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Preparation and structure of quaternary mixed sulphide $Li(Lu,M)S_2$ (M=U,Ce)

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Abstract

The $Li(Lu,M)S_2$ (M=U,Ce) compounds were prepared by the reaction of the weighed mixture of Li_2CO_3, Lu_2O_3 and UO_2 or CeO_2 in a CS_2+N_2 gas mixture at 800°C for 2 h. It was proved that a series of $Li(Lu_yU_{1-y})S_2$ compounds showed an NaCl-type structure in a wide range of y values from 0.2 to 0.8, while the ternary sulphides $LiLuS_2$ and Li_2US_3 crystallized in hexagonal α-$NaFeO_2$-type structure (R3m) and monoclinic structure (C2/m), respectively. The Rietveld refinement showed that the compound was $Li_{1.5}Lu_{0.5}U_{0.5}S_{2.5}$ with cubic lattice parameter 5.420 Å and that the space group was Fm3m with the final R_I value of 0.027. A series of $Li(Lu_yCe_{1-y})S_2$ compounds also showed the NaCl structure in a range of y values from 0.4 to 0.8, though $LiCeS_2$ adopts a Th_3P_4 structure. The final R_I value for the compound $Li_{1.17}Lu_{0.5}Ce_{0.5}S_{2.17}$ with cubic lattice parameter 5.531 Å was 0.052 after the Rietveld refinement. © 1998 Elsevier Science S.A.

Keywords: Ternary sulphides; Rietveld refinement; Structure

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1. Introduction

A series of rare-earth ternary sulphides, $ALnS_2$ (A= alkali metal, Ln= rare-earth elements) are known to crystallize in either a cubic structure or a hexagonal one [1,2]. For $NaLnS_2$ with Ln=La and Ce, the structure is cubic NaCl-type with the random distribution of Na and Ln over the metal sites, while the structure is hexagonal α-$NaFeO_2$-type if Ln=Gd, Tb, Dy, Ho, Er and Yb [3]. In the latter case, two different kinds of cations occupy alternately the metal sites on the (111) cubic planes forming a layer-ordered superstructure. Ballestracci and Bertaut [4] reported that the lithium compounds, $LiLnS_2$, adopted the NaCl structure for Ln=Pr to Tb and Y, and the α-$NaFeO_2$ structure for Ln=Ho to Lu. According to Ohtani et al. [5], on the other hand, $LiLnS_2$ compounds take both the NaCl and α-$NaFeO_2$ structures for Ln=Dy, Ho, Er or Y but only the NaCl structure for Ln=Nd to Tb. Furthermore, $LiLnS_2$ compounds (Ln=La or Ce) have neither the NaCl nor α-$NaFeO_2$ structure, but Th_3P_4 structure.

When the rare-earth elements in $ALnS_2$ (A=Li and Na) are replaced by uranium, a ternary uranium sulphide, A_2US_3, is formed which is crystallized in a monoclinic system with space group C2/m [6]. Since this compound can be rewritten as $A(A_{1/3}U_{2/3})S_2$, one third of uranium atoms in a uranium layer is replaced regularly by alkali metals in order to satisfy the electrical neutrality condition. Then, the possibility of formation of solid solution between rare-earth element and uranium can be considered. The Lu^{3+} ion has the smallest crystal radius in the rare-earth elements, and its value 1.001 Å (CN=6) is close to 1.03 Å (CN=6) of U^{4+} [7].

In the present paper, preparation and structure of quaternary mixed sulphides $Li(Lu,U)S_2$ were studied by changing the Lu/U ratios. The formation of quaternary sulphide $Li(Lu,Ce)S_2$ was also studied since cerium takes on trivalent state in addition to the tetravalent state as uranium. The crystal structure change was studied in relation to the metal ratio and composition.

2. Experimental

Analytical grade CS_2(b.p. 46–47°C and max. H_2O 0.02%) and Li_2CO_3 were obtained from Wako Pure Chemical Ind. Co., Ltd., and used as received. Commercial grade CeO_2 and Lu_2O_3 of 99.9% purities obtained from Nihon Yttrium Co., Ltd., were used as received. Uranium dioxide was synthesized by the reduction of purified UO_3 with H_2 at 1000°C for 4 h. A weighed mixture of Li_2CO_3,

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Lu_2O_3 and UO_2 in a platinum or carbon boat was set in the quartz reaction tube and reacted at 800°C for 2 h in a stream of CS_2/N_2 gas mixture, which was obtained by passing N_2 through liquid CS_2 at room temperature. After the reaction, the product was treated in an inert glove box for powder X-ray diffractometry since the compounds containing lithium are very hygroscopic.

X-ray powder diffractometry was carried out with a Rigaku Type RAD-IC diffractometer with CuKα radiation (40 kV, 20 mA) monochromatized with curved pyrolytic graphite. The slit system used was 0.5°–0.6 mm–0.5°–0.05 mm. The intensity calculation and lattice parameter calculation by the least-squares method were carried out with the LAZY-PULVERIX [8] and the LCR2 [9] programs, respectively. The program RIETAN [10] was used for refining the powder data. The composition of Ln, U and S were determined by the EPMA system using Hitachi X-560 Scanning Electron Microanalyzer. The lithium amount was determined by the iodometric titration method following the periodate precipitation [11].

3. Results and discussion

When the weighed mixtures of Li_2CO_3, Lu_2O_3 and UO_2 with different ratios of Lu/U were reacted with CS_2 at 800°C for 2 h, a series of black compounds $Li_2Lu_yU_{1-y}S_z$ were obtained. The X-ray diffraction patterns for these compounds are shown in Fig. 1. The hexagonal $LiLuS_2$ (S.G.:$R\bar{3}m$) [4] and monoclinic Li_2US_3 (S.G.:C2/m) [6] were obtained at $y=1.0$ and 0.0, respectively. However, the NaCl-type structure (S.G.:Fm3m), which has been seen for $LiLnS_2$ (Ln=Nd and Tb) [5], appeared in a wide range of y values from 0.2 to 0.8. When $y=0.5$, a small very broad peak was seen near $2\theta=15°$, which might be caused by the short range ordering structure. When the y value decreased from 0.5 to 0.2, the small peaks of hexagonal structure appeared near the broad peak, while those for monoclinic structure appeared with increasing y value from 0.5 to 0.8. As reported by Ohtani et al. [5], the α-$NaFeO_2$ structure of $ALnS_2$ is obtained by the ordering of the two kind of cations (A and Ln) in the NaCl structure. On the other hand, the crystal symmetry was decreased for Na_2US_3 by the substitution of one third of uranium atom in the uranium layer of the hexagonal cell with sodium resulting in formation of the monoclinic structure [6]. The above results show that the three types of the cations (Li, Lu, U) in a series of $Li_xLu_yU_{1-y}S_z$ compounds are distributed randomly over cation sites forming the NaCl structure.

When the lithium concentration x of $Li_xLu_{0.5}U_{0.5}S_z$ ($1\leq x\leq 2$) was changed, a single phase compound was obtained at an apparent x value of 1.7. At $x\geq 1.8$, the impurity phase Li_2S [12] was observed to exist as well as the NaCl-type phase. The other phases such as Li_2US_3 [6], Lu_2O_2S [13] were identified at $x=1.5$ and 1.6. Furthermore, $LiLuS_2$ phase was observed as well as the above phases at $x=1.0$. From the results of EPMA measurement for the single phase compound, the atom fractions of Lu, U and S were determined as 14.5, 14.5 and 70.5%, respectively. Lithium content was 3.01 wt.% by chemical analysis. These values with experimental errors gave the chemical formula of this quaternary compound as $Li_{1.42\pm0.06}Lu_{0.5}U_{0.5}S_{2.43\pm0.06}$.

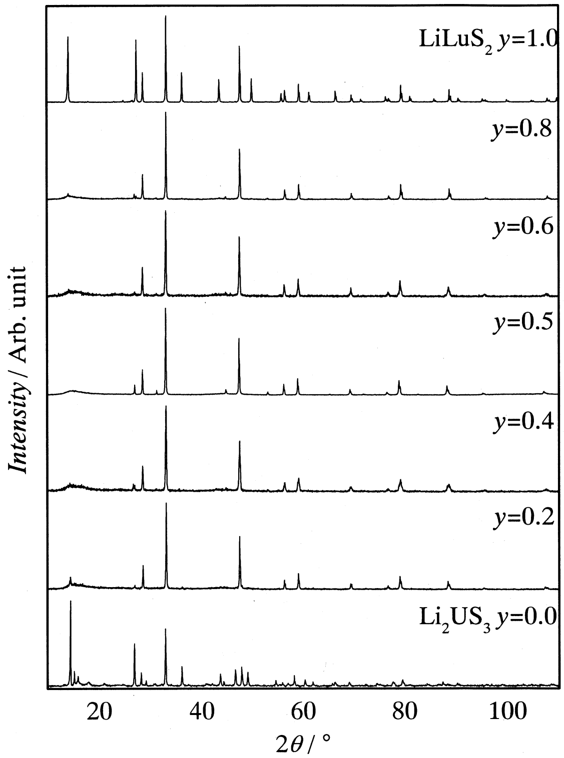

Fig. 1. Change of X-ray diffraction patterns for $Li_{2.0}Lu_yU_{1-y}S_z$ with y values ($y=0.0$–1.0).

The Rietveld refinement [10] of the X-ray data was carried out for the single phase compound. Result of calculation of the R_I value with the x value of $Li_xLu_{(1-x)/2}U_{(1-x)/2}S$ between 0.5 to 0.7 is depicted in Fig. 2. The R_I value showed a minimum at $x=0.6$ which gave the chemical formula to be $Li_{1.5}Lu_{0.5}U_{0.5}S_{2.5}$. This formula agrees well with that obtained by chemical and EPMA analyses. The obtained crystallographic data are given in Table 1. The cubic lattice parameter, a, of the compound was 5.420 Å. The final R_I and R_F factors of $Li_{1.5}Lu_{0.5}U_{0.5}S_{2.5}$ were 0.027 and 0.019, respectively. By using the crystal radii of Li^+, Lu^{3+}, U^{4+} and S^{2-} in six coordination [7], the fractional mean of crystal radii of cations of $Li_{1.5}Lu_{0.5}U_{0.5}S_{2.5}$ i.e. 0.946 Å and S^{2-} was summed to be 2.646 Å which was in good agreement with the 2.710 Å obtained by the lattice parameter. The small difference may be caused from the covalent contribution between cations and sulphur.

The X-ray diffraction patterns for wine red colour cerium compounds, $LiLu_yCe_{1-y}S_2$, of various y values

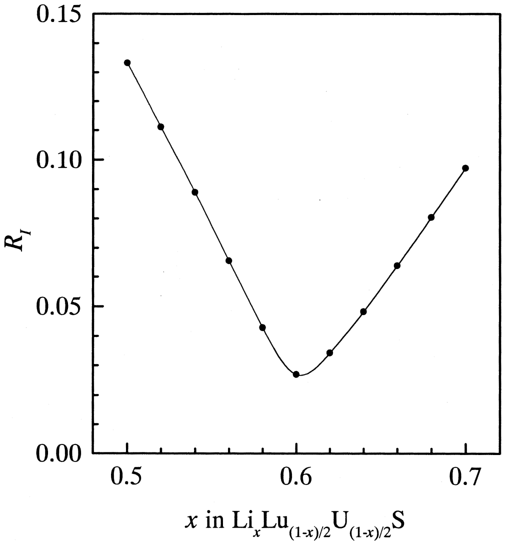

Fig. 2. Change of R_I value as a function of x of $Li_xLu_{(1-x)/2}U_{(1-x)/2}S_z$.

from 0 to 1 are shown in Fig. 3. The hexagonal $LiLuS_2$ (α-$NaFeO_2$-type) [4] was observed at $y=1.0$. The cubic $LiCeS_2$ phase (Th_3P_4-type) [5] was identified with other impurity phases such as Li_2S [12] and $Ce_4O_4S_3$ [14] at $y=0$. A mixture of the cubic phases of the NaCl and Th_3P_4 structures as well as the above impurity phases was obtained at $y=0.2$. The NaCl structure with small amounts of Li_2S, $Ce_4O_4S_3$ phases was observed at y values from 0.4 to 0.8. The Lu_2O_2S phase coexisted at y values higher than 0.5. The diffraction pattern at $y=0.5$ showed the smallest peak intensities for Li_2S, $Ce_4O_4S_3$ and Lu_2O_2S phases from which their amounts were estimated to be 4, 3 and 3%, respectively.

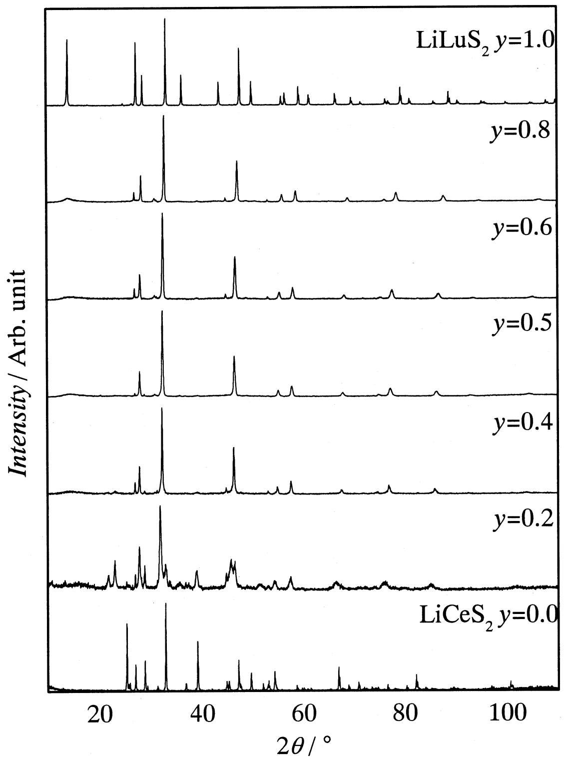

Fig. 3. Change of X-ray diffraction patterns for $LiLu_yCe_{1-y}S_2$ y values ($y=0.0$–1.0).

From the results of EPMA and chemical analyses, the chemical formula of this compound was determined as $Li_{1.92\pm0.06}Lu_{0.5}Ce_{0.5}S_{2.18\pm0.06}$. The refinement of the crystal structure was carried out for $Li_{1.92}Lu_{0.5}Ce_{0.5}S_{2.18}$ by the Rietveld method [10]. Since the compound was a mixture with small amounts of Li_2S, $Ce_4O_4S_3$ and Lu_2O_2S, calculation was made without including the peaks for these impurities. When the R_I value was calculated with the x value of $Li_xLu_{(1-x)/2}Ce_{(1-x)/2}S$ between 0.4 to 0.6, the R_I value showed a minimum at $x=0.54$ which gave the chemical formula as $Li_{1.17}Lu_{0.5}Ce_{0.5}S_{2.17}$. Good agreement was observed between the calculated and observed sulphur amounts, while the chemically analyzed lithium amount was larger than the calculated value. This difference may be caused by the error in the Rietveld analysis because of the small atomic scattering factor of the lithium atom. The obtained crystallographic data are given in Table 1. The cubic lattice parameter, a, of the compounds was 5.531 Å. The final R_I and R_F factors of $Li_{1.17}Lu_{0.5}Ce_{0.5}S_{2.17}$ were 0.052 and 0.029, respectively.

Table 1
Crystallographic data of $Li_xLu_{0.5}M_{0.5}S_z$ (M=U,Ce). Space group: Fm3m, Atomic position: Li,Lu,M in 4a (0, 0, 0), S in 4b (1/2, 1/2, 1/2)

	$Li_xLu_{0.5}U_{0.5}S_z$	$Li_xLu_{0.5}Ce_{0.5}S_z$
Lattice parameter (Å)	5.420	5.531
Occupation factor		
Li in 4a	0.6	0.54
Lu in 4a	0.2	0.23
M in 4a	0.2	0.23
S in 4b	1.0	1.0
Isotropic temperature factor B $(Å)^2$		
Li,Lu,M	0.54	0.59
S	0.35	0.74
R_I	0.027	0.052
R_F	0.019	0.029

When lanthanum was used instead of uranium or cerium, the synthesis of the NaCl ternary sulphide was unsuccessful. Since uranium and cerium can take on both tri- and tetravalent states, the mixed valence state of M in $Li(Lu,M)S_2$ seems to play an important role in giving the NaCl structure.

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