J Mater Sci (2008) 43:2962–2966
DOI 10.1007/s10853-006-1472-y

Mechanochemical synthesis of indium complex oxides ($InAO_4$; A = P, V, Nb, Ta, Sb) and their solid solutions

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Received: 7 September 2006 / Accepted: 19 December 2006 / Published online: 26 April 2007

Abstract Indium complex oxides, $InAO_4$ (A = P, V, Nb, Ta, Sb), were synthesized by milling of the In_2O_3 and A_2O_5 mixture using planetary ball mill at room temperature. Formation of these compounds was monitored by powder X-ray diffraction (XRD) and was found to be complete with 240 or 480 min. This method has been successfully extended to the synthesis of solid solutions, $InP_{1-x}V_xO_4$ and $InTa_{1-x}Nb_xO_4$, between these indium complex oxides.

Introduction

Indium complex oxides, ($InAO_4$; A = P, V, Nb, Ta, Sb), are of interest in their unique properties such as microporous materials [1, 2], electrode materials for Li-ion secondary battery [3, 4], phosphors [5, 6] and transparent conducting oxides (TCO) [7, 8]. In recent years, the photocatalytic properties of $InVO_4$, $InNbO_4$ and $InTaO_4$ under visible light have been discovered and intensively investigated, where substitution of nickel for indium in $InTaO_4$ is very effective to develop the photocatalytic properties [9–16].

Generally, these complex oxides have been synthesized by a conventional ceramic powder elaboration or wet methods. The former method is simple to operate, however, it requires high reaction temperature and considerable reaction time. Besides, the degree of chemical homogeneity is limited. The latter methods can provide fine and homogeneous particle products. However, complex processes are involved in the methods, where accurate pH and temperature adjustment is necessary, and reagents used in the methods are normally expensive. On the other hand, especially, the synthesis methods of $InTaO_4$ or $InNbO_4$ are limited to the solid state reaction at high temperature such as 1,100 or 850 °C, respectively, because it is difficult to prepare reagents including Nb or Ta elements for wet process from high durability of Nb_2O_5 or Ta_2O_5 against acid or base solutions. Therefore, there has been growing demands to develop simple and economic methods for synthesizing indium complex oxides. Another route to prepare the indium complex oxides may be a mechanochemical method using constituent oxides as starting materials. This method has been proven to be versatile for synthesizing of various compounds in our laboratory [17–20].

We are conducting systematic investigations on mechanochemical solid state reaction between trivalent oxides M_2O_3 and pentavalent oxides A_2O_5 to form MAO_4. As a part of them, the main purpose of this work is to provide basic information of synthesis of $InAO_4$ (A = P, V, Nb, Ta, Sb) compounds by mechanochemical method. In addition, further attempt has been made to synthesize solid solutions between these complex oxides, $InP_{1-x}V_xO_4$ and $InTa_{1-x}Nb_xO_4$ (x = 0–1), which are seldom discussed [6, 21].

Experimental

In_2O_3, P_2O_5, V_2O_5, Nb_2O_5 and Ta_2O_5 were supplied from Wako Pure Chemical Industries Ltd. (Japan), and Sb_2O_5 from Sigma-Aldrich (USA). In_2O_3 was mixed with these pentoxides at equal molar ratio as starting mixtures for milling. Two grams of the mixture were put into a zirconia

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pot of 45 cm^3 inner volume with seven zirconia balls of 15 mm diameter. A planetary ball mill (Pulverisette-7, Fritsch, Germany) was used for milling the starting mixture. Milling was operated in air at 700 rpm. The milled samples were characterized by X-ray diffraction (XRD) analysis (RINT 2200, Rigaku Co., Japan) method using CuKα radiation (wave length, λ = 1.541838 Å) to identify the phases formed in the milling. Furthermore, four or more peak-tops of each XRD pattern were determined by peak fitting analysis with a pseudo-Voigt profile function and the lattice parameters of the samples were calculated with the CellCalc [22] based on RSLC3 algorithm [23]. Morphology of the ground samples was observed by a scanning electron microscope (SEM, S4100-L, Hitachi, Japan).

Results

Synthesis of $InAO_4$ (A = P, V, Nb, Ta, Sb)

Figure 1 shows the XRD patterns of In_2O_3 and Ta_2O_5 mixture milled for different periods of times, from 15 to 240 min. New peaks appear around 24.0 and 29.6° in the pattern of 30-min-milled sample. The intensity of these peaks increases with an increase of milling time, and such increment levels off in the XRD pattern of the mixtures milled for 120 min or more. No peaks of starting materials are observed in the pattern of the sample milled for 120 min or more. The new phase is identified as $InTaO_4$ (monoclinic, JCPDS No. 81-1196), suggesting that $InTaO_4$ has been synthesized mechanochemically by milling the mixture. The synthesis reaction can be expressed by following formula:

$$In_2O_3 + Ta_2O_5 \rightarrow 2InTaO_4 \quad (1)$$

Figure 2 shows the SEM photographs of the sample milled for 240 min. According to the photo, the product seems to be agglomerates having their size of several microns, and it is found that the agglomerates consist of grains with sizes less than several hundred nano meters.

Synthesis of $InPO_4$, $InVO_4$, $InNbO_4$ and $InSbO_4$ has been also attempted through the mechanochemical method. Figure 3 shows the XRD patterns of the In_2O_3 and the pentoxide (P_2O_5, V_2O_5, Nb_2O_5 or Sb_2O_5) mixture milled for 240 min (or 480 min in In_2O_3–V_2O_5 system). $InPO_4$ (orthorhombic, JCPDS No. 72-1132), $InVO_4$ (orthorhombic, JCPDS No. 71-1689), $InNbO_4$ (monoclinic, JCPDS No. 83-1780) and $InSbO_4$ (monoclinic, JCPDS No. 31-0588) are formed by milling the mixtures. Both of $InPO_4$ and $InVO_4$ synthesized by mechanochemical method have same crystal structure categorized into space group No. 63; orthorhombic *C*mcm $Z = 4$, and both of $InTaO_4$ and $InNbO_4$ into space group No. 13; monoclinic $P2/a$ $Z = 2$. The reactions can be described as follows:

$$In_2O_3 + P_2O_5 \rightarrow 2InPO_4 \quad (2)$$

$$In_2O_3 + V_2O_5 \rightarrow 2InVO_4 \quad (3)$$

$$In_2O_3 + Nb_2O_5 \rightarrow 2InNbO_4 \quad (4)$$

$$In_2O_3 + Sb_2O_5 \rightarrow 2InSbO_4 \quad (5)$$

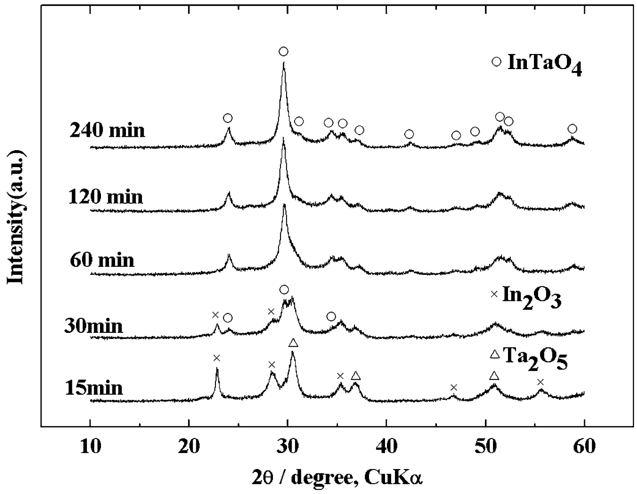


Fig. 1 XRD patterns of the In_2O_3 and Ta_2O_5 mixture milled for different periods of time

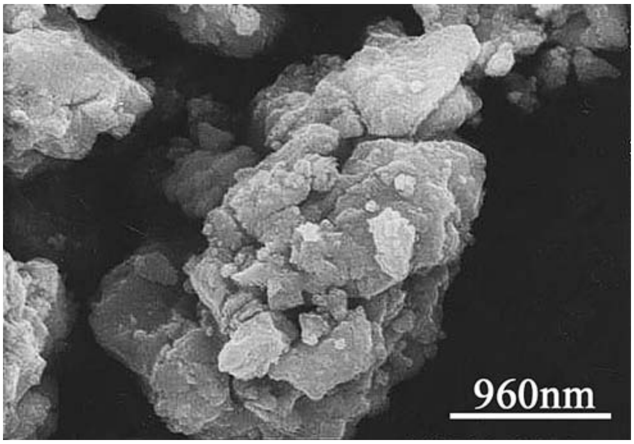


Fig. 2 SEM photographs of the In_2O_3 and Ta_2O_5 mixture milled for 240 min

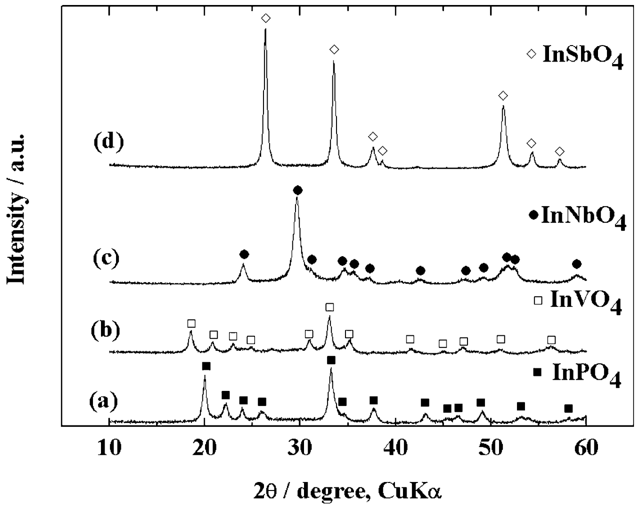


Fig. 3 XRD patterns of the In_2O_3 and X_2O_5 (X = P, Nb and Sb) mixture milled for 240 min, and In_2O_3–V_2O_5 mixture milled for 480 min. (a: In_2O_3–P_2O_5, b: In_2O_3–V_2O_5, c: In_2O_3–Nb_2O_5, d: In_2O_3–Sb_2O_5)

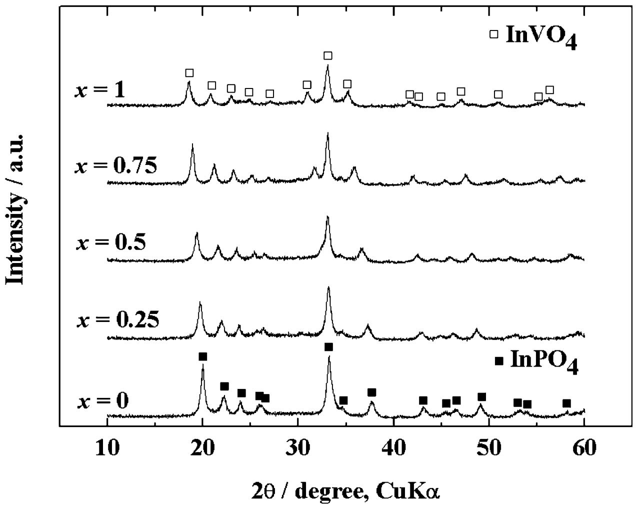
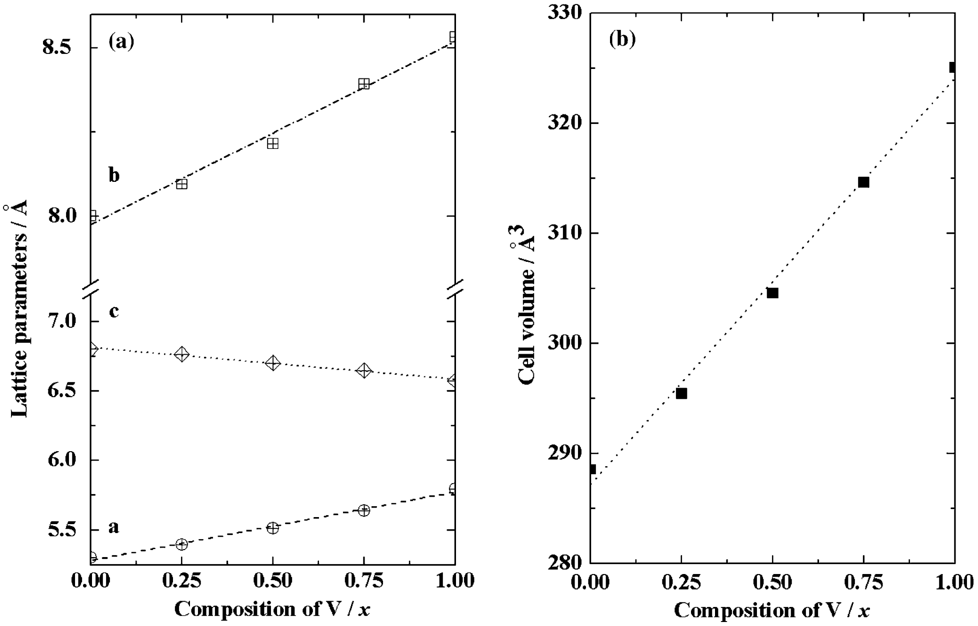


Fig. 4 XRD patterns of the $InP_{1-x}V_xO_4$ mixture milled for 480 min

Synthesis of solid solutions, $InP_{1-x}V_xO_4$ and $InTa_{1-x}Nb_xO_4$

The achievement of the mechanochemical synthesis $InPO_4$ and $InVO_4$, or $InNbO_4$ and $InTaO_4$, with the same crystal structure leads us to synthesize their solid solutions, namely $InP_{1-x}V_xO_4$ and $InTa_{1-x}Nb_xO_4$ (x = 0–1). Figure 4 shows XRD patterns of the samples of five sets of mixtures of In_2O_3, P_2O_5 and V_2O_5 with different composition ratios milled for 480 min. Each pattern of products shows regular shifts of XRD peaks towards somewhat lower angles with the increase of x in the composition. All the XRD patterns could be categorized into an orthorhombic structure for the solid solutions. No splitting of the reflections or appearance of new reflections can be seen in these patterns, indicating that no intermediate phase in $InP_{1-x}V_xO_4$ series and no formation of other material besides solid solutions could be observed. Figure 5 shows the lattice parameters and cell volume of these mixtures as a function of the mole fraction x of V in the products. With an increase in the number of x, the lattice parameters and cell volume change linearly. These results are approximately consistent with Vegard's low, and well agree with an increase of the radii of the pentavalent element ions, from 0.17 (P^{5+} with fourfold

Fig. 5 Unit cell parameters in the $InP_{1-x}V_xO_4$ mixture milled for 480 min as a function of x



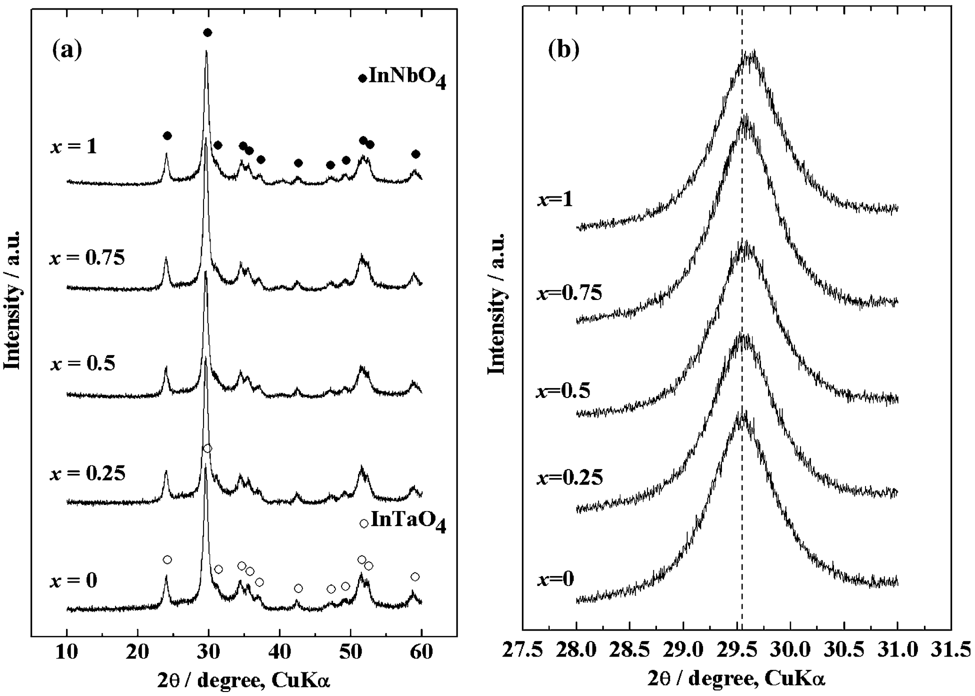


Fig. 6 XRD patterns of the $InTa_{1-x}Nb_xO_4$ mixture milled for 240 min

oxide coordination) to 0.355 Å (V^{5+} with fourfold oxide coordination) [24]. These can prove that the solid solutions of $InP_{1-x}V_xO_4$ are mechanochemically synthesized through the grinding the mixture of In_2O_3, P_2O_5 and V_2O_5. The reaction in the formation of $InP_{1-x}V_xO_4$ can be given as follows:

$$In_2O_3 + (1-x)P_2O_5 + xV_2O_5 \rightarrow 2InP_{1-x}V_xO_4 \qquad (6)$$

Figure 6a shows the XRD patterns of the $InTa_{1-x}Nb_xO_4$ mixture milled for 240 min, and Fig. 6b shows the first peaks of these patterns as a magnified figure. Although the remarkable differences between the patterns in Fig. 6a are not observed, the first peaks slightly shift to higher 2θ degrees with the increase of Nb content as shown in Fig. 6b. Figure 7 shows lattice parameters and cell volumes as a function of the mole fraction x of Nb in the products. These parameters approximately change linearly with an increase of Nb content, though both of the Ta and Nb pentavalent ionic radii are same value according to the literature by Shannon (0.64 Å for Nb^{5+} with sixfold oxide coordination; 0.64 Å for Ta^{5+} with sixfold oxide coordination) [24]. This implies that the radius of Nb pentavalent

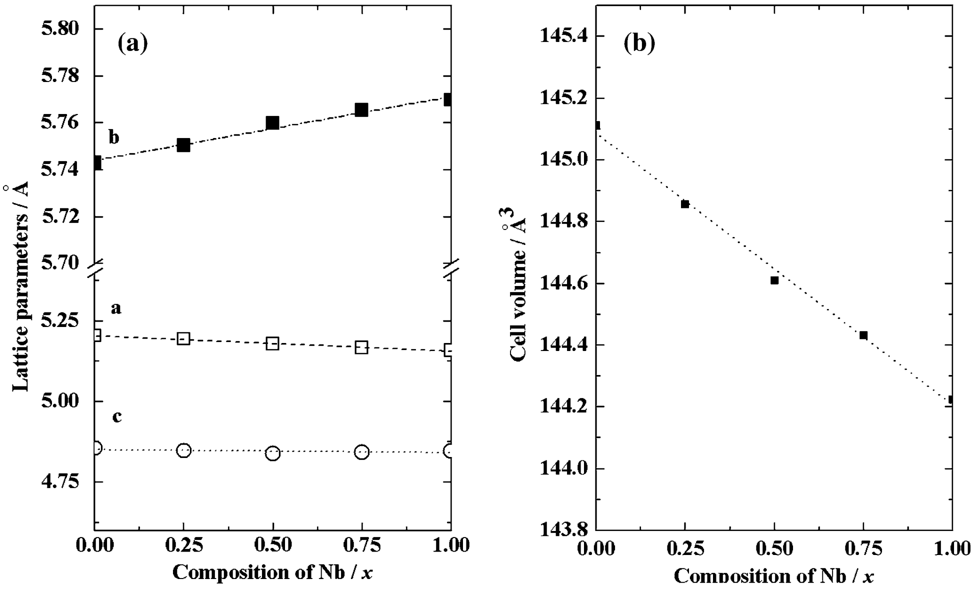


Fig. 7 Unit cell parameters in the $InTa_{1-x}Nb_xO_4$ mixture milled for 240 min as a function of x

ion is smaller than that of Ta pentavalent ion in the structure of $InTa_{1-x}Nb_xO_4$. Brixner and Chen reported similar results [6]. These results indicate that the solid solutions between $InTaO_4$ and $InNbO_4$ may be synthesized by mechanochemical method. The reaction can be described as follows:

$$In_2O_3 + (1-x)Ta_2O_5 + xNb_2O_5 \rightarrow 2InTa_{1-x}Nb_xO_4$$

Conclusion

The following conclusions can be made based on the present experimental results: (i) $InAO_4$ (A = P, V, Nb, Ta, Sb) can be synthesized mechanochemically by milling the mixture of In_2O_3 and A_2O_5 at room temperature. (ii) The solid solutions between $InPO_4$ and $InVO_4$, $InP_{1-x}V_xO_4$, can be synthesized by milling corresponding mixture of In_2O_3, P_2O_5 and V_2O_5 for 480 min. (iii) The solid solutions between $InTaO_4$ and $InNbO_4$, $InTa_{1-x}Nb_xO_4$ may be synthesized by milling the mixture of In_2O_3, Nb_2O_5 and Ta_2O_5 for 240 min.

References

1. Koh LL, Xu Y, Du HB, Pang WQ (1997) Progress in Zeolite and Microporous Materials, PTS A-C Studies in Surface Science and Catalysis 105(Part A–C):373
2. Xu Y, Koh LL, An LH, Xu RR, Qiu SL (1995) J Solid State Chem 117:373
3. Cimino N, Artuso F, Decker F, Orel B, Šurca Vuk A, Zanoni R (2003) Solid State Ion 165:89
4. Denis S, Baudrin E, Touboul M, Tarascon JM (1997) J Electrochem Soc 144(12):4099
5. Blasse G, Bril A (1969) J Chem Phys 50(7):2974
6. Brixner LH, Chen H-Y (1980) Mat Res Bull 15:607
7. Kikuchi N, Hosono H, Kawazoe H, Tanegashima O, Ota I, Kimura Y (2002) Vacuum 65:81
8. Song PK, Shimada Y, Shigesato Y, Hattori T, Ishida M, Saegusa K (2003) Thin Solid Films 442:184
9. Zou ZG, Ye JH, Sayama K, Arakawa H (2001) Nature 414(6864):625
10. Ye JH, Zou ZG, Oshikiri M, Matsushita A, Shimoda M, Imai M, Shishido T (2002) Chem Phys Lett 356(3–4):221
11. Ye J, Zou Z, Arakawa H, Oshikiri M, Shimoda M, Matsushita A, Shishido T (2002) J Photochem Photobiol A: Chem 148:79
12. Oshikiri M, Boero M, Ye J, Zou Z, Kido G (2002) J Chem Phys 117(15):7313
13. Zou ZG, Ye JH, Arakawa H (2001) Mater Res Bull 36:1185
14. Zou ZG, Ye JH, Arakawa H (2000) Chem Phys Lett 332:271
15. Ye JH, Zou ZG (2005) J Phys Chem Solids 66:266
16. Irie H, Hashimoto K (2005) J Am Ceram Soc 88(11):3137
17. Zhang Q, Saito F (2000) J Am Ceram Soc 83(2):493
18. Lee J, Zhang Q, Saito F (2001) J Solid State Chem 160:469
19. Lu J, Zhang Q, Saito F (2002) Chem Lett 31(12):1176
20. Tojo T, Zhang Q, Saito F (2006) J Solid State Chem 179:433
21. Hajek B, Muck A, Santava E (1985) Collect Czech Chem Commun 50(7):1465
22. Miura H (2003) J Cryst Soc Jpn 45(2):145
23. Sakurai T (1967) Crystal analysis: universal program system (II) the crystallographic. Society of Japan, Tokyo
24. Shannon RD (1976) Acta Cryst A 32:751