

Rapid communication

Site occupancy determination for manganese in some spinel-type oxides by $K\beta$ X-ray fluorescence spectra

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Abstract

Site occupancy of cations in spinel-type oxides is sometimes extremely difficult to solve by the conventional crystallographic analysis based on diffraction methods. The present report describes successful determination for manganese spinels by analyzing $K\beta$ X-ray fluorescence spectra, which are essentially sensitive to chemical environments such as oxidation and/or coordination numbers. Instead of looking at peak positions and/or shapes of the spectra, the intensity ratios of $K\beta'$ satellite and $K\beta_5$ lines were investigated in detail. It has been found that the spectra are apparently classified depending on the manganese site occupancy whether tetrahedral A or octahedral B. Applications to some spinel-type oxides, for which the manganese states have not yet been fully solved so far, were also discussed.

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1. Introduction

Spinel-type oxides, AB_2O_4 , take a structure described as a densely packed oxygen array with A and B cations in tetrahedral and octahedral coordination, respectively. Because 3d-transition metals often take various oxidation states, and occupy either sites A or B in spinel-type oxides, the determination of those structural parameters has become an important subject. Manganese behavior in spinels is also complex due to the tendency of Mn to exist in two main oxidation states, Mn(II) and Mn(III). Because the knowledge of cation distribution is important in gaining an understanding of the physical and magnetic properties of Mn ferrites in a single example, elaborate studies using X-ray diffraction (XRD) [1] or X-ray absorption fine structure (XAFS) [2] have been performed.

In this study, X-ray fluorescence (XRF) was employed to determine oxidation states and site occupancy. XRF analysis is a convenient method for identifying elements and determining the quantity contained in a material. It can not only investigate the composition of a material, but also indicate the chemical states of elements. For example, slight shifts in the energy of XRF lines or detailed changes in spectral profiles show chemical effects. In order to observe such faint signals, high-energy resolution (lower than 1 eV) is required for spectral observation. However, one can also observe chemical effects in terms of the changes in the relative intensity of XRF lines provided that middle-energy resolution (around 10 eV for 3d-transition metals) is maintained. Recently, a wavelength-dispersive spectrometer with downsized Johansson-type focusing optics was successfully developed as an alternative to a conventional Si(Li) detector system, and applied to trace XRF analysis using synchrotron radiation (SR) [3–6]. The present spectrometer is not only highly sensitive with respect to ultra trace elements, but is also

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extremely feasible for obtaining chemical information, because the suitable downsizing satisfied both detection efficiency and reasonable energy resolution. $K\beta$ XRF spectra of Mn compounds were observed using the spectrometer, and $K\beta'$ and $K\beta_5$ intensities were obtained. The $K\beta'$ – $K\beta_5$ correlation map demonstrated that chemical species are classified by their location on the map, indicating that the $K\beta$ spectrum of an unknown sample can identify the state of the Mn it contains [7]. In this study, Mn $K\beta$ spectra for a dozen spinel-type double oxides were observed. The relation between $K\beta$ spectra and both oxidation number and site occupancy of Mn are discussed, and the manganese states for some compounds, MnGa₂O₄, MnCo₂O₄ and CrMnCoO₄, are determined.

2. Experimental

2.1. Preparation of samples

A dozen manganese-containing spinel-type double oxides were prepared as follows:

- LiMn₂O₄: Li₂CO₃ and MnO₂ (molar ratio Mn:Li = 2:1) were mixed with an agate mortar, pressed into a pellet, and heated at 800 °C for 15 h in a furnace.
- Li(Mg_{1/6}Mn_{11/6})O₄: Synthesized powder from carbonates [8] was supplied by Ishizawa et al.
- ZnMn₂O₄ and Zn_{1-x}Mn_{2+x}O₄ ($x=0.25, 0.5, 0.75$): Pellets of Mn₂O₃ and ZnO mixtures (Mn:Zn = 2:1 and 2 + x :1 - x) heated at 950 °C, 12 h.
- MnCr₂O₄ and Mn_{1+y}Cr_{2-y}O₄ ($y=0.25, 0.5, 0.75, 0.8$): Pellets of Mn₃O₄ and Cr₂O₃ mixtures (Mn:Cr = 1:2 and 1 + y :2 - y), heated at 1550 °C, 10 h.
- MnGa₂O₄: A pellet of MnO and Ga₂O₃ mixture (Mn:Ga = 1:2) heated at 1000 °C, 3 h followed by heating at 1200 °C, 3 h.
- MnCo₂O₄: An aqueous solution containing MnCl₂ and CoCl₂ (Mn:Co = 1:2) with concentrated HNO₃ was heated in a beaker on a hotplate, and evaporated to dryness. The collected residue was heated at 800 °C for 10 h in a furnace.
- CrMnCoO₄: An aqueous solution containing equimolar CrCl₃, MnCl₂ and CoCl₂ was heated in a beaker on a hotplate, and evaporated to dryness. Heating was continued at 350 °C until the deposit turned black [9].

Each product was checked by X-ray diffraction using CuK α radiation. It was also analyzed by X-ray absorption fine structure (XAFS) spectra using SR. A chip of each product was used for $K\beta$ spectral measurement. Some samples obtained as powder were pressed into small pellets and used for measurements.

Pellets of some manganese oxides were also prepared from powders of chemicals (MnO, Mn₃O₄, Mn₂O₃ and MnO₂, 99.9%, Furuuchi Chemicals Co.).

2.2. Spectral observation

$K\beta$ spectra were observed with quasi-monochromatic X-rays at BL40XU, SPring-8. The ID gap was set at 10.8 mm so that the fundamental peak came to 10.0 keV. The spectrometer used in this experiment for $K\beta$ spectra collection was an efficient compact spectrometer [5] with a Ge(220), $R=100$ mm Johansson analyzing crystal (CRISMATEC, France) and a YAP:Ce scintillation detector. In order to prevent the saturation of the detector as well as radiation damage to the sample, a 0.6-mm thick aluminum plate was used as X-ray absorber to attenuate incident X-rays. The X-ray beam was restricted by a slit to a size of 0.07 mm (H) \times 0.03 mm (V) at the sample surface. The X-ray fluorescence spectrum was observed by step scanning of the crystal and the scintillation counter. The measuring time was 5–10 s/point, and \approx 15–30 min for 180 points to obtain a spectrum.

3. Results and discussion

Formal oxidation numbers and site occupancy of Mn in some spinel-type double oxides are already known. They are summarized in Table 1 ((1)–(6)). In LiMn₂O₄, Li prefers site A and Mn prefers site B as long as the deviation from the stoichiometry is small [10,11]. Therefore, almost all Mn occupy site B (normal spinel) and have a formal oxidation number of 3.5. Li(Mg_{1/6}Mn_{11/6})O₄ was analyzed precisely by synchrotron X-ray, and octahedrally coordinated Mn atoms have been confirmed by both Mn-K XAFS and powder diffraction studies [8]. The same sample was used in this study. In the near edge part of XAFS spectrum, the above LiMn₂O₄ and Li(Mg_{1/6}Mn_{11/6})O₄ were similar to each other, and a slight shift of the absorption edge of Li(Mg_{1/6}Mn_{11/6})O₄ to higher energy was very reasonable as Mn in it has the formal oxidation number of 3.64. ZnMn₂O₄ is also a normal spinel and Mn(III) occupies site B [12]. When the Mn/Zn ratio is more than 2, excess Mn ions replace Zn ions in site A as Mn(II) [13]. In XAFS spectra, the chemical shift toward lower energy indicates the decrease of average oxidation number, one can see that the pre-edge peak intensity, which is characteristic for Mn in site A, becomes significant with the increase of x in Zn_{1-x}Mn_{2+x}O₄. MnCr₂O₄ is also a normal spinel and Mn(II) occupies site A in this case [14]. When the Mn/Cr ratio is more than $\frac{1}{2}$ excess Mn ions replace chromium ions in site B as Mn(III) [15,16]. This was also confirmed by XAFS spectra for the samples prepared in this research. For the three oxides

Table 1
Spinel-type double oxides prepared in this research and manganese states in them

Compounds	Oxidation numbers	Occupancy		Reference no.
		Site A	Site B	
(1) LiMn_2O_4	3.5	0	2	[10,11]
(2) $\text{Li}(\text{Mg}_{1/6}\text{Mn}_{11/6})\text{O}_4$	3.64	0	2	[8]
(3) ZnMn_2O_4	3	0	2	[12]
(4) $\text{Zn}_{1-x}\text{Mn}_{2+x}\text{O}_4$ ($x = 0.25, 0.5, 0.75$)	$(6 + 2x)/(2 + x)$	x	2	[13]
(5) MnCr_2O_4	2	1	0	[14]
(6) $\text{Mn}_{1+y}\text{Cr}_{2-y}\text{O}_4$ ($y = 0.25, 0.5, 0.75, 0.8$)	$(2 + 3y)/(1 + y)$	1	y	[15,16]
(7) MnGa_2O_4	2	<1	>0	[17] & this study
(8) MnCo_2O_4	3	0	1	[18] & this study
(9) CrMnCoO_4	3	0	1	This study

Here, occupancy is described by the number of Mn atoms in each site per chemical formula.

(1)–(6): normal spinel, (7) partly inverse spinel and (8) inverse spinel.

in the lower column in Table 1 ((7)–(9)), it was not clear which site the Mn occupied. The oxidation numbers in (8) and (9) also remained to be determined. The manganese states of the three oxides were determined and verified in this research as described later.

$K\beta$ spectra observed in this experiment are shown in Figs. 1(a)–(c). It is possible to see satellite lines $K\beta'$ (observed at the lower energy side of $K\beta_{1,3}$) and $K\beta''$ (higher energy side of $K\beta_{1,3}$). The $K\beta_5$ line is observable at the higher energy side of $K\beta''$. It is known that the $\text{Mn}K\beta_{1,3}$ shows a shift towards lower energy with increasing Mn oxidation state [19], and that the magnitude of energy splitting between $K\beta'$ and $K\beta_{1,3}$ depends on each compound [20] as observed in high-resolution spectrum. In the present research, however, instead of looking at the peak position, the line intensities of $K\beta'$ and $K\beta_5$ are investigated. Apparently, the experiment does not require such a high-energy resolution, and therefore the analysis is fairly stable. Fig. 1(a) shows the spectra for manganese oxides of different oxidation states. These spectra have been well studied in past years, and as clearly seen in the figure, the intensity of $K\beta'$, which is caused by an exchange interaction and/or plasmon oscillation [21–23], tends to decrease, while $K\beta_5$, to which cross-over transitions from O-2p to Mn-1s contribute [24], tends to increase when the Mn oxidation number increases. In this study, normalized values of $K\beta'$ and $K\beta_5$ were calculated for numerical investigations. Raw intensities were simply obtained by integration from a linear baseline instead of a more sophisticated but complicated way, i.e. curve fitting etc. The baseline was drawn under $K\beta'$ line to be tangential to the slope of low-energy side of $K\beta_{1,3}$. The intensities were normalized by net intensity of the whole $K\beta$ spectra. From a statistical point of view, the intensities obtained here are satisfactory, because even relatively weak $K\beta_5$ gives typically more than 10k counts. Therefore, the statistical error of counting is less than 1%. A more serious error may come about through spectral distortion caused by a misalignment of

the X-ray optics, though the error range is difficult to estimate exactly. In this research, in order to reduce such error, spectral measurement was repeated over three times per sample and an average intensity was adopted. The $K\beta'$ and $K\beta_5$ intensities of oxides obtained from the spectra in Fig. 1(a) and double oxides some spectra of them are shown in Fig. 1(b) are listed in Table 2. In order to compare $K\beta'$ intensities for many samples clearly, oxidation number versus $K\beta'$ relative intensity are plotted in Fig. 2(a). As seen in the figure $K\beta'$ intensity of the oxides shows almost linear dependence on the oxidation number.

In Fig. 2(b) average coordination number versus $K\beta_5$ relative intensity is given. Oxides MnO , Mn_2O_3 and MnO_2 have Mn ions coordinated by six O ions. Mn_3O_4 takes spinel structure also, though it is distorted, therefore one-third of the Mn has a coordination number four (site A) and two-thirds have six (site B). For a spinel-type oxide, MnCr_2O_4 has a Mn(II) ion occupying site A, therefore coordination number is four. In contrast, both LiMn_2O_4 and ZnMn_2O_4 have Mn in site B, coordination number six. As shown in the figure, $K\beta_5$ intensity shows almost linear correlation to the coordination number. However the oxides of coordination number six show dispersion, and they arrange in the order of oxidation number with the $K\beta_5$ increase, except for Mn_2O_3 . The result shows that the $K\beta_5$ intensity is affected by not only coordination number, but also by oxidation number. In the case of Mn_2O_3 , it takes scandium-oxide structure, and in which there are two types of Mn ions coordinated by six O ions. One of them (three quarters of Mn in Mn_2O_3) is coordinated by four O in shorter distances and two O in relatively longer distance, while both MnO and MnO_2 have regularly coordinated Mn ions as far as distance is concerned. The square-like coordination by four O in Mn_2O_3 may make the $K\beta_5$ intensity smaller.

$K\beta'$ – $K\beta_5$ relative intensity correlation map are shown in Fig. 2(c). On the map the spinel series are on the correlation curve in the order of the oxidation numbers

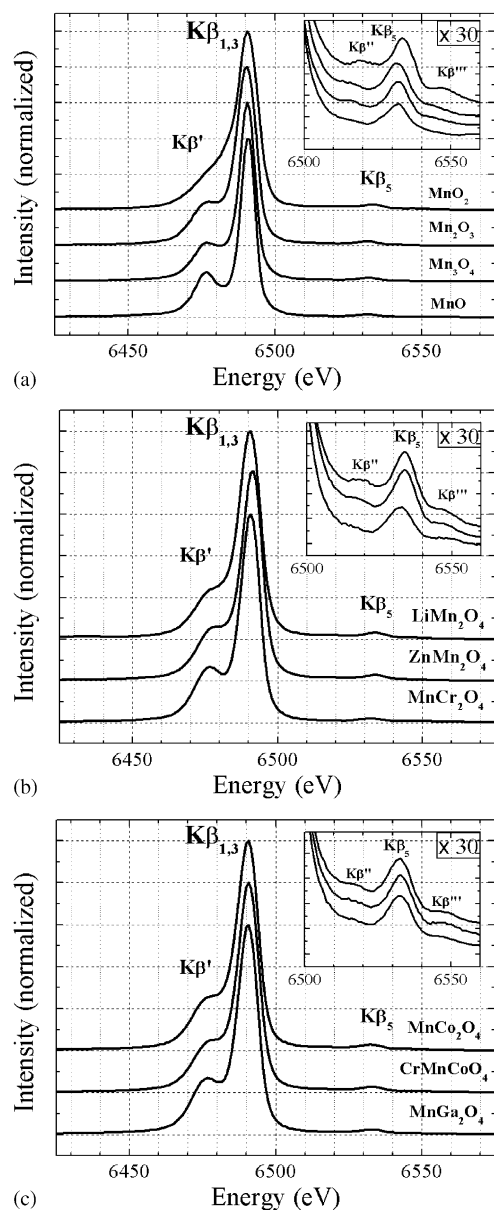


Fig. 1. $K\beta$ spectra of manganese spinel oxides. The measurement was 180 points for one spectrum and the measuring time was 5–10 s/point: (a) manganese oxides of different oxidation numbers, (b) LiMn_2O_4 , ZnMn_2O_4 and MnCr_2O_4 , and (c) MnCo_2O_4 , CrMnCoO_4 and MnGa_2O_4 .

and site B occupancies. MnCr_2O_4 is located in the lower-right part, while both LiMn_2O_4 and ZnMn_2O_4 are located in the upper-left part in the order of oxidation number. The increase in x in $\text{Zn}_{1-x}\text{Mn}_{2+x}\text{O}_4$ (up to 1, Mn_3O_4) makes the position shift to lower-right direction with the decrease of site B occupancy and manganese oxidation number. The increase in y in $\text{Mn}_{1+y}\text{Cr}_{2-y}\text{O}_4$ brings upper-left direction in the map with the increases in both manganese oxidation number and site B occupancy. Although Mn(III) exhibits the Jahn-Teller effect and Mn_3O_4 and ZnMn_2O_4 have tetragonal distortions, the effect seems to have no special influence

Table 2

Relative integrated intensities of $K\beta'$ and $K\beta_5$

Compounds	$K\beta'/K\beta$ ($\times 10^{-2}$)	$K\beta_5/K\beta$ ($\times 10^{-3}$)
MnO	7.63	10.0
Mn_3O_4	4.31	10.1
Mn_2O_3	3.47	9.62
MnO_2	0.792	11.0
LiMn_2O_4	1.37	10.9
$\text{Li}(\text{Mg}_{1/6}\text{Mn}_{11/6})\text{O}_4$	1.58	10.9
ZnMn_2O_4	2.63	10.7
$\text{Zn}_{1-x}\text{Mn}_{2+x}\text{O}_4$		
$x = 0.25$	3.11	10.3
$x = 0.5$	3.36	10.3
$x = 0.75$	3.64	10.3
MnCr_2O_4	6.07	7.96
$\text{Mn}_{1+y}\text{Cr}_{2-y}\text{O}_4$		
$y = 0.25$	5.28	8.10
$y = 0.5$	5.38	8.75
$y = 0.75$	5.09	9.02
$y = 0.8$	5.07	8.94
MnGa_2O_4	5.45	9.43
MnCo_2O_4	2.21	10.6
CrMnCoO_4	2.35	10.6

Values are averages of repeated measurements.

on their order on the map. At least, the clear correlation is shown in the compounds with the same structural type, and the trend in the map is consistent with the following explanation: an increase in oxidation number decreases $K\beta'$ intensity mainly because of a decrease in the number of unpaired 3d electrons in the Mn atom, while an increase in coordination number increases $K\beta_5$ intensity mainly because of an increase in the odds of cross-over transition of electrons originated in oxygen.

Now the $K\beta'$ and $K\beta_5$ intensities of unclear spinel-type compounds MnCo_2O_4 , CrMnCoO_4 , and MnGa_2O_4 were obtained from the spectra in Fig. 1(c), and plotted on the map. MnCo_2O_4 and CrMnCoO_4 are located near ZnMn_2O_4 , and thus it was confirmed that the Mn in them occupies site B and is trivalent. Both normal and partly inverse spinels were reported as the structure of MnCo_2O_4 [18,25]. The distribution of Mn and Co in the structure is easily affected by the synthesis method. MnCo_2O_4 prepared in this study was proved to be an inverse spinel $[\text{Co}]^{\text{A}}[\text{Mn}, \text{Co}]^{\text{B}}\text{O}_4$, similar to that reported by Boucher et al. [18]. CrMnCoO_4 was prepared by a new low-temperature synthesis method in this study [9]. It has Mn in a very similar condition to MnCo_2O_4 , therefore the atomic arrangement in it is derived from MnCo_2O_4 by the substitution of half of the cobalt ions by chromium ions. Even though the distribution of chromium and cobalt between sites A and B was not examined by Mn $K\beta$ spectra, this structural description is completely different from that made by Kulkarni et al. [26], as they concluded that Mn was divalent and occupied site A. The difference in synthesis method must bring about a different structure

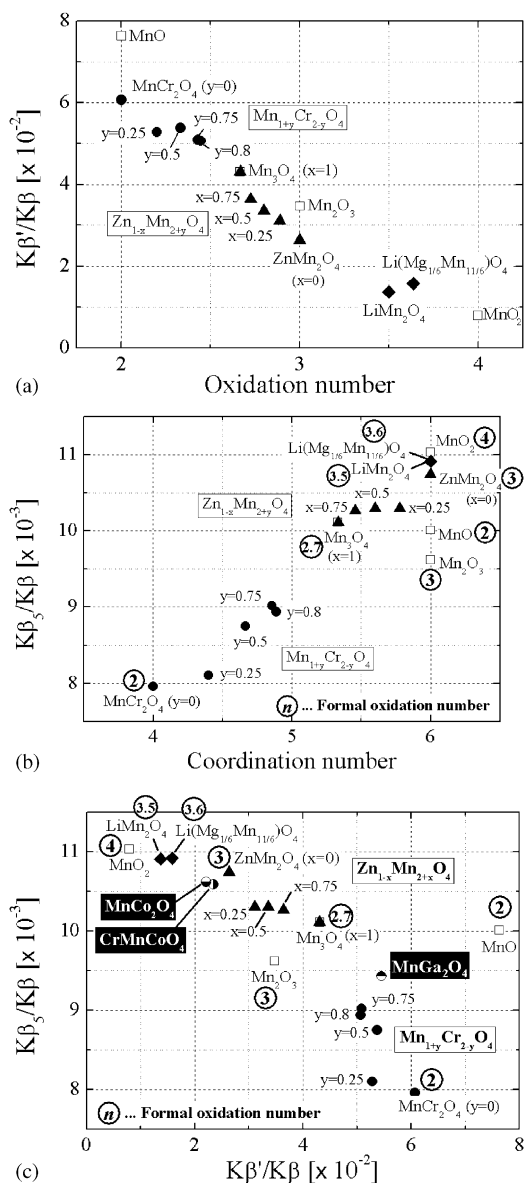


Fig. 2. (a) Correlations between formal oxidation number and $K\beta'$ relative intensity of manganese oxides and double oxides. (b) Correlations between average coordination number and $K\beta_5$ relative intensity of manganese oxides and double oxides. (c) Correlations between $K\beta'$ and $K\beta_5$ relative intensities of manganese oxides and double oxides.

even though the chemical formula is the same. In contrast, $MnGa_2O_4$ is located near the $Mn_{1+y}Cr_{2-y}O_4$ group, and especially near the higher y position. Mn in $MnGa_2O_4$ is divalent (because Ga is assuredly trivalent) and seems to occupy both sites A and B, though Mn(II) is likely to occupy only site A as observed in $MnCr_2O_4$. Therefore a partly inverse spinel structure is taken by $MnGa_2O_4$. The result is consistent with that reported by Casado et al., who concluded Mn occupancy in site A is about 0.7 by X-ray diffraction [17]. We also observed Mn-K XANES for $MnCo_2O_4$, $CrMnCoO_4$, and $MnGa_2O_4$ also. The absorption edge energy and the

spectral shape of $MnCo_2O_4$ and $CrMnCoO_4$ were similar to each other, and those of $MnGa_2O_4$ resemble $Mn_{1+y}Cr_{2-y}O_4$ of high y .

The observation of $K\beta$ spectra is an analytical method to determine the oxidation states and site occupancy in compounds efficiently, especially when the spectra are compared for the same structural type. Because the method is not a diffraction technique, it is also applicable for poorly crystallized or nanoscale materials. Although the usual XRD method has difficulty in distinguishing elements that have very close atomic numbers, such as Cr, Mn and Co in this study, or Mn and Fe in Mn ferrite, XRF spectral observation has no such problem. When this XRF method is compared with XAFS measurement, XRF has the advantage of ease of sample preparation. That is to say, XRF can treat almost all kinds of samples in various conditions, while it takes effort to prepare controlled samples for XAFS experiments. Thus, if fluorescence XAFS experiments are performed, sample restrictions are not so severe. However, the XAFS fluorescence spectrum is easily distorted and actually it is difficult to determine the coordination number. Therefore, the $K\beta$ spectral method is more useful for analysis of various samples and materials.

4. Conclusion

$K\beta$ XRF spectra can be utilized to observe manganese states in spinels. The intensities of $K\beta'$ and $K\beta_5$ were measured for a dozen spinel-type oxides, and a correlation map was drawn. Because the oxides were distributed on the map based on site occupancy and oxidation number, these parameters could be determined for samples with uncertain structures. In the case of $MnCo_2O_4$, it was confirmed that the spinel is an inverse one with trivalent Mn in site B. In $CrMnCoO_4$, trivalent Mn is also in site B. It is appropriate to consider $MnGa_2O_4$ as an inverse spinel.

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References

- [1] A. Okita, F. Saito, S. Sasaki, T. Toyoda, H. Koinuma, Jpn. J. Appl. Phys. 37 (6A) (1998) 3441–3445.
- [2] S. Calvin, E.E. Carpenter, V.G. Harris, S.A. Morrison, Appl. Phys. Lett. 81 (20) (2002) 3828–3830.

- [3] K. Sakurai, H. Eba, *Jpn. J. Appl. Phys. Suppl.* 38–1 (1999) 650.
- [4] H. Eba, C. Numako, J. Iihara, K. Sakurai, *Anal. Chem.* 72 (2000) 2613.
- [5] K. Sakurai, H. Eba, K. Inoue, N. Yagi, *Nucl. Instrum. Methods A* 467–468 (2001) 1549.
- [6] K. Sakurai, H. Eba, K. Inoue, N. Yagi, *Anal. Chem.* 74 (2002) 4532–4535.
- [7] K. Sakurai, H. Eba, *Nucl. Instrum. Methods B* 199 (2003) 391–395.
- [8] N. Ishizawa, D. du Boulay, M. Hayatsu, S. Kuze, Y. Matsushima, H. Ikuta, M. Wakihara, Y. Tabira, J.R. Hester, *J. Solid State Chem.* 174 (2003) 167–174.
- [9] H. Eba, K. Sakurai, to be submitted.
- [10] Y. Shimakawa, T. Numata, J. Tabuchi, *J. Solid State Chem.* 131 (1997) 138–143.
- [11] J. Akimoto, Y. Takahashi, Y. Gotoh, S. Mizuta, *Chem. Mat.* 12 (2000) 3246–3248.
- [12] M. Nagues, P. Poix, *Ann. Chim. (Paris)* 1972 (1972) 301–314; M. Nagues, P. Poix, *J. Phys. Chem. Solids* 25 (1962) 711–727.
- [13] F. Bosi, S. Lucchesi, A. della Giusta, *Am. Mineral.* 87 (2002) 1121–1127.
- [14] J.M. Hastings, L.M. Corliss, *Phys. Rev.* 126 (1962) 556–565; J.M. Hastings, L.M. Corliss, *J. Appl. Phys.* 33 (1962) 1138.
- [15] S. Lucchesi, U. Russo, A. della Giusta, *Eur. J. Mineral.* 9 (1997) 31–42.
- [16] J.-L. Gautier, J. Ortiz, G. Zelada, G. Poillerat, *J. Chim. Phys.* PCB 86 (9) (1989) 1889–1917.
- [17] P. Garcia Gasado, I. Rasines, *Z. Kristallogr.* 160 (1982) 33–37.
- [18] B. Boucher, R. Buhl, R. Di Bella, M. Perrin, *J. Phys.* 31 (1970) 113.
- [19] G. Peng, F.M.F. de Groot, K. Hämäläinen, J.A. Moore, X. Wang, M.M. Grush, J.B. Hastings, D.P. Siddons, W.H. Armstrong, O.C. Mullins, S.P. Cramer, *J. Am. Chem. Soc.* 116 (1994) 2914–2920.
- [20] S.D. Gamblin, D.S. Urch, *J. Electron Spectrosc. Relat. Phenom.* 113 (2001) 179–192.
- [21] K. Tsutsumi, *J. Phys. Soc. Jpn.* 14 (1959) 1969.
- [22] K. Tsutsumi, H. Nakamori, K. Ichikawa, *Phys. Rev. B* 13 (1976) 929.
- [23] M. Deutsch, H. Hölzer, J. Hartwig, J. Wolf, M. Fritsch, E. Förster, *Phys. Rev. A* 51 (1995) 283.
- [24] A.S. Koster, G.D. Rieck, *J. Phys. Chem. Solids* 31 (1970) 2505.
- [25] N. Yamamoto, S. Higashi, S. Kawano, N. Achiwa, *J. Mater. Sci. Lett.* 2 (1983) 525–526.
- [26] D.K. Kulkarni, C. Mande, *Acta Cryst. B* 27 (1971) 1044–1047.