Netsu Sokutei, W**39** 23-28

Article

Preparation of $Al_{2-x}Sc_x(MoO_4)_3$ with Low Thermal Expansion and Analysis of Its Structural Phase Transition Behavior

Choushichiroh Kitahara, Takayuki Sugimoto and Takuya Hashimoto*

Department of Integrated Sciences in Physics and Biology, College of Humanities and Sciences,
Nihon University
3-25-40 Sakurajousui, Setagaya-ku, Tokyo 156-8550, Japan
*takuya@chs.nihon-u.ac.jp

(Received October. 3, 2011; Accepted November. 25, 2011)

Single phase of $Al_{2-x}Sc_x(MoO_4)_3$ (x = 0.0, 0.5, 1.0, 1.5, 2.0) ceramics were successfully prepared at sintering temperature as low as 800 °C. Specimens with more homogeneous cation distribution were obtained by Pechini method using aqueous solution of $Al(NO_3)_3$•$9H_2O$, Sc_2O_3 and MoO_3 than those prepared by solid state reaction method using mixture of Al_2O_3, Sc_2O_3 and MoO_3 powder. Sc substitution of only 0.5 decreased the temperature of the structural phase transition from monoclinic to orthorhombic observed in $Al_2(MoO_4)_3$ from 200 °C below -50 °C, resulting in low thermal expansion of the specimens with x more than 0.5 above -50 °C. The abrupt decrease of the structural phase transition temperature with x as low as 0.5 suggested existence of miscibility gap, showing agreement with observation of both monoclinic and orthorhombic phases in the specimens with $0.0 < x < 0.5$.

Keywords: $Al_{2-x}Sc_x(MoO_4)_3$, Thermal expansion, Phase transition, Miscibility gap, X-ray diffraction, Phase diagram.

1. Introduction

Materials with low thermal expansion or zero thermal expansion are required for various industrial applications such as ferrule of optical fiber, basement for mechanical or optical equipments with precise positioning and so on. $Al_2(WO_4)_3$-based system is one of the candidate materials since $Al_2(WO_4)_3$ exhibits low thermal expansion from room temperature to 300 °C.1) However, it shows the abrupt volume change due to the first order structural phase transition from monoclinic phase with positive thermal expansion to orthorhombic one with low thermal expansion at -22 °C.1-3) For application to optical devices, the structural phase transition should be below -50 °C. In the preceding study,1) we have succeeded in preparation of zero-thermal expansion material in temperature range from -50 to 200 °C with decreasing the structural phase transition temperature by partial substitution of Sc for Al site in $Al_2(WO_4)_3$.

Since crystal structure of $Al_2(MoO_4)_3$ at room temperature is identical to that of low temperature monoclinic phase of $Al_2(WO_4)_3$,4) it can be expected that orthorhombic phase with low thermal expansion might be obtained by increasing temperature or partial cation substitution in $Al_2(MoO_4)_3$ system. Tyagi and coworkers reported that $Al_2(MoO_4)_3$ showed structural phase transition at about 200 °C involving abrupt volume expansion and that negative thermal expansion was observed in high temperature phase.5) It was expected that the phase transition behavior could be controlled and materials with zero thermal expansion between -50 ~ 200 °C might be prepared with partial substitution of Sc for Al site in $Al_2(MoO_4)_3$ as was the case of $Al_2(WO_4)_3$.

In order to prepare specimens with homogeneous distribution of Al and Sc with solid state reaction method, high sintering temperature might be necessary. For $Al_{2-x}Sc_x(WO_4)_3$, sintering temperature can be high as 1100 °C, since volatility of WO_3 is negligible at the temperature; however, such a high temperature cannot be employed for preparation of $Al_{2-x}Sc_x(MoO_4)_3$ since saturated vapor pressure of MoO_3, evaluated by using thermodynamic calculation program MALT-2,6) is higher in order as Fig. 1 shows. Therefore, not solid state reaction method but solution mixing method, which can be low temperature process due to shorter cation diffusion length for preparation,7) might be necessary to prepare $Al_{2-x}Sc_x(MoO_4)_3$ with homogeneous cation distribution.

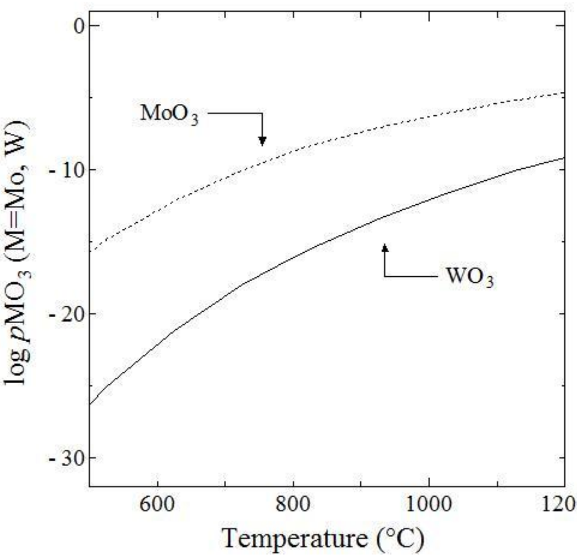

Fig. 1 Saturated vapor pressure of WO_3 and MoO_3 calculated using MALT-2

In this paper, we have prepared $Al_{2-x}Sc_x(MoO_4)_3$ polycrystalline ceramics by solid state reaction method or Pechini method,[8] which is representative solution mixing method, and homogeneity of the specimens prepared by the both methods has been compared. The Sc distribution and effect of Sc substitution on crystal structure, phase transition behavior and thermal expansion property have been evaluated by temperature-regulated X-ray diffraction, differential scanning calorimetry (DSC) and dilatometry in order to estimate possibility of $Al_{2-x}Sc_x(MoO_4)_3$ for application as zero thermal expansion material.

2. Experimental

Ceramic $Al_{2-x}Sc_x(MoO_4)_3$ specimens were prepared by solid state reaction or Pechini method. For solid state reaction method, nominal amount of powdery α-Al_2O_3 (99.9 %, Furuuchi Chem. Corp.), Sc_2O_3 (99.9 %, Furuuchi Chem. Corp.) and MoO_3 (99.9 %, Kojundo Chem. Lab. Co., Ltd.) were mixed in planet-type ball mill made from yttria stabilized ZrO_2 (YSZ) followed by pressing into pellet. The pellet was sintered below 800 °C for 12 h in air to avoid evaporation of Mo. For Pechini method, $Al(NO_3)_3•9H_2O$ (Wako Pure Chemical Industry Ltd.) was employed for Al source instead of α-Al_2O_3 and source of Sc and Mo was the same as those for solid state reaction method. Therefore, compositional difference of prepared specimens would be small between the both methods. $Al(NO_3)_3•9H_2O$ was dissolved by distilled H_2O. Sc_2O_3 was dissolved by mixture of conc. H_2SO_4, H_2O_2 and hot H_2O. For solution of MoO_3, 10 % aqueous NH_3 and H_2O_2 were used. Each solution containing nominal amount of cation was mixed. After addition of citric acid and ethylene glycol, the mixed solution was heated at about 400 °C. The solvent was evaporated and residue was successively fired. After calcinations of obtained powder at 650 °C for 48 h in air, the powder was pulverized by YSZ planet-type ball mill and pressed into pellet. The pellet was heated at 700 °C for 24 h in air, followed by pulverization and pressed. Finally, the specimens were heated at 800 °C for 12 h in air. Crystal structure of obtained pellet was investigated by powder X-ray diffraction (XRD) using RINT-2500 (CuKα: 50 kV, 250 mA, Rigaku Co., Ltd.).

The thermal expansion property of obtained pellets between -130 and 400 °C was measured by dilatometry using TMA8310 (Rigaku Co., Ltd.). SiO_2 was employed as material for push rod and reference. The heating rate was 10 °C/min. In order to characterize phase transition behavior, DSC and XRD at various temperatures were measured from -150 to 250 °C. For DSC measurements using DSC8230 (Rigaku Co., Ltd.), the powder specimen with about 30 mg was crimped in Al cell and Al_2O_3 powder with about 30 mg crimped in Al cell was used as reference. The heating rate was 10 °C/min. The XRD patterns of the specimens at high temperatures were measured by using RINT-2500 equipped with Pt heater. XRD patterns at temperatures between -150 and 150 °C were measured using temperature controlled N_2 gas from liquid nitrogen.

3. Results and discussion

3.1. Preparation of $Al_{2-x}Sc_x(MoO_4)_3$ (x = 0.0, 0.5, 1.0, 1.5 and 2.0)

Figure 2 shows X-ray diffraction patterns of $Al_{2-x}Sc_x(MoO_4)_3$ (x =0.0, 0.5, 1.0, 1.5 and 2.0) prepared by the Pechini method at room temperature. The diffraction pattern of $Al_2(MoO_4)_3$ could be indexed as single phase $P2_1/n$ (No.14) monoclinic, which was identical to that of low temperature phase of $Al_2(WO_4)_3$, with a_m = 15.498 Å, b_m = 18.194 Å, c_m = 8.961 Å and γ = 125.8 °. With Sc substitution more than 0.5, the peaks represented by arrows and indicating monoclinic symmetry disappeared. The diffraction patterns of the specimens with x larger than 0.5 could be indexed as single phase *Pbcn* (No. 60) orthorhombic symmetry, which was identical to crystal system of $Al_2(WO_4)_3$ at high temperature. Figure 3 shows variation of lattice constants and molar volume of $Al_{2-x}Sc_x(MoO_4)_3$ on Sc content. For $Al_2(MoO_4)_3$, monoclinic lattice parameters, a_m, b_m and c_m were converted to $\left|\vec{a}_\mathrm{m}-\frac{\vec{b}_\mathrm{m}}{2}\right|$, $\frac{b_\mathrm{m}}{2}$ and c_m, respectively, for comparison with a_o, b_o and c_o which are corresponding orthorhombic lattice parameters of $Al_{2-x}Sc_x(MoO_4)_3$ [2, 3]. Almost linear expansion with Sc content from 0.5 to 2.0 indicates successful substitution of Sc for Al site. Deviation of linear expansion on the specimen with x = 0.0 can be attributed to the difference of crystal structure. The variation of the crystal system on Sc content suggests that temperature of structural phase transition of $Al_2(MoO_4)_3$ decreases with Sc content as is also observed for $Al_2(WO_4)_3$, which will be discussed later.

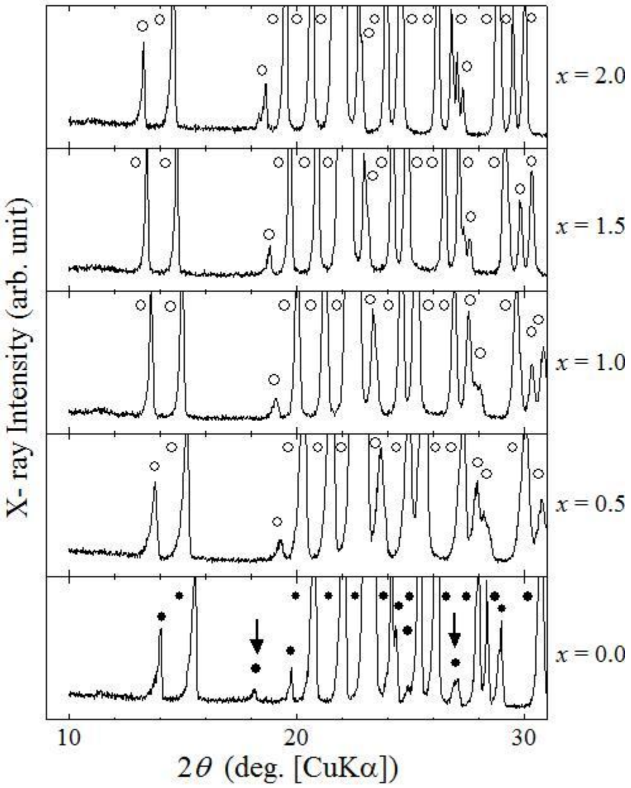

Fig. 2 XRD patterns of $Al_{2-x}Sc_x(MoO_4)_3$ (x = 0.0, 0.5, 1.0, 1.5 and 2.0) prepared by Pechini method at room temperature. Peaks indexed as monoclinic and orthorhombic are represented by ● and ○, respectively. The peaks indicated by arrows represent ones identified as monoclinic which disappear in orthorhombic symmetry.

By solid state reaction method, single phase of $Al_{2-x}Sc_x(MoO_4)_3$ (x = 0.0, 0.5, 1.0, 1.5 and 2.0) with the same crystal symmetry as those prepared by Pechini method could be obtained. However, difference of full width of half maximum (FWHM) of the XRD peaks was detected in the specimens with x = 0.5, 1.0 and 1.5 as shown in Fig. 4. The broad FWHM of the diffraction peak of $Al_{2-x}Sc_x(MoO_4)_3$ prepared by solid state reaction method could be ascribed to less homogeneous distribution of Al and Sc. The influence of the inhomogeneity on thermal property will be discussed in the next section.

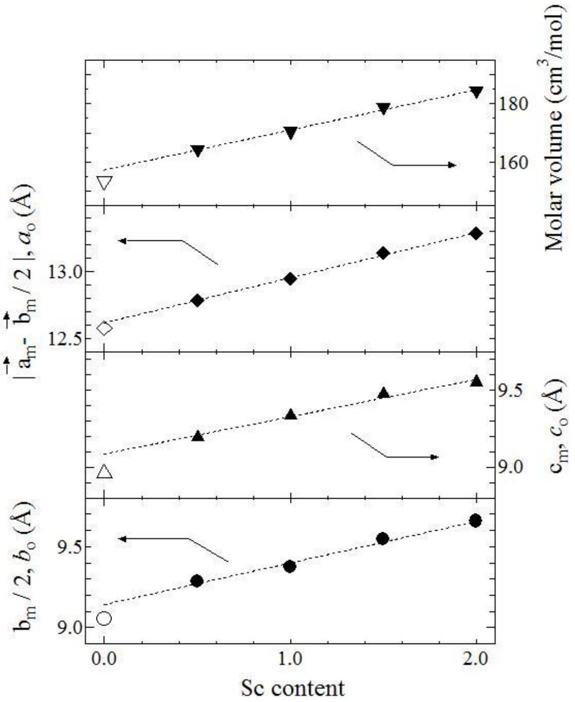

Fig. 3 Variation of lattice constants and molar volume of $Al_{2-x}Sc_x(MoO_4)_3$ on Sc content. Open and closed symbols represent lattice constants and molar volumes of monoclinic symmetry and orthorhombic ones, respectively.

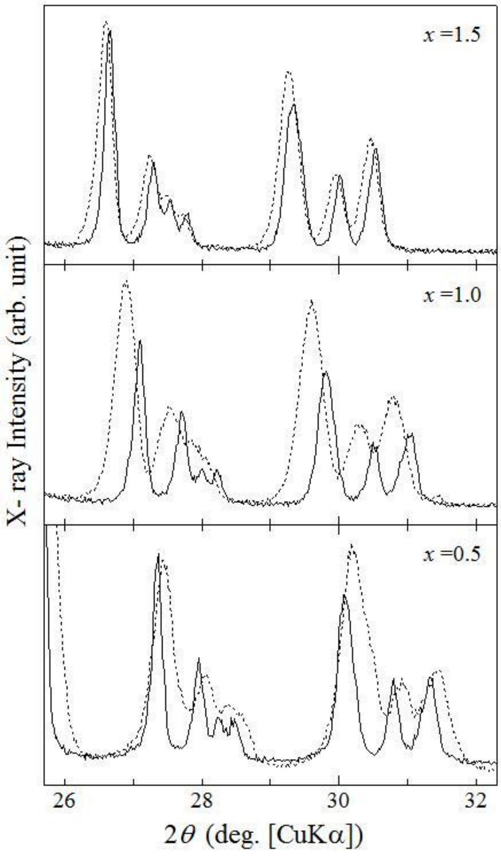

Fig. 4 Representative XRD peaks of $Al_{2-x}Sc_x(MoO_4)_3$ prepared by solid state reaction method (dashed curve) and Pechini method (solid curve). FWHM's of the peaks of the specimens prepared by Pechini method are narrower.

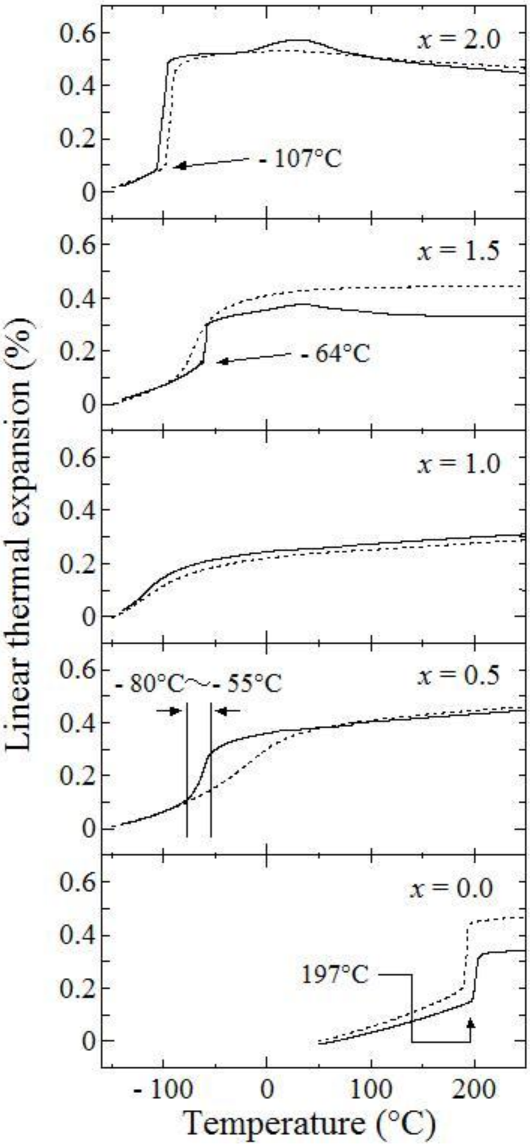

Fig. 5 Thermal expansion behavior of $Al_{2-x}Sc_x(MoO_4)_3$ prepared by solid state reaction method (dashed curve) and Pechni method (solid curve).

3.2 Thermal analyses of $Al_{2-x}Sc_x(MoO_4)_3$ (x = 0.0, 0.5, 1.0, 1.5 and 2.0)-the effect of the structural phase transition

Figure 5 shows thermal expansion behavior of $Al_{2-x}Sc_x(MoO_4)_3$ (x = 0.0, 0.5, 1.0, 1.5 and 2.0). Solid curves and dashed ones represent thermal expansion of the specimens prepared by Pechini method and solid state reaction method, respectively. For $Al_2(MoO_4)_3$, abrupt expansion was observed at about 197 °C showing agreement with the report by Tyagi and coworkers.[5] The abrupt increase could be ascribed to the first order structural phase transition from monoclinic to orthorhombic, which was also confirmed by high temperature XRD measurements depicted in Fig. 6. For $Sc_2(MoO_4)_3$, the abrupt expansion due to the structural phase transition was observed at -107 °C, which showed agreement with the results of XRD measurements at low temperature depicted in Fig. 7. Since this suggested that structural phase transition temperature would decrease with Sc substitution, thermal expansion behavior of the specimens with x = 0.5, 1.0 and 1.5 was investigated. For the specimens prepared by solid state reaction method, abrupt expansion was observed;

however, the phase transition temperature could not be clearly determined because of broad transition behavior. Since it was regarded that the broad transition originated from inhomogeneous cation distribution, the expansion behavior of the specimens with x = 0.5, 1.0 and 1.5 prepared by Pechini method was investigated. Abrupt expansion due to the first order phase transition was observed more clearly for the specimens with x = 0.5 and 1.5, indicating that Sc substitution with only x = 0.5 decreased the phase transition temperature below -50 °C. The drastic decrease of the phase transition temperature by Sc substitution was also confirmed with low temperature XRD measurements depicted in Figs 8 and 9 and DSC measurements shown in Fig. 10. For the specimen with x = 1.0, the transition behavior observed by dilatometry was broad and clear transition temperature could not be determined. However, the endothermic peak, in spite of broad and small, was observed in DSC curve and XRD patterns at low temperature revealed that the phase transition existed at about -78 °C in $Al_{1.0}Sc_{1.0}(MoO_4)_3$. It was suggested that the broad phase transition could be attributed to deficient homogeneity of cation distribution even in $Al_{1.0}Sc_{1.0}(MoO_4)_3$ prepared by Pechini method.

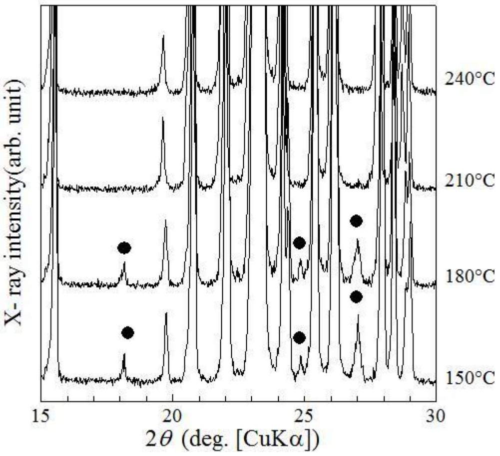

Fig. 6 High temperature XRD patterns of $Al_2(MoO_4)_3$ prepared by Pechini method. The peaks represented by ● are observed in only monoclinic symmetry. The disappearance of the peaks indicates that the crystal symmetry above 210 °C is orthorhombic.

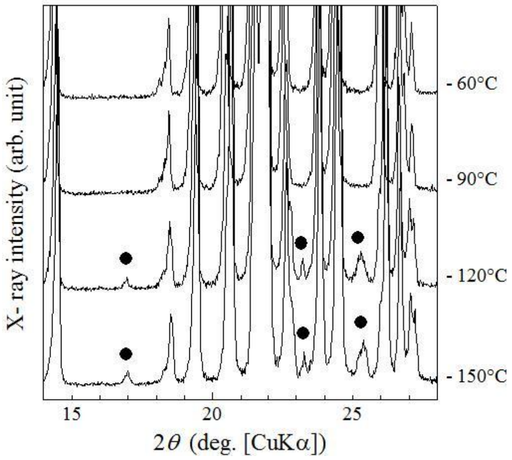

Fig. 7 Low temperature XRD patterns of $Sc_2(MoO_4)_3$ prepared by Pechini method. The peaks represented by ● are observed in only monoclinic symmetry. The disappearance of the peaks indicates that the crystal symmetry above -90 °C is orthorhombic.

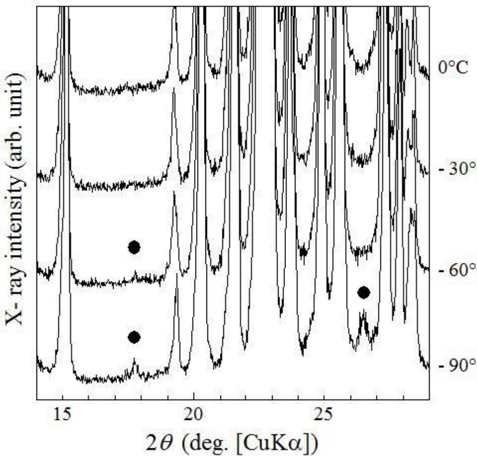

Fig. 8 Low temperature XRD patterns of $Al_{1.5}Sc_{0.5}(MoO_4)_3$ prepared by Pechini method. The peaks represented by ● are observed in only monoclinic symmetry. The disappearance of the peaks indicates that the crystal symmetry above -30 °C is orthorhombic.

With Sc substitution, we have succeeded in decreasing phase transition temperature, resulting in preparation of low thermal expansion material between -50 and 250 °C. Especially, the mean thermal expansion coefficient of $Al_{0.5}Sc_{1.5}(MoO_4)_3$ between -50 and 250 °C is nearly zero.

3.3 Miscibility gap of $Al_{2-x}Sc_x(MoO_4)_3$ between x = 0.0 and x = 0.5

As shown in Figs 5 and 10, the phase transition temperature of $Al_2(MoO_4)_3$ at about 200 °C drastically decreased to -50 °C with substitution of Sc at even 0.5. Gradual decrease of the phase transition was observed with further Sc substitution. This tendency showed contrast to the continuous decrease of phase transition temperature of $Al_{2-x}Sc_x(WO_4)_3$ on Sc content.$^{1)}$ One of the possible reasons of the drastic decrease can be a miscibility gap between x = 0.0 and x = 0.5 in $Al_{2-x}Sc_x(MoO_4)_3$.

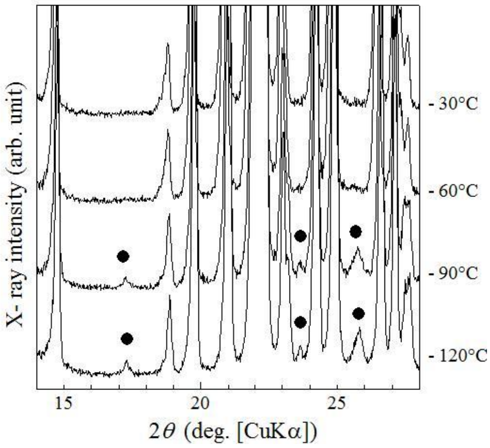

Fig. 9 Low temperature XRD patterns of $Al_{0.5}Sc_{1.5}(MoO_4)_3$ prepared by Pechini method. The peaks represented by ● are observed in only monoclinic symmetry. The disappearance of the peaks indicates that the crystal symmetry above -60 °C is orthorhombic.

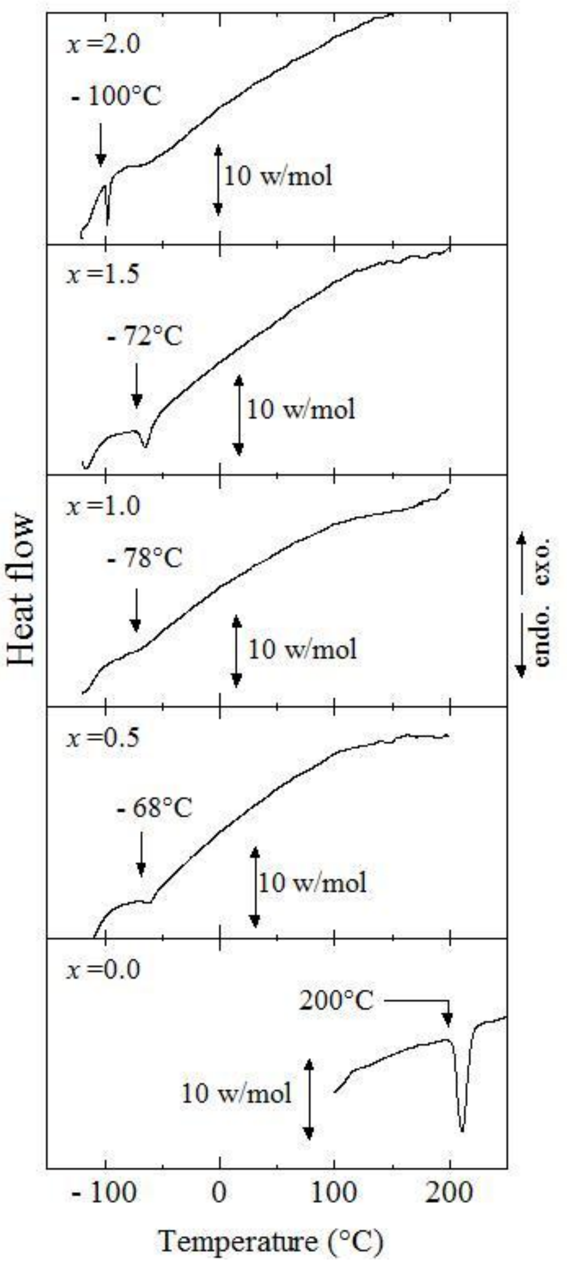

Fig. 10 DSC curves of $Al_{2-x}Sc_x(MoO_4)_3$ prepared by Pechini method.

Figure 11 shows XRD patterns of $Al_{2-x}Sc_x(MoO_4)_3$ with $x = 0.0 \sim 0.5$. All the peaks of $Al_2(MoO_4)_3$ and $Al_{1.5}Sc_{0.5}(MoO_4)_3$ can be indexed as monoclinic and orthorhombic symmetry, respectively. In the diffraction patterns of the specimens with $x = 0.1 \sim 0.4$, the peaks both identified as monoclinic and those as orthorhombic were observed. Figure 12 shows magnified XRD peaks in 2θ range of 20 ~ 21 °, where both peaks indexed as monoclinic and orthorhombic are clearly observed. With the increase of Sc content, intensity of the monoclinic peak decreased and that of orthorhombic one increased without variation of Bragg angles, indicating that miscibility gap in the specimens with $x = 0.1 \sim 0.4$ where monoclinic phase with small Sc content and orthorhombic one with large Sc content coexist.

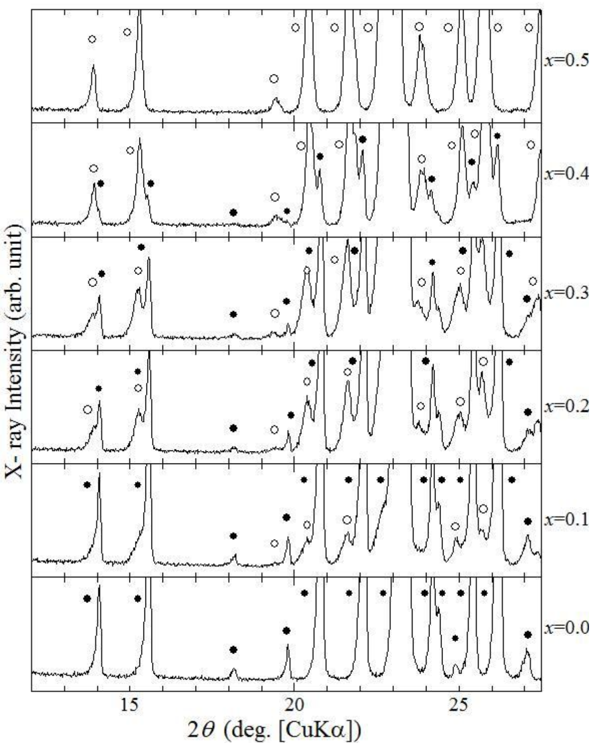

Fig. 11 XRD patterns of $Al_{2-x}Sc_x(MoO_4)_3$ ($x = 0.0\sim0.5$) prepared by Pechini method at room temperature. Peaks indexed as monoclinic and orthorhombic are represented by ● and ○, respectively.

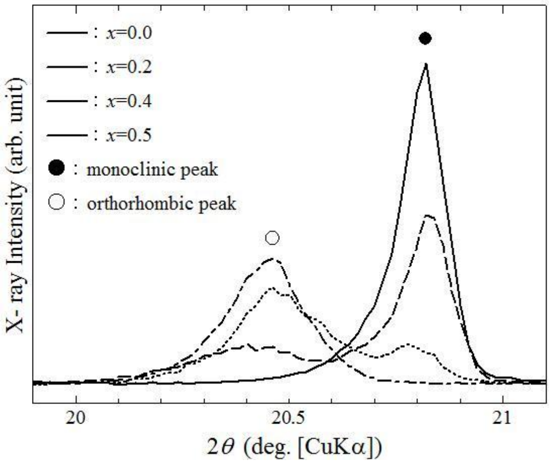

Fig. 12 XRD peaks of $Al_{2-x}Sc_x(MoO_4)_3$ ($x = 0.0\sim0.5$) prepared by Pechini method at room temperature in 2θ range of 20 ~ 21 °. The symbols ● and ○ represent monoclinic and orthorhombic symmetry, respectively.

The miscibility gap influences the thermal expansion property as shown in Fig. 13. The anomaly of the thermal expansion coefficient of $Al_2(MoO_4)_3$ due to the structural phase transition was observed around 200 °C. The temperature where the anomaly was observed decreased to around 150 °C with Sc substitution and was maintained from x=0.1 to x=0.4. For the specimen with $x = 0.2 \sim 0.4$, additional anomaly was observed below 0 °C in the thermal expansion coefficient and its intensity increased with increasing Sc content. Thus, it is concluded that miscibility gap exists in the specimens with $x = 0.1 \sim 0.4$ in $Al_{2-x}Sc_x(MoO_4)_3$, which has not been detected in $Al_{2-x}Sc_x(WO_4)_3$ system.

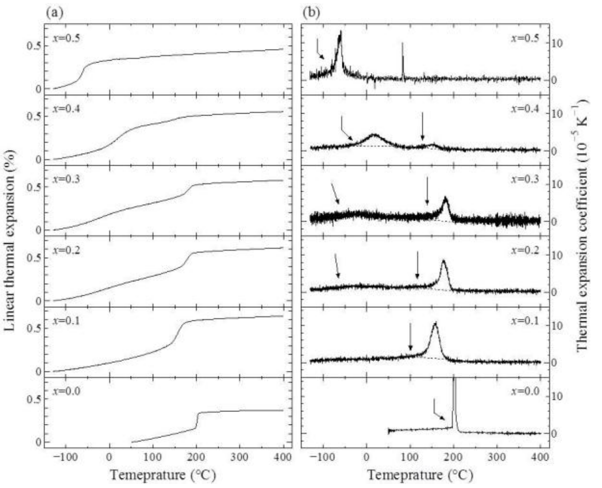

Fig. 13 (a) Linear thermal expansion and (b) thermal expansion coefficient of $Al_{2-x}Sc_x(MoO_4)_3$ (x=0.0~0.5). Anomalies observed in thermal expansion coefficient are represented by arrows.

Figure 14 shows phase diagram of $Al_{2-x}Sc_x(MoO_4)_3$ proposed in this study. In $Al_2(MoO_4)_3$, crystal structures above and below 200 °C are orthorhombic and monoclinic, abbreviated as $O_{(I)}$ and $M_{(I)}$, respectively.[5)] For the specimens with x lager than 0.5, crystal structure above about -50 ~ -100 °C is $Sc_2(MoO_4)_3$-type orthorhombic, abbreviated $O_{(II)}$, whereas it changes $Sc_2(MoO_4)_3$-type monoclinic, abbreviated as $M_{(II)}$ is the diagram, below the temperature.[9)] For the specimens with x = 0.1 ~ 0.4, miscibility gap existed resulting in mixture of $M_{(I)}$ and $O_{(II)}$ at room temperature. In the miscibility gap, two kinds of phase transitions were observed. One was from $M_{(II)}$ to $O_{(II)}$ around -50 °C, the other was from $M_{(I)}$ to $O_{(I)}$ around 150 °C as represented in Fig. 14.

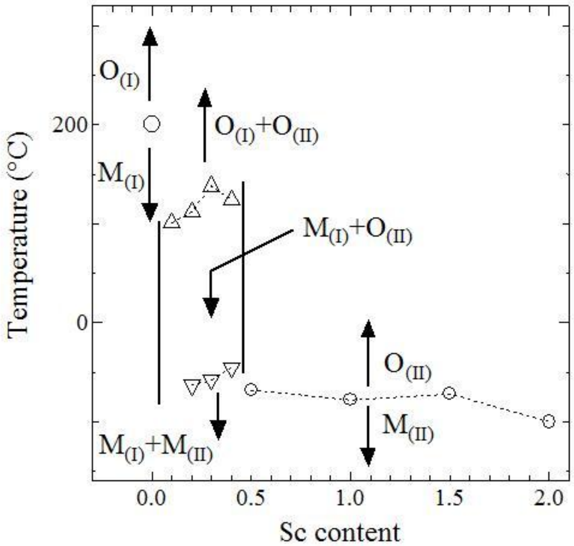

Fig. 14 Proposed phase diagram of $Al_{2-x}Sc_x(MoO_4)_3$ in this study. Miscibility gap was observed in $0.0 < x < 0.5$. $O_{(I)}$: Orthorhombic phase of $Al_2(MoO_4)_3$, $O_{(II)}$: Orthorhombic phase of $Sc_2(MoO_4)_3$, $M_{(I)}$: Monoclinic phase of $Al_2(MoO_4)_3$, $M_{(II)}$: Monoclinic phase of $Sc_2(MoO_4)_3$.

4. Conclusion

$Al_{2-x}Sc_x(MoO_4)_3$ (x = 0.0, 0.5, 1.0, 1.5 and 2.0) with homogeneous cation distribution has successfully been prepared by Pechini method. The first order structural phase transition from monoclinic to orthorhombic was observed at about 200 °C for $Al_2(MoO_4)_3$. The phase transition temperature decreased below -50 °C with Sc substitution of only 0.5, resulting that orthorhombic phase with low thermal expansion was stable above -50 °C. Especially, the mean thermal expansion coefficient of $Al_{0.5}Sc_{1.5}(MoO_4)_3$ between -50 and 250 °C was nearly zero. Abrupt decrease of the phase transition temperature with Sc substitution only by 0.5 suggested existence of miscibility gap, which could be confirmed by X-ray diffraction and thermal expansion measurements.

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