New crystals in the lithium sulfate family

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The preparation and structures of caesium lithium sulfate, $Cs_{1.15}Li_{2.85}(SO_4)_2$, and caesium lithium rubidium sulfate, $Cs_{0.90}Li_{2.88}Rb_{0.22}(SO_4)_2$, are described and discussed in the context of simple and double sulfate polymorphism. The latter structure is related to the former through the substitution of Rb for Cs. In both crystals, the sulfate ions occupy two non-equivalent sites, but the ions are disordered in $Cs_{1.15}Li_{2.85}(SO_4)_2$.

Comment

Double sulfate crystals ($LiASO_4$, with A = Na, K, Rb, Cs and NH_4) have been widely studied because of the rich variety of properties and phase transitions exhibited by this family. Among the compounds with this chemical formula, crystals can be found displaying ferroelectricity (Shiroishi et al., 1976), ferroelasticity (Pakulski et al., 1983), superionic conduction (Karlsson & McGreevy, 1995) and incommensurate phases (Mashiyama et al., 1979). In general, double sulfates crystallize in a tridymite-like structure, where A^+ cations are piled along the c axis at the vertices of pseudo-hexagonal networks, which are distributed inside layers of SO_4 tetrahedra. Li^+ cations are located at vacancies of the network between the layers (Aleksandrov, 1993).

Two polymorphic families are observed in double sulfate compounds because of distortions of the pseudo-hexagonal lattice. The first corresponds to lattices with hexagonal basis vectors or closely related structures, such as, for example, a monoclinic lattice with $a_h \simeq b_h$ and $\beta \simeq 120°$. Another form of polymorphism is characterized by a set of orthogonal axes, which are related to the hexagonal axes by $a_o = a_h$, $b_o = a_h$ and $c_o = c_h$, or also a monoclinic lattice, characterized by slight distortion of the orthogonal translations, with one of the internal angles close to 90°. It is known that the formation of these polymorphs is closely related to the dynamics and possible orientations of the tetrahedral sulfate anions in the

structure and the ionic radius of the A^+ cation. As an example of these polymorphs, we show in Fig. 1 the crystal structures of Cs_2SO_4 and $KLiSO_4$, where the distorted and regular hexagonal lattices can be observed. The A^+ cation lattice dependence is particularly evident in mixed crystals $[Li(A'A'')SO_4]$, in which the crystal structure and the phase-transition sequence are strongly dependent on the concentration and radius of the alkali cations.

Usually, simple and mixed double sulfates grow from aqueous solutions containing stoichiometric mixtures of the simple sulfate salts $Li_2SO_4·H_2O$, A'_2SO_2 and, if necessary, A''_2SO_4. Generally, alkaline sulfate salts give rise to structures with the same characteristics as double sulfates. However, Li_2SO_4 and $Li_2SO_4·H_2O$ crystallize in a different structure pattern because the small lithium radius is not able to support the pseudo-hexagonal network, and consequently Li^+ cations are approximately aligned to the basal plane of the SO_4 tetrahedra.

Recently, on the basis of X-ray powder diffraction and Raman scattering, a new phase in the $LiRbSO_4–LiCsSO_4$ system was characterized (Lima et al., 2000). This phase seems to be stable over variations of the growing conditions. Polarized Raman spectra and X-ray powder diffraction suggest that the crystal structure is monoclinic, with point group C_s. Moreover, the lattice parameters [$a = 15.983$ (6), $b = 5.050$ (4), $c = 5.191$ (7) Å and $\beta = 90.22°$] cannot be interpreted as a simple distortion of the tridymite network.

Based on these results, several attempts were made to grow high-quality single crystals with the structure reported by Lima et al. (2000) suitable for structure determination. We report here single-crystal X-ray diffraction studies of two crystals obtained from different salt mixtures, with formulae $Cs_{1.15}Li_{2.85}(SO_4)_2$, (I), and $Cs_{0.90}Li_{2.88}Rb_{0.22}(SO_4)_2$, (II), which have structures, established from least-squares refinement, closely related to those reported by Lima et al. (2000). These structures do not exhibit the same features as most other alkali
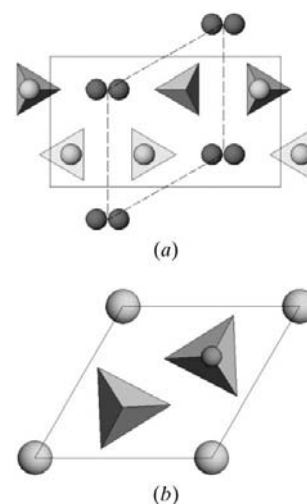

Figure 1
Projection of the crystals structures of (a) Cs_2SO_4 along the a axis and (b) $KLiSO_4$ along the c axis. Cs and Li atoms are represented by large and small spheres, respectively. Dashed lines show the pseudo-hexagonal network.

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sulfates, where pseudo-hexagonal networks composed of sulfate anions and one kind of cation are piled along the c axis (typical of the tridymite-like structures) and the other kind of cation is located at vacancies in the network between the layers (Aleksandrov, 1993

Compound (I) is orthorhombic, and projections of the structure on the ac and bc planes are shown in Figs. 2(a) and 2(b). The Cs^+ ions occupy two different Wyckoff positions, $viz.$ a and b. Several refinement tests indicated that atoms in position a have full occupancy, while atoms in position b have partial occupancy [0.15 (2)]. Li^+ ions were refined with their site occupancies constrained such that, taking into account the Cs^+ ions, the total charge is two. The structure was found to be a racemic twin, the fractional component of the inverted structure being 0.53 (6) (Flack, 1983). Besides the Li and Cs occupational disorder observed in the structure, the O atoms located at the basal plane of the sulfate anion are also disordered, thus allowing two possible orientations for this group. As shown in Fig. 2(c), O11 atoms are located at the apices of the tetrahedra centered on S1, while the two possible bases are determined by each set of O21, O12 and O14 atoms. The coordination of the S2 atom is shown in Fig. 2(d) and is similar to the coordination around S1.

Compound (II) is monoclinic, and projections of the structure on the ac and bc planes are shown in Figs. 3(a) and 3(b). The Cs^+ and Rb^+ ions occupy two different general positions, both with partial occupancies. Several refinement tests ruled out the possibility that these sites are shared by both ions. Li^+ ions were refined, as in the previous structure, with their site-occupation factors constrained such that, taking into account the Cs^+ and Rb^+ ions, the total charge is two. No disorder of the sulfate anions was observed in this crystal. Furthermore, the structure is consistent with the previous Raman scattering study, which indicated a monoclinic lattice with C_s symmetry (Lima et $al.$, 2000).

Despite the fact that both refinements were carried out independently, with different space groups and chemical formulae, the structures are nearly isomorphous. In fact, each structure can be refined with the diffraction data of the other, although the refinements converge to higher $R1$ factors. A comparison of the two crystal structures (Figs. 2 and 3) reveals the main similarities and differences between them. Note that the unit cell of (I) has been shifted by $(0,0,\frac{1}{4})$ in order to help the comparison. In (II) the monoclinic angle β of 90.297 (2)° may be thought of as a distortion from the orthorhombic angle of 90°, which results in the removal of the mirror plane. Cation substitution influences the ordering of the sulfate anions in the crystal structure. In the orthorhombic structure, (I), the sulfate anions are found with two equally probable orientations, while in the monoclinic structure, (II), the sulfate anions are well ordered. Although orientational disorder of the sulfate anions is only observed in (I), the main orientation of these groups is the same as that in (II). Atoms Li2 and Li1 do not change their positions relative to the sulfate anions, while in (II) atom Li3 is almost aligned with Li1, thus forming a plane perpendicular to the [001] direction. The main difference between the two structures is the Li4 and heavy-cation distribution. In (I), the Cs^+ cations are aligned in the [100] direction, alternating between full and partially occupied sites, and the Li4 atoms are intercalated among one of the sulfate layers. In (II), the Rb^+ ions are shifted from the line determined by the Cs^+ cations and partially occupy the Li4 site, as this site is vacant..

Finally, we would like to comment on the reported structures in the context of simple and double sulfate poly-
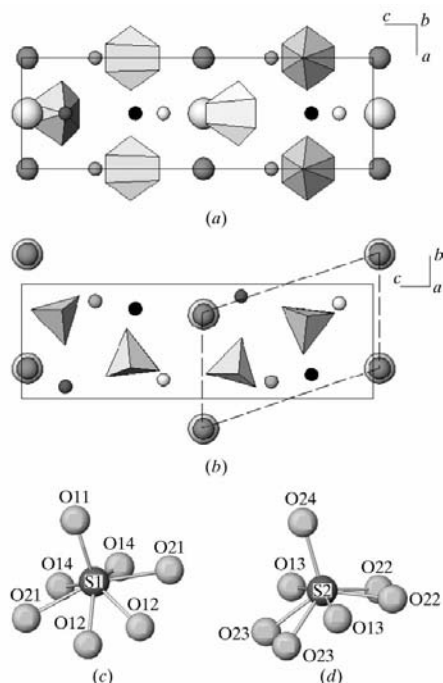

Figure 2
Projections of the crystal structure of $Cs_{1.15}Li_{2.85}(SO_4)_2$ along the (a) b and (b) a axis. Large, medium and small spheres represent Cs2, Cs1 and Li atoms, respectively. The small spheres become darker, indicating different Li-atom positions (from 1 to 4). The dashed lines show the pseudo-hexagonal network. The atomic coordination of (c) S1 and (d) S2 is also shown.
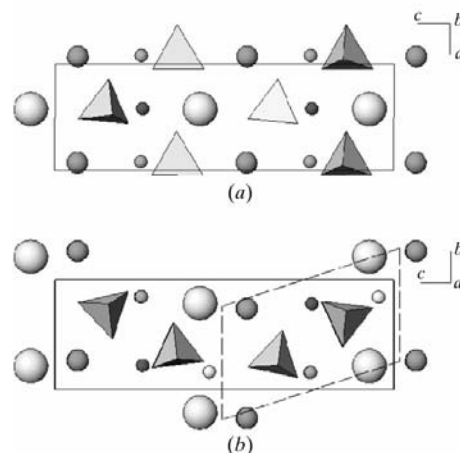

Figure 3
Projections of the crystal structure of $Cs_{0.90}Li_{2.88}Rb_{0.22}(SO_4)_2$ along the (a) b and (b) a axis. Large, medium and small spheres represent Rb, Cs and Li atoms, respectively. The small spheres become darker, indicating different Li-atom positions (from 1 to 3). The dashed lines show the pseudo-hexagonal network.

morphism. It has been pointed out that double sulfates are characterized by a pseudo-hexagonal network determined by the heavy ions, within which layers of sulfate anions perpendicular to the pseudo-hexagonal axis are distributed. A comparison of structures representative of simple and double sulfate polymorphism (Fig. 1), with the projection of (I) (Fig. 2b) and (II) (Fig. 3b) on the bc plane, reveals an atomic pattern similar to that observed in the pseudo-hexagonal network; this pattern is represented by dashed lines in the figures. On the basis of this lattice, we can associate the a_h and c_h hexagonal axes with the a_o (a_m) and b_o (b_m) axes of the orthorhombic (monoclinic) cell, respectively. Note that the a_b pseudo-axis value corresponds approximately to that measured in double sulfates, but the c_h pseudo-axis is much shorter. This contraction is due to the low occupation of the heavy-ion sites, which are responsible for the pseudo-hexagonal framework. Furthermore, in the structures reported in this work, the sulfate anions are not intercalated between the planes determined by the heavy ions but lie in the same planes (see Figs. 2a and 3a). The c_h-axis contraction does not allow Li^+ ions to be placed on top of the SO_4 tetrahedra (see Fig. 1b), but the Li^+ ions occupy interstitial sites between these groups. According to the previous discussion, the c axis of the monoclinic and orthorhombic lattices reported in this work should be associated with the b_o axis of the orthorhombic polymorph of sulfate crystals, which is expected to be a multiple of $3^{1/2}a_h$. Thus, in spite of the small contraction, it is observed that $c \simeq 2(3)^{1/2}a$. These results confirm the correspondence of the crystal structures of (I) and (II) with the usual polymorphism of simple and double sulfate crystals.

Experimental

Small single crystals of (I) and (II) were grown by the vapor-diffusion technique (Henisch, 1996) at controlled temperature (293 K) and pH (9). Two saturated solutions containing a 2:1:1 molar ratio of Li_2SO_4, Cs_2SO_4 and Rb_2SO_4, and a 1:0.1 ratio of Li_2SO_4 and Cs_2SO_4 were prepared in distilled and de-ionized water, producing small crystals of (I) and (II), respectively.

Compound (I)

Crystal data

$Cs_{1.15}Li_{2.85}(SO_4)_2$
$M_r = 364.77$
Orthorhombic, $Pmc2_1$
$a = 5.0620$ (2) Å
$b = 5.2230$ (3) Å
$c = 16.0060$ (9) Å
$V = 423.18$ (4) Å^3
$Z = 2$
$D_x = 2.872$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 17 795 reflections
$\theta = 1.0–27.5°$
$\mu = 5.55$ mm^{-1}
$T = 293$ (2) K
Prism, colorless
$0.29 \times 0.19 \times 0.08$ mm

Data collection

Nonius KappaCCD diffractometer
φ scans and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.290$, $T_{max} = 0.661$
1740 measured reflections
1065 independent reflections

1053 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 27.5°$
$h = -6 \rightarrow 6$
$k = -6 \rightarrow 6$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.133$
$S = 1.07$
1064 reflections
109 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0969P)^2 + 0.7843P]$
    where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.96$ e Å^{-3}
$\Delta\rho_{min} = -0.87$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.166 (17)
Absolute structure: Flack (1983)
Flack parameter = 0.50 (6)

Compound (II)

Crystal data

$Cs_{0.90}Li_{2.88}Rb_{0.22}(SO_4)_2$
$M_r = 350.53$
Monoclinic, Pc
$a = 5.0530$ (2) Å
$b = 5.1990$ (4) Å
$c = 15.9840$ (8) Å
$\beta = 90.297$ (3)°
$V = 419.90$ (4) Å^3
$Z = 2$

$D_x = 2.772$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8702 reflections
$\theta = 1.0–27.5°$
$\mu = 5.75$ mm^{-1}
$T = 293$ (2) K
Prism, colorless
$0.09 \times 0.08 \times 0.06$ mm

Data collection

Nonius KappaCCD diffractometer
φ scans and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.632$, $T_{max} = 0.750$
12 898 measured reflections
1833 independent reflections

1810 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 27.5°$
$h = -6 \rightarrow 6$
$k = -6 \rightarrow 6$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.082$
$S = 1.22$
1833 reflections
137 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 0.1683P]$
    where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.07$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.038 (3)
Absolute structure: Flack (1983)
Flack parameter = −0.05 (2)

Colorless prismatic single crystals of both title compounds were selected with the aid of a polarizing microscope. The occupancies of the cations were initially refined and were then fixed for the final refinement. Occupancies for (I) were found to be 0.15 (2) for Cs2, 0.32 (3) for Li2, 0.20 (2) for Li3 and 0.40 (3) for Li4, while occupancies for (II) were found to be 0.90 (1) for Cs, 0.22 (1) for Rb, 0.92 (2) for Li1 and 0.96 (2) for Li2.

For both compounds, data collection: *COLLECT* (Enraf–Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

inorganic compounds

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1399). Services for accessing these data are described at the back of the journal.

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