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Elution of lead from lead zirconate titanate ceramics to acid rain

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The amount of lead that eluted from lead zirconate titanate (PZT) ceramics to artificial acid rain was evaluated. Four kinds of PZT ceramics, namely, pure PZT at MPB composition, CuO-added PZT, PZT with 10 mol % substitution of Ba for Pb, and CuO-added PZT with 10 mol % substitution of Ba for Pb, were used as samples of the elution test. These PZT ceramics of 8 mm² and 1.1–1.2 mm thickness were suspended in 300 ml of H_2SO_4 solution of pH 4.0. The concentration of lead eluted from PZT was in the range from 0.2 to 0.8 ppm. It was found that both liquid phase formation by the addition of CuO and the substitution of Ba for Pb were effective to reduce the amount of lead that eluted. By fitting the leaching out curve with a classical equation, a master curve assuming no sampling effect was obtained. The lead concentration evaluated from the amount of lead that eluted from a commercial PZT plate to H_2SO_4 solution of pH 5.3 was almost the same as the limit in city water. It is concluded that PZT is not harmful to health and the environment and the amount of lead that eluted from PZT can be controlled by modifying PZT composition. © 2017 The Japan Society of Applied Physics

1. Introduction

Presently, lead zirconate titanate (PZT) ceramics are widely used in various piezoelectric devices such as actuators, sensors and transducers.[1,2] However, motions to prohibit or regulate the usage of PZT ceramics in electronic components are under way because of the toxicity of lead. The Restriction of Hazardous Substances (RoHS) Directive adopted by the European Union restricts the use of heavy metals. The maximum permitted concentration of lead in nonexempt products is 0.1 wt % but PZT is currently listed as an exempt product in 7(c)-I. Under this circumstance, lead-free piezo-electric ceramics have been investigated by many researchers since 2000s. In 2004, Saito et al.[3] reported that highly textured potassium sodium niobate (KNN)-based ceramics exhibited a very high piezoelectric constant d_{33} of 416 pC/N. Many studies on KNN-based ceramics have been carried out in order to improve the piezoelectric property.[4–20] Another candidate of lead-free piezo-ceramics is the $(Bi,Na)TiO_3$ (BNT)-based system, which was proposed by Takenaka et al.[21–26] and many studies have been carried out over the past 15 years. However, a lead-free material that exceeds the performance of PZT has not been found so far.

Lead in a PZT lattice is stable in air. In this sense, PZT is not dangerous as long as it is used in electric components. Lead toxicity is a concern when electric components with PZT are scrapped and exposed in acid rain. The elution of lead from PZT to acid rain may cause environmental pollution. However, no experimental data have been reported so far on the exact amount of lead that eluted from PZT to acid rain. Without these data, we cannot comment on the regulation of PZT as scientists. However, once we have these data, it is our duty to state our opinion that further regulations of PZT should be based on clear experimental evidence.

The purpose of this study is very simple. We will provide results of the amount of lead that eluted from PZT to artificial acid rain and on the basis of scientific evidence, we can conclude whether PZT is dangerous or not.

2. Experimental procedure

2.1 Sample preparation

Laboratory-made PZT (hereafter, lab.-made PZT) and commercial PZT ceramics (Fuji Ceramics C-6) were prepared for the elution test. Lab.-made PZT ceramics were fabricated by a conventional solid-state ceramic fabrication technique. Four kinds of ceramic samples, $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT), 1 mol % CuO-added PZT ceramics (PZT-CuO), 10 mol % Ba-doped PZT ceramics with the composition $(Pb_{0.9}Ba_{0.1})(Zr_{0.52}Ti_{0.48})O_3$ (PZT-Ba), and 1 mol % CuO-added Ba-PZT ceramics (PZT-Ba/CuO) were prepared. Powders of PbO (Sigma-Aldrich, purity 3N), ZrO_2 (Nippon Denko, purity 3N), TiO_2 (Toho Titanium, purity 3N), $BaCO_3$ (Junsei Chemical, purity 3N), and CuO (Rare Metallic, purity 3N) were used as starting raw materials. Stoichiometric amounts of oxides and carbonates corresponding to PZT and PZT-Ba were weighed, mixed with ethanol medium to form thin slurries and milled for 20 h with 3 mmϕ yttrium-stabilized zirconia (YSZ) balls. The slurries were dried and then calcined at 950 °C for 3.5 h. Then, 1 mol % CuO was added to parts of PZT and PZT-Ba powders to prepare PZT-CuO and PZT-Ba/CuO ceramic samples. These powders were re-illed in ethanol for 20 h, then dried and pelletized in a cold isostatic press at 100 MPa. The resulting pellets were heated at 500 °C for 2 h to burn out the binder and sintered at 1250 °C for 4 h. The sintered ceramic samples were cut to 8 mm² using a dicing saw (DISCO DAD3220).

For phase identification, pulverized samples were scanned within a 2θ range of 20–80°, by powder X-ray diffractometer (Rigaku). Density was measured by the Archimedes method using distilled water as the immersion medium. Microstructure of the surface of the samples on which Au was sputtered at 5 mA for 10 min was observed by scanning electron microscope (SEM; JEOL JCM-6000).

2.2 Elution test

Four kinds of lab.-made PZT ceramics mentioned above and commercial PZT ceramics with the composition $Pb(Zr_{0.52}Ti_{0.48})O_3$ (Fuji Ceramics C-6) were used as the samples of the elution test. Noted that we used ceramic samples for the test rather than powders. None of the manufactures will crash PZT ceramics to powders before disposal because crashing is one of the most expensive procedures in ceramic processing. In this sense, powder samples are not realistic for the elution test. If bulk ceramics are used as samples, the normalization of samples should be based on the apparent surface area, rather than the weight of samples. Acid rain is defined as the rain with a pH lower
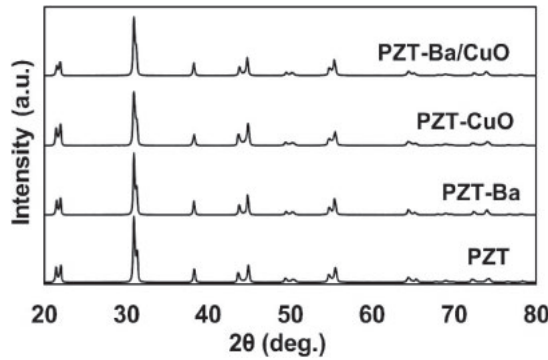
Fig. 1. XRD profiles of the PZT ceramics.

Table I. Unit cell volume ($\mathring{A}^3$) and c/a ratio of the PZT ceramics.

Sample	V	c/a
PZT	67.56	1.028
PZT-CuO	67.62	1.026
PZT-Ba	67.57	1.022
PZT-Ba/CuO	67.63	1.021

than 5.6, and in some severe cases, pH dropped to 4.2–4.4. On the basis of this information, the pH of artificial acid rain was fixed at 4.0. The temperature of the artificial acid rain was fixed at 40 °C, which is higher than the average temperature of any places in the world.

Lab.-made PZT ceramics of 8 mm^2 and 1.1–1.2 mm thickness were suspended in a polyethylene beaker containing 300 ml of aqueous H_2SO_4 solution of pH 4.0. The beaker with the sample was put in an incubator at 40 °C. The aqueous H_2SO_4 solution was stirred at 200 rpm with a magnetic stirrer. The elution test took four days (96 h) in total. 15 ml of the solution was taken out from the beaker for the measurement of lead concentration. Sampling was carried out 13 times until 96 h after the immersion of a sample. To maintain the volume of the solution, 15 ml of aqueous H_2SO_4 solution of pH 4.0 was returned to the solution immediately after each sampling, which means that the solution was diluted at each sampling. The lead concentration in the solution was determined by inductively coupled plasma atomic-emission spectroscopy (ICP-AES; Thermo Fisher Scientific iCAP 6300 DUO View).

3. Results and discussion

3.1 Characterization of samples

Figure 1 shows powder XRD profiles of the ceramic samples. All samples were identified to have a single phase of tetragonal perovskite. Table I shows the unit cell volume and the c/a ratio of the samples. The unit cell volume of PZT-Ba was larger than that of PZT because of the substitution of larger Ba^{2+} ions (1.61 Å for CN = 12[27]) for Pb^{2+} ions (1.49 Å for CN = 12[27]). The addition of CuO markedly increased the unit cell volume which may indicate that a part of Cu^{2+} (0.73 Å for CN = 6[27]) substituted Ti^{4+} (0.605 Å for CN = 6[27]) and Zr^{4+} (0.73 Å for CN = 6[27]) with a smaller average ionic radius. The decrease in c/a ratio by the substitution of Ba^{2+} ions corresponds to the decrease in Curie temperature.
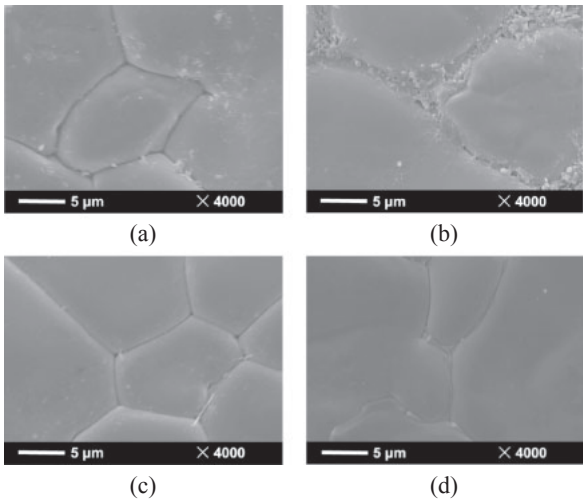

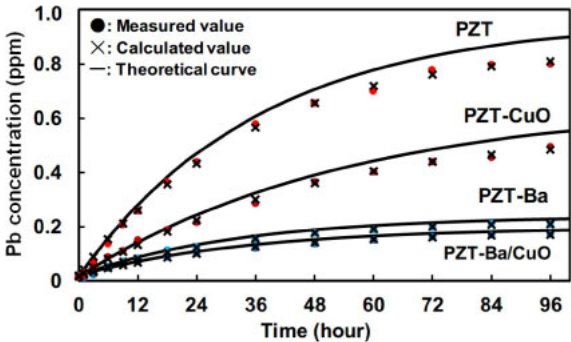**Fig. 2.** SEM images of the surfaces of (a) PZT, (b) PZT-CuO, (c) PZT-Ba, and (d) PZT-Ba/CuO.

Fig. 3. (Color online) Elution curves of various PZT ceramics. Solid circles are the result as measured, crosses are the result of fitting and solid lines are master curves assuming no sampling.

The relative densities were 93.7% for PZT, 91.3% for PZT-CuO, 94.0% for PZT-Ba and 90.8% for PZT-Ba/CuO. Figure 2 shows SEM images of the sample surfaces. It is notable that traces of the liquid phase were observed in CuO-added samples.

3.2 Result of elution test

The results of the elution test for the samples of 8 mm^2 and 1.1–1.2 mm thickness are summarized in Fig. 3. The solid circles indicate the measured lead concentrations. The amount of lead in the solution increased with time and tended to saturate depending on the sample composition. The lead concentrations in the solution after 96 h were 0.80 ppm for PZT, 0.50 ppm for PZT-CuO, 0.21 ppm for PZT-Ba, and 0.17 ppm in PZT-Ba/CuO. Noted that the maximum lead concentration calculated from the solubility of $PbSO_4$ is about 81 ppm, indicating that the lead concentrations observed in this study are much lower than this value. By comparing lead concentrations from different PZTs, we found that the both the substitution of Ba^{2+} for Pb^{2+} and CuO addition were effective in reducing the amount of lead that eluted from PZT to acid rain.

Ramam and Lopez[28] reported the effects of Ba on the ferroelectric and piezoelectric properties of PZT ceramics. The k_p, k_t, and d_{33} values shows maximum values at 30 mol % Ba-doped PZT ceramics because of the decrease in Curie temperature. The results in Fig. 3 indicate that the sub-

stitution of 10 mol % Ba for Pb was effective in reducing the amount of lead that eluted from PZT. Substitution of 10 mol % Ba is acceptable from the viewpoint of the piezoelectric performance and the Curie temperature. Swilam and Mgadalla[29] and Nonaka et al.[30] reported the formation of the liquid phase in BaTiO$_3$ ceramics following the addition of CuO. Goo et al.[31] reported that addition of excess PbO may form the liquid phase during sintering at the grain boundary of PZT ceramics and Dong[32] also reported that PbO and CuO may form the liquid phase during sintering, which changed to an amorphous phase when solidified at the grain boundary of Pb(Zr,Ti)O$_3$–BiFeO$_3$–Ba(Cu$_{0.5}$W$_{0.5}$)O$_3$ ceramics. By considering these results, it is reasonable to conclude that the liquid phase was formed at grain boundaries of CuO-added PZT ceramics, and the liquid phase captured lead at grain boundaries, resulting in the suppression of lead elution from PZT to acid rain. In the later section, we will show the results of commercial PZT sintered under an optimum condition with a small amount of lead at grain boundaries. The lead elution from commercial PZT is much less than that from lab.-made PZTs. From these results, we believe that the amount of lead that eluted from PZT is determined by the amount of lead at grain boundaries. This conclusion is very important because it automatically implies that lead in PZT lattices is stable even when immersed in acid rain.

It is important to examine the elution of lead from PZT thin films. If a sample is normalized with respect to the apparent surface area, a comparison between bulk samples and thin films will be possible. We think that the amount of lead that eluted from PZT thin films is larger than those from PZT ceramics. The amount of lead that eluted from PZT is determined by the amount of lead at structurally imperfect accommodating sites such as grain boundaries. Electrode interfaces may work as accommodating sites. Normally PZT thin films involve excess lead over the stoichiometric composition. These may enhance lead elution from PZT thin films in comparison with bulk ceramics. In this sense, it is important to continue the development of lead-free or lead-less piezoelectric thin films, especially for MEM applications.

The leaching out curve in Fig. 3 was analyzed with the following classical equation.[33]

$$\frac{dC}{dt} = k(C_s - C), \tag{1}$$

where C is the lead concentration as a function of time (t), k is the rate constant and C_s is the concentration of the saturated solution. The solution of Eq. (1) gives the time evolution of lead concentration as follows:

$$C = C_s + (C_0 - C_s)e^{-kt}, \tag{2}$$

where C_0 is the initial concentration. In the measurement in this study, after sampling 15 ml of H$_2$SO$_4$ solution, the same amount of the solution with pH 4.0 was returned to keep the volume of the solution constant. The experimental data shown as solid circles in Fig. 3 were fitted by changing the parameters C_s and k as well as taking into account the diluting effect during sampling. Calculated results were plotted as crosses in Fig. 3. The agreement between observation and calculation results was very good for all samples, indicating that lead elution from PZT to acid rain

Table II. Parameters obtained by fitting.

Sample	C_s (ppm)	k
PZT	0.963	0.027
PZT-CuO	0.657	0.018
PZT-Ba	0.241	0.030
PZT-Ba/CuO	0.198	0.029

was expressed using classical Eqs. (1) and (2). The analysis in this study enables us to eliminate the effect of sampling, which is very important when we consider the standardization of lead elution from PZT-based materials to acid rain.

The solid lines in Fig. 3 are the results of calculation assuming no sampling. They are the so-called master curves of lead elution from each PZT ceramic. The parameters used for calculation are listed in Table II. The amount of eluted lead should be normalized per unit surface area as W (µg/cm^2) using the following equation:

$$W = \frac{L(C_s - C_0)}{S}, \tag{3}$$

where L (ml) is the volume of solution and S (cm^2) is the apparent sample surface area. The W values were 171.4 µg/cm^2 for PZT, 116.1 µg/cm^2 for PZT-CuO, 40.36 µg/cm^2 for PZT-Ba, and 32.25 µg/cm^2 for PZT-Ba/CuO. We think that the W should be used for evaluating the impact of lead elution from different PZT ceramics and to screen for suitable or unsuitable PZT ceramics for environmental protection.

3.3 Lead elution from commercial PZT

We similarly conducted elution test of commercial PZT. Seven PZT plates (Fuji Ceramics) with the dimensions of 5 × 15 mm^2 and 0.8 mm thickness were suspended in H$_2$SO$_4$ solution (300 ml) of pH 4.0 and the amount of lead that eluted from PZT ceramics was measured with time. The elution curve of the commercial PZT ceramics was compared with that of lab.-made PZT in Fig. 4. It was found that the amount of lead that eluted from commercial PZT was about one-tenth of that from lab.-made PZT.

Lead elution from Sn$_{63}$–Pb$_{37}$ solder to nitric acid of PH 3.0 was examined by Hara et al.[34] The amount of eluted lead was 40.3 mg/L, which was much larger than that from PZT ceramics examined in this study. The experimental evidence indicates that the regulation of lead in Pb solders and PZT ceramics should not be discussed in the same way.

We try to determine how much PZT ceramics can be included in city water. The concentration of lead in city water is strictly limited. For example, Japanese regulation demands that the amount of lead should be lower than 0.01 ppm and the pH should be between 5.8 to 8.6. We used H$_2$SO$_4$ solution of pH 5.3 for H$_2$SO$_4$ solution (200 ml) and suspended in this solution five commercial PZT (Fuji Ceramics) plates with the same dimensions as above for 24 h to increase lead concentration to a measurable range. The amount of lead from PZT with normalized dimensions (10 × 10 mm^2 square and 1 mm thickness) to normalized volume (1,000 ml) of H$_2$SO$_4$ solution of pH 5.3 was evaluated. This condition means 1,000 PZT plates in 1 m^3 water, which is much more than we can expect in daily life
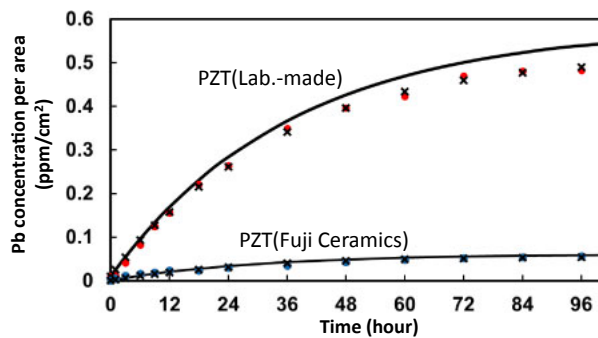
Fig. 4. (Color online) Elution curves of lab.-made PZT and commercial PZT ceramics.

because we never use such big PZT plates for electric components. The lead concentration after 24 h immersion was about 0.01 ppm, which means that the water is drinkable. It should be stress that the PZT used in this measurement was pure PZT without Ba and CuO. It is obviously possible to reduce the amount of lead that eluted from PZT by using such dopants. From the results obtained in this study, we conclude as scientists that PZT ceramics are not harmful to health and the environment and the impact of lead elution can be controlled by materials science.

Lead is not a rare earth element and is widely distributed everywhere on this planet. We calculated the average concentration of lead with respect to silicon in Earth's crust[35] to be about 14 ppm. We have never encountered actually such high a concentration of lead in this study. If the elution test in this study is adopted to screen for PZT ceramics for environmental protection, the maximum lead content permitted in the solution will be less than 0.01 ppm, which is less than one-thousandth of 14 ppm. If we take such experimental results objectively as scientists, we have to conclude Earth must be regulated first before PZT.

4. Conclusions

The amount of lead that eluted from PZT ceramics to artificial acid rain was evaluated. Four kinds of PZT ceramics, PZT, PZT-CuO, PZT-Ba, and PZT-Ba/CuO were used as samples of the elution test. H_2SO_4 solution of pH 4.0 at 40 °C was employed as an artificial acid rain. The amount of lead that eluted from PZT ceramics of 8 mm^2 and 1.1–1.2 mm thickness to 300 ml of the acid solution was in the range from 0.2 to 0.8 ppm. It was found that the liquid phase formed by the addition of CuO was effective in reducing the amount of eluted lead because lead at grain boundaries may be captured by the liquid phase. The substitution of Ba for Pb was also effective in reducing the amount of lead that eluted from PZT. The elution curve was fitted by a classical equation and the effect of sampling was eliminated to obtain a master curve of lead elution from PZT. The amount of lead eluted from commercial PZT ceramics was much less than that from lab.-made PZTs because the amount of lead at grain boundaries is smaller in commercial PZT. The results indicate that the amount of lead that eluted is determined by lead at grain boundaries and lead in the PZT lattice is stable in acid rain. The lead concentration evaluated

for commercial PZT plates in 1,000 ml of H_2SO_4 solution with pH 5.3 was almost the same as the limit in city water. We concluded that PZT ceramics are not harmful to health and the environment and the amount of lead elution can be controlled by modifying PZT composition.

1) E. Cross, Nature **432**, 24 (2004).
2) W. Jo, R. Dittmer, M. Acosta, J. Zang, C. Groh, E. Sapper, K. Wang, and J. Rodel, J. Electroceram. **29**, 71 (2012).
3) Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, and M. Nakamura, Nature **432**, 84 (2004).
4) S. Zhang, R. Xia, T. R. Shrout, G. Zang, and J. Wang, J. Appl. Phys. **100**, 104108 (2006).
5) S. Zhang, R. Xia, and T. Shrout, Appl. Phys. Lett. **91**, 132913 (2007).
6) D. Lin, K. W. Kwok, and H. L. W. Chan, J. Appl. Phys. **103**, 064105 (2008).
7) E. K. Akdoğan, K. Kerman, M. Abazari, and A. Safari, Appl. Phys. Lett. **92**, 112908 (2008).
8) K. Wang and J.-F. Li, Adv. Funct. Mater. **20**, 1924 (2010).
9) R. Zuo, J. Rödel, Re. Chen, and L. Li, J. Am. Ceram. Soc. **89**, 2010 (2006).
10) Y. Guo, K. Kakimoto, and H. Ohsato, Appl. Phys. Lett. **85**, 4121 (2004).
11) J. Rödel, W. Jo, K. T. P. Seifert, E.-M. Anton, T. Granzow, and D. Damjanovic, J. Am. Ceram. Soc. **92**, 1153 (2009).
12) W. Liang, Z. Wang, D. Xiao, J. Wu, W. Wu, T. Huang, and J. Zhu, Integrated Ferroelectr. **139**, 63 (2012).
13) X. Wang, J. Wu, D. Xiao, J. Zhu, X. Cheng, T. Zheng, B. Zhang, X. Lou, and X. Wang, J. Am. Chem. Soc. **136**, 2905 (2014).
14) B. Malic, J. Bernard, J. Holc, D. Jenko, and M. Kosec, J. Eur. Ceram. Soc. **25**, 2707 (2005).
15) B. Malic, J. Bernard, A. Bencan, and M. Kosec, J. Eur. Ceram. Soc. **28**, 1191 (2008).
16) R. Zuo and J. Fu, J. Am. Ceram. Soc. **94**, 1467 (2011).
17) Y. B. Wei, Z. Wu, Y. M. Jia, J. Wu, Y. C. Shen, and H. S. Luo, Appl. Phys. Lett. **105**, 042902 (2014).
18) J. Gao, Y. Hao, S. Ren, T. Kimoto, M. Fang, H. Li, Y. Wang, L. Zhong, S. Li, and X. Ren, J. Appl. Phys. **117**, 084106 (2015).
19) T. Zheng, J. G. Wu, X. J. Cheng, X. P. Wang, B. Y. Zhang, D. Q. Xiao, J. G. Zhu, X. J. Wang, and X. J. Lou, J. Mater. Chem. C **2**, 8796 (2014).
20) X. P. Wang, J. G. Wu, D. Q. Xiao, J. G. Zhu, X. J. Cheng, T. Zheng, B. Y. Zhang, X. J. Lou, and X. J. Wang, J. Am. Chem. Soc. **136**, 2905 (2014).
21) T. Takenaka, T. Okuda, and K. Takegahara, Ferroelectrics **196**, 175 (1997).
22) H. Nagata, N. Koizumi, N. Kuroda, I. Igarash, and T. Takenaka, Ferroelectrics **229**, 273 (1999).
23) K. Yoshii, Y. Hiruma, H. Nagata, and T. Takenaka, Jpn. J. Appl. Phys. **45**, 4493 (2006).
24) Y. Hiruma, H. Nagata, and T. Takenaka, IEEE Trans. Ultrason. Ferroelectr. Freq. Control **54**, 2493 (2007).
25) Y. Watanabe, Y. Hiruma, H. Nagata, and T. Takenaka, Ferroelectrics **358**, 139 (2007).
26) H. Muramatsu, H. Nagata, and T. Takenaka, Jpn. J. Appl. Phys. **55**, 10TB07 (2016).
27) R. D. Shannon, Acta Crystallogr., Sect. A **32**, 751 (1976).
28) K. Ramam and M. Lopez, J. Phys. D **39**, 4466 (2006).
29) M. N. Swilam and A. Mgadalla, Trans. J. Br. Ceram. Soc. **74**, 165 (1975).
30) K. Nonaka, Y. Onishi, S. Hayashi, K. Okada, T. Yano, K. Uematsu, A. Saito, and N. Otsuka, J. Ceram. Soc. Jpn. **98**, 794 (1990).
31) E. K. W. Goo, R. K. Mishra, and G. Thomas, J. Am. Ceram. Soc. **64**, 517 (1981).
32) D. Dong, Dr. Thesis, Faculty of Engineering, Shizuoka University, Shizuoka (1995).
33) A. A. Noyes and W. R. Whitney, J. Am. Chem. Soc. **19**, 930 (1897).
34) M. Hara, K. Nakazawa, K. Katayama, H. Sakamura, and I. Ysui, Electronics Jisso Gakkaishi **6**, 173 (2003) [in Japanese].
35) J. Emsley, *Nature's Building Blocks* (Oxford University Press, New York, 2001) p. 231.