tilting and rotation angles of

the BO_6 octahedron, the structures of Ce- and Nb-perovskites can be considered to be more distorted than pure CaTiO_3 . The transition temperatures from the orthorhombic phase to tetragonal and cubic phases may be higher in Ce- and Nb-perovskites.

Local distortions around titanium, zirconium, and niobium in solid solutions detected by XANES spectra

Characterization of the K -edge XANES spectra of $3d$ and $4d$ transition metals is useful for understanding materials in earth sciences. XANES features are sensitive to electronic and geometric structures around the X-ray absorbing central atom (Vedrinskii et al., 1998; Yamamoto, 2008; Boye et al., 2011; Yogi et al., 2011). The pre-edge peak features at the Ti K -edge have been widely studied by comparing the XANES spectra of different compositions (Grunes, 1983; Ravel et al., 1993; Ravel and Stern, 1995; Farges et al., 1997; Joly et al., 1999; Wang et al., 2011). Three clear pre-edge peaks of six-coordinated titanium oxide have been observed in many compounds and are usually called A1, A2, and A3 peaks in the order of increasing energy. The A1 and A3 peaks are assigned to the electric quadrupole and electric dipole transitions, respectively (Joly et al., 1999). Absorption into the orbital that forms the A2 peak is allowed by a mixture of dipole and quadrupole transitions. The absorption of the A2 peak can increase, owing to distortions around Ti atoms (Yamamoto, 2008). The pre-edge peak intensity of the X-ray absorbing atoms depends on the degree of distortion induced by temperature, pressure, electron orbital hybridization, and compositional changes (Itié et al., 2006; Yoshiasa et al., 2018). The differences in the intensities of the three pre-edge peaks reflect the magnitude of various local distortions. The intensities of the pre-edge peaks increase with increasing local distortions around the X-ray absorbing atom.

The Ti K -edge XANES spectra for Ce- and Nb-perovskites are shown in Figure 3a with the XANES spectra of pure synthetic CaTiO_3 as a reference. The A1, A2, and A3 peaks in the Ce- and Nb-perovskites have different intensities from pure synthetic CaTiO_3 (Fig. 3b). The heights of the A2 peaks for Ce- and Nb-perovskites are higher than those for pure CaTiO_3 , and the shapes of the A3 peak are different from those of pure CaTiO_3 . The A2 peak is the highest in Ce-perovskite. The A3 peak in Nb-perovskite is characteristically split into two peaks: A3 and A3'. The probability of electron transition from orbital $1s$ to $3d$ of Ti atoms in Ce- and Nb-perovskites is different from that in pure CaTiO_3 . This observation indicates that local distortions around Ti atoms in Ce- and Nb-perovskite solid solutions increase (Hiratoko et al., 2013; Naka-

Figure 3. (a) The Ti K -edge XANES spectra of Ce-perovskite, Nb-perovskite, and pure CaTiO_3 . (b) A detailed comparison of the Ti K -edge XANES spectra around the pre-edge peaks of Ce-perovskite, Nb-perovskite, and pure CaTiO_3 .

tani et al., 2016; Tobase et al., 2018; Yoshiasa et al., 2018). The heights of the post-edge peaks are lower in Ce- and Nb-perovskites, and the shapes are broader than those in CaTiO_3 .

The effects of local distortions, such as declination vibration, on the shape of the XANES spectrum differ between the pre-edge and post-edge peaks behind the threshold energy of the X-ray absorption edge. The heights of the pre-edge peaks increase with increasing distortion, while those of the post-edge peaks decrease due to the Debye-Waller type damping effect (Hiratoko et al., 2013; Yoshiasa et al., 2018). Figure 4 shows the Zr K -edge XANES spectra in Ce- and Nb-perovskites. The shapes of these XANES spectra are similar to those reported for other perovskite-type compounds (e.g., Greigor et al., 2001). However, the heights of the pre-shoulder and the first and second peaks are different. Although the XANES spectra of both samples are different, no chemical shifts are observed at the threshold energy. Therefore, it can be concluded that the oxidation state of Zr is the same in both samples. The second top peak intensity in the XANES spectrum of Ce-perovskite is lower than that of Nb-perovskite. Figure 5 shows the Nb K -edge XANES spectrum in Ce- and Nb-perovskite. XANES spectra with similar patterns have been reported for other perovskite-type compounds (Nakayama et al., 2003). It is considered that there is no difference in the valence state of Nb between both samples. Although

Figure 4. Zr K -edge XANES spectra of Ce- and Nb-perovskites.

Figure 5. Nb K -edge XANES spectra of Ce- and Nb-perovskites.

the XANES shapes of both samples are essentially similar, the top peak intensity in the XANES spectrum of Ce-perovskite is lower than that of Nb-perovskite.

The decrease in the top peak intensities of the Zr and Nb K -edge XANES spectra is evident in Ce-perovskite, and the tendency for changes is common in both spectra. The intensity of the top peak decreases, the valleys become shallower, and local distortions increase (Farges and Rossano, 2000; Piilonen et al., 2006). Local environments around Zr and Nb at the octahedral site in Ce-perovskite are more distorted than those in Nb-perovskite. The displacement parameters (U_{eq}) of the B-, O1-, and O2-atoms of Ce-perovskite determined by diffraction experiments (Table 4) are almost twice the displacement parameters of Nb-perovskite. The value of U_{eq} for the A-atom is also 1.4 times larger. The local distortions around Zr and Nb, which occupy the six-coordinate octahedral sites in Ce-perovskite, are much larger than the distortions

Figure 6. Th L_{III} -edge XANES spectra of Ce-perovskite and Th-bearing $CaSiO_3$ (Greaux et al., 2012).

in Nb-perovskite and do not correspond to the concentration of these elements. Many years have passed since the crystallization of these natural samples. As will be discussed later, this is considered to be due to the influence of radioactive Th in Ce-perovskite. There is a high possibility that metamictization will proceed in Ce-perovskite due to the damage caused by radiation destruction.

Effects of radioactive decay of actinoid element Th on Ce-perovskite

Figure 6 shows the Th L_{III} -edge XANES spectrum of Ce-perovskite. No significant amount of Th was detected in Nb-perovskite. The XANES spectrum of Ce-perovskite was compared with synthesized high-pressure cubic perovskite-type $CaSiO_3$ containing Th (Greaux et al., 2012). Although the chemical compositions and site symmetry of both samples are different, the XANES shapes are essentially similar. Since natural Ce-perovskite is a solid solution of many heavy elements such as REEs and Fe, the backscattering amplitude of X-ray scattering atoms in Ce-perovskite is large. Therefore, most peak heights should be higher than those in $CaSiO_3$. The height of the second peak is significantly shorter in natural Ce-perovskite. This is probably a damping effect due to increased distortion (Farges and Rossano, 2000; Piilonen et al., 2006). This attenuation may have occurred by local damage caused by the radioactive decay of Th.

Displacement parameter of each atom in Ce- and Nb-perovskite

Table 4 presents the anisotropic displacement parameters of each atom in Ce-perovskite, Nb-perovskite, and

Figure 7. Crystal structures of Ce-perovskite, Nb-perovskite (in this study), and CaTiO₃ (Beran and Libowitzky, 1996) projected along the *c*-axis. Displacement ellipsoids represent a 90% probability. Color version is available online from <https://doi.org/10.2465/jmps.200424>.

CaTiO₃ (data from Beran and Libowitzky, 1996) collected through diffraction experiments. Figure 7 shows displacement ellipsoids with a probability of 90%. The displacement ellipsoids of all atoms in Ce-perovskite expand while maintaining their anisotropic shapes. Displacement parameters obtained from diffraction experiments include the effects of static and dynamic disorders. The anisotropic displacement parameters of all Ce-perovskite atoms are considerable compared to those of Nb-perovskite and pure CaTiO₃ (Table 4). In particular, the displacement values of the B-sites and O-sites in Ce-perovskite are more than 1.5 times those in Nb-perovskite and pure CaTiO₃, indicating that the structural fluctuation due to static disorder is large. In Ce-perovskite, 83% of A-sites and 96% of B-sites are occupied by Ca and Ti, respectively. In Nb-perovskite, 94% of A-sites are occupied by Ca, and 76% of B-sites are occupied by Ti. The difference in ionic radii (Shannon, 1976) between Ti ($r_{\text{Ti}^{4+}}^{\text{VI}} = 0.605 \text{ \AA}$) and Nb ($r_{\text{Nb}^{5+}}^{\text{VI}} = 0.64 \text{ \AA}$), which occupy the B-sites, is significantly larger than that between Ca and other ions, which occupy the A-sites.

Therefore, the effects of ions of various sizes on positional displacements estimated to be less than $0.005 \text{ \AA}$ should be maximized at the B-site in Nb-perovskite. The root mean square displacements of U_{eq} at the B-sites in Ce-perovskite and Nb-perovskite are 0.101 and $0.079 \text{ \AA}$, respectively, and the difference between these values is $0.022 \text{ \AA}$. The difference between the values of the O1 sites in Ce-perovskite and Nb-perovskite is $0.033 \text{ \AA}$. Such differences between the sites in both perovskites indicate that the positional displacements in Ce-perovskite are several times greater than those resulting from the substitution of ions of different sizes (Table 4). It is believed that Ce-perovskite crystals become metamictic due to the radioactive decay of the actinoid element Th. The amounts of Zr and Nb at the octahedral sites in Ce-perovskite are less than those in Nb-perovskite, and the effect of ion size is small. However, the positional displacements around the B-sites in Ce-perovskite are considerably large due to damage from radioactive decay.

Compared to Nb-perovskite, the increase in U_{eq} of the A-atom in Ce-perovskite is smaller than that of the B-, O1-, and O2- atoms (Table 4). This phenomenon may be explained by the extensive damage around the A-site occupied by Th. The increased displacement parameter due to radioactive decay damage can also be observed for zircon in ZrSiO₄ (Tokuda et al., 2019).

CONCLUSION

The natural CaTiO₃ perovskite solid solutions contain various elements. Various lanthanoid and actinoid elements such as Th are substituted for Ca at the A-site, while Fe^{3+} , Fe^{2+} , Zr, and Nb occupy the B-site by replacing Ti. Although Fe^{3+} substitutions have been reported mainly in CaTiO₃ solid solutions, the oxidation state of the divalent Fe ions observed in Ce-perovskite was different for each perovskite solid solution. In these samples, the total charges at the A- and B-sites were strictly divalent and tetravalent, respectively, and an ideal charge balance was achieved at each site. Because of the substitution of Zr, Nb, and Fe, the local distortion of Ti at the octahedral site of the solid solution is greater than that of the CaTiO₃ endmember. Therefore, the pre-edge intensity of electron transitions from the $1s$ orbital to the $3d$ orbital is high. In a perovskite solid solution containing the actinoid element Th, the radioactive decay of Th seems to affect the crystal structure. Displacement parameters, including the effects of the static disorder, characteristically increase with metamictization, particularly at the B- and O-sites. Differences in the degree of distortion of perovskite-type structures, such as those associated with the tolerance factors in Ce- and Nb-perovskites, arise from differences in chemical composition. The effect of metamictization primarily appears as an increase in the displacement parameters of all atoms.

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SUPPLEMENTARY MATERIAL

Color version of Figure 7 is available online from <https://doi.org/10.2465/jmps.200424>.

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