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Li_2BeCl_4 and Na_2BeCl_4: Two Olivine-Type Chlorides

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Li_2BeCl_4 and Na_2BeCl_4, the only ternary compounds in the systems $M^ICl–BeCl_2$ (M^I = Li, Na), are reinvestigated by X-ray, IR, and Raman methods. Both compounds are not polymorphic. They crystallize in the olivine structure (a = 1251.2(2), b = 733.6(1), and c = 580.8(1) and a = 1334.0(3), b = 809.3(2), and c = 609.1(1) pm, respectively), as shown from vibrational spectra, x-ray intensity calculations, and the relation of the unit-cell dimensions, which is 1 : 0.590 : 0.467 for olivine-type compounds within a narrow range. © 1992 Academic Press, Inc.

Introduction

Li_2BeCl_4 and Na_2BeCl_4 are the only ternary compounds of the systems $M^ICl–BeCl_2$ (M^I = Li, Na) (*1–4*). The crystal structures and most physical properties are not known so far. Within the scope of our studies on ternary and quaternary lithium chlorides with fast ionic conductivity (*5*, *6*), we reinvestigated these chlorides by X-ray diffraction, high-temperature X-ray, IR, and Raman spectroscopic methods.

Experimental

Microcrystalline samples of $M^I_2BeCl_4$ (M^I = Li, Na) were prepared by fusing stoichiometric mixtures of M^ICl and $BeCl_2$ at 380°C and slowly cooling down to ambient temperature. Details of the experimental procedures (X-ray, high-temperature X-ray, IR, and Raman studies) are given elsewhere (*5*).

Results and Discussion

Contrary to most ternary lithium chlorides, Li_2MCl_4 (M = Mg, Mn, Fe, Co, Zn, Cd) (*5–8*), Li_2BeCl_4 is not polymorphic. The same is true for Na_2BeCl_4. The phase transition reported in (*4*) was not confirmed by our high-temperature X-ray experiments.

Both compounds are isostructural. They crystallize in the orthorhombic system with a = 1251.2(2), b = 733.61(1), and c = 580.8(1) pm (Li_2BeCl_4), and a = 1334.0(3), b = 809.3(2), and c = 609.1(1) pm (Na_2BeCl_4) (a = 1336, b = 812, c = 606 pm (*3*)) (Z = 4), as computed from X-ray Guinier powder data. (The monoclinic cell reported for Li_2BeCl_4 (*1*) is not confirmed.) As revealed from systematic absences possible space groups are *Pnma* and $Pn2_1a$. The noncentrosymmetric space group $Pn2_1a$, however, is ruled out, because the mutual exclusion principle of the Raman and IR spectra (see Figs. 1 and 2) is obeyed.

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Comparing the Raman and IR spectra of Li_2BeCl_4 and Na_2BeCl_4 with those of other $M^{\rm I}_2M{\rm Cl}_4$ ($M^{\rm I}$ = Li, Na) compounds, as, for example, with those of Li_2ZnCl_4 and Na_2ZnCl_4 (*5*), the olivine structure is suggested for the ternary beryllium chlorides under investigation. This (also proposed by Fink *et al.* (*9*)) is confirmed by Lazy-Pulverix (*10*) calculations of the X-ray intensities as well as by the relations of the unit-cell dimensions $a:b:c$, which vary for olivine-type compounds only in a narrow range of 2–3% (mean value for olivine-type oxides and chalcogenides cited in (*11*) 1 : 0.590 : 0.467). The respective data of the olivine-type halides are 1 : 0.586 : 0.464 (Li_2BeCl_4), 1 : 0.606 : 0.457 (Na_2BeCl_4), 1 : 602 : 448 (γ-Na_2BeF_4) (*12*), 1 : 0.581 : 0.478 (Li_2ZnCl_4 (*5*), 1 : 582 : 476 (Li_2ZnBr_4) (*13*), 1 : 578 : 474 (Li_2ZnI_4) (*14*), and 1 : 0.588 : 0.468 (Na_2ZnCl_4 (*5*)).

The Raman spectra (see Fig. 1) exhibit strong scattering peaks at 294 and 301 cm^{-1}, respectively, which are assigned to $BeCl_4$ breathing modes (*3*). The increase in mode frequencies on going from Na_2BeCl_4 to Li_2BeCl_4 is caused by the increasing cohesive energy rather than by the lower mass of Li compared to Na. The IR spectra (see Fig. 2) are only slightly structured as is usual for ternary lithium chlorides (*15*). The bands in the range of 500–580 cm^{-1} are due to asymmetric BeCl stretching modes. Contrary to (*1*), modes involving Li^+ ion motions are assigned to the spectral range of 260–360 cm^{-1}. A group-theoretical treatment of the lattice vibrations of olivine-type compounds is given in (*5*).

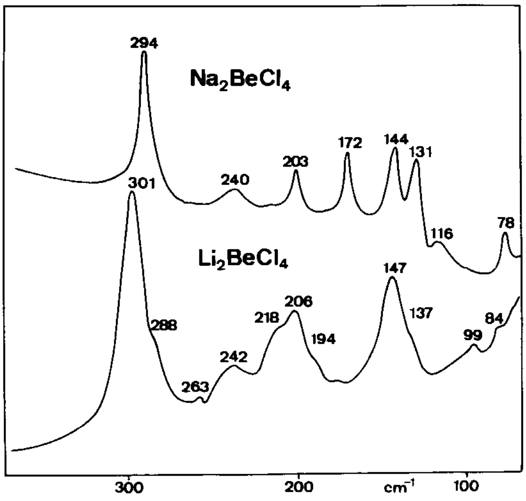

FIG. 1. Raman spectra of Li_2BeCl_4 and Na_2BeCl_4 (Dilor Omars 89, 514.5-nm excitation).

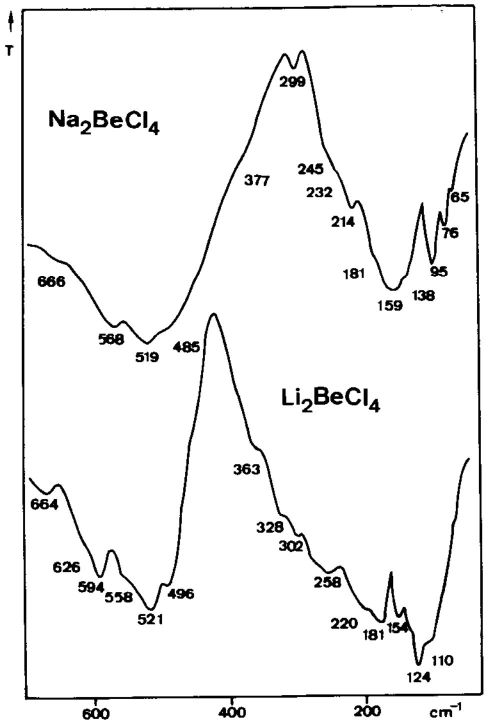

FIG. 2. IR absorption spectra of Li_2BeCl_4 and Na_2BeCl_4 (Bruker IFS 114, paraffine oil).

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