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A New Ferroelastic Transition in Some $A_2(MO_4)_3$ Molybdates and Tungstates

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We have found for the first time a ferroelastic transition in many molybdates and tungstates with the $Sc_2(MoO_4)_3$-type structure. Below the transition these phases are monoclinic ($P2_1/a$), and above the transition they are orthorhombic ($Pnca$). Observed transition temperatures are: $Al_2(MoO_4)_3$, 200°C; $Al_2(WO_4)_3$, −6°C; $Cr_2(MoO_4)_3$, 385°C; $Fe_2(MoO_4)_3$, 499°C; $In_2(MoO_4)_3$, 335°C; $In_2(WO_4)_3$, 252°C; and $Sc_2(MoO_4)_3$, 9°C.

Introduction

Many compounds of the type $A_2^{3+}(WO_4)_3$ and $A_2^{3+}(MoO_4)_3$ are known and have been the subject of recent publications (*1–8*). Four different structure types have been clearly established, and all contain discrete MO_4 tetrahedra. The $Eu_2(WO_4)_3$ structure (*9*) is found for $A_2(WO_4)_3$ compounds where A is a large rare earth (1, 3) and for the low-temperature modifications of $A_2(MoO_4)_3$ compounds where A is Sm–Ho (*6*). The α-$La_2(MoO_4)_3$ structure exists for $Ce_2(MoO_4)_3$, α-$Pr_2(MoO_4)_3$, α-$Nd_2(MoO_4)_3$ and α-$La_2(MoO_4)_3$ (*8*). The β-$Gd_2(MoO_4)_3$ structure can exist for $A_2(MoO_4)_3$ compounds where A is Pr–Ho (*6*). The $Sc_2(MoO_4)_3$ structure type (*10*) is found for $A_2(WO_4)_3$ and $A_2(MoO_4)_3$ compounds where A is Al, In or a small rare earth and for $Fe_2(MoO_4)_3$ and $Cr_2(MoO_4)_3$.

Many of the $A_2(MO_4)_3$ molybdates and tungstates are dimorphic; that is, they can exist in two of the above-mentioned structure types. Transitions between these structure types are diffusion controlled and thus often very slow. Rapid displacive transitions occur for compounds with the β-$Gd_2(MoO_4)_3$ structure. The symmetry of this structure is tetragonal ($P\bar{4}2_1m$) above the transition but distorts to orthorhombic ($Pba2$) below the transition. This transition is ferroelastic and ferroelectric.

The purpose of this paper is to show that many compounds with the $Sc_2(MoO_4)_3$-type structure also possess a displacive-type transition which is ferroelastic but not ferroelectric.

Experimental Methods

All reactants used had listed purities of 99.9% or better. Appropriate quantities of the reactants were intimately mixed and heated at 600 to 1000°C in air for 10 hr. Any compound which showed a tendency to pick up water was transferred directly from the furnace to a desiccator.

X-Ray powder patterns were obtained at 25°C both with a Hägg-Guinier camera using $CuK\alpha_1$ radiation and an internal standard of KCl ($a = 6.2931$ Å) and with an IRDAB-XDC-700 Guinier camera using $CrK\alpha_1$ radiation and an internal standard of Co_3O_4 ($a = 8.0832$ Å). The cell dimensions were refined by least squares using the Guinier data. Only uniquely indexed lines were used in the refinement, but all lines were accounted for. A Nonius high-temperature Guinier camera was used to examine $Cr_2(MoO_4)_3$.

Differential scanning calorimetry (DSC) data were obtained over the temperature range −80 to +600°C.

Results

Although compounds with the $Sc_2(MoO_4)_3$-type structure are generally referred to as orthorhombic (3), some compounds of this structure

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* Contribution No. 1968.

type are clearly distorted to monoclinic symmetry. The degree of distortion in these cases is, however, small and difficult to detect. Ordinary X-ray powder patterns do not show the line splitting indicative of the distortion, and even a Guinier camera frequently does not show the distortion. However, our IRD Guinier camera using Cr radiation gives sufficient resolution to always clearly show the distortion when it exists.

In order to be certain that the complex monoclinic patterns were indexed properly, intensities were calculated in these cases based on the reported positional parameters for $Fe_2(MoO_4)_3$ (*11*). The qualitative agreement between calculated and observed intensities was very good. For the simpler orthorhombic patterns, intensities were not always calculated, but the space group *Pnca* was always assumed. The refined cell dimensions at 25°C are given in Table I. The failure to observe a second harmonic signal in any of the phases listed in Table I is further evidence that both the monoclinic and orthorhombic versions of the $Sc_2(MoO_4)_3$ structure are centrosymmetric.

For compounds which are monoclinic at room temperature, DSC always showed a transition between 25 and 600°C. Compounds which are orthorhombic at room temperature showed no transitions between 25 and 600°C, but in some cases transitions below room temperature were found. The transition temperatures are given in Table I. In the case of $Cr_2(MoO_4)_3$, high-temperature Guinier data showed that the transition found by DSC was indeed the expected monoclinic to orthorhombic transition.

Compounds with the $Sc_2(MoO_4)_3$-type structure are not significantly hygroscopic when the A cation is not a rare earth; however, both the molybdates and the tungstates of this structure type hydrate easily and quickly when the A cation is a rare earth. The tendency to hydrate increases with the size of the rare earth cation; thus, reliable data were not obtained when the A cation was larger than Yb.

Discussion

The structures of three compounds with the $Sc_2(MoO_4)_3$ structure have been determined. The orthorhombic space group *Pnca* was found for $Sc_2(MoO_4)_3$ (*10*) and $Al_2(WO_4)_3$ (*12*). The monoclinic space group $P2_1/a$ was found for $Fe_2(MoO_4)_3$ (*11*). Our results indicate that the *Pnca* space group applies to all the orthorhombic compounds and that the space group $P2_1/a$ applies to all the monoclinic compounds in Table I.

A transition from *Pnca* to $P2_1/a$ is a point group change of $mmm \rightarrow 2/m$. According to Aizu (*13*) such a transition is ferroelastic. Of course, since the monoclinic compounds are centrosymmetric, they are not ferroelectric.

The transition temperatures found for the compounds in Table I clearly do not depend on

TABLE I

CELL DIMENSIONS AND TRANSITION TEMPERATURES

Compound	a (Å)	b (Å)	c (Å)	β (°)	V^a (Å^3)	T (°C)
$Al_2(MoO_4)_3$	15.382	9.041	17.874	125.37	2026.8	200
$Al_2(WO_4)_3$	9.136	12.592	9.057		2083.8	−6
$Cr_2(MoO_4)_3$	15.572	9.159	18.105	125.31	2107.1	385
$Fe_2(MoO_4)_3$	15.693	9.231	18.211	125.25	2154.4	499
$In_2(MoO_4)_3$	16.267	9.586	18.904	125.26	2406.9	335
$In_2(WO_4)_3$	16.359	9.632	19.006	125.30	2444.2	252
$Sc_2(MoO_4)_3$	9.656	13.274	9.563		2451.4	9
$Sc_2(WO_4)_3$	9.669	13.327	9.581		2469.2	
$Lu_2(MoO_4)_3$	9.929	13.689	9.834		2673.2	
$Lu_2(WO_4)_3$	9.963	13.771	9.872		2708.7	
$Yb_2(WO_4)_3$	9.987	13.806	9.897		2729.2	

[a] Volume has been doubled for orthorhombic phases to allow direct comparison to the volumes of the monoclinic phases.

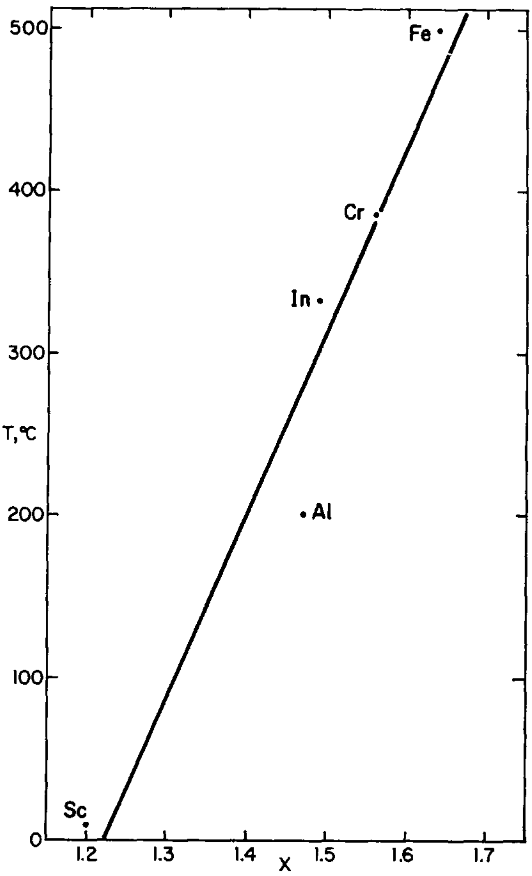

FIG. 1. Transition temperature vs electronegativity of A for the $A_2(MoO_4)_3$ series. The electronegativity values are taken from A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.* **5**, 264 (1968).

the size of the A cation. The important consideration seems to be the electronegativity of the A cation. The transition temperatures for the $A_2(MoO_4)_3$ series increase with the increasing electronegativity of the A cation (Fig. 1). The correlation is excellent considering the uncertainties in electronegativity values. Such a plot for $A_2(WO_4)_3$ compounds would not be significant since there would only be two points. However, those two points would show the same trend.

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