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Structure and thermal expansion properties of solid solution $Nd_{2-x}Er_xW_3O_{12}$ ($0.0 \leqslant x \leqslant 0.6$ and $1.5 \leqslant x \leqslant 2.0$)

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Abstract

Solid solutions of $Nd_{2-x}Er_xW_3O_{12}$ ($0.0 \leqslant x \leqslant 0.6$ and $1.5 \leqslant x \leqslant 2.0$) have been successfully prepared and their structures have been investigated by X-ray and neutron powder diffraction. The thermal expansion properties of $Nd_{2-x}Er_xW_3O_{12}$ ($x = 0.2$, 0.4, 1.5, 1.7 and 1.9) were studied with high temperature X-ray diffraction. Positive thermal expansions of compounds $Nd_{2-x}Er_xW_3O_{12}$ with $0.0 \leqslant x \leqslant 0.6$ are found to be anisotropic along the three crystallographic directions where the ***a***-axis expands in the 25–200 °C range and contracts in the 200–800 °C range, while ***b***- and ***c***-axes show expansion in the whole temperature range. Negative thermal expansion coefficient α_l of compounds $Nd_{2-x}Er_xW_3O_{12}$ with $1.5 \leqslant x \leqslant 2.0$ becomes more negative from -6.032×10^{-6} to $-6.28 \times 10^{-6}\ {}^\circ C^{-1}$ with the neodymium content increasing.

Keywords: Thermal expansion; Tungstates; Neutron powder diffraction; X-ray diffraction

1. Introduction

Most materials expand lattice on heating owing to the anharmonic lattice dynamics [1]. However, a growing number of compounds have been found to contract on heating, which typically originates from the presence of low-energy transverse vibrations or volume-reducing cooperative rotations of rigid corner-sharing polyhedra [2–6]. Materials with negative thermal expansion are of considerable scientific and technological interest, especially their composite. It is reported that composite materials containing negative thermal expansion (NTE) materials can be produced with tuned thermal expansion coefficients to be negative, positive or almost zero [7–9]. Controlled expansion composites can be widely used in electronic applications, printed circuit boards, optical applications, biomedical applications and so on, where the NTE materials can be used to compensate the changes in the devices and avoid cracks or separation between materials [7,8,10–13].

Negative thermal expansion (NTE) has been observed in many tungstates and molybdates with the general formula of $A_2M_3O_{12}$ (A ranging from Al^{3+} to some of the heavier trivalent rare earth cations) [14–19]. It was reported that $Er_2W_3O_{12}$ shows NTE in the temperature range of 473–1073 K with thermal expansion coefficient (TEC) of -6.74×10^{-6}/K and $Nd_2W_3O_{12}$ exhibits positive thermal expansion with TEC of 5.54×10^{-6}/K in the temperature range of RT-1073 K [16,20]. It is thus very interesting to make $Nd_{2-x}Er_xW_3O_{12}$ and study their thermal expansion properties. By adjusting the Nd/Er ratio, it is possible to make compounds $Nd_{2-x}Er_xW_3O_{12}$ have controllable thermal expansion coefficients. Here we report our work on synthesis, structure and thermal expansion properties of $Nd_{2-x}Er_xW_3O_{12}$ ($0.0 \leqslant x \leqslant 0.6$ and $1.5 \leqslant x \leqslant 2.0$).

2. Experiment

Solid solutions with nominal formulas $Nd_{2-x}Er_xW_3O_{12}$ ($0.0 \leqslant x \leqslant 0.6$ and $1.5 \leqslant x \leqslant 2.0$) were prepared by conventional solid-state reaction from a mixture of Er_2O_3 (purity 99.9%), Nd_2O_3 (purity 99.9%) and WO_3 (purity $\geqslant$ 99.0%). All the starting materials were preheated at 500 °C before weight-

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ing to protect from H_2O and CO_2. Stoichiometric ratios of the reactants were thoroughly ground and calcined at 1000–1100 °C for 48 h with intermediate regrinding.

X-ray and neutron powder diffractions were performed to determine the crystallographic structure. The room temperature X-ray diffraction data were recorded on MSAL-XD2 using Cu K_α radiation at Laboratory of Inorganic Materials of Graduate University of the Chinese Academy of Sciences. High-temperature XRD data were collected on PAN X'Pert PRO MPD with Cu K_α radiation at Beijing Normal University. Data were refined using the Rietveld software, FULLPROF [21]. Neutron powder diffraction data for $Nd_{2-x}Er_xW_3O_{12}$ ($x = 0.2$ and 0.4) were collected on the Special Environment Powder Diffractometer (SEPD) at room temperature at Argonne's Intense Pulsed Neutron Source (IPNS). Neutron diffraction data were refined using the program GSAS [22].

3. Results and discussion

3.1. Phase formation

To partially substitute one or more elements in a compound, the substituting limit is related to the sizes of the elements being replaced and the size of the substituents. According to Hume–Rothery rule [23], the atomic size factor is defined as $\delta = (r_A - r_B)/r_A$, where r_A and r_B are the atomic size of atom A and B, respectively. If the atomic size of atom B differs by more than 15% from that of atom A, the resulting structure will be unstable. In this study the atomic radius of Er and Nd are 2.45 and 2.64 Å, and the atomic size factor δ is calculated to be 7.2% and thus, $Er_2W_3O_{12}$ and $Nd_2W_3O_{12}$ should be able to form solid solutions in a finite range. In fact solid solutions of $Nd_{2-x}Er_xW_3O_{12}$ for $0.0 \leqslant x \leqslant 0.6$ and $1.5 \leqslant x \leqslant 2.0$ have been successfully prepared in this study.

Samples with orthorhombic structure are highly hygroscopic at room temperature, which has been observed in all the orthorhombic rare earth tungstates with rare earth ranging from Y to Lu [16,20]. These tungstates can form a stable trihydrate structure at room temperature when stored under saturated NH_4Cl, and the water of hydration can be removed when temperature is above 333 K. The hydrated XRD patterns of $Nd_{2-x}Er_xW_3O_{12}$ ($1.5 \leqslant x \leqslant 2.0$) are similar to the pattern of $Yb_2W_3O_{12}$ previously reported by Sumithra et al. [20], which is quite different from the patterns of unhydrated samples.

3.2. XRD data

The room temperature X-ray powder diffraction patterns of the nominal compositions $Nd_{2-x}Er_xW_3O_{12}$ ($0.0 \leqslant x \leqslant 0.6$ and $1.5 \leqslant x \leqslant 2.0$) indicate that (1) for $0.0 \leqslant x \leqslant 0.6$, the resulting solid solution will keep the $Nd_2W_3O_{12}$ structure and crystallize in monoclinic space group $C2/c$; (2) for $1.5 \leqslant x \leqslant 2.0$, the resulting solid solution will keep the $Er_2W_3O_{12}$ structure and crystallize in orthorhombic space group P*nca*.

Refinements of the X-ray powder diffraction patterns were carried out by using program Fullprof Suite 2000. Lattice parameters of $Nd_{2-x}Er_xW_3O_{12}$ ($0.0 \leqslant x \leqslant 0.6$) and $Nd_{2-x}Er_xW_3O_{12}$ ($1.5 \leqslant x \leqslant 2.0$) are given in Fig. 1 and Fig. 2, respectively. From Fig. 1, it can be seen that the lattice parameters ***a***, ***b***, ***c*** and ***V*** decrease linearly with increasing erbium content as expected because of the difference in the ionic sizes of Er^{3+} (88 pm) and Nd^{3+} (100 pm) ion. Fig. 2 shows that the lattice parameter ***b***, ***c*** and ***V*** of $Nd_{2-x}Er_xW_3O_{12}$ ($1.5 \leqslant x \leqslant 2.0$) also decrease monotonically with increasing erbium content due to the same reason just mentioned. However, ***a***-axis increases with the increase of erbium content, indicating the anisotropy of $Nd_{2-x}Er_xW_3O_{12}$ ($1.5 \leqslant x \leqslant 2.0$). The dependence of the lattice parameter on erbium content follows the Vegard's law [24, 25], which proved that solid solution of $Nd_{2-x}Er_xW_3O_{12}$ has been successfully prepared in this study.

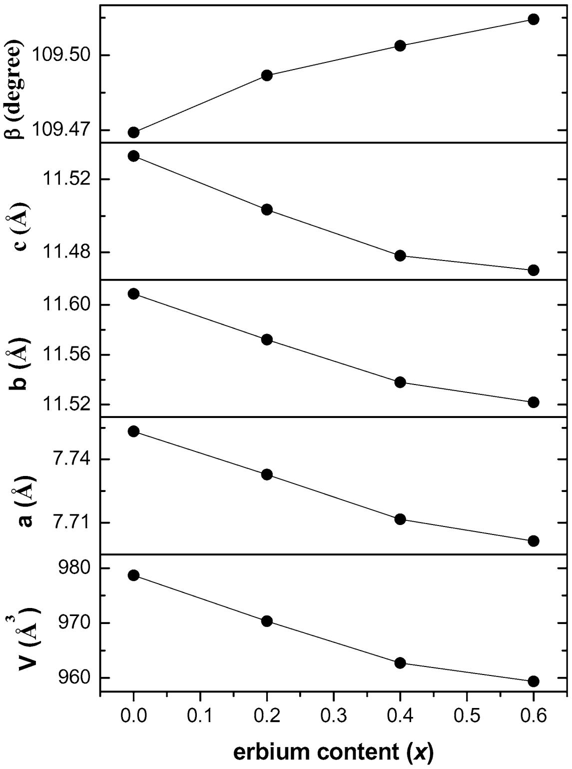

Fig. 1. The dependence of the cell parameters of $Nd_{2-x}Er_xW_3O_{12}$ ($0.0 \leqslant x \leqslant 0.6$) on the erbium content.

3.3. NPD data

Neutron powder diffraction data of $Nd_{2-x}Er_xW_3O_{12}$ ($x = 0.2$ and 0.4) were collected and refined by the Rietveld method using program GSAS. The refinement results are shown in Fig. 3 and the detail structure information is listed in Table 1. Selected bond lengths and angles are given in Table 2. Fig. 4 shows the structure of $Nd_{2-x}Er_xW_3O_{12}$ ($x = 0.2$ and 0.4), which has a distorted scheelite structure with space group $C_{2/c}$. This structure is identical to those reported for $La_2W_3O_{12}$ and $Eu_2W_3O_{12}$ [26,27]. Each Nd(Er) atom has eight oxygen neighbors, and the average bond length for Nd–O is 2.44 and 2.428 Å for $Nd_{1.8}Er_{0.2}W_3O_{12}$ and $Nd_{1.6}Er_{0.4}W_3O_{12}$, respectively. Obviously, the substitution of Nd (III) by smaller Er (III) leads to the decrease of Rare Earth–Oxygen bond length. W1 atom is in tetrahedral coordination with oxygen atoms, and the edges