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DIFFERENTIAL SCANNING CALORIMETRIC STUDIES OF FERROELECTRIC RARE-EARTH MOLYBDATES

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ABSTRACT

Gadolinium and samarium molybdates in their pure forms and substituted with other homovalent rare-earth ions (in small concentrations) have been studied using the DSC technique. The ferroelectric phase transitions in the said compounds have been detected using this technique. It has been observed that there is no change in the ferroelectric phase transition temperature when the homovalent cation is substituted to a small extent.

INTRODUCTION

Rare-earth molybdates $R_2(MoO_4)_3$, (R = trivalent rare-earth ion) are very important materials for manufacturing various devices in different fields of modern technology because of their interesting fluorescence, laser, piezoelectric, ferroelectric and ferroelastic properties [1–4]. Most of the physical properties used for practial applications are very sensitive to the preparative conditions, the quality and quantity of impurities and to small variations from the stoichiometry. These rare-earth molybdates have several polymorphs [2] and the most important form is the β' in the orthorhombic modification of space group Pba2 [5]. The β' form is in the metastable state at room temperature and its β form is quite stable at high temperatures (above 850 °C) [6]. Most of the other forms, such as the α form which is quite stable below 850 °C [2] and γ form which is not very stable, are found at very high temperatures near the melting point of the compound [2]. We are mainly interested in the β' form of the compound because of its technical importance. Various stable phases in these molybdates can be obtained by long term heating at certain higher temperatures. It is interesting to investigate the formation condition and phase transitions of these molybdates, in particular gadolinium molybdate (GMO) and samarium molybdate (SMO), with different small-concentration substitutions of other homovalent rare-earth ions. This leads to a better understanding of the

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transition mechanism and the occurrence of some interesting physical properties. We have made isoelectronic cation substitutions on sintered polycrystalline (ceramic) samples of $Gd_2(MoO_4)_3$ (GMO) and $Sm_2(MoO_4)_3$ (SMO). Sm^{3+} and Dy^{3+} have been used (in small concentrations) as substitutes for Gd^{3+}, and Nd^{3+} and Gd^{3+} have been used for Sm^{3+}. An extensive differential scanning calorimetric (DSC) study of all these compounds has been completed.

EXPERIMENTAL DETAILS

Sample preparation

The compounds $(Gd_{1-x}Sm_x)_2(MoO_4)_3$, $(Gd_{1-x}Dy_x)_2(MoO_4)_3$, $(Sm_{1-x}Nd_x)_2(MoO_4)_3$ and $(Sm_{1-x}Gd_x)_2(MoO_4)_3$ with different values of x ($0 < x < 0.1$) were prepared with the component oxides Gd_2O_3, Sm_2O_3, Nd_2O_3, Dy_2O_3 (M/s Indian Rare-Earth Ltd., 99.99% pure) and MoO_3 (BDH, England, 99.5% pure). Stoichiometric amounts of these oxides were mixed and ground in an agate mortar with ethanol and calcined at 800 °C for 24 h in a platinum crucible. The calcined powders were again mixed, ground and pressed into cylindrical pellets. These pellets were sintered at 1100 °C for 24 h and were quenched from 1000 °C to room temperature (RT) to obtain the desired β' phase [7,8].

Formation of the single phase compounds was confirmed by X-ray diffraction and scanning electron microscopical (SEM) (including elemental analysis) techniques.

DSC studies

DSC studies on all the samples have been carried out on a DuPont 910 differential scanning calorimeter coupled with a DuPont 990 and R90 TA program. Both the temperature and heat exchange associated with transition in the materials have been rapidly measured by this system. The thermal measurement can provide qualitative and quantitative data that relates to the physical and chemical changes in the materials, involving endothermic (heat absorption) or exothermic (heat evolution) processes [9] in the proposed compounds. A chromel–alumel thermocouple was used as a temperature sensing device. The heating rate employed in this experiment was 5 °C min^{-1} in a temperature range from room temperature to 600 °C in a static air atmosphere. Non-hermetically crimped aluminium pans were used with an empty pan as reference. The calibration coefficient of the cell, which is used to calculate the enthalpy changes and the specific heat, was determined and found to be constant. The change in enthalpy or heat of fusion ΔH and specific heat C_p at transition temperature T_c has been calculated using the following formulae [10,11]

$$\Delta H = \frac{E60AB\,\Delta qs}{m}\,\mathrm{J\,g^{-1}} \tag{1}$$

and

$$C_p = \frac{E60\,\Delta qsY}{H_r m}\,\mathrm{J\,g^{-1}\,K^{-1}} \tag{2}$$

where E is the cell calibration coefficient in mW $\mathrm{mV^{-1}}$, m is the mass of the sample in g, A is the peak area in $\mathrm{cm^2}$, B is the time-base setting in min $\mathrm{cm^{-1}}$, Δqs is the y-axis sensitivity in mV $\mathrm{cm^{-1}}$, H_r is the heating rate in °C $\mathrm{min^{-1}}$ and Y is the difference, in cm, in the y-axis deflection between the sample and reference curves at the temperature of interest.

RESULTS AND DISCUSSION

DSC curves of pure GMO and GMO substituted (in small quantities) with Sm and Dy are shown in Figs. 1 and 2. From the figures it is clear that the pure GMO compound undergoes an endothermic ferroelectric phase transition at 159°C which is consistent with the reported value [12]. By substituting different small concentrations (x) of homovalent Sm and Dy (with $x = 0.01$, 0.02, 0.05 or 0.1) into GMO, which take up cation lattice sites, it has been observed that there are no significant changes in the

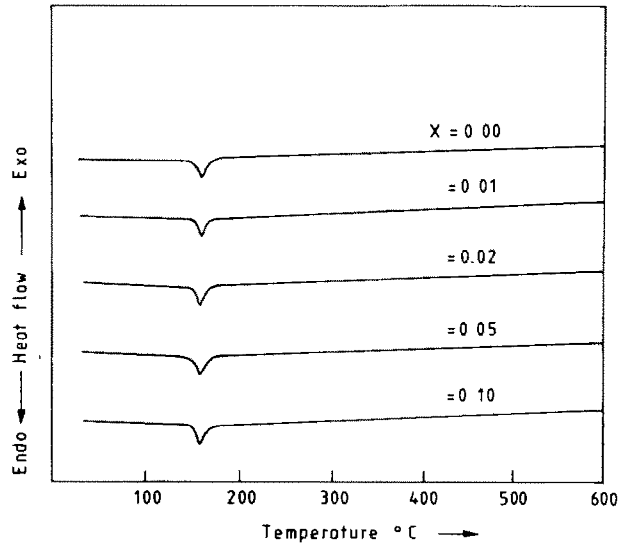

Fig. 1. DSC curves of $(\mathrm{Gd}_{1-x}\mathrm{Sm}_x)_2(\mathrm{MoO_4})_3$.

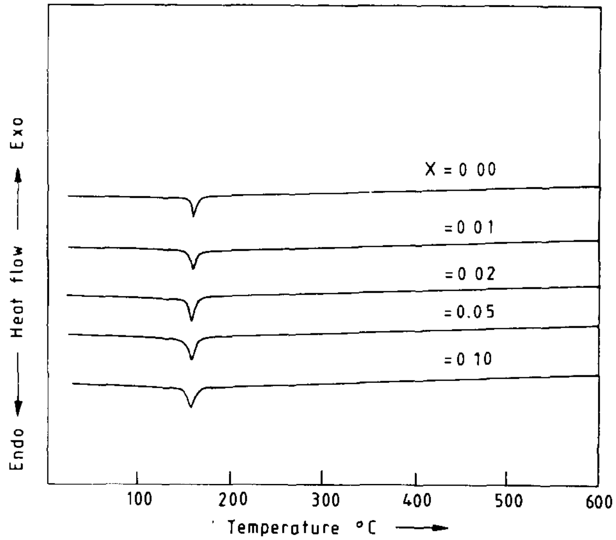

Fig. 2. DSC curves of $(Gd_{1-x}Dy_x)_2(MoO_4)_3$.

transition temperature, ΔH and C_p, indicating that these homovalent substitutions in the cation lattice sites do not create much distortion in the structure. Our previous X-ray and thermal studies [13–15] support the present observations. In the case of pure $Sm_2(MoO_4)_3$, an endothermic peak associated with the ferroelectric phase transition was observed at 197 °C as evidenced by the other physical properties measured [16]. On substituting

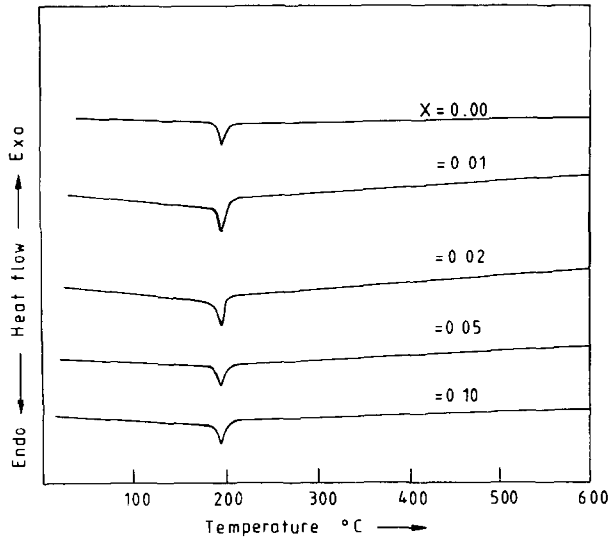

Fig. 3. DSC curves of $(Sm_{1-x}Nd_x)_2(MoO_4)_3$.

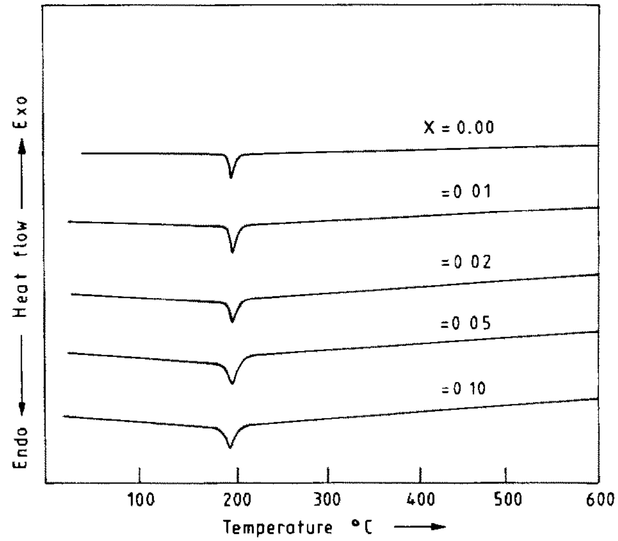

Fig. 4. DSC curves of $(Sm_{1-x}Gd_x)_2(MoO_4)_3$.

different small concentrations ($x = 0.01$, 0.02, 0.05 or 0.1) of Nd and Gd in SMO, which take exactly the same lattice cation positions as in the case of GMO, no appreciable change in their ferroelectric phase transition temperature was observed (Figs. 3 and 4). The symmetrical shape of the DSC peaks of the above compounds suggests that the phase changes are not accompanied by a decomposition reaction or any other changes associated with the thermal effect. The data obtained from our DSC experiment were used to

TABLE 1

T_c, ΔH and C_p values of Sm- and Dy-substituted $Gd_2(MoO_4)_3$

Compounds	Transition temperature T_c (°C)	ΔH (J g^{-1})	C_p J g^{-1} K^{-1})
$(Gd_{1-x}Sm_x)_2(MoO_4)_3$			
$x = 0.00$	159	16.20	2.40
$x = 0.01$	159	16.15	2.38
$x = 0.02$	159	16.25	2.41
$x = 0.05$	159	16.10	2.39
$x = 0.10$	159	16.21	2.41
$(Gd_{1-x}Dy_x)_2(MoO_4)_3$			
$x = 0.00$	159	16.20	2.40
$x = 0.01$	159	16.00	2.38
$x = 0.02$	159	16.18	2.35
$x = 0.05$	159	16.15	2.40
$x = 0.10$	159	16.17	2.41

TABLE 2

T_c, ΔH and C_p values of Nd- and Gd-substituted $Sm_2(MoO_4)_3$

Compounds	Transition temperature (T_c) °C	ΔH ($J\,g^{-1}$)	C_p ($J\,g^{-1}\,K^{-1}$)
$(Sm_{1-x}Nd_x)_2(MoO_4)_3$			
$x = 0.00$	197	15.00	1.98
$x = 0.01$	197	15.00	1.95
$x = 0.02$	197	15.10	1.88
$x = 0.05$	197	15.00	1.92
$x = 0.10$	197	15.20	2.00
$(Sm_{1-x}Gd_x)_2(MoO_4)_3$			
$x = 0.00$	197	15.00	1.98
$x = 0.01$	197	14.95	1.87
$x = 0.02$	197	15.15	1.92
$x = 0.05$	197	15.08	1.95
$x = 0.10$	197	15.20	1.99

determine the enthalpy changes and specific heat at the transition temperature. The estimated values of ΔH and C_p at the transition temperature are shown in Tables 1 and 2. These estimated values of C_p are in good agreement with the reported value [17].

It is interesting to note that little change in the quantity of heat absorbed or evolved was observed on the substitution of an isoelectronic element in small quantity into the cation lattice sites.

Additionally, the mass balance measurements on the mixed specimen verified that neither decomposition or vaporization occured during heating.

CONCLUSION

From the DSC studies of the pure GMO, SMO and their other compounds substituted in small concentrations by the different homovalent cations, it can be concluded that the small-concentration substitution does not affect the phase transition temperature, enthalpy change, specific heat or the basic structure. This is also evident from measurements of other physical properties of the said compounds.

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